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Correlation of Electron Delocalisation with Pseudocapacitance in Nanostructured Carbon

By

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Thesis submitted to the University of Nottingham for
the degree of Doctor of Philosophy

Department of Chemical and Environmental Engineering
The University of Nottingham

May 2018

Abstract

The unique electronic structure - partial electron delocalisation (PED) - has been for the first time correlated with pseudocapacitance in graphene-based electrode materials in this study. Pseudocapacitive charge storage was observed on electrodes fabricated from graphene and related materials with different degrees of electron delocalisation (DED%), including graphene oxide (GO), partially oxidised graphene (POG) and polycrystalline monolayer graphene (PMG).

GO working electrodes were electrochemically reduced (ECR) via different potential cycling controls to prepare POGs with different DED%. Raman spectroscopy and X-ray photoelectrons spectroscopy (XPS) were used to qualitatively correlate the DED% with the state of oxidation of GOs. It was found that when the ECR was increased from 0 to 1000 potential cycles, the DED% of GO improved from 12.5% to 60.4%. Electrochemical characterisations were used to monitor the charge storage of ECR-treated GOs, i.e. POGs, in 3.0 M KCl and 1.0 M H₂SO₄, respectively. Cyclic voltammetry (CV) results showed that as the DED of GO was improved, the specific capacitance (C_m) increased from 0.1 to 38.0 F/g in 3.0 M KCl and 0.2 to 62.0 F/g in 1.0 M H₂SO₄. Electrochemical impedance spectroscopy (EIS) indicated that the improvement of charge storage could be mainly attributed to pseudocapacitance.

In the case of PMG, the CV results showed that the value of C_m was ca. 28.0 F/g in 3.0 M KCl and ca. 64.0 F/g in 3.0 M HCl, respectively, although the DED% of PMG was almost 95.0% as derived from the XPS results. The EIS analyses again indicated that the pseudocapacitive contribution predominated the total charge storage.

The electronic structures of representative GO models with DED% varying from 0 to 100% were established based on the density functional theory (DFT) modelling. The results showed that extra electronic states only emerged around the Fermi level of POG species ($0\% < \text{DED\%} < 100\%$), but not in fully oxidised graphene ($\text{DED\%} = 0\%$), nor in pure graphene ($\text{DED\%} = 100\%$). These states should have originated from the partially delocalised valence electrons rather than those localised electrons. A non-linear relationship between the charge storage capacity and the DED% was found with a peak at between 65.0 and 75.0% of the DED.

Finally, by sorting the specific capacitance of the above mentioned graphene species in the order of their DED%, a non-linear relationship has been found again with a peak between 65.0 to 75.0% of the DED. Both the experimental observations and theoretical predictions have revealed a consistent correlation between the pseudocapacitance and the DED% in graphene oxide electrode materials.

Acknowledgement

Firstly, my heartfelt thanks should give my late grandmother Xiuying Wang. Also my parents Chaobin Li and Zhouli Na for their emotional support, encouragement complete supporting and patience during my PhD studying.

My great thanks should also give my sponsor, employer Aviation Industry Corporation of China (AVIC) and China Scholarship Council (CSC) for their foresight and sagacity to give me this valuable chance for overseas study.

Secondly, I would like to thank my supervisors Prof. George Z. Chen and Dr Xianghui Hou for their supervision and guidance throughout the project. My deepest gratitude goes to Linpo Yu, Grace Li, Wen Zhu, Nawar Kader Al-Shara, Happiness Ijje, Stevenson Anthony, Ossama Al-Juboori, Athil Al-Shihabi Al-Ani and other members of the research group for their help.

I also would like to thank Douglas Brown, Bryce Marion, David Mee, Hannah Beska, Mckenzie Katy and all other L3 technicians at the Department of Chemical and Environmental Engineering for their assistance.

Special thanks to Dr Fang Xu and Dr Junpeng Liu for their warm-hearted help and constructive suggestions during my equipment training and sample characterisation. Dr Rance Graham and Dr Emily Smith based in the Nanoscale and Microscale Research Centre - NMRC in the University of Nottingham for technical support on the Raman and XPS characterisations, respectively. Marion Roe and Nigel neat for giving training on SEM and TEM.

The last but not the least, my heartfelt thanks would like to give my Yanchen Zhang and Liang Liu.

**This page is specially preserved to my late grandmother
Xiuying Wang, 90 years' old. She, as a kindness grandmother,
mother and mother-in-law, suffered a heavy cerebral infarction
after broken her thighbone and a successful surgery at that
time. Although accompanied by my painful parents and I, after
six months long struggling and fighting, the serious illness
finally took her life away on 19th April 2017.**

**This work is dedicated to my grandmother for memorising her
with gratitude and feel sad often for not being able to repay her
for her kindness in raising me up.**

—— Your grandson Junfu Li

List of Publications

Journal paper:

- Junfu Li, James O'Shea, Xianghui Hou, and George Z. Chen, *Faradaic Processes beyond Nernst's Law: Density Functional Theory Assisted Modelling of Partial Electron Delocalisation and Pseudocapacitance in Graphene Oxides*. Chem. Commun., 2017. DOI: 10.1039/C7CC04344A.
- Junfu Li, Xianghui Hou, and George Z. Chen, *Spectroscopic and electrochemical investigations of charge storage in polycrystalline monolayer graphene*. (Under preparation).

Presentation:

- Poster presentation: J.F. Li, and C. Z. George, *Electron delocalisation in nanostructured carbon materials and its implication for energy storage technology*. Midlands Electrochemistry Group Conference, University of Warwick, 13th June 2014.
- Oral presentation: J.F. Li, *Study on the electronic structure of graphene oxides with various electron delocalisation degrees through DFT calculation*. The 23rd Joint Annual Conference of CSCST-SCI, University of Nottingham, 3rd September 2016.

Conference attended:

- Midlands Electrochemistry Group Conference, University of Warwick, 13th June 2014.
- A Sustainable Future through New Materials for Energy, Energy Technologies Research Institute (ETRI) Conference, Jubilee Campus, University of Nottingham, 10th January 2017.

Abbreviations

0D	Zero-dimensional
2D	Two-dimensional
3D	Three-dimensional
AC(s)	Activated carbon(s)
AFM	Atomic force microscopy
BET	Brunauer–Emmett–Teller
[Bu ₄ N]BF ₄	Tetrabutylammonium tetrafluoroborate
CE	Counter electrode
Chi ²	χ^2
CNT(s)	Carbon nanotube(s)
C _P	Pseudocapacitance
CPE	Constant phase element
CPR	Capacitive potential range
CV	Cyclic voltammetry
CVD	Chemical vapour deposition
PMG	Polycrystalline monolayer graphene
D_i	Diffusion coefficient
D(s)ED	Degree(s) of electron delocalisation
DI	Deionized
DFT	Density of theory
EES	Electrochemical energy storage
EC	Equivalent circuit
ECC(s)	Electrochemical characterisation(s)
ECP(s)	Electric conducting polymer(s)
ED	Electron delocalisation
EDA	Electron delocalisation area
EDL(C) or C _{dl}	Electrical double layer (capacitance)
EDX/EDS	Energy Dispersive X-Ray Microanalysis
E _{eq}	Equilibrium potential
E _F	Fermi level
EIS	Electrochemical impedance spectroscopy
emf/EMF	Electromotive force
ESR	Equivalent series resistance
FOG	Fully oxidised graphene
FTIR	Fourier transform infrared spectroscopy

FWHM	Full wave at half maximum
GCD	Galvanostatic charging-discharging
GF(s)	Graphite flakes
GGA	Generalized gradient approximation
GO(s)	Graphene oxide(s)
H _{ads}	Adsorbed H
HOMO	Highest occupied molecular orbital
IHL	Inner Helmholtz layer
J_i	Flux
LUMO	Lowest unoccupied molecular orbital
MOs	Molecular orbitals
MOFs	Metal-organic frameworks
MSDS	Material Safety Data Sheets
NG	Nitrogen-doping graphene
OCGs	Oxygen-containing groups
OCP	Open circuit potential
OCV	Open circuit voltage
OHL	Outer Helmholtz layer
OPR	Operating potential range
Ox	Oxidant
η	Overpotential
PANI	Polyaniline
PBE	Perdew Burke Ernherzhof
PDE	Partial differential equation
PG	Pure graphene
PMG	Polycrystalline monolayer graphene
POG	Partially oxidised graphene
PPY	Polypyrrole
PS	Particle size
PTP	Polythiophene
PtWE	Platinum working electrode
PZC	Potential of zero charge
R _a	Surface roughness
Re	Reductant
RE	Reference electrode
RT	Room temperature
SAED	Selected area electron diffraction

SAEP	Selected area electron pattern
SCF	Self-consistent field
SE	Secondary electrons
SEM	Scanning electron microscopy
SSA(s)	Specific surface area(s)
TBAOH	Tetrabutylammonium hydroxide
TEM	Transmission electron microscopy
TiWE	Titanium working electrode
TLM	Transmission line model
TMO(s)	Transition metal oxide(s)
UV-Vis	Ultraviolet-Visible
WE	Working electrode
XAS	X-ray absorption spectroscopy
XPS	X-ray photoelectron spectroscopy

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Chapter 1 Introduction

Nanostructured carbons, such as carbon nanotubes (CNTs), graphene and their derivatives, have been experimentally demonstrated as promising candidates for high performance electrochemical energy storage (EES) devices, including supercapacitors and supercapatteries. As a major category of the potential electrode materials used in supercapacitors, nanostructured carbons have been found in many studies [1-5] to make pseudocapacitive contributions that could account for a great fraction of the total charge storage.

The charge and energy storage capacities due to pseudocapacitance could increase by up to five times from that due to the traditional electrical double layer (EDL) capacitance [6]. Therefore, the development of excellent pseudocapacitive electrode materials will undoubtedly broaden the application horizon of electrochemical capacitors or supercapacitors, especially for the highly demanding electricity storage and delivery.

On the other hand, the electronic structures of materials, especially which related to valence electrons whose energy states are close to the Fermi level, play a crucial role in deciding the physiochemical and electrochemical properties of the materials. However, relevant studies considering the pseudocapacitance from the aspect of electronic structure of the electrode materials is exceptionally rare in the literature, especially in nanostructured carbons, such as carbon nanotubes and graphenes.

In order to lay a foundation for the strong motivation, and the achievable aim and objectives of this study, the fundamental knowledge and the most recent research progresses in the field of electrochemical energy storage in nanostructured carbons will be reviewed in the following Section 1.1. It includes the major types of electrochemical charge storage, nanostructured carbon materials, supercapacitor electrodes made from graphene and related materials, and the electron delocalisation phenomenon in materials.

1.1 Literature review

1.1.1 Basics of electrochemical energy storage (EES)

According to the advanced development in the field of energy storage,

popular EES technologies include three main types [7]:

- Rechargeable batteries based on the classic redox reaction;
- Electrochemical capacitors which are more widely known as supercapacitors;
- Hybrids of battery and supercapacitor, so-called supercapattery and supercabattery.

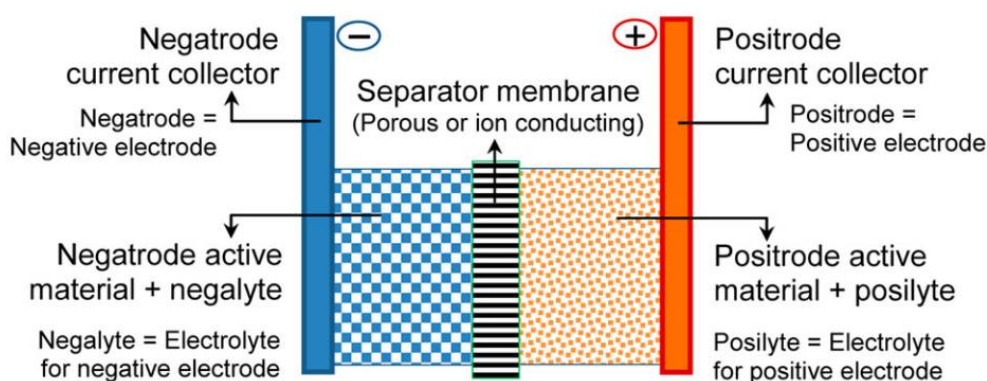


Figure 1-1. Schematic illustrations of a single cell of typical EES devices [7].

All EES devices are composed of a positive electrode, a negative electrode and an electrolyte separator, as illustrated in Figure 1-1. These components are packed in one or another way in a cell (i.e. the EES device). The electrolyte separator, which is the separator membrane in Figure 1-1, can be a liquid (acid solution or neutral solution), a solid, or more commonly a porous membrane filled with a liquid electrolyte (for example, the glass fibre or gel membrane in supercapacitors). The positive and negative electrodes are made of materials with high electronic conductivity, such as various metals, carbons, ceramics and their composites with polymers. The electrodes are used in two ways in EES devices. First, the electronic conductor is used mainly for loading an active material for charge storage by coating or another method. This case applies to both rechargeable batteries and supercapacitors, and the electronically conducting substrate is called current collector which should be chemically and electrochemically inert in the cell environment. The second use of the electrode is to conduct electrons from or into the redox active ions or molecules in the electrolyte and this case is common in redox flow batteries.

As the title of this thesis goes, one of the main topics of this study is 'pseudocapacitance'. Thus a straight-forward question, one may come up with immediately, is: *what exactly the 'pseudocapacitance' is?* It is almost impossible to give a clear definition at this stage without any background knowledge of EES. Superficially, the word 'pseudocapacitance' is the association of the prefix 'pseudo' and capacitance. Originally, the term 'pseudocapacitance' was created in order to describe the properties of an electrode that behaves like a capacitor in its electrochemical signature. Therefore, the 'pseudo' should be understood as the meaning of (1) not actually but having the appearance of and (2) almost, approaching, or trying to be, in the present case [8]. That is to say, the pseudocapacitance is a type of capacitance, while it is based on a completely different charge storage mechanism in contrast with the original capacitance.

The word '*capacitance*' should be distinguished from the notion of '*capacity*', *especially in the EES devices*. In the field of energy storage, the energy storage capacity with units of joules (J) or watt-second (W·s) and their multiples, is the amount of energy that can be stored in a storage system [9]. Thus, the capacity is the amount of electric charge that can be stored with units of coulombs (C) or ampere-hours (A·s), for example in batteries. The total charge of one mole of unit charges, such as electrons or ions with unit charge (C^+ or A^-), is 1 farad (F) = 96485 C/mol. The capacitance is the property of a capacitor which determines how much charge can be stored in the capacitor at a certain voltage and measured in farads (F). A 1 farad capacitor, when charged with 1 coulomb of electric charge, has a potential difference of 1 volt across its electrodes [10].

In essence, batteries and capacitors are based on totally different charge storage mechanisms. Simply speaking, the former stores electrical energy electrochemically, while electrostatically for the latter. Batteries store and delivery charges based on redox reaction on the electrode materials. Electrical energy and chemical energy are interconverted on the electrode materials through classic redox reactions including oxidation - losing electrons and reduction - gaining electrons. Charge transfer, or more precisely the transfer of electrons, happens at the interface between the electrode and redox active substances. A schematic shown in Figure 1-2 illustrates the fundamental principles and electrode processes of a secondary or rechargeable battery

under the situation of charging (left panel) and discharging (right panel).

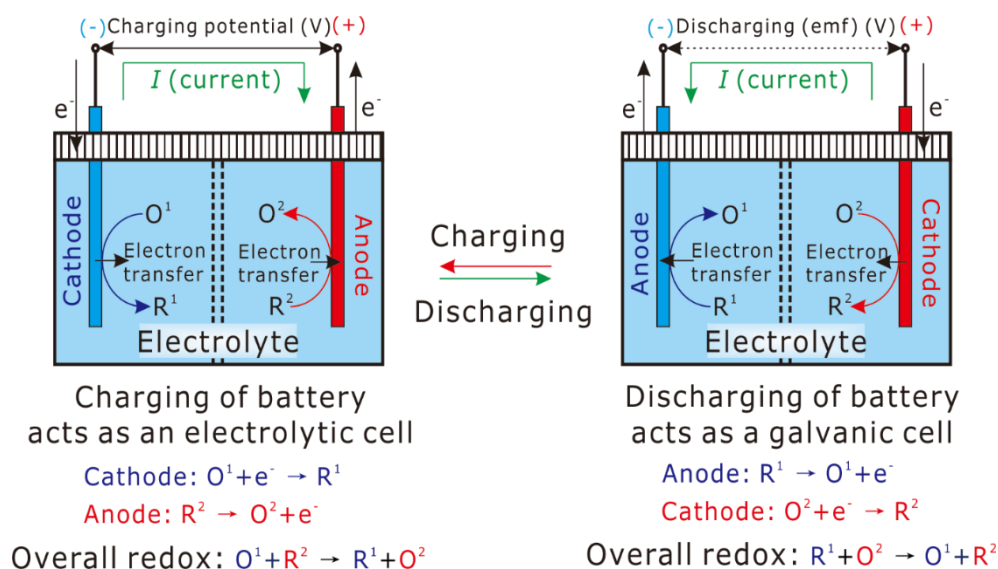


Figure 1-2. Schematic of a typical rechargeable battery. R^1/O^1 and R^2/O^2 denote the first and second redox couple taking part in the redox reaction on the left and right electrode respectively. $R^1 + O^2 \rightarrow O^1 + R^2$ is the thermodynamically favourable reaction, therefore, can happen spontaneously to convert chemical energy to electrical energy. Cathode denotes the electrode at which electrons flow from electrode to electrolyte, while at the anode electrons flow from electrolyte to electrode.

In this rechargeable battery, two metal electrodes are involved, a negative electrode (M1, in blue) on the left and a positive electrode (M2, in red) on the right. In between, a liquid or solid ionic conductor which terms as electrolyte contacts with the two electrodes to supply the conducting connection. Different choices of electrode-electrolyte configurations make various types of battery. Main types include primary (non-rechargeable) and secondary (rechargeable) batteries. The former can only be used once after complete discharge, for example, the well-known galvanic copper-zinc primary cell, voltaic cell and zinc-carbon dry battery. The secondary battery is rechargeable because the relevant redox reactions in this battery can be reversed, meaning the reactants can be regenerated by a suitable reversal of the voltage across the cell. That is to say, when the secondary battery is discharging the forward redox reaction, in this case $R^1 + O^2 \rightarrow O^1 + R^2$, is thermodynamically favourable and can happen automatically, which is the battery's capability to convert chemical energy into electric energy in essence. While, during the period of

discharging, the backward redox reaction ($R^1 + O^2 \leftarrow O^1 + R^2$) is not thermodynamically favourable. It cannot happen automatically. Only a certain magnitudes of electromotive force (emf) supplied by the external power source can drive the backward reaction and convert the products of the forward reaction (O^1, R^2) into the initial reactants (R^1, O^2). The equilibrium potential of the R^1/O^1 couple endows the anode a negative electrode potential (ϕ^-). The same, the equilibrium potential of R^2/O^2 couple endows the cathode a positive electrode potential (ϕ^+). Redox reaction at this electrode is the reduction of the O^2 into the R^2 , with a half-cell reaction of $O^2 + e^- \rightarrow R^2$. The voltage established between the negative (-) and positive (+) electrodes is the electromotive force (emf) of the cell, which equals to the difference $\phi^+ - \phi^-$ (V). If an external load, such as a resistor, lamp, is then connected between the two electrodes, a spontaneous forward redox reaction is happening electrons are extracted from the R^1 on the anode and flows to the cathode to reduce the O^2 via an external load, during which the electrochemical energy is converted into electrical work to drive the external load. When the battery is charged the potential (E) applied on the two electrodes will lead the establishment of an over-potential (η) ($\eta = E - E_{eq}$) because of the difference between the applied potential (E) and the equilibrium electrode potential of the redox couple of R^1/O^1 on negative electrode, R^2/O^2 on positive electrode. Then, the backward redox reaction, $R^1 + O^2 \leftarrow O^1 + R^2$ is now thermodynamically favourable and can happen under the driving of the external power source, during which the electrical energy supplied by the external source can be stored and converted into chemical energy in the battery again. During the charging of the battery, the cell acts as an electrolytic cell. The above electrochemical operations and the set-up in this case can be simplified by a shorthand notation: $M1/R^1, O^1//O^2, R^2/M2$. The '/' denotes the interface between the electrode and the electrolyte. In practical copper-zinc primary cell, this notation becomes $Zn/Zn^{2+}_{(aq)}, Cu^{2+}_{(aq)}/Cu$, and $Pb/Pb^{2+}_{(aq)}, SO_4^{2-}_{(aq)}/PbO_2/Pb$ in a lead-acid secondary battery.

As a matter of fact, the above schematic is only an over-simplified description. While it still illustrates the main principles and phenomena happening in the charging/discharging of a battery. In detail, there are many steps that can happen close to the electrode before and after the relevant redox

reactions. The following Figure 1-3 presents a detailed pathway of a general electrode reaction, i.e. $O + ne^- \leftrightarrow R$. Such an electrode reaction, practically, is composed of a series of steps relative to chemical reaction, adsorption/desorption and electron transfer processes.

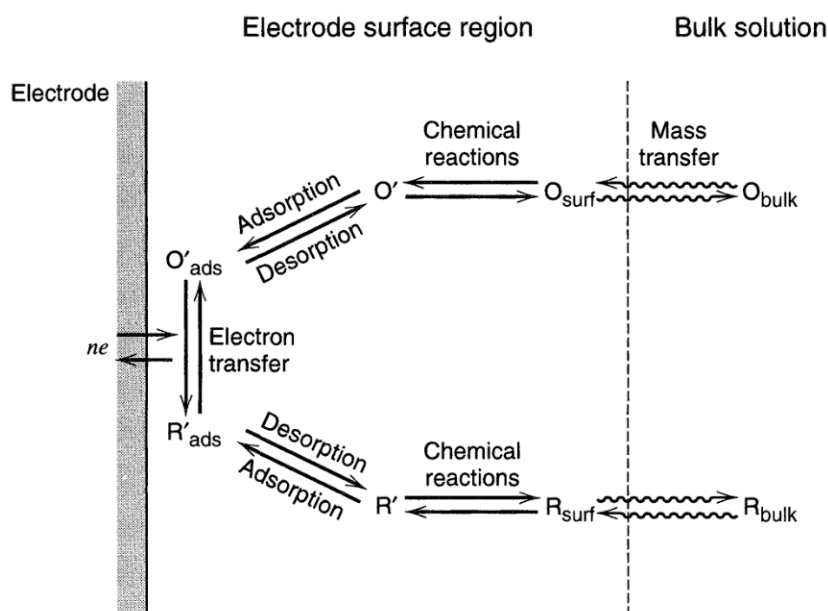


Figure 1-3. Pathway of a general electrode reaction [11].

The main note in describing electrochemical energy storage and the redox reaction in a battery can be summarised below:

- The electrode material has to be in contact with the electrolyte;
- Redox reactions happen at the interface of electrode | electrolyte;
- Charge transfer occurs across the interface of electrode | electrolyte;
- Electrical energy storage performance is characterised by the capacity of the device;
- Charge storage ability of electrons in the battery is equivalent to 1-3 electrons per atom or molecule of the bulk phase [6].

The energy storage capacity of a battery is determined by the total charges (Q_b) that is stored within a given charging time. If a constant current is used in charging and discharging of the battery the ideal capacity (Q_b) equals to the current multiplied by the time, namely $Q_b = I \times t$ with a unit of

ampere-second (A·s). Of course, the capacity in actual devices is also dependent on the amount of electrode materials, reactants and redox active phases. Additional fundamental considerations will be reviewed in Section 1.1.1.1.

With regards to the other electrical energy storage devices, i.e. capacitors, the mechanism is totally different. The ideal example of a capacitor is the plane condenser in which two flat metal plate acts as electrode in this condenser. In between the two electrodes, the dielectric layer can only be vacuum, air or other insulating materials, namely dielectric materials as shown in Figure 1-4.

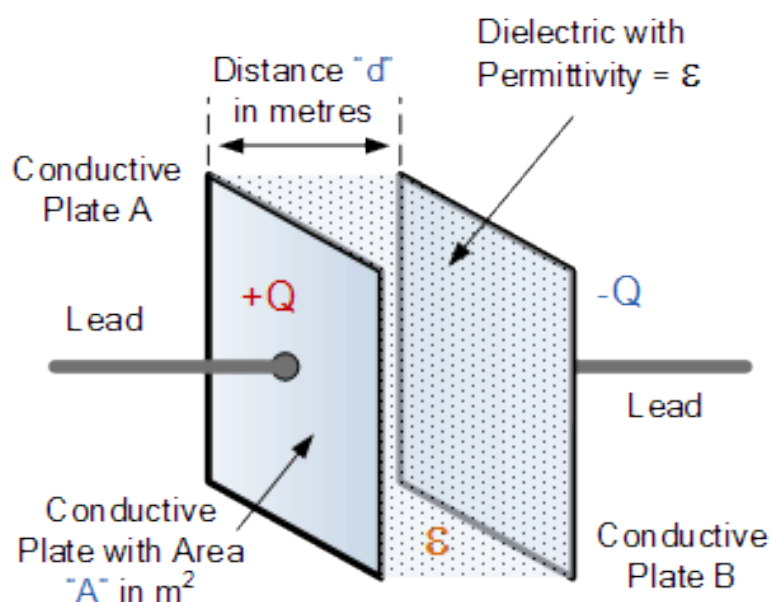


Figure 1-4. Plate condenser or plate capacitor [12]

Charging this capacitor can be achieved by applying a voltage across the two electrodes, during which equivalent amount of electrons are extracted from the left plate causing the deficiency of electrons and injected to the right plate causing the excess of electrons. That is to say, equivalent counter charges are stored on the two plates (electrodes) of the capacitor. Then an electric field can be established at the certain voltage in between the two electrodes. The amount of charges that can be stored on the electrodes are finite. When it

saturated on the metal plate no further charges can be stored. During the charge storage in a capacitor the charges which can be stored is linear proportional to the voltage applied on the two electrodes. The constant ratio of proportionality is the capacitance (C) of the capacitor. If the external voltage is removed, and an external load, e.g. a resistor, is connected to the two electrodes of the capacitor, charges stored on one of the two electrodes will flow via the load to neutralise the counter charges on the other electrode because of the potential difference established in between the two electrodes, thus a certain amount of electric work is done. This is the discharging course or the delivery of the stored electrical energy. Some key points to be noted with the charge stored in a capacitor can be summarised below:

- No redox reactions happen during the energy storage in a capacitor;
- Charge storage is based on only pure electrostatic process;
- No charge transfer occurs at the interface between the electrode and the dielectric;
- Electrical energy storage performance is characterised by the capacitance of the device;

In such a simplest plate capacitor, it is found that the capacitance (C) has an equation with the area of electrode (A), the distance between the two electrode plates (d) and the dielectric constant (permittivity, $\epsilon = \epsilon_r \times \epsilon_0$) of the dielectric material, namely $C = (A \times \epsilon_r \times \epsilon_0) / d$, where $\epsilon_0 = 8.854187817 \times 10^{-12}$ (F/m) is the permittivity of vacuum and ϵ_r the relative permittivity of dielectric material. Thus, one can easily calculate the capacitance of this kind of capacitor is about $0.0008859 \text{ } (\mu\text{F}) = 885.6 \text{ } (\text{pF})$ if air is the dielectric with $\epsilon_r \approx 1.00053$ and both electrode plate are 1 m^2 in area with a distance of 1 cm between them. If this capacitor can be fully charged at 1 volt the total charges (Q_c) stored in this capacitor is only about $0.0008859 \text{ } (\mu\text{C})$, and the area-specific capacitance and the surface charge density is only $8.9 \times 10^{-8} \text{ } \mu\text{F}/\text{cm}^2$ and $8.9 \times 10^{-8} \text{ } \mu\text{C}/\text{cm}^2$ respectively. These are quite small values of charge storage in capacitors. As known from the capacitance equation of the plate capacitor, the capacitance is inversely proportional to the distance (d) between the two plates. That is to say, the smaller the distance, the larger the capacitance, and the same, the larger

the electrode area, the larger the capacitance. Therefore, manufacturers started producing capacitors with thinner interval electrode distance and larger specific surface area (SSA) in order to achieve as a high capacitance as possible. Research and development went via electrolytic capacitors, such as Al-Al₂O₃ and Ta-Ta₂O₅ system, to nowadays' electrochemical capacitors or supercapacitors as it was realised that the activated carbon (AC) has very large SSA and good conductivity in 1960s [6]. This goes into a new era of capacitors with few tens to hundreds F/g or $\mu\text{F}/\text{cm}^2$ of high specific capacitance in contrast with that of the previous generations, which is only on the level of pF or just μF in practical devices [6].

The electrochemical capacitor with its high specific capacitance is beneficial from two main aspects. The one is the extremely large SSA of electrode materials. Normally in the activated carbon the SSA is around 1000-3000 m^2/g . This value is far larger than the common metallic electrode materials. The other one is the highly compacting electrical double layer (EDL) characterised by close packing counter charges, such as electrons/holes in the electrode side and ions in the electrolyte side, resulting in a distance (d) between the counter charges of only 0.5-0.6 nm ($\text{nm} = 1 \times 10^{-9} \text{ m}$) [6].

Specifically, the same as the case in traditional capacitors, when a voltage is applied on the two electrodes of the cell, excessive electrons (or holes) can populate on the outer surface of electrodes. If the electrode is in contact with an ion-conducting electrolyte, for example, the aqueous electrolyte with freely moving ions, the equivalent amounts of anions and cations can be separated and accumulate onto the counter electrode because of the electrostatic attraction. As long as the applied potential difference between the two electrodes is less than the discharge voltage of the corresponding counter ions or lower than the decomposition voltage of the electrolyte, no charge transfer can happen at the interface of electrode | electrolyte. On each electrode, there are two compactly charged layers. The one is on the surface of electrode, and the second virtual plate that is the inner interfacial limit of the electrolyte. Both of these two layers constitute the so-called electrical double layer (EDL), or the well-known Helmholtz EDL model as shown in Figure 1-5.

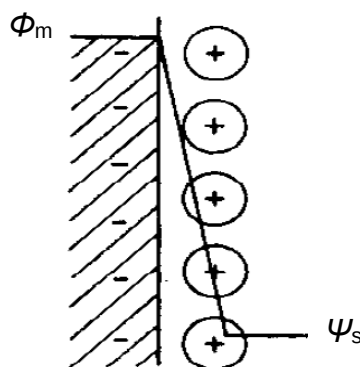


Figure 1-5. Helmholtz model of double-layer [6]

This model was first adopted by von Helmholtz [13] to describe the distribution of opposite charges, quasi-2-dimensionally, at the interface of colloidal particles being referred to as the Helmholtz double-layer model. In this model, excessive charges on the electrode (left shaded area) lead to a potential of Φ_m , and the equal amount of counter ions in the electrolyte side (right) reduces the potential down to Ψ_s . Hence the potential difference at the interface of this EDL is $|\Phi_m - \Psi_s|$. It is important to note that in the Helmholtz double-layer model the counter ions is assumed to be an ideal point charge. Therefore, electrochemical capacitors based on the EDL are called double-layer type electrochemical capacitors. In practice, a relatively large specific capacitance of 20 to 50 $\mu\text{F}/\text{cm}^2$ can arise because of the small thickness of the compacting layer [6]. Table 1-1 enumerates the EDL capacitances (EDLCs) of common metallic and carbonaceous electrode materials.

Table 1-1. Typical values of EDLC in common metal and carbonaceous materials [6,14]

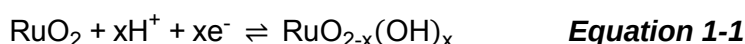
Metal material	Electrolyte	Area-specific EDLC (C_a) ($\mu\text{F}/\text{cm}^2$)	SSA (m^2/g)	Approx. specific capacitance (C_m) (F/g)
Platinum (Pt)	0.01 N NaCl	64.2	N/A	/
Sliver (Ag)	0.01 N NaCl	52.8	N/A	/
Gold (Au)	0.01 N NaCl	30.9	N/A	/
Gold (Au)	Water	23*	N/A	/
Stainless steel	0.01 N NaCl	39.8	N/A	/
Hg	Water	28*	N/A	/

Tl(Ga)	Water	34*	N/A	/
Bi	Water	36*	N/A	/
Sn	Water	39*	N/A	/
Pb	Water	40*	N/A	/
Cd	Water	52*	N/A	/
In(Ga)	Water	60*	N/A	/
Zn	Water	100*	N/A	/
Ga	Water	135*	N/A	/
Carbonaceous material	Electrolyte	Area-specific EDLC (C_a) ($\mu\text{F}/\text{cm}^2$)	SSA (m^2/g)	Approx. specific capacitance (C_m) (F/g)
Activated carbon	10% NaCl	19	ca. 1200	228
Carbon black	1.0 M H_2SO_4	8	80 - 230	6.4 - 18.4
	31 wt.% KOH	10	80 - 230	8 - 23
Carbon fiber cloth	0.51 M Et_4NBF_4 in propylene carbonate	6.9	1630	112.5
Highly oriented pyrolytic graphite: Basal plane	0.9 N NaF	3	N/A	/
Highly oriented pyrolytic graphite: Edge plane	0.9 N NaF	50 - 70	N/A	/
Graphite powder	10% NaCl	35	4	1.4
Graphite cloth	0.168 N NaCl	10.7	630	67.4
Glassy carbon	0.9 N NaF	ca. 13	N/A	/
Carbon aerogel	4M KOH	23	650	149.5

* Inner-layer differential capacitance at the potential-of-zero charge.

Originally, in the field of capacitive charge storage, in addition to the traditional EDLC (C_{dl}), electrochemical capacitors also comprises of another significant mechanism known as the so-called '*pseudocapacitance*' (C_ϕ). The behaviour of pseudocapacitance was first observed by Trasatti [15] in the thermally decomposed films of some special transition metal oxides (TMOs, e.g., RuO_2 , IrO_2). These TMOs are characterised by their distinguishing metallic conductivity. When the current response was measured under a constant charging/discharging potential rate in the electrolyte solution 1.0 M HClO_4 , both a semi-rectangular current-voltage (i/E) response and a linear dependence of the charge stored with changing potential within certain potential range were observed. These relationships can be obtained normally by ECC, e.g. cyclic voltammetry (CV), which will be described further in methodology sections. In

such a semi-capacitive charging/discharging behaviour, charge storage originates from electron-transfer mechanisms rather than simply relies on the accumulation of ions in the electrical double layer (as with EDLC) [8]. As a matter of fact, redox related to Ru^{n+} ($n = 4, 3$ and 2) ions can be detected during the charging/discharging processes. The redox reaction shown in Equation 1-1 [15] with regards the electrons-protons double-injection/-ejection was first used to explain the charge storage mechanism of RuO_2 .



Since then, this specific faradaic capacitance was also observed and investigated in other metal oxides (MnO_2 [16,17]), electrically conducting polymers (ECPs) (polypyrrole (PPY) and polyaniline (PANI) [18]), even in many carbonaceous materials [6], nano-structural materials (carbon nanotubes (CNTs), graphene, graphene oxides and heteroatom doping derivatives [3,4,19-28]), metal organic frameworks (MOFs) [29,30] and mesoporous metallic conductors [31]. Some researchers [32] believed that the pseudocapacitive behaviour may be only a combination between faradaic behaviour and the double layer behaviour, but in essence, these two behaviours display totally different mechanisms of charge storage. In short, the main properties of pseudocapacitance can be summarised as follows:

- Redox reactions occurs in the electrode materials during the charging/discharging process;
- The charge accumulation is not mainly due to electrostatic attractions;
- Charge transfer occurs during the charging/discharging processes;
- Electrical energy storage performance of the device can be characterised by the capacitance;
- Taking the common pseudocapacitance value, e.g. ca. $500 \mu\text{F}/\text{cm}^2$, as an example, it is equal to $500 \mu\text{C}$ for a 1 volt cell, the charge storage ability of electrons in pseudocapacitive materials is equal to ca. 2.5 electrons per atom of the accessible surface [6].

The common value of pseudocapacitance (C_ϕ) normally is higher than 200 F/g which corresponds to an area-specific normalised value larger than 100

$\mu\text{F}/\text{cm}^2$, e.g. the data obtained in RuO_2 . Some common values of pseudocapacitance from some seminal research are given in Table 1-2.

Table 1-2. Typical values of the specific capacitance in pseudocapacitance materials

Electrode material	Material states	Area-specific EDLC (C_a) ($\mu\text{F}/\text{cm}^2$)	SSA (m^2/g)	Approx. specific capacitance (C_m) (F/g)	Ref.
RuO_2	Thermal decomposition film	ca. 14800-75000 ^a	N/A	/	[15]
RuO_2	Thin film	291.7	120	350	[33]
RuO_2	Crystalline	292.3	130	380	[34]
$\text{RuO}_2 \cdot x\text{H}_2\text{O}$	Amorphous	760 - 1800	40 - 95	720	[35]
$\text{RuO}_2 \cdot x\text{H}_2\text{O}$	Thin film prepared by electrostatic spray deposition	N/A	N/A	650	[36]
$\text{MnO}_2 \cdot n\text{H}_2\text{O}$	Amorphous	66	303	200	[16]
MnO_2	Ultrathin, dip-coated sol-gel-derived films	N/A	N/A	698	[17]
Mn/Mo oxides	Electrodeposition on thin film	N/A	N/A	190	[37]
PANi	Interfacial polymerization	N/A	N/A	554	[38]
PPy	Interfacial polymerization	N/A	N/A	261	[39]
	Chemical oxidation	N/A	N/A	576	[40]
	In-situ polymerization	N/A	N/A	325	[41]
	Electro-polymerization	N/A	N/A	343	[42]
PTh	Dilute polymerization	N/A	N/A	134	[43]
	Dilute polymerization	N/A	N/A	156	[44]
	Successive ionic layer adsorption and reaction	N/A	N/A	252	[45]
	Chemical bath deposition	N/A	N/A	300	[46]
Graphene oxides	Chemically reduced by hydrazine	N/A	N/A	194	[23]

	reacts with KOH and followed by chemical reduction with hydrazine	N/A	N/A	253	[28]
	solvothermal method and controlled reduction of GO	N/A	N/A	276	[4]
	Electrochemically reduced	N/A	N/A	223	[27]
	Electrochemically reduced	N/A	N/A	279	[3]
Nitrogen-doping graphene oxides	Chemically reduced by hydrazine to NG by thermal reduction of the RGO in NH_3 gas.	N/A	N/A	144	[22]
	simple plasma process	N/A	N/A	ca. 280	[20]
	Crumpled NG nanosheets with ultrahigh pore volume	N/A	N/A	248 302	[47]

a. Results were estimated from the CV obtained under 40 mV/s and the Table 1 of Ref. [15];

The aforementioned class of electrochemical energy storage: battery and capacitor (including EDLC and pseudocapacitance), have been shown to be based on different mechanisms of storing charge. Therefore, in order to learn more about these mechanisms, a detailed review of their fundamentals and the most recent progressing will be provided in the subsequent sections. This will starts from the mechanism of charge storage in the batteries - faradaic charge storage, after which EDLC (C_{dl}) would be described. Furthermore, the still to be completely understood capacitive faradaic charge storage (pseudocapacitance, C_ϕ) would be reviewed.

1.1.1.1 Faradaic charge storage

In the field of EES, electron transfer reactions always refers to those occurring at the interface connecting two or more phases (solid, liquid or gas). The interface between two phases includes 'current collector | active material'

and 'electrode | electrolyte', but an interline (or point) between three (or more) phases. Such charge transfer reactions are known as faradaic reactions or processes. Different from the electron transfer direction in common chemical redox, i.e. only from the reductant to the oxidant, the transferred electrons in a faradaic process (heterogeneous reaction) can be withdrawn from or injected into the electrodes via the external circuit [7].

Technically, the current response (i) to the applied cell voltage (E), be it the charging (electrical energy storage) or discharging (electrical energy delivery) processes, can reveal the characteristics of a faradaic charge storage process.

Take the most commonly used cyclic voltammetry in a three-electrode cell for example, this technique applied a linearly varied potential cycling, e.g. $E(t) = E_i \pm v t$, across the working electrode (WE), where E_i is the initial potential point of the WE, t is time. This potential variation is achieved by passing a correspondingly various current (i) across the WE and a counter electrode (CE). Then, the real-time WE potential (Φ_{WE} , or E_{WE}) can be detected versus a reference electrode (RE), such as the standard hydrogen electrode (SHE) and Ag/AgCl electrode, which has an inherently stable electrode potential (Φ_{RE} , or E_{RE}) in the electrochemical system. The inherently stable electrode potential held on the RE is based on the fact that the RE can always maintain its electrode reaction in an equilibrium state, e.g. the equilibrium of



in the Ag/AgCl RE and



in the SHE.

The electrode potential of the SHE is set to 0 V as the internationally accepted primary reference [48]. Therefore, the other REs held their own fixed electrode potential vs. SHE, e.g. 0.2223 V for Ag/AgCl vs. SHE, can be used as a reference in various electrochemical environments for the measurement of potentials across WEs.

For a typical faradaic process, the current response is simultaneously happening as a potential (E) is applied across the WE. If only a single-direction linear potential sweep is considered the faradaic process will give a characteristic peak shape voltammogram as shown in Figure 1-6.

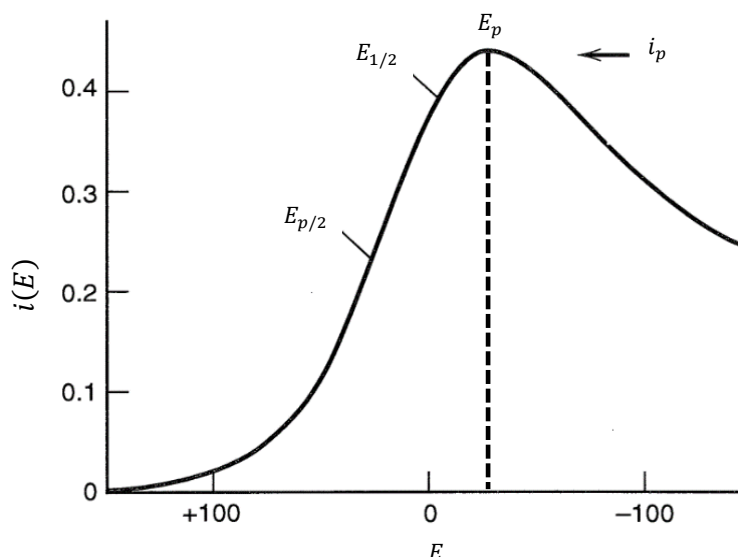


Figure 1-6. Single-direction linear potential sweep voltammogram. i_p the peak current, E_p the peak potential, $E_{p/2}$ the half-peak potential and $E_{1/2}$ [11].

Strict mathematical deduction gave the following current response formula [11]:

$$i_f(t) = nFAC^* \sqrt{\frac{nF}{RT}} u \sqrt{\pi D} \chi\left(\frac{nF}{RT} E\right) \quad \text{Equation 1-4}$$

where $i_f(t)$ is the faradaic current; n the stoichiometric number of electrons consumed or transferred in the electrode reaction; F Faraday constant; A the area of the electrode; C^* the initial concentration of the reactant in the bulk solution; R is the ideal gas constant; T the temperature; $u = dE/dt$ the rate of potential sweep; D the diffusion coefficient of the reactant in the solution and E the potential applied on the working electrode.

In this equation, at any given point, $\chi\left(\frac{nF}{RT} E\right)$ is a pure number, so that Equation 1-4 gives the functional relationship between the current at any point

on the cyclic voltammogram and the variables. Noteworthy, the faradaic current respons, i_f , is proportional to C^* and $\sqrt{u}$.

In essence, Nernst equation is the core of the mathematical deduction for the faradaic current response because it correlates the electrode potential (E) with the concentration of redox couples directly as shown in Equation 1-5.

$$E = E^0 + \frac{RT}{nF} \ln \frac{a_{Ox}}{a_{Re}} \quad \text{Equation 1-5}$$

where a_{Ox} and a_{Re} are the activity of oxidants and reductants respectively. The activity is $a_i = \gamma_i(C_i/C^0)$, where C_i is the concentration of the solute; C^0 the standard concentration (usually 1 M), and γ_i the activity coefficient which is dimensionless.

Therefore, faradaic process should follow the Nernst equation which results in peak-shaped CVs. Concentration gradient of reactants leads to the diffusion of the reactants, therefore, shifts the anodic (oxidation) peak towards the positive direction and the cathodic (reduction) peak in the reverse.

One more extreme case is the redox behaviour of adsorbed species, for example, a thin layer coating of a redox active material on the electrode. Following an analogous deduction by substituting the C^* with a $\Gamma_t (= \Gamma_{Re} + \Gamma_{Ox})$, the total surface area covered by the reduced (Γ_{Re}) and oxidised (Γ_{Ox}) sites, and more simple boundary conditions. The current response towards the linear potential change can be expressed as Equation 1-6 [11]

$$i_f = \frac{n^2 F^2 A \Gamma_t}{RT} U \frac{e^{\left[\frac{(E-E^0)nF}{RT}\right]}}{\left\{1 + e^{\left[\frac{(E-E^0)nF}{RT}\right]}\right\}^2} \quad \text{Equation 1-6}$$

where i_f , A, T, R, F, u, n and E has the same meaning with those in Equation 1-4. $\Gamma_t (= \Gamma_{Re} + \Gamma_{Ox})$ is the total surface area covered by the reduced (Γ_{Re}) and oxidised (Γ_{Ox}) sites; E^0 is the equilibrium potential of the redox couple. Assuming $n = 1$, $A = 1 \text{ cm}^2$, $\Gamma_t = 0.05$, $T = 300 \text{ K}$, the CVs calculated from Equation 1-6 at three different scan rates are presented in Figure 1-7a. The corresponding galvanostatic charge-discharge (GCD) curves under different current densities are shown in Figure 1-7b.

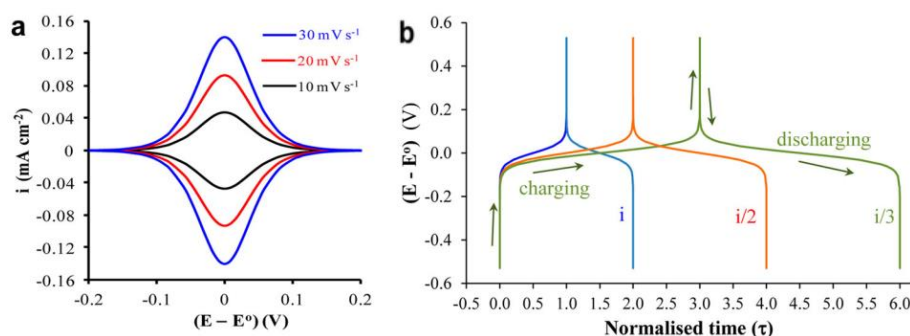


Figure 1-7. (a) CVs derived from equation (1) at indicated potential scan rates, and (b) GCD plots derived from equation (3) at indicated constant currents of i , $i/2$, $i/3$ for a reversible faradaic-Nernstian reaction with localised electron transfer to and from isolated redox sites on the electrode [49].

It can be seen that the current response i_f for adsorbed species or thin layer coating of a redox active material on the electrode is proportional to the u ($=dE/dt$) rather than $\sqrt{u}$. In addition, a unique form of Nernst Equation 1-7 [11] is also used in the deduction of this extreme case of thin layer redox reaction.

$$E = E^0 + \frac{RT}{nF} \ln\left(\frac{1-x}{x}\right) \quad \text{Equation 1-7}$$

where $x = \Gamma_{\text{Re}}/\Gamma_t$ is the mole fraction of reduced species (or sites) on the electrode surface at time t . Under reversible conditions (i.e. the process is governed by the Nernst equation), x is linked to the amount of charge passed by the Faraday's law as follows:

$$x = \frac{i_f t}{nF\Gamma_t} \quad \text{Equation 1-8}$$

Below are some key features for a typical faradaic charge storage:

- Charge transfer occurs across the interface of electrode | electrolyte;
- CV shows a characteristic pair of peaks regarding to the oxidation and reduction current responses;
- The current response i_f of a faradaic process can be proportional to $\sqrt{u}$ or u ($= dE/dt$) determined by whether or not there is the diffusion control:

$$i_f(\text{diffusion control}) \sim \left(nFAC^* \sqrt{\pi D} \sqrt{\frac{nF}{RT}} \right) \sqrt{U} \quad \text{Equation 1-9}$$

$$i_f(\text{non-diffusion control}) \sim \left(\frac{n^2 F^2 A \Gamma_i}{RT} \right) U \quad \text{Equation 1-10}$$

- GCD has typical charging/discharging plateaus maintaining an almost constant value corresponding to the charging/discharging potentials;
- Diffusion process of reactants shifts the anodic (oxidation) and cathodic (reduction) peaks more positively and more negatively respectively, and causes two different charging/discharging plateaus in the GCD.

Another keyword in the title of this dissertation is the ‘electron delocalisation’. Therefore, the electronic structure of electrode materials is highly concerned in this study. As such the remaining aspects of this review would present alternative theoretical approaches that can be used to explain the mechanism of faradaic process at the electrode | electrolyte interface, based on the distributions of electronic energy states in the electrode and the electrolyte.

This theoretical approach, applied to heterogeneous electrode kinetics, is based on a model of the overlap between electronic states of the electrode and those of the reactants in the solution [6,11], as presented in Figure 1-8a to c. This model is particularly useful for treating electron transfer at electrode materials, e.g. semiconductor, where the electronic structure of the electrode is important [11]. The main idea is that an electron transfer can take place from any occupied energy state that is matched in energy, E , with an unoccupied receiving state. If the process is a reduction, the occupied state is on the electrode and the receiving state is on a reactant, O. For an oxidation, the occupied state is on species R in solution, and the receiving state is on the electrode.

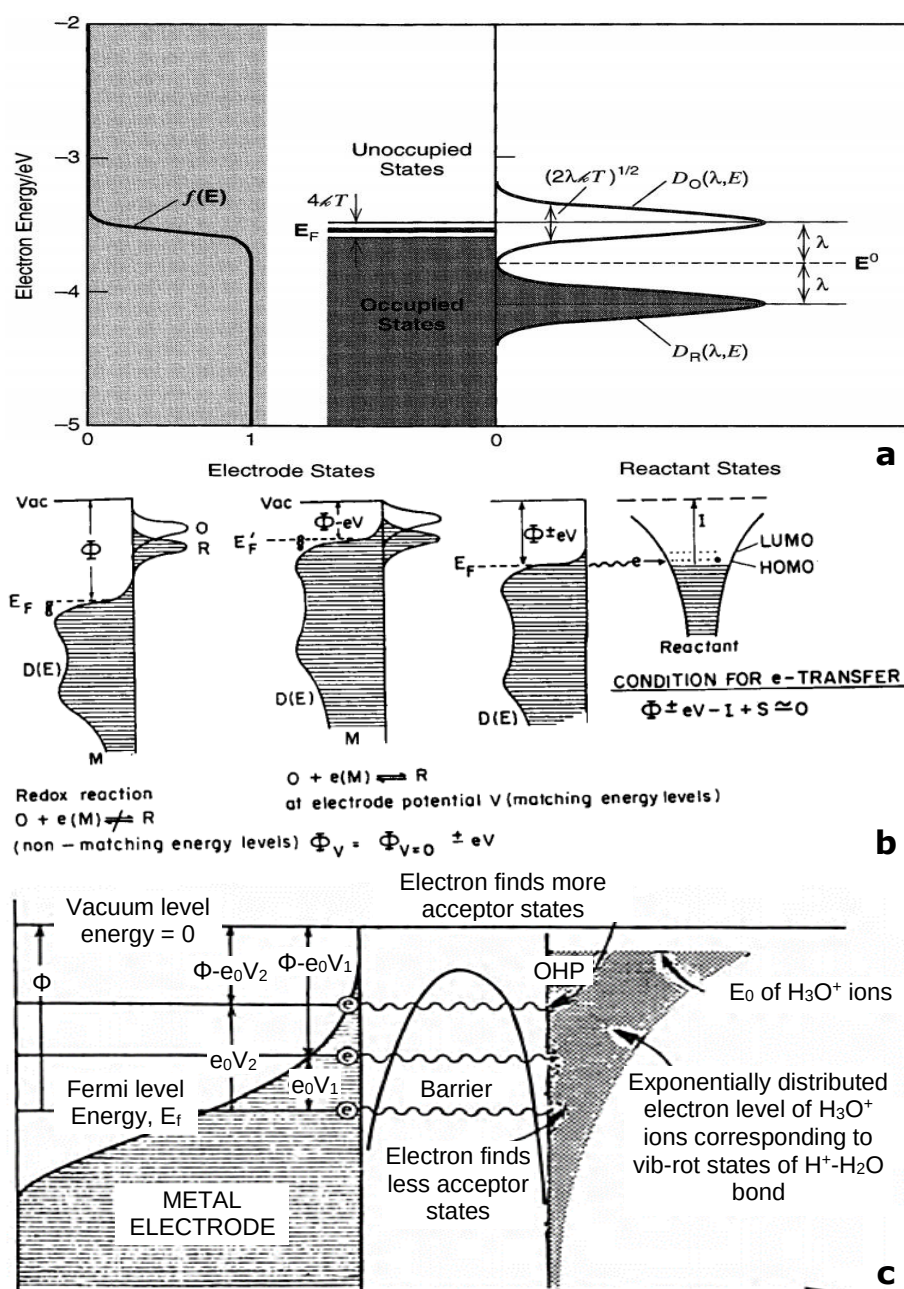


Figure 1-8. (a) Relationships among electronic states at an interface between a metal electrode and a solution containing species oxidants (O) and reductants (R) at equal concentrations; (b) Conditions for energy mismatching (the most left figure in (b)) and energy matching (the middle one in (b)) at the electrode Fermi level for facile electron transfer to occur in a radiationless process [6]. and (c) Schematic diagram of the potential energy barrier at the interface [48].

In general, the eligible states extend over a range of energies, and the total rate is an integral of the rates at each energy [11]. As shown in Figure 1-8a, the vertical axis is electron energy, E . The arrow Indicated place on the

electrode side is a zone $4kT$ wide centred on the Fermi level, E_F . The graph of $f(E)$ is the well-known Fermi-Dirac distribution function of electrons (which is a type of Fermion) in the condensed solid state. $f(E)$ makes the transition of the population of electrons from a value of nearly 1 below the zone to a value of virtually zero above. On the solution side, the state density distributions are shown for oxidants (O) and reductants (R). These are Gaussian's type of distributions having the same shapes as the probability density functions, $W_O(\lambda, E)$ and $W_R(\lambda, E)$. It is important to note that, $D_O(\lambda, E)$ and $D_R(\lambda, E)$ are the concentration density functions, which equal to the corresponding probability density functions, W times the concentration of reactants on the electrode surface and Avogadro's number, $D_i(\lambda, E) = N_A \times C_i(0, t) \times W_i(\lambda, E)$, where λ is reorganization energy which has a large effect on the predicted current-potential response.

The electron energy corresponding to the standard potential, E° of this redox couple, is ca. -3.8 eV, and $\lambda = 0.3$ eV. The Fermi energy corresponds to an electrode potential of ca. -250 mV vs. E° . Filled states are denoted on both sides of the interface by dark shading. Since filled electrode states overlap with (empty) O states, the reduction can proceed accompanying with charge transfer from the electronic states in the electrode to the oxidation states in oxidants. Since the (filled) R states overlap only with filled electrode states, oxidation is blocked. If the potential on the electrode is positively polarised vs. E° , the filled states on the electrode side will be dragged down within or below the (filled) R states, in other words, unoccupied states in electrode extends to the comparable energy level of the (filled) R states. Thus oxidation can proceed accompanying with charge transfer from the (filled) R states to the unoccupied states in the electrode. Since the unoccupied states in the electrode overlaps with (empty) O states, the reduction is forbidden. This mechanism can be further illustrated in Figure 1-8b and c by the notion of the radiationless electron transfer. The energy condition for radiationless electron transfer is, for significant rates of charge transfer to occur, energy levels at or near the Fermi level in the metal must be matched with suitable vacant (LUMO) or occupied (HOMO) orbitals in the reactant. Normally, an applied potential, V , is required to modify the electron work function Φ to some value $\Phi \pm eV$ to achieve the condition of balance, shown

in the bottom of Figure 1-8b, required for facile electron transfer to take place at the potential V . Figure 1-8c is a detailed schematic of when the electron finds its way to transfer from the surface of the electrode to the ionic energy level of a H_3O^+ ion through tunnelling effect across the ionic potential barrier.

Since this model in terms of overlapping state distributions is linked directly to the Marcus theory, many of its predictions are compatible with those of the previous thermodynamic explanations. The principal difference is that this model allows explicitly for contributions from states far from the Fermi level, which can be important in reactions at semiconductor electrodes or involve bound monolayers on metals, such as adsorbed species or thin layer coating of a redox active material.

Some important notes should be highlighted. Firstly, both thermodynamic method and electron states model consider just the charge transfer between the electrode and the redox couples in solution, adsorbed species or thin layer coating redox active materials during the faradaic process, rather than the electrode material itself. The standard equilibrium potential (E^0) of the redox couple and the Fermi level (or the equilibrium potential E_{eq}) of the electrode material are invariable during the faradaic charge transfer process.

Secondly, the charge transfer occurs between the highest occupied electronic states of the electrode material (e.g. the outermost fully delocalised electronic states on the metal electrode) and the discrete valence states of the reactants (e.g. molecular orbitals or ionic orbitals). Both aforementioned two aspects indicate that the charge transfer and the charge storage during the faradaic process can only occur at a specific potential or energy level at which the energy states on both electrode and reactants can match in energy. This results in the characteristic peak-shaped cyclic voltammogram for the Nernst equation governed faradaic process.

1.1.1.2 Electric double layer charge storage

As primarily reviewed, the mechanism of EDL capacitance is purely physical electrostatic attraction. The capacity can be dramatically boosted by the very large SSA of the electrode materials, excellent dielectric property of liquid electrolyte, high mobility of the counter charges (ions) in the liquid

electrolyte and fairly short separation distance between the counter charges at the electrode | electrolyte interface.

Traditionally, there are two types of conventional capacitors, both of which are composed of a positive electrode plate, a negative electrode plate and, between the two plates, a dielectric or ionic medium which must be non-conductive to electrons.

In the first type of capacitors, the medium is a dielectric material, e.g. mica, in which the dipoles can be polarised to accumulate electric charge (Q) at the interface between the electrode plate and the dielectric medium. In the second type of capacitors, the medium is a liquid or solid ionic conductor which is also often called electrolyte. In such a case, charge storage is achieved by the accumulation of positive ions (cations) at the interface between the negative electrode and the electrolyte, and negative ions (anions) of an equal amount of charge at the interface between the positive electrode and the electrolyte. Figure 1-9 illustrates these two typical capacitors [50].

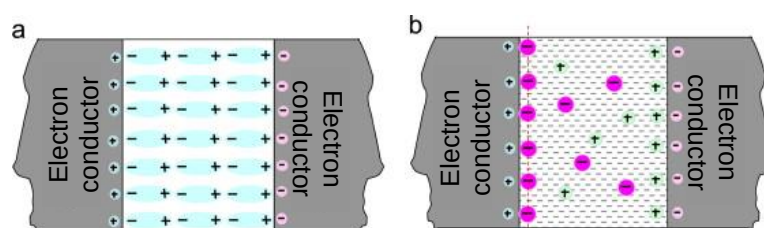


Figure 1-9. Charge storage in conventional capacitors, (a) a solid dielectric media where the non-mobile dipoles are alternatively arranged in terms of charge distribution, (b) a liquid or solid electrolyte with freely mobile ions in the bulk, but packed ions in the electrolyte side next to the electrode surfaces [50].

Both the dielectric and electrolytic media are insulating to electrons. However, freely movable ions in the electrolyte can pack on the surface of the electrode in the electrolytic capacitor with a higher density of accumulation in comparison with the unmovable dipoles in the dielectric capacitor. Thus, a much greater charge density can be achieved at the electrode | electrolyte interface than at the electrode | dielectric interface. This is the reason why the capacitance is often in the magnitude of mF for electrolyte capacitors, while in the magnitude of μ F for dielectric capacitors.

In the two types of capacitors just described, the amount of charge stored (Q) and the strength of the applied electric field or the voltage (U) between the two electrodes can be expressed by Equation 1-11

$$C = \frac{Q}{U} = \frac{\epsilon_0 \epsilon A}{d} \quad \text{Equation 1-11}$$

The charge (Q) stored in the capacitor equals to $C \times U$. Then differentiating Q with respect to time (t) results in Equation 1-12, with C considered as a constant, i.e. $\frac{dC}{dt} = 0$.

$$\frac{dQ}{dt} = C \frac{dU}{dt} + U \frac{dC}{dt} = C \frac{dU}{dt} \quad \text{Equation 1-12}$$

If linearly varied voltage, i.e. $U = U^0 \pm ut$, is applied, where U^0 is the starting voltage which may be zero, and u is the voltage or potential scan rate. Considering that $\frac{dQ}{dt} = i$ (current), Equation 1-12 can be further simplified to correlate the current with the scan rate.

$$i = Cu \quad \text{Equation 1-13}$$

Equation 1-13 shows that the current, i , charging into or discharging from a capacitor is proportional to the potential scanning rate, u , whilst independent of the applied potential, U , itself. In the case of potential cycling, the scan rate can be positive or negative for increasing or decreasing voltage respectively. That is to say, the current can also be positive or negative. That means a sudden reversion of voltage scan will result in a current jump from a positive value to a negative value. This feature gives a characteristic rectangular cyclic voltammogram (CV) at different voltage scan rates as shown in Figure 1-10a. This characteristic CV is an experimental criterion for qualitatively judging the capacitive behaviour of a device or electrode made from the synthesis of a pure or composite material of interest because it is highly distinguishable from the peak-shaped CV of the faradaic process as introduced in the last section.

On the other hand, if a constant current is applied to charge or discharge the capacitor, Equation 1-13 predicts a constant rate of voltage. Thus, a typical triangular curve of voltage against time is expected during a constant current

charging and discharging cycles as shown in Figure 1-10b. This graph of Figure 1-10b is so-called galvanostatic charging - discharging (GCD).

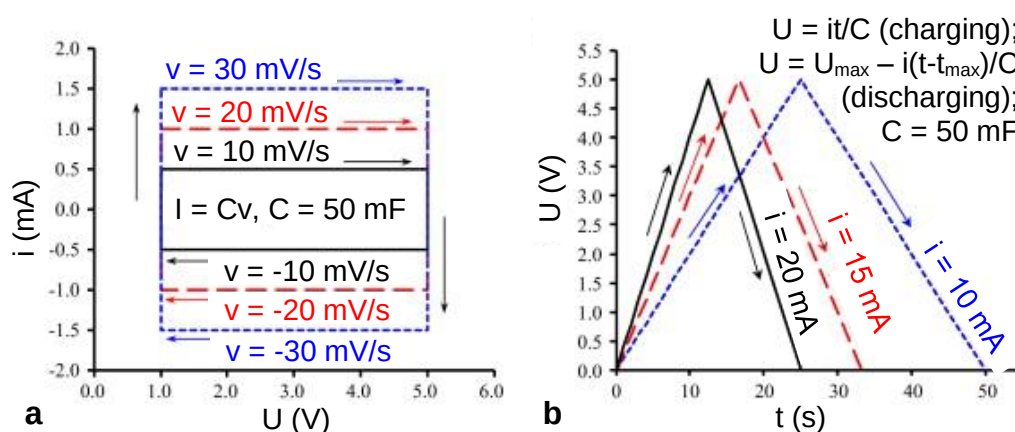


Figure 1-10. (a) CVs at indicated voltage scan rates, and (b) GCD plots at indicated constant currents as derived from Equation 1-13 for a 50 mF capacitor with $U_{\max}=5$ V. In the GCD plots in (b), $t_{\max}=U_{\max}C/i$ [50].

As can be seen that the structure and feature of the electric double layer (EDL) play a crucial role in deciding the performance of the electrochemical capacitor based on this type of energy storage mechanism.

In order to describe the EDL in detail, the simple Helmholtz double-layer model shown in Figure 1-5 can be illustrated by a more detailed schematic. Figure 1-11a shows a full picture of the EDL on a surface of a metal electrode. A simplified schematic is shown in Figure 1-11b.

Owing to the high density of free electrons in the metal (approximately 1 e/atom), any net charge density at the surface is strongly screened. This results in the gradient of electron density at a charged metal interface is highly constrained over a distance of only 0.05 to 0.2 nm in depth. Due to the extension of the wave function amplitudes outside the actual electrode surface plane, there is significant spill over of electron density into the double layer on the solution side of the interface [51,52], and this effect is potential dependent. The practical Helmholtz layer can be divided into an inner and outer layer. The inner Helmholtz layer (IHL) is mainly composed of the highly oriented solvent molecules, such as water molecules, and quite small amounts of specifically

adsorbed anions and other neutral molecules. The IHL is also known as the compact layer. The outer Helmholtz layer (OHL) consists of partially oriented solvent molecules, electrostatically adsorbed cations with its solvated shell. Outside of the outer Helmholtz layer, it is the diffuse layer with randomly distributed solute cations and anions because of the effects of thermal fluctuation according to the Boltzmann principle [6].

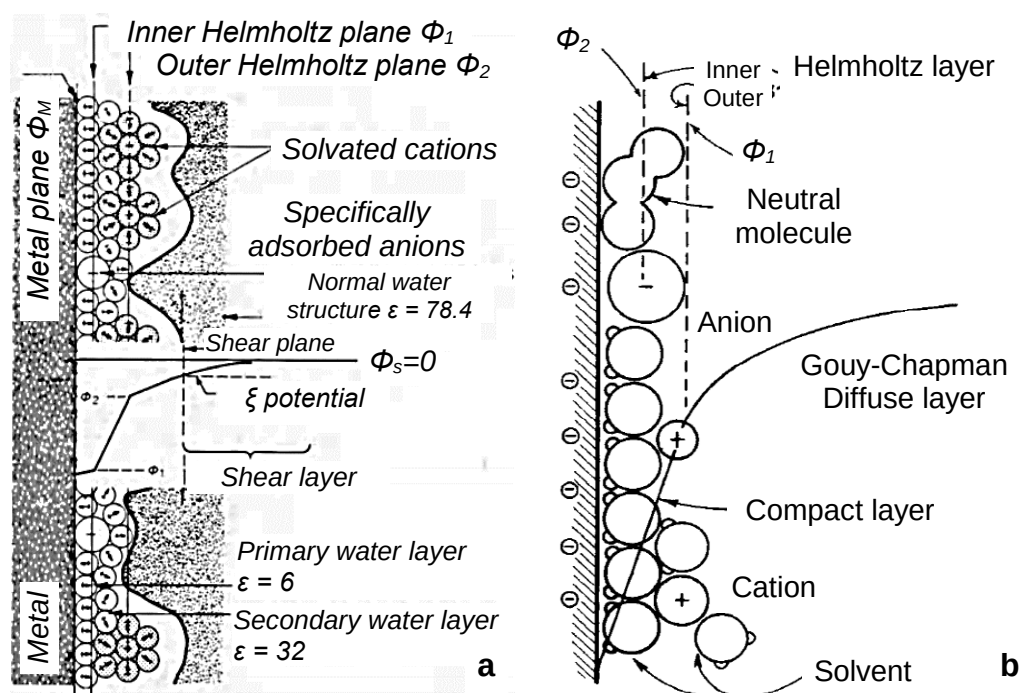


Figure 1-11. A detailed model of the double layer (a) [48] and a simplified schematic (b) [6]. Electrode electronic structure is ignored. Schematic potential change is superimposed, from the surface to the shear plane and through the shear layer to the bulk electrolyte.

If we use an electric circuit to express each component in the EDL a candidate sketched in Figure 1-12a can be a relatively complete representation. In the circuit, on the one hand, the EDL and the diffuse layer is delegated by Helmholtz capacitance (C_H or C_{EDL}) in series with a diffuse layer capacitance ($C_{Diffuse\ layer}$); on the other hand, R_M , R_s and $R_{Leakage}$ represent the resistance terms originated from the metal electrode, the solution and the leakage resistance of the EDL respectively. If the electrode is interfacing a concentrated or saturated solution the $C_{Diffuse\ layer}$ will be far larger than the C_H . Thus the total interfacial capacitance can be simplified by only considering the C_H because of

the relationship of $1/C_{\text{total}} = 1/C_H + 1/C_{\text{Diffuse layer}}$. If the R_M and R_S are combined to an equivalent series resistance (ESR), and the R_{Leakage} is further ignored the EDL circuit model can be further reduced into a simple R-C series circuit as shown in Figure 1-12b.

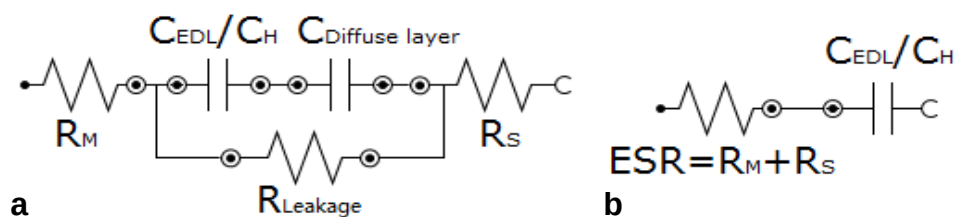


Figure 1-12. The equivalent circuits of EDL on the interfacial of metal and electrolyte. The full circuit (a), and a simplified circuit (b).

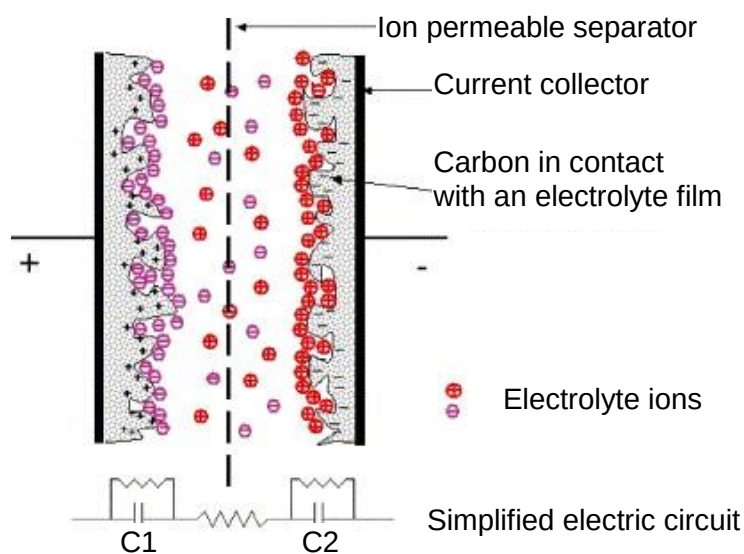


Figure 1-13. Representation of an electric double layer capacitor (charged state) [53].

In practical electrochemical capacitors which is based on the EDL charge storage mechanism, the electrode materials are usually porous, e.g. activated carbon (AC), with good conductivity and large SSA. Figure 1-13 shows a sketch of an EDL capacitor with porous electrodes. As can be seen, during the charging process the positive surface of the electric double layer capacitor (EDLC) is generally electro-neutralised by a net-negative charge contribution from the dissolved ions, and the opposite occurs at the negative electrode [53].

The electrolyte ions approach the electrode material but do not react with it, meaning no charge transfer between the polarised electrodes and electrolyte ions. The capacitance can generally be linked to the SSA of the electrode, the type of electrolyte and the effective thickness of the double layer, according to the Equation 1-11.

The first generation electrochemical capacitors use porous carbon materials with high SSA to achieve excellent electrostatic energy storage in the EDL. Thus the specific capacitance is improved by a factor of several orders of magnitude because of the very large SSA. Although porous carbonaceous materials have been used to fabricate commercial supercapacitors for a long time, some disadvantages such as high SSA of some carbons leading to reduced electronic conductivity, or high micro-porosity resulting in a reduction of mechanical strength, etc., affects their practical performance in devices. The other issue is that not all the internal surface area, such as those that makes up the walls of micro-pores, can be accessed by ions for charge storage. Thus, although their SSAs are typically 1000 to 3000 m²/g, the specific capacitance is normally smaller than 100 F/g [54].

On the other hand, finite charge distribution densities in the EDL, ca. 16 to 50 $\mu\text{C}/\text{cm}^2$, further restrict the capacity of charge storage. Taking an average charge density value of 30 $\mu\text{F}/\text{cm}^2$ or 30 $\mu\text{C}/\text{V}$ for example and considering an atom density of about 10^{15} per cm^2 at a smooth electrode surface, thus, only about $30/10^{15}$ μC of charge which is equal to $30 \times (10^{-6}/10^5) \times 6.02 \times 10^{23}/10^{15} \approx 0.2$ electrons/atom can be stored when the EDL is charged to 1.0 V of potential [6].

Below some key features of the EDL charge storage is summarised:

- No faradaic charge transfer occurs across the electrode;
- Characteristic rectangular or semi-rectangular CVs shows constant current response vs. linear potential sweep;
- The current response i_{EDLC} for a capacitive charge storage can only be proportional to u ;
- GCD plot has a characteristic linear charging/discharging feature with a constant slope vs. time;

Based on the current understanding of the EDLC, it has to be highlighted that the electronic structure of electrode materials, e.g metal, is totally neglected. Only a small portion of spill-out electron or excessive charge at the outmost surface of the electrode is considered. Most of the electrons in the metal are strongly screened from the excessive charges by the tremendous amounts of free and semi-free electrons in the bulk metal.

1.1.1.3 Pseudocapacitance - capacitive faradaic charge storage

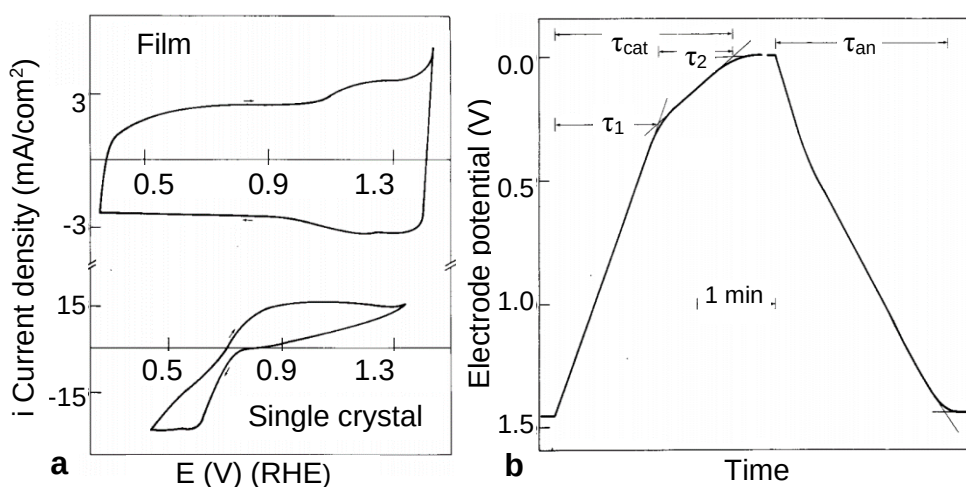


Figure 1-14. CVs for films and single crystals of RuO_2 in 1 M HClO_4 at 40 mV/s, and Cathodic and anodic charging curves [15], GCD showed upside down.

From the very beginning, people already realised that faradaic reactions must happen during the pseudocapacitive charge storage as promoted in the electrochemical reaction Equation 1-1. However, according to the review of Section 1.1.1.1 about the faradaic charge storage, it was well understood that the faradaic process on the electrode should be governed by the Nernst equation and should have characteristic peak-shaped CVs. The position of the peak potential is directly correlated with the equilibrium electrode potential of relevant redox couple, concentration and temperature, etc. Diffusion control shifts the anodic current peak more positively and the cathodic wave more negatively. The current response of a CV for a faradaic process on the electrode can be proportional to $\sqrt{u}$, or u , with, or without diffusion control respectively. While actually neither characteristic current peaks nor charging/discharging plateaus can be observed in the CV and GCD plot of the pseudocapacitive

electrode materials. Phenomenologically, just as reported in Ref. [15] (Figure 1-14a and b), it is almost impossible to distinguish the CVs and GCDs of pseudocapacitance from those behaviours originating from EDL capacitance.

As can be seen in Figure 1-14, the thermally decomposed RuO_2 film shows a typical semi-rectangular CV, while the CV of the single crystal RuO_2 is a characteristic redox process. Two well-defined regions (τ_1 and τ_2) can be identified in the GCD of RuO_2 films in Figure 1-14b.

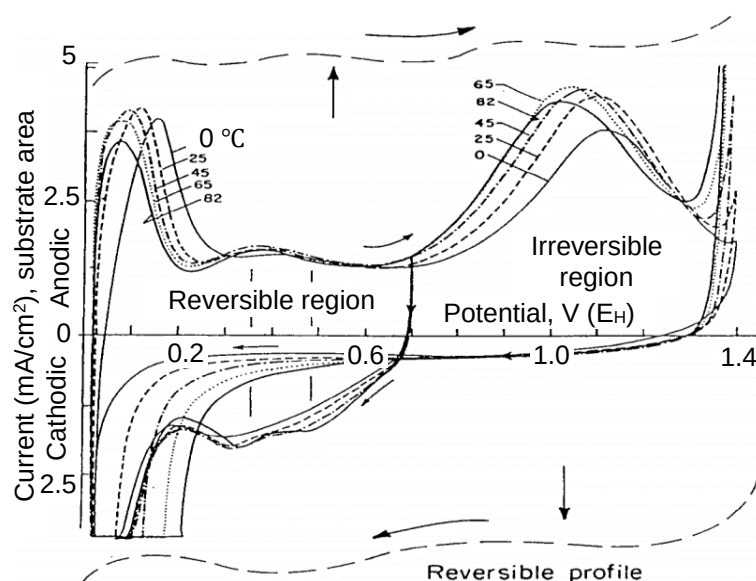


Figure 1-15. CVs for Ru metal in aqueous 1.0 M H_2SO_4 at 298 K showing behaviour of initial cycles where monolayer oxide formation and reduction [6].

In an earlier described investigation, pseudocapacitive behaviour was not observed in the initial cycles of the CV when only monolayer oxide forms on the Ru in an acidic electrolyte. In contrast, apparent faradaic current waves with reversible and irreversible regions were detected in several initial CVs as shown in Figure 1-15. Such a phenomenon was identified and extensively studied by B. E. Conway [6], and it was found that the oxidation of Ru, or in other words, the formation of the RuO_2 film, underwent a transformation from monolayer to multilayers.

In addition, good metallic conductance can be maintained even in RuO_2 during the oxidation of Ru. It was thought for a long time that the outstanding

capacitance performance in RuO₂ film originated from the EDL capacitance of the conductive RuO₂ film. If a simple calculation is done by using the usual value of area-specific EDL capacitance 20-50 $\mu\text{F}/\text{cm}^2$ and referring to the common SSA of RuO₂ film 40-300 m^2/g in Table 1-2, the possible capacitance contributed from the EDL can be estimated only ca. 8-150 F/g. However, as reviewed in Table 1-2, the minimum pseudocapacitance in the RuO₂ film is larger than 300 F/g. That is to say, more than 50% of the capacitance does not originate from the EDL.

In the carbonaceous electrode materials, such as activated carbon, the normal value of specific capacitance is lower than 100 F/g [6]. As reviewed in Table 1-2, however, some graphene oxides and doping derivatives give excellent capacitance performance at least 150% higher than the capacitance that should result from the EDL mechanism.

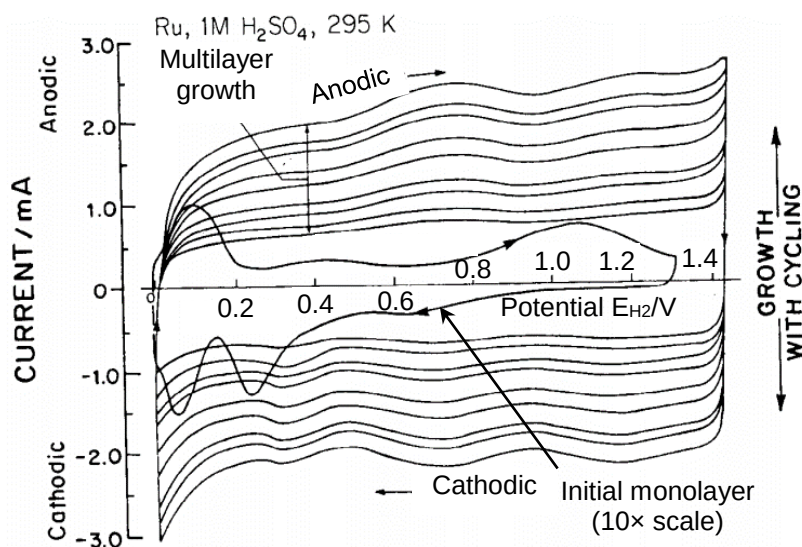


Figure 1-16. Progressive increase of oxide film growth potential cycling at Ru, exhibiting increase of capacitive reversible current response [6].

The earliest systematic investigation and explanation on the origin of pseudocapacitance in RuO₂ was illustrated extensively by Trasatti [15] and B. E. Conway's research groups [6]. The charging and discharging of Ru electrode in H₂SO₄ is one of the classic examples, which is attributed to a coupled electron-proton double-injection process [55,56]. A quasi-rectangular CV shown

in Figure 1-16 demonstrates the typical pseudocapacitive behaviour of RuO_2 , it has a capacitive potential range which extends to up to 1.4 V [15,57].

The unique quasi-metallic conductivity of RuO_2 [58] allows facile charge transfer into and through its matrix. Furthermore, the hydrous structure of RuO_2 allows facile proton transfer into and through the bulk. The wide capacitive potential window may originate from several overlapping redox processes within the potential range as sketched in Figure 1-17.

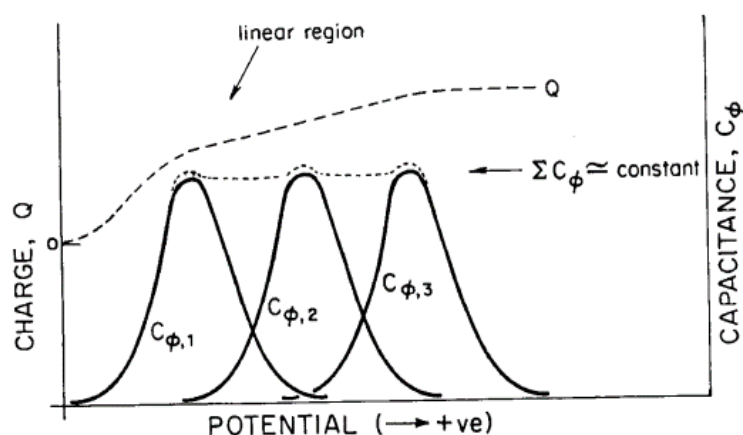
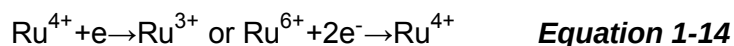


Figure 1-17. Illustrating overlap of three redox capacitance (C_ϕ) responses required to give almost constant net capacitance over an appreciable potential range, as observed with RuO_2 . Q is the accumulated charge (schematic) [6].

Three or more continuous and sequential redox steps can be recognised that involve oxidation states of Ru^{2+} , Ru^{3+} , Ru^{4+} , and probably also Ru^{6+} , such as the multiple steps of reduction processes



with



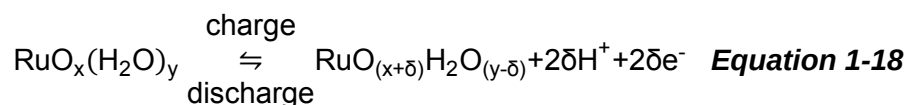
or further



with



The overall electrochemical reaction can be reorganised as follow:



Based on this multistep redox explanation, as illustrated in Figure 1-18b in Ref. [59], an almost constant pseudocapacitance can only be achieved when the reversible potentials for each redox couple are widely separated, and the saturation charge or the corresponding coverage (θ) of subsequent couple is greater than that of preceding one. However, if the maximum charge associated with the saturation coverage of θ_1 and θ_2 is the same, only a single capacitance peak is observed, no matter how wide the reversible potential of these species are separated as shown in Figure 1-18a [59].

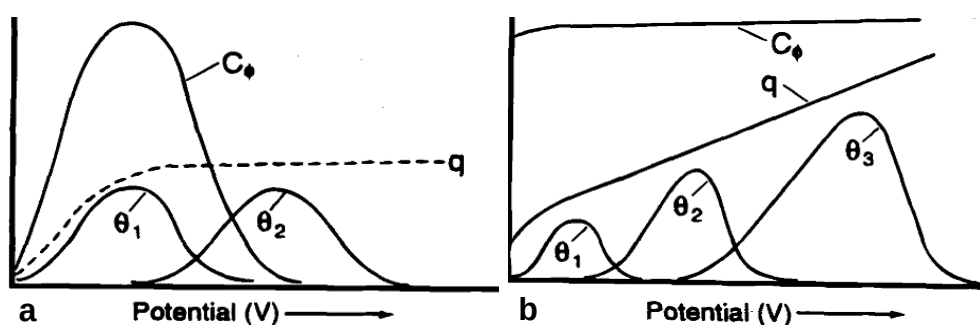
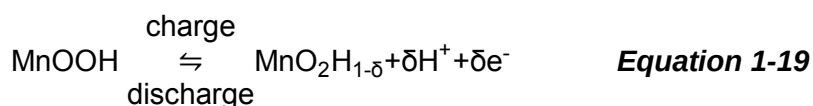


Figure 1-18. Coverage (θ), charge (q), and C_p variation when more than two adsorbed intermediates participate in the surface reactions [59].

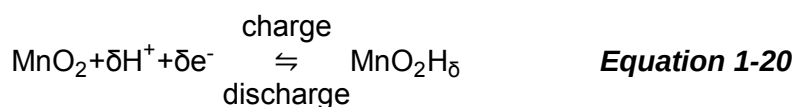
This argument, however, is still quite controversial, although this peak-like behaviour was also denoted by pseudocapacitance (C_p) in Ref. [59]. In addition, the above redox reactions experience an interaction effect between the Ru sites in various oxidation states, which displays the characteristic of spreading out the energies required for progressive oxidation of Ru species over a voltage range of 0-1.1 V or more. This type of effect involving charges in a redox system spreads across the redox potentials over a wide range of about 1.0 V is what results to the broad and quasi-rectangular CV for RuO_2 [6].

Pseudocapacitance later was also observed in many other TMOs, e.g. magnesium dioxides [16,17,60]. However, the charge storage mechanism in these TMOs is still under extensive study both theoretically and experimentally.

Inspired by the charging/discharging process of manganese dioxide in neutral electrolytes [61,62], Ref. [17] postulated that redox reactions occurring in MnO_2 thin-film involve proton 'intercalation' or insertion between the positive and negative electrodes as follows



in the positive electrode, and



in the negative electrode, and the overall

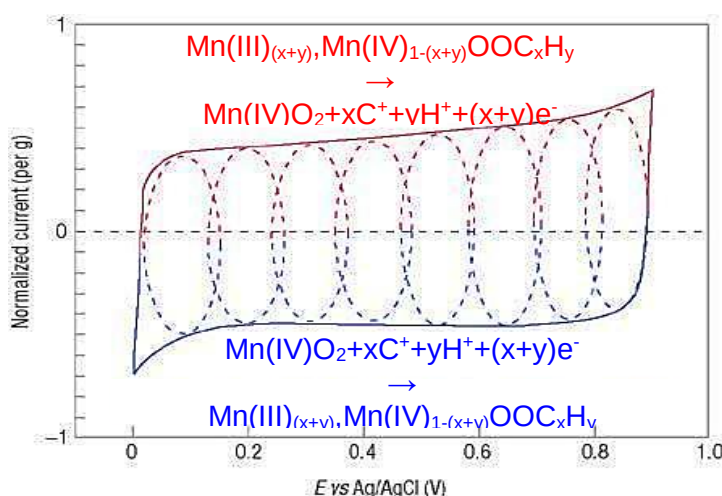
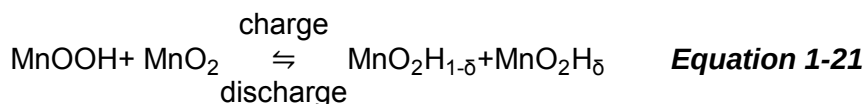


Figure 1-19. Schematic of cyclic voltammetry for a MnO_2 -electrode cell in a mild aqueous electrolyte (with cations C^+ (K^+ , Na^+ ...)) as well as proton incorporation) shows the successive multiple surface redox reactions leading to the pseudocapacitance. The red (upper) part is related to the oxidation from Mn(III) to Mn(IV) and the blue (lower) part refers to the reduction from Mn(IV) to Mn(III) [63].

This explanation based on the protons' insertion is very similar to the process which occurs in the RuO_2 film. Therefore, for a long time, the pseudocapacitive behaviour in MnO_2 was attributed to the successive multiple

surface redox reactions accompanying the intercalation of cations and protons [63], as illustrated in Figure 1-19. However, till now, there is no solid experimental evidence which shows that such successive multiple surface redox reactions can give rise to the semi-rectangular CVs.

Theoretical breakthroughs on the origin of rectangular CVs and their corresponding microscopic mechanisms were explored in Ref. [64] and [65] respectively. A linear dependence between the equilibrium potential (E_{eq}) of the redox reaction in the MnO_2 matrix and the local (i.e. at the solid-electrolyte interface) oxidation state was assumed. In other words, as the charge/discharge progresses the oxidation state of the MnO_2 matrix increases/decreases, resulting in a positive/negative movement of the E_{eq} , namely the equilibrium potential has the following dependency with the oxidation state (Os) of the electrode material

$$E_{eq} = a \times Os + b \quad \text{Equation 1-22}$$

This linear dependence of the E_{eq} of MnO_2 as a function of oxidation state has also been confirmed by some experimental observations made with in-situ X-ray absorption spectroscopy (XAS) [66-68]. With these the authors' deduced a formula for an ideal pseudocapacitance

$$C_P^{ideal} = \frac{F \cdot n_0}{a} = \frac{F \cdot n_0 (Os_{max} - Os_{min})}{U_{max} - U_{min}} \quad \text{Equation 1-23}$$

where n_0 is the total amount of Mn mole (per volume unit) in the solid available for the redox reaction; U_{max} the upper limit of the potential window and U_{min} the lower limit of the potential window. Os_{max} and Os_{min} are the corresponding maximum and minimum oxidation states. Obviously, the product $F \cdot n_0 \cdot (Os_{max} - Os_{min})$ is the maximum quantity of the available charge in the solid phase.

Furthermore, a transmission line model (TLM) was based on, and the finite element method was used to solve these sets of partial differential equations established under some hypotheses, which includes: homogeneous medium, potential independent C_{EDL} , isothermal system, unaffected by side reactions and uniform ionic concentration. Finally the author of Ref. [64] obtained a series of simulation results

which satisfactorily displays the characteristic semi-rectangular CV that was observed in the pseudocapacitive behaviour of MnO_2 species.

Ref. [65] proposed a possible theoretical explanation of the origin of pseudocapacitance in $\alpha\text{-MnO}_2$ -based electrode from the aspects of electronic structure and the special interstitial structures of the crystal lattice of $\alpha\text{-MnO}_2$. It proposed that the so-called ‘charge-switching states’ introduced by interstitial cations in the MnO_2 lattice play a critical role in allowing a moving equilibrium potential and extra charge storage states forming in the middle way of the energy gap. These mechanisms, as illustrated in Figure 1-20, work in unison to facilitate the charge storage in the $\alpha\text{-MnO}_2$ -based electrode.

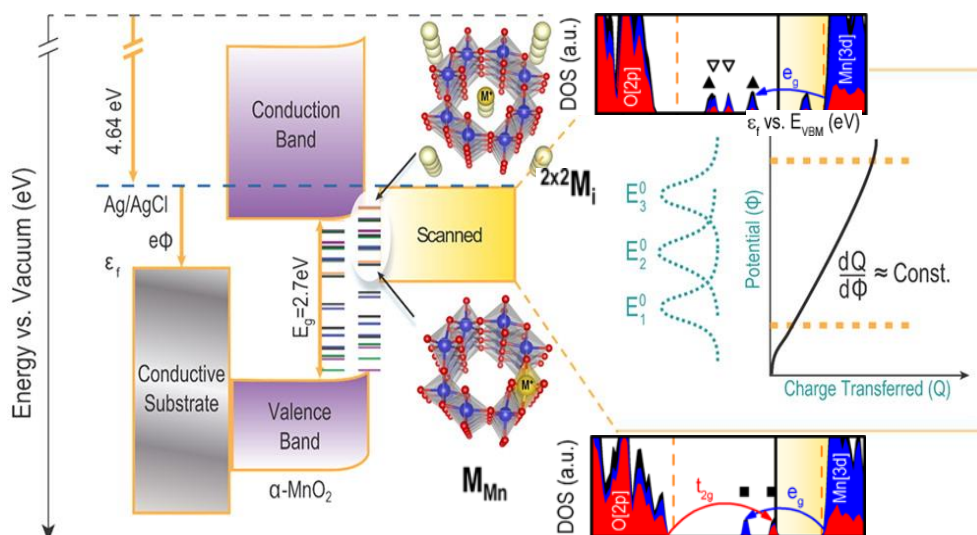


Figure 1-20. Band diagram (on the left hand side) and charge-switching alignment of an electrochemical supercapacitor electrode. In the middle, illustration of incorporated interstitial (top, $2 \times 2M_i$) and substitutional (bottom, M_{Mn}) cations M^+ that create charge-switching states in $\alpha\text{-MnO}_2$, and two diagrams of the projected density of states (PDOS) for the negatively charged interstitial proton defects are shown beside the corresponding interstitial structure and the dominant orbital character of the states is denoted by the coloured arrows in the PDOS. This Figure is modified from [65].

According to the theory proposed in Ref. [65], the $\alpha\text{-MnO}_2$ -based electrode is composed of an electrically conducting current collector, an electrochemically active electrode material ($\alpha\text{-MnO}_2$) with a bulk band gap (E_g), and an electrolyte with a known stability window. Electrochemically active materials ($\alpha\text{-MnO}_2$) possess many defect structures, such as the interstitial

defects. These defects with their own electronic energy levels within the band gap of the matrix material ($\alpha\text{-MnO}_2$) can undergo electrochemical reduction/oxidation, resulting in the gain or loss of electrons, hence storage or release of charge. The authors' termed these defect levels that lead to charge storage as 'charge-switching states'. The operating window is limited to the region of potentials where the electrode band gap and electrolyte stability window overlap. Charge-switching states at potentials (E_n^0) are broadened by interactions with their surroundings, resulting in a nearly linear relationship between potential and stored charge, hence a constant capacitance [65].

Pseudocapacitance in electrical conducting polymers (ECPs), such as polyaniline (PANI), polypyrrole (PPY) and polythiophene (PTP), was realised because of the possibility of introducing positive or negative charge centres on electronically conjugated polymer chains by means of electrochemical oxidation or reduction reactions, the extents of which depend on electrode potential. This aspect of charge storage has attracted substantial earlier and current interests as materials for supercapacitors [6]. ECPs got its name because of its unique 'metallic' conductivity. Polyacetylene, and the other three aromatic substances: polyaniline (PANI), polypyrrole (PPY) and polythiophene (PTP) all belong to this unique family and are characterised by a large degree of π -orbital conjugation that gives rise to their electronic conductivity. One of the important features of the conjugated structure is their ability to be electrochemically oxidised or reduced by withdrawal or injection of electrons, respectively, either directly at an anode or a cathode interface [69].

The electrochemical processes at the conducting polymers are electrochemical redox reactions associated with sequential Lewis acid- or Lewis base-producing steps so that the polymer molecules are converted to multiply charged structures through electrochemical Lewis-type reactions involving electron withdrawal or electron donation [6]. Thus ECPs can be positively (p-doped) or negatively (n-doped) charged with ion insertion on electronically conjugated polymer chains to balance the injected charge by means of electrochemical oxidation or reduction reactions. This is a typical faradaic process that gives the capacitive behaviour in ECPs, i.e. pseudocapacitance.

Figure 1-21 presents the charge-discharge or p-/n-type doping and energy storage mechanism of this kind of pseudocapacitive electrode material.

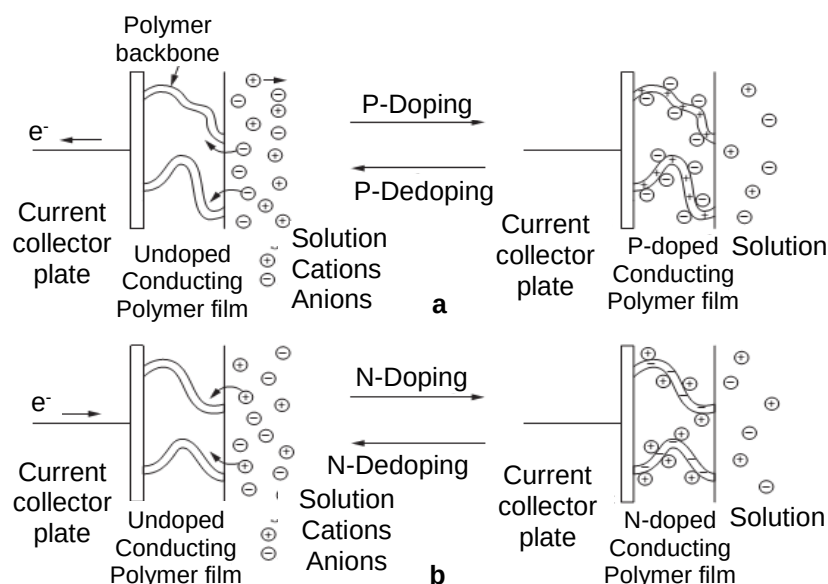


Figure 1-21. Doping/dedoping redox mechanism of the pseudocapacitance in ECPs [18]

Based on the vast experimental and theoretical findings with regards to the pseudocapacitive mechanisms in RuO_2 , MnO_2 and ECPs, Conway [6] proposed several faradaic mechanisms that may result in capacitive electrochemical charge storage. These mechanism, as collected in Figure 1-22, include:

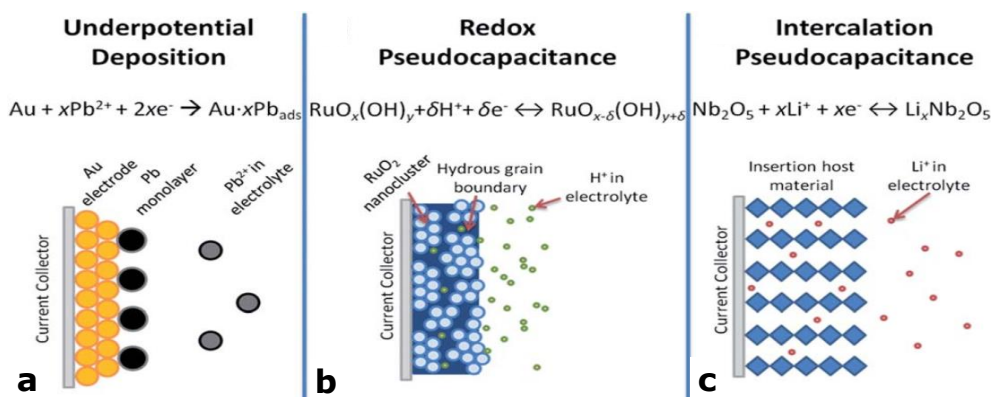


Figure 1-22. Three proposed pseudocapacitance mechanisms based on reversible redox [70].

- (1) Underpotential deposition (UPD);
- (2) Redox pseudocapacitance (as in $\text{RuO}_2 \cdot n\text{H}_2\text{O}$), and
- (3) Intercalation pseudocapacitance.

In spite of these fruitful achievements on the explanation of pseudocapacitance, a very recent theoretical analysis [32] with detailed mathematical deduction and experimental investigation directly questioned the existence of pseudocapacitance in electrode materials. It was pointed out that, as long as the calculation of current to potential (i/E) response is based on the Nernst equation, there will be no chance to obtain a rectangular or even semi-rectangular CVs that is a distinguishable characteristic of capacitive charge storage. This report claims that, even if the linear dependency between the equilibrium potential and the oxidation state of the electrode material is considered, what can be observed would be a broadening of the current wave with the characteristic exponential increase at the foot of the wave, and as is well known, this is different from a typical capacitor charging profile. Therefore, a qualitative representation of the pseudocapacitance was proposed in this publication, which believed that the so-called pseudocapacitance is only a simple addition between the EDLC and broadening peaks originating from surface faradaic reactions. Figure 1-23 suggests the possible means through which the two contributions can be coupled with each other.

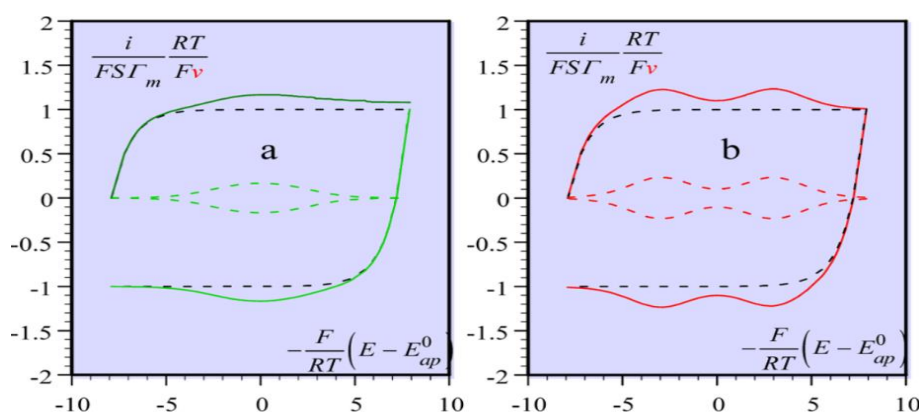


Figure 1-23. Examples of current-potential CV responses mixing double layer charging and surface faradaic processes. (a) Single faradaic surface reaction. (b) Two successive faradaic surface reactions [32].

So far, according to the above literature review, it can be seen that there are still some irreconcilable contradictions existing in the explanation of pseudocapacitance by simply combining the classic faradaic process governed by Nernst equation with the EDL mechanism.

Although the qualitative explanation was proposed in [71] and [60] through a use of the band theory of semiconductors as described briefly in Figure 1-24 [7]. Unfortunately, the real mechanism of electrochemical charge storage in these pseudocapacitive materials is still not well-understood generally.

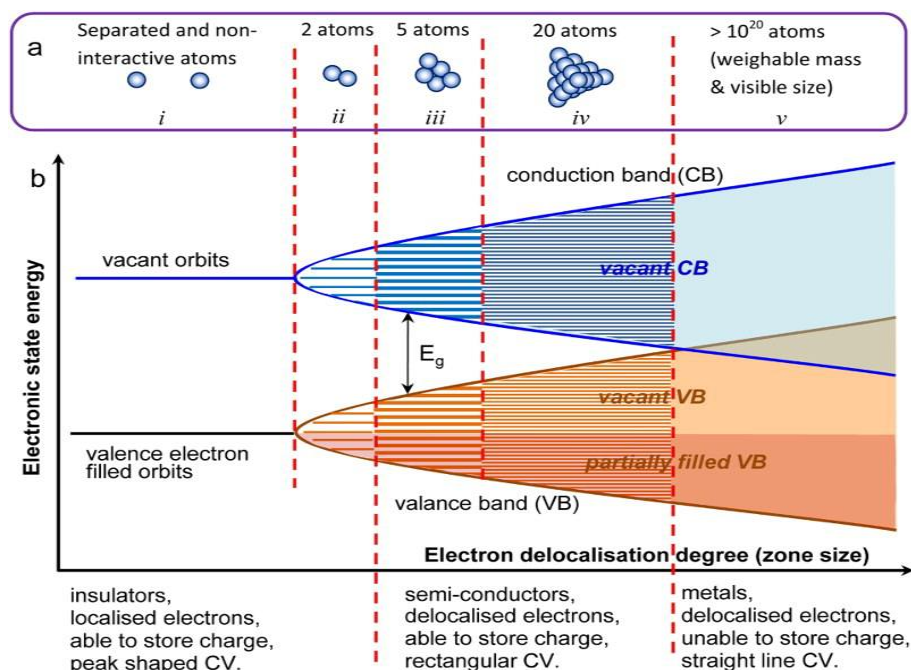


Figure 1-24. Schematic illustrations of the band model for chemical bonding [7] (a) between metal atoms that are (i) separated and non-interactive, and (ii – v) forming clusters of (ii) 2, (iii) 5, (iv) 20 and (v) 10²⁰ atoms, and (b) the corresponding energy levels of the valence electrons as a function of the degree (or zone size) of delocalisation of valence electrons in the cluster of metal atoms.

According to this theory, electron injection to (or removal from) an electrode may occur in electronically interactive or separated redox active sites, very much depending on the conductivity of the material. Well separated (or isolated) sites should have equal or fairly close energy states, and hence accept (or donate) electrons at potentials very close to each other, leading to the peak-

shaped CV in a very narrow potential range. However, if these redox active sites can interact with each other due to either short separations or good electronic conductivity or both, their energy states can merge into a broad band with negligibly small differences between the neighbouring states. Such a situation corresponds to the conduction band in semiconductors, and is also comparable to the electron delocalisation in conjugated chemical bonds, such as in ECPs, resulting from overlapping electron orbits between neighbouring atoms.

As a result, electron transfer into (or from) each energy state in this broad band becomes continuous over a wide range of potentials, which might be responsible for the constant current flow and hence the rectangular CV [50]. Furthermore, these unique semiconductor energy band structures and delocalised electrons hold big possibility on deciding the capability of charge storage in this type of material by contributing to pseudocapacitance which originates from some special charge storage mechanisms such as additional sub-energy levels or charge transfer states. To our best knowledge, this theory is the first trial, and it is also part of the inspiration of this thesis; which aims to study pseudocapacitance from the viewpoint of electronic structure and the energy band structure of electrode material itself.

Some key features of pseudocapacitive behaviour are summarised below:

- Partially reversible faradaic charge transfer happens in the electrode material;
- Typical rectangular or semi-rectangular CVs shows nearly constant current response vs. potential variation;
- The current response i_P of a capacitive charge storage process can only be proportional to u , i.e.

$$i_P = C_P \times u \quad \textbf{Equation 1-24}$$

where, C_P is pseudocapacitance, u is the scan rate during the cyclic voltammetry;

- GCD has typical linear charging/discharging feature with constant slope;

1.1.2 Carbon nanomaterials

1.1.2.1 Carbon nanotubes (CNTs)

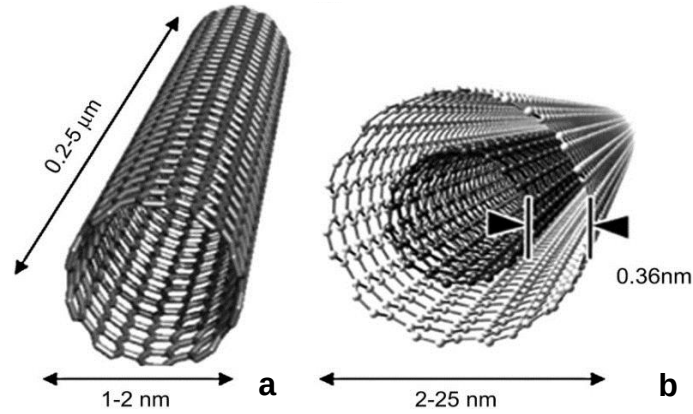


Figure 1-25. Geometry structure of SWNT (a) and MWNT (b) [72].

So far, researchers have synthesised two main types of CNTs, these includes single-wall CNTs (SWNTs) which is the simplest structure, and multi-walled CNTs (MWNTs) [72]. The diameter of most SWNTs is about 1 to 2 nm, and the length of individual tube can be millions of times longer than the diameter as shown in Figure 1-25a and b.

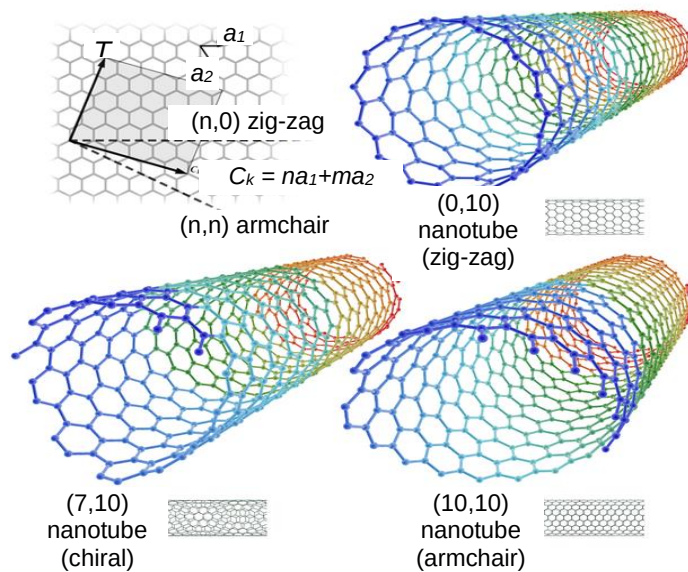


Figure 1-26. Wrapping direction of graphene layer and SWNT geometrical indices (n, m) [73].

Conceptually, it is possible to wrap up a single layer of graphene into a seamless cylinder to obtain the special structure of SWNTs. The wrapping direction of graphene layer can be represented by a couple of integers (n, m). The integer n and m represent the number of unit vectors a_1 and a_2 along two directions in the honeycomb net lattice of graphene as shown in the following Figure 1-26.

For example, when m equals to 0, zigzag nanotubes can be wrapped up along the horizontal direction in Figure 1-26, and armchair nanotubes can be built up as n equals to m. Otherwise, chiral structured nanotubes are formed with a different value of n and m. Equation 1-25 can be used to calculate the diameter, d , in pm, of an ideal nanotube if its (n, m) indices are known [74].

$$d = \frac{a}{\pi} \sqrt{(n^2 + nm + m^2)} = 78.3 \sqrt{((n+m)^2 - nm)} \quad \text{Equation 1-25}$$

where $a = 0.246$ nm.

MWNTs are constructed by several rolled planes of graphene with a concentric tube configuration. Two structural configuration models can be utilised to describe the geometry of MWNTs. The first is “Russian Doll model”, in which single wall carbon nanotubes with different diameters are arranged concentrically, for instance, a SWNT of (0, 8) is inserted into another larger SWNT of (0, 17). The second is “Parchment model”, wherein one layer of graphene is rolled in around itself, similar to a rolled newspaper or a scroll of parchment. An interlayer distance of about 3.4 Å has been calculated for MWNTs which is close to the width between two layers in the ideal crystalline graphite. In practice, the earlier structural model i.e. “Russian Doll model” is usually observed [74].

Ideal CNTs have very excellent mechanical properties, such as the highest longitudinal elastic modulus and tensile strength, making them one of the stiffest known materials. It has been ascertained that the sp^2 covalent bonds of carbon atoms in the structure is responsible for this outstanding strength of the tiny tubes. A very high tensile strength of 63 GPa, close to 9.1×10^6 psi, has been recorded in a MWNT [75]. Individual CNT tested in investigations

conducted in 2008, has a strength of nearly 100 GPa (1.5×10^7 psi), this result was consistent with quantum/atomistic predictions [76]. In comparison with the specific strength of high-carbon steel (154 kN·m/kg), CNTs displays a high specific strength of up to 4.8×10^5 kN·m/kg, which is impressive considering that it has a low density of 1.3 - 1.4 g/cm³ in the solid state [77].

Very good thermal conductivity is displayed by all CNTs because of the excellent "ballistic conduction" along the tube, however, this property is not exhibited in the direction along the radius of the tube. Under ambient temperature, copper which is well-known as a good thermal conductor has a thermal conductivity of 385 W/m·K, impressively, SWNT displays an excellent thermal conductivity of ca. 3500 W/m·K along its tube, which is almost 10 times in comparison with copper [78]. However, the thermal conductivity along the radial direction of SWNT is only 1.52 W/m·K [79]. As was estimated in [80], carbon nanotubes can exist stably up to 2800 °C in a vacuum and ca. 750 °C in the atmosphere.

Carbon nanotubes display significant optical properties, and these properties can in turn be used to routinely quantify its quality [81]. So far, besides the common optical absorption between 0-5 eV [82], photoluminescence [83], electroluminescence [84], Raman [85] and Anti-Stokes scattering [86] have all been observed in CNTs. Some of these scattering properties, such as those observed from Raman or XPS, are of particular interest because of the significant role they play in the detailed characterisation of CNTs.

Table 1-3. Main Raman vibration modes of CNTs

Terms	Range	Origin	Relationship	Ref.
Radial breathing mode (RBM)	100-350 cm ⁻¹	radial expansion-contraction of the tube	$\omega(\text{RBM}) = A/d + B$ d: nanotube diameter; A and B: environmental constants	[85,86]
Bundling mode	strongly depending on	collective vibration in a	/	[87]

	the excitation energy	bundle of single tubes		
G mode	1580 cm ⁻¹ and split into several peaks	planar vibrations of carbon atoms	depend on the tube structure and excitation energy	[88]
D mode	between 1300 and 1350 cm ⁻¹	structural defects	conventionally used to quantify the structural quality of carbon nanotubes	[88]
G' mode	depends on the diameter of nanotubes	the overtone of the defect-induced D mode	can be used roughly to estimate the SWCNT diameter	[88]

As has been described from various findings, bundling and other interactions between CNTs widen the detectable optical peaks. This strongly affects the photoluminescence spectra but has a much weaker effect on the optical absorption and Raman spectra. However, since SWNTs displays good sensitivity and spatial resolution (ca. 0.5 μm) of Raman maps, only minimal sample is required to obtain most of the desired characteristics. Therefore Raman scattering behaviour of CNTs is an effective and probably the most popular technique used for its characterisation. In general, the resonant type is the predominant feature of Raman scattering of SWCNTs, this occurs when the tubes have one of the bandgap that equals the energy of the laser used to create the excitation [85,86]. It is important to note that the Raman spectrum can be used to identify both semiconducting and metallic tubes, however, it is less sensitive to nanotube bundling compared to photoluminescence. The Raman spectrum of SWCNT displays several scattering modes as summarised in Table 1-3.

With regards to its electrical performance, CNTs have structure-dependent electrical properties which is determined by the symmetrical honeycomb carbon net and special electronic structure. For instance, a (n, m) nanotube whose $n = m$ behaves metallically; whilst a nanotube with $|n - m| = 3k$, where k is an integer, is a narrow band gap semiconductor or displays a

moderate semiconducting characteristic. This means that, all armchair nanotubes with $n = m$ indices are metallic, and nanotubes with indices of (6, 4), (9, 1), etc. display semiconducting behaviour, this is illustrated in Figure 1-26 [89].

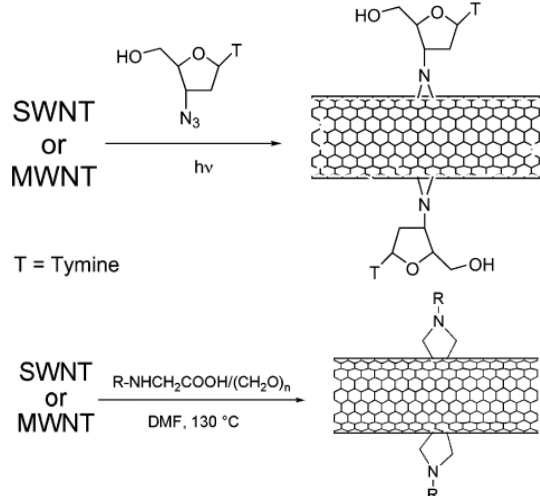
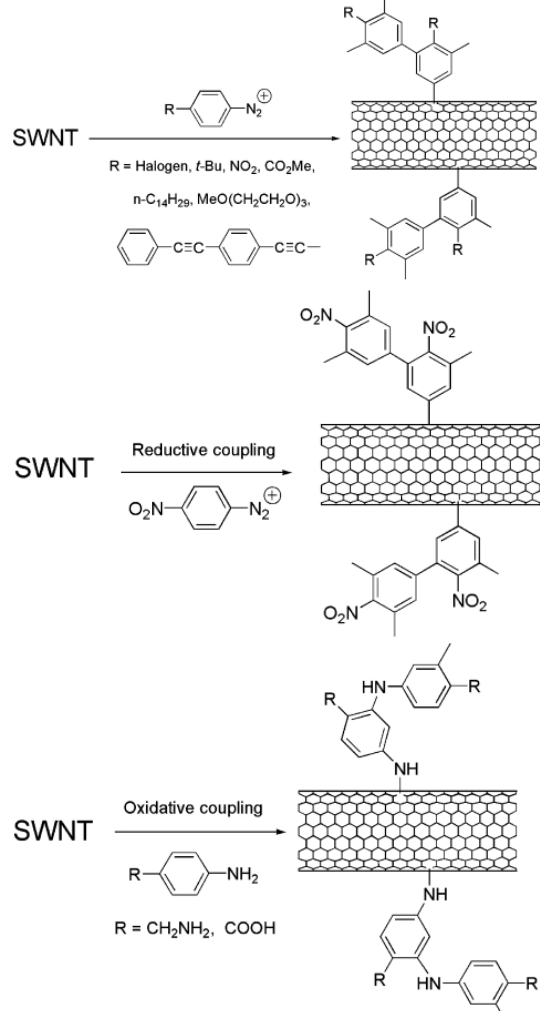
As a type of special quasi one-dimensional structure, CNTs participate in plenty of chemical reactions which results in different degrees of modification or functionalisation [90].

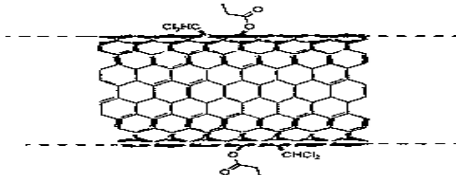
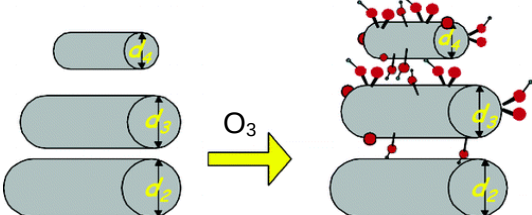
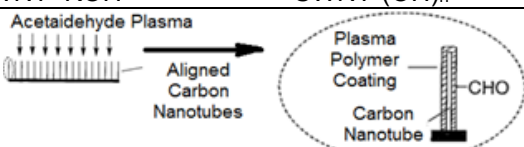
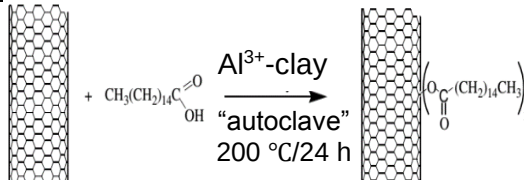
The main methods through which CNTs can be chemically functionalised can be summarised into three categories:

- (1) Reactions between the π -conjugated skeleton of CNTs and chemical group forming a covalent attachment, this is summarised in Table 1-4;
- (2) Non-covalent interactions, such as adsorption or wrapping, between CNTs and other functional molecules;
- (3) The endohedral filling of the inner empty space of CNTs.

Table 1-4. Main covalent reactions of CNTs

Items	Reaction scheme	Refs.
Sidewall halogenation	SWNT or MWNT $\xrightarrow{F_2, 25-600\text{ }^\circ\text{C}}$ Fluorinated nanotube Side reaction: NH_2NH_2 in $i\text{-PrOH}$ $\rightarrow$ Fluorinated nanotube	[90] [91] [92]
Hydrogenation	$C_{11}H$. Detailed bonding nature of hydrogen and the local configuration of the C-H bonds formed need further structural studies.	[93]
Cycloadditions	SWNT or MWNT $\xrightarrow{\text{PhHgCCl}_2\text{Br/toluene or CHCl}_3/\text{NaOH}}$ Dichloride adduct SWNT $\xrightarrow[\text{b}]{\text{ROOC-N}_3, \Delta}$ Azide adduct	[94] [95] [96] [97] [98]

	 SWNT or MWNT $\xrightarrow{h\nu}$ [Structure] T = Tyminyl SWNT or MWNT $\xrightarrow[\text{DMF, 130 } ^\circ\text{C}]{\text{R-NHCH}_2\text{COOH}/(\text{CH}_2\text{O})_n}$ [Structure]	
Radical additions	 SWNT $\xrightarrow{\text{R-C}_6\text{H}_4\text{-N}_2^+}$ [Structure] R = Halogen, <i>t</i>-Bu, NO₂, CO₂Me, <i>n</i>-C₁₄H₂₉, MeO(CH₂CH₂O)₃, $\text{C}_6\text{H}_5\text{-C}\equiv\text{C-C}_6\text{H}_5\text{-C}\equiv\text{C-}$ SWNT $\xrightarrow[\text{O}_2\text{N-C}_6\text{H}_4\text{-N}_2^+]{\text{Reductive coupling}}$ [Structure] SWNT $\xrightarrow[\text{R-C}_6\text{H}_4\text{-NH}_2]{\text{Oxidative coupling}}$ [Structure] R = CH₂NH₂, COOH	[99] [100] [101] [102] [103] [104] [105]

Electrophilic additions		[106]
Addition of inorganic compounds	$\text{NT(nanotube)} + \text{OsO}_4 \rightarrow [\text{NTOsO}_4] \rightarrow \text{NT} + \text{OsO}_4^-$	[107]
Ozonolysis	Diameter selectivity in the ozonation of SWNTs 	[108] [109]
Mechanochemical functionalisations	Ball-milling $\text{MWNT} \xrightarrow{\text{Reactive atmospheres}}$ Functional MWNT with groups like amines, amide, thiols and mercaptans SWNT+KOH $\xrightarrow{\text{solid-phase milling}}$ SWNT-(OH)_n	[110] [111]
Plasma activation		[112]
Nucleophilic additions		[113]
Grafting of polymers	$\left[\begin{array}{c} \text{CH}_2\text{CH} \\ \\ \text{Ph} \end{array} \right]_n \text{CH}_2\text{CH}(\text{N}_3) \xrightarrow[\text{o-DCB, } \Delta]{\text{SWNT}} \left[\begin{array}{c} \text{CH}_2\text{CH} \\ \\ \text{Ph} \end{array} \right]_n \text{CH}_2\text{CH}(\text{N}-\text{CNT})$ $\text{SWNT} + \text{CH}_2=\text{C}(\text{SO}_3\text{Na})-\text{C}_6\text{H}_4-\text{CH}=\text{CH}_2 \xrightarrow[\text{H}_2\text{O, } \Delta]{\text{K}_2\text{S}_2\text{O}_8} \left[\text{CH}_2\text{CH}(\text{C}_6\text{H}_4\text{SO}_3\text{Na})-\text{CH}_2\text{CH}(\text{C}_6\text{H}_4\text{SO}_3\text{Na}) \right]_n$	[114] [115]

The unique tubular structure of CNT endows it with a unique physical symmetry, and this is the basis for its peculiar electronic structure, which

strongly affects its displayed electrical properties. Geometrically, CNT can be thought of as a closed cylinder wrapped up by single or few layers of graphene. Therefore, the 1-dimensional energy band structure for a nanotube can be obtained by using the 2-dimensional energy band structure of graphene. Take armchair nanotube, with a (n, n) structural parameter, as an example; there are $4n$ rather than $2n$ valence electrons that belong to its 1-dimensional unit-cell because $2n$ graphene unit-cells are cast into one unit-cell, where n refers to the integer of wrapping indices. There are only 2π -electrons in one graphene unit cell. Furthermore, because of special selection rules, the transportation of electrons in CNTs is an inter-band transitional process [116]. This kind of scattering process allows electrons to move without a change in their direction of motion, namely (constant) velocity, which means that no additional electrical resistance is introduced. This is the reason for the large mean free path of armchair CNTs.

The periodic boundary condition of CNTs is equivalent to a situation in which the graphene layer is rolled into a seamless tube. Hence, quasi-1-dimensional electronic states are quantised in different wrapping directions but remains unconstrained in the direction along the tube. Thus, one can use a series of parallel lines intersected in the 2-dimensional Brillouin zone of graphene to “map” the sub-bands in various angles in reciprocal space [117].

Two distinct cases of electronic structure for nanotubes $(5, 5)$ and $(7, 3)$ are shown in Figure 1-27.

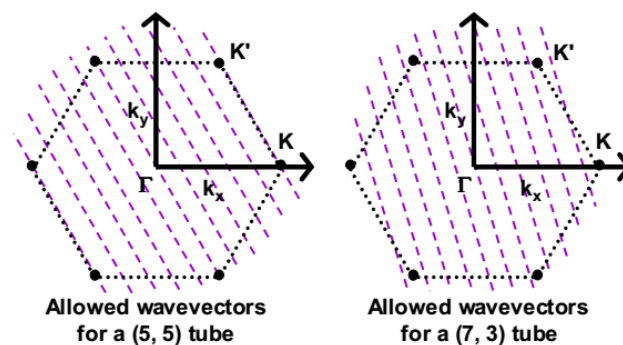


Figure 1-27. Allowed electronic states (dashed lines) of two different nanotubes, superimposed upon the graphene Brillouin zone to illustrate the two distinct types of electronic behaviours [117].

CNTs will have metallic behaviour if a Fermi K point is an allowed state because the conduction and valence bands will link to each other at the K point. Otherwise, the CNTs will display semiconducting property with a tiny energy gap between the conduction and valence bands. Thus the chiral structure indices (n, m) can be utilised to predict the characteristic of any tube. Two typical energy band structure and the density of states for metallic and semiconducting SWCNTs are shown in Figure 1-28.

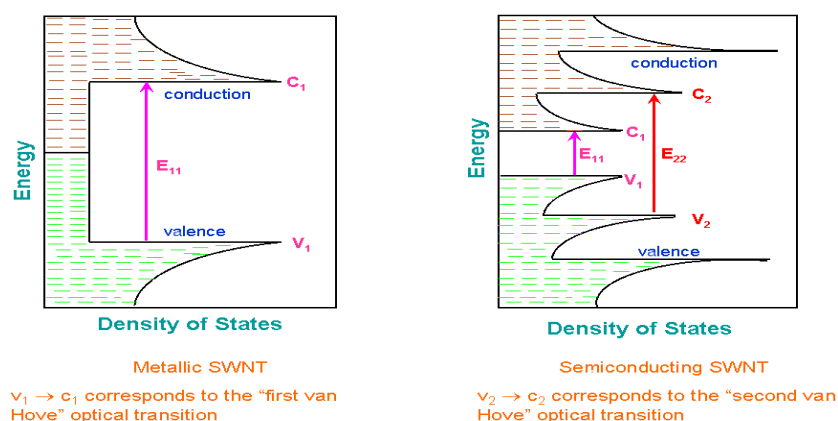


Figure 1-28. Typical energy band structure and densities of states as a function of energy for metallic and semiconducting single-wall carbon nanotubes (SWCNTs) [116].

1.1.2.2 Graphene and its derivatives

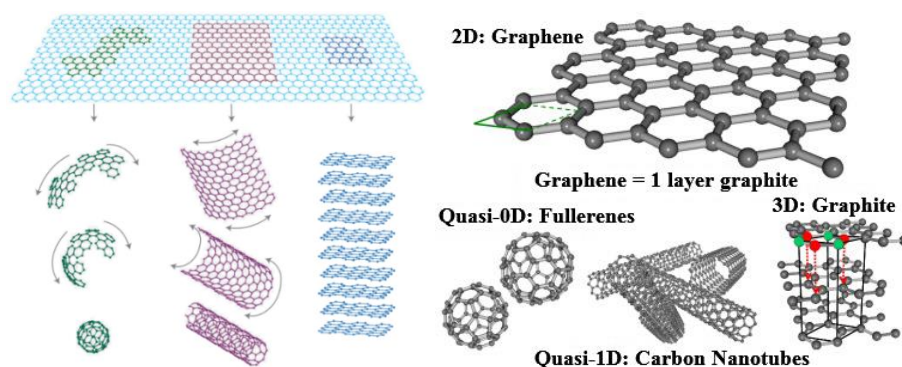


Figure 1-29. The structure of graphene and geometric relation with other carbon species from 0D (buck balls) to 1D (nanotube) to 3D (graphite) [118,119].

As a single-atom-thick layer with only sp^2 -bonded carbon atoms, graphene is densely packed in a two-dimensional (2D) honeycomb crystal lattice. The nearest-neighbour atomic distance in graphene is 1.42 Å. Almost all

structures in the carbon family can be constructed by graphene, such as zero-dimensional (0D) fullerenes, one-dimensional (1D) CNTs and three-dimensional (3D) bulk graphite. Figure 1-29 shows relevant conformational operations of graphene structures and some allotropes of carbon.

The stability of graphene results from very strong carbon-carbon bonds formed by the sp^2 hybridised orbital and its special periodic hex-ring net. The carbon to carbon σ -bond is constituted by the combination of orbitals p_x and p_y . There are one π -bond and three σ -bonds in the unit cell of a graphene lattice. The π -bond is made up of free p_z electrons shared by the neighbouring carbon atoms, i.e. electron delocalisation, which is critical to the half-filled energy band that allows fast-moving electrons and holes [120].

The unique 2D atomic crystal lattice structure coupled with its ultrathin laminar feature endows graphene with numerous attractive properties, such as extremely high mechanical strength, ultrahigh thermal conductivity, very good optical transparency, and impressive carrier mobility, making it an excellent material for mechanics, heat transport, electronics, optoelectronics, etc. [121].

Relating to the mechanical strength of graphene, a ca. ten times higher specific penetration energy than that of macroscopic steel sheet was found in Ref. [122] by shooting the multilayer graphene sample with 3.7 μm silica sphere bullets. Although this incredible strength is definitely a strict function of the quality of the sample, nevertheless, graphene powders with very tiny lateral width can still display good mechanical properties, as such they could be combined with other materials to prepare composites which display improved durability and service performance [123].

On the thermal behaviour, graphene has a very excellent thermal conductivity of nearly 5300 W/m·K which originates from its special π -conjugation electronic structure [121]. This advantage, again, holds a significant potential for applications in electronic devices with self-cooling ability.

The optical transparency of graphene is one of its most attractive properties, if this is combined with its excellent electrical conductivity, graphene could be considered as the next generation transparent electrodes. Although this aspect is not the main concern of the present study, the properties of

graphene obtained from spectroscopic techniques such as Raman, UV-Vis and XP are very useful in characterising graphene and its derivatives, hence these properties are further reviewed.

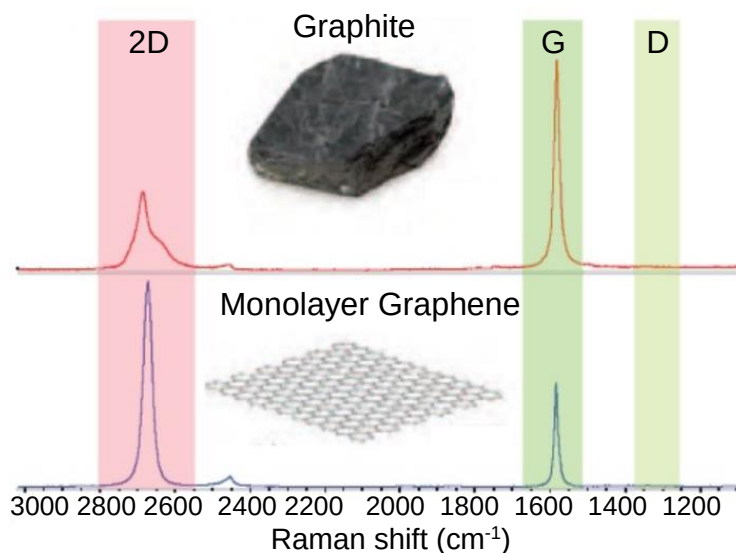


Figure 1-30. Typical Raman spectra of monolayer graphene and graphite, collected with 532 nm excitation [124].

The Raman scattering behaviour of graphene is fairly similar to that of graphite because of the same sp^2 atomic bonding and layer like lattice. However, the subtle structural differences, such as numbers of the layer and the manner of stacking, gives graphene a distinct Raman spectrum. Hence numerous studies are utilising Raman maps as a powerful tool to investigate graphene. Typical Raman spectra of a monolayer graphene and graphite are shown in Figure 1-30.

The origin and applications of the main peaks and bands of the Raman spectra of graphene are summarised in Table 1-5. A large amount of significant information in terms of structure and defects can be obtained from the subtle differences in the spectrum. More details on Raman scattering technology will be given in the methodology section.

Table 1-5. Principal Raman bands of graphene [124]

Terms	Position & Range	Origination	Applications
D band	between 1250 and 1400 cm^{-1}	Ring breathing mode from carbon rings and structural defects	Conventionally used to quantify the structural quality of graphene. Only defected materials have a significant D band
G band	Sharp symmetrical around 1580 cm^{-1}	In-plane vibrational mode of sp^2 carbon atoms	To determine the layer thickness as its position is highly sensitive to the number of layers present in the sample.
D' band	Always as a weak peak or shoulder beside G band ca. 1620 cm^{-1}	Defects and/or edge related vibration	Can be used to determine the degree of defects.
2D band (G' band)	between 2550 and 2800 cm^{-1}	the overtone of the defect-induced D mode	To be effective in differentiating the layer thickness between single and multilayer graphene of less than four layers.

Owing to the unusual electron delocalisation and periodic six-atomic carbon structure, pure graphene displays excellent electronic performances, for instance, tests have shown that the highest electrical conductivity resulting from electron mobility is above $1.5 \times 10^4 \text{ cm}^2/\text{V}\cdot\text{s}$. Theoretically, this carrier mobility can be up to $2 \times 10^5 \text{ cm}^2/\text{V}\cdot\text{s}$. This means that charge carriers i.e. electrons and holes, can travel sub-micrometre distances without any scattering, this phenomenon which is known as ballistic transport is the reason why graphene is a marvellous electrical conductor.

Some important physical properties are collected and listed in Table 1-6. The impressive values of these properties has the potential for revolutionary technological applications, such as: advanced optical electronic devices, high-performing photo-voltaic solar cells, high-powered batteries and novel energy storage technologies [125].

Table 1-6. Main physical properties of graphene

Property terms	Theoretical and measured value	Ref.
Tensile strength (GPa)	130	[126]
Young's modulus (TPa)	1, (1.5×10^8 psi)	[126]

Thermal conductivity near-room temperature (W/m·K)	$4.84 \pm 0.44 \times 10^3 - 5.30 \pm 0.48 \times 10^3$	[127,128]
Optical absorbing / optical transparency	$\pi\alpha \approx 2.3\% / \text{ca. } 97.7\%$	[129]
Charge carrier mobility (at ambient temperature) ($\text{cm}^2/\text{V}\cdot\text{s}$)	$>2 \times 10^5$ and $>10^6$ (at low temperature)	[130,131]
Specific areas (m^2/g)	2630	[132]
Specific capacitance (electric double layer) (F/g)	526	[132]

Although the large π -conjugation passivates graphene to most of the chemical reactions, chemical functionalisation and modification are not completely impossible and have been achieved efficiently through various routes. Through chemical modification, most of the physical properties of graphene can be effectively modulated by means of covalent chemistry. Some of these routes convert the sp^2 bonding to sp^3 forms, thus novel 2D super-lattice materials with intriguing traits beyond graphene itself could be constructed from its framework, vastly widening the graphene derivative family and their applications [121]. Furthermore, due to the accessibility of carbon atoms in the graphene sheet, covalent chemical reaction provides a powerful tool to modify the physical properties of pristine graphene [133-138].

Different from the other carbonaceous allotropes, carbon atoms in graphene planes are susceptible to chemical reactions from either side because of the unique 2D lattice structure. Naturally, the edge-site atoms of graphene have a very high chemical activity for lone pair electron and hanging bonds, and compared to other forms of framework, the edge carbons of graphene have the highest chemical activity. Furthermore, chemical activity is also increased by different types of defects within the layer [139]. The basal plane of monolayer graphene can be oxidised by oxygen starting at less than 260°C [140], and the single graphene sheets can be burnt from a very low temperature of about 350°C [141]. In practise, graphene has the highest reactivity amongst all forms of carbon structures, and this in turn can be attributed to the availability of carbon atoms on both sides of the plane. Normally oxygen- and nitrogen-functional groups can modify graphene effectively, and these functional

structures can be characterised by XPS and Fourier transform infrared spectroscopy (FTIR) [142,143].

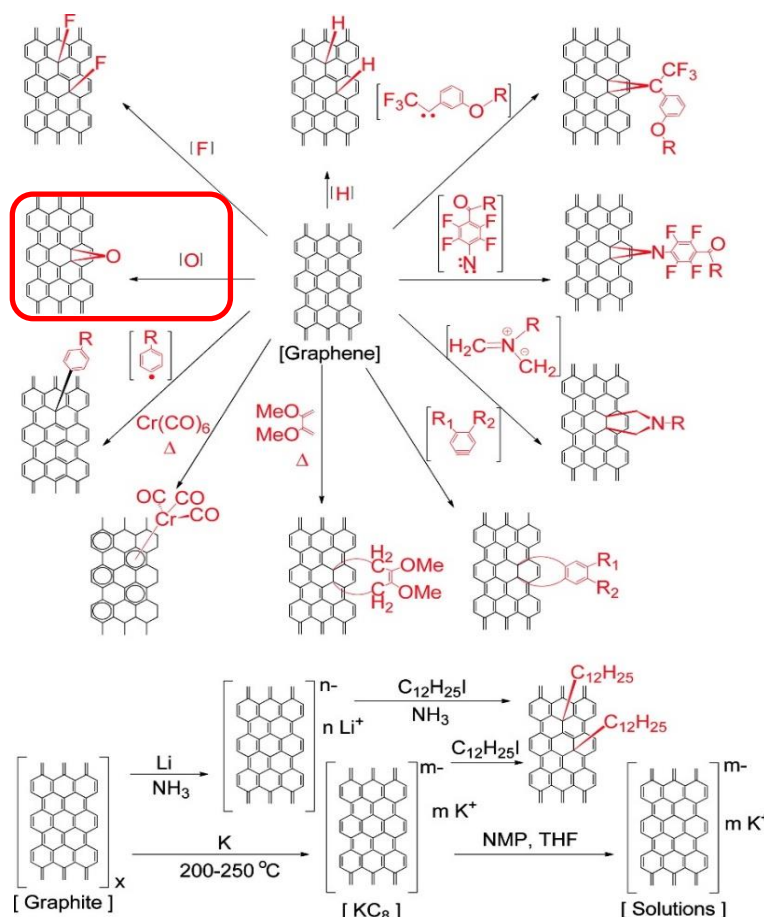


Figure 1-31. Typical chemical reactions and functionalisation of graphene [144]

Besides, a large number of $-C=C-$ bond reactions, such as radical addition and cycloaddition determined for benzene ring can also be achieved on graphene [121]. Some researchers have also reported that single-atom thick graphene sheet are a hundred times more chemically active than a stack of few sheets [145]. In order to know more details and find out suitable chemical methods for this study, relevant reactions, modifications and functionalisation conducted on graphene and graphene oxide are collected in the Figure 1-31 and 1-32. It can be seen that the oxidation of graphene is the most noticeable one, resulting in a more convenient and effective modification or functionalisation. This is the reason why the oxidation of graphene is the most

common functionalisation route adopted by most researchers.

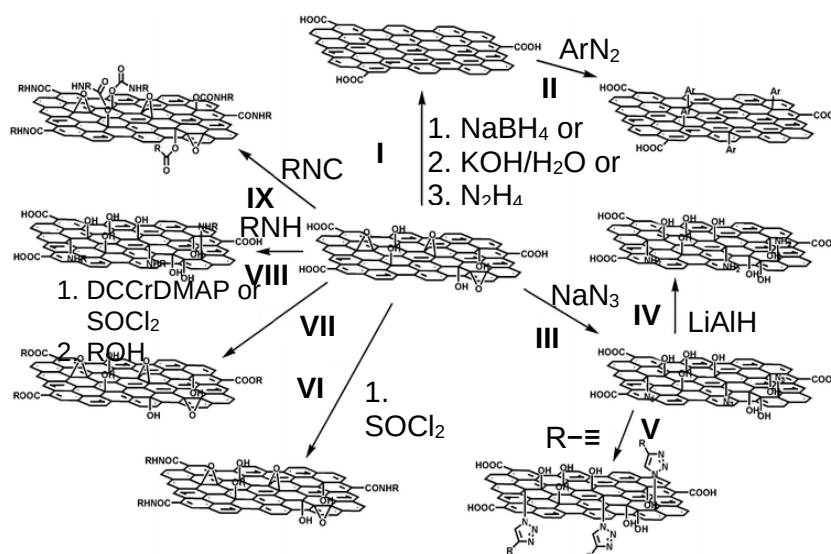


Figure 1-32. Schematic of covalent functionalisation chemistry of GO [146]

Theoretical calculation of the electronic structure of graphite and graphene was pioneered by Wallace [147]. In order to characterise the binding within the basal planes, a 'tight-binding approximation' was used. Based on this approximation the dispersion relation displaying electronic energy with the electron's wave vector, k , can be expressed by the equation below [147,148].

$$E = \pm \sqrt{V_0^2 \left(1 + 4\cos^2 \frac{k_y b}{2} + 4\cos \frac{k_y b}{2} \cdot \cos \frac{k_x \sqrt{3}b}{2} \right)} \quad \text{Equation 1-26}$$

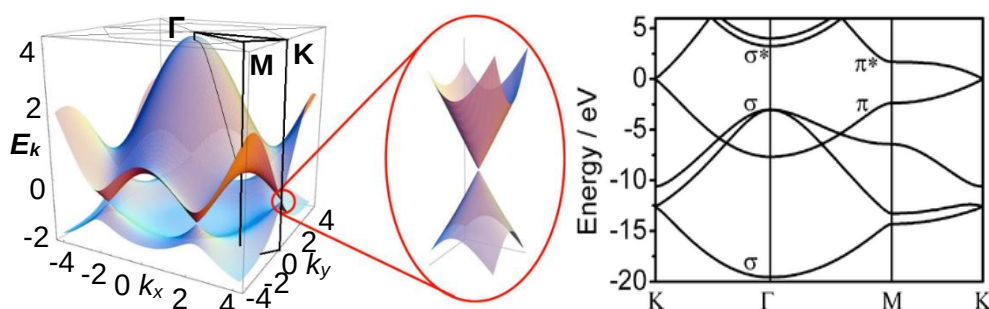


Figure 1-33. Electronic dispersion and energy band structure of ideal graphene [149,150].

In Equation 1-26 the lowest unoccupied orbitals, i.e. conduction band (π^*) corresponds to the plus sign E , and the highest occupied orbitals, valence band (π), is the minus sign E term, where γ_0 is the hopping energy of the nearest-neighbour about 2.8 eV and b is about 2.46 Å referring to the reciprocal space lattice constant. In the first Brillouin zone, the reciprocal space of graphene lattice, there are six unusual K-points at which the conduction and valence band shrink and touch each other resulting in a zero-gap semiconductor with a linear dispersion of energy near the K-point as shown in Figure 1-33 [148-151]. This unique energy vs. momentum dispersion is the reason why electrons in graphene display unusual physical behaviours.

In fact, in monolayer graphene the valence electrons, which construct the π -conjugation system by shearing between two neighbouring carbon atoms, behave like massless Dirac fermions. External electric and/or magnetic fields can then be applied to control these Dirac fermions directly, this can also be achieved by altering the sample geometry and/or topology [150,152]. For example, the band gap of bilayer graphene system can be opened and controlled in the presence of bias electrochemical potential, and this phenomenon has been confirmed experimentally.

Moreover, the electronic and energy band structure can be affected by geometrical size, defects and doping, etc. For instance, electronic properties of graphene can be effectively modified by deposition of various atoms and molecules doping [153]. Large amounts of efforts on chemical doping have been intensively investigated to modify the versatile conjugationally electronic structure in graphene [154]. In summary, the practical electronic structures of graphene species can be modified and even controlled through various physical and chemical methods.

1.1.3 Electrode materials based on graphene and its derivatives

Many nanostructured carbon materials, such as carbon nanotubes [155], graphene [5], have been extensively studied for use as electrode materials in EES devices. The pristine graphene play a big role in recent publications because of its distinct high SSA, electrical conductivity, and mechanical stability [156,157]. In addition, chemically reduced graphene [23,158], activated

graphene [159,160] and graphene nanocomposites [161,162] have also been broadly investigated for their outstanding energy storage performance. Almost all investigations demonstrated that pseudocapacitance widely exists in these nanostructured graphene species. The following sections review the most recent publications, and pay more attention to the applications of graphene and its derivatives as electrodes in electrochemical capacitors.

1.1.3.1 Graphene and its derivatives

The theoretical SSA of a single graphene sheet is $2630 \text{ m}^2/\text{g}$ [163], resulting in the largest theoretical EDLC of up to 526.0 F/g [164], which also corresponds to the highest theoretical area-specific capacitance of ca. $20.0 \text{ }\mu\text{F}/\text{cm}^2$. Therefore, the highly aromatic 2D macromolecular graphene, with exceptionally low intrinsic electrical resistivity, is a potential candidate as a novel electrode material for electrochemical energy storage applications [165-167]. The performance characteristics of graphene which are directly related to the quality, in terms of the number of layers and the surface area, are superior to that of single-walled and multi-walled carbon nanotubes [168].

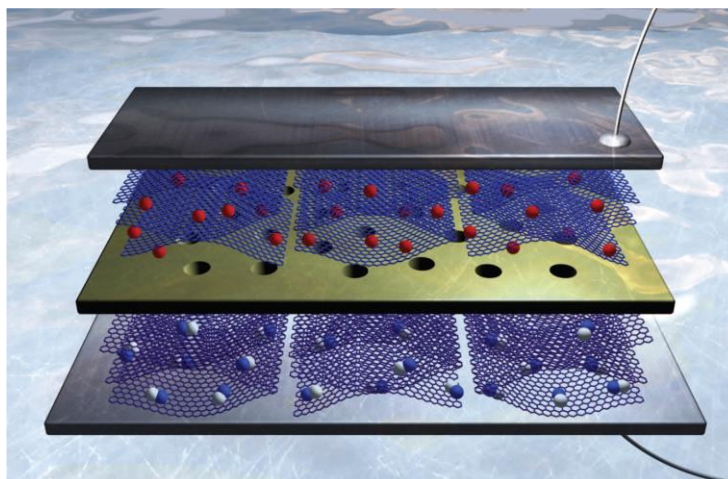


Figure 1-34. A kind of supercapacitor device based on graphene electrodes [169].

Currently, the prototype of graphene-based electrochemical capacitors [163] leads the field in capacitance, energy and power densities. Although the characteristics of graphene supercapacitors are very encouraging, there are still issues about the energy storage mechanism especially for the modified

graphene with pseudocapacitance which is still not clearly explained. Figure 1-34 shows an idealised supercapacitor cell based on graphene electrodes.

1.1.3.2 Graphene oxides (GOs)

Graphite oxides can be prepared through various means, including Hummer's method [170], electrochemical processes [171] or other modifications of the Hummer or related methods [172,173]. The presence of oxygen-containing functional groups, reduces the inter-planar forces and imparts hydrophilic character, thereby promoting complete exfoliation of single graphene oxide layers in aqueous media. On the other hand, oxygen-related functional groups can further modify the electronic structure by energy gap opening. Theoretical studies suggested that the oxygen-containing groups are clustered into rows or islands, resulting in graphitic regions intermixed with islands of oxygen-functionalised atoms [174]. The structure of the GO sheets is best described by intact, nanometre-sized graphitic domains separated by defect clusters. This structural feature results in hopping conduction as the dominant charge-transport mechanism in GOs. High-resolution microscopic investigations reveal further details about the defect nature and identify the location of oxygenated functionalities which presumably remain in a low concentration. Such knowledge is of relevance in attempts to tune the electronic structure of graphene via chemical oxidative functionalisation [175,176].

In practice, the aggregation of graphene sheets is a big problem. As a result, the thermally annealed graphene performs like graphite, and this decreases the effective diffusion of ions in the graphene matrix. However, the presence of hydrophilic functional groups on the graphene sheets efficiently improves the wetting between graphene and polar electrolytes, and also inhibits the aggregation of graphene sheets [28]. Additionally, some oxygen functional groups contributes to pseudocapacitance together with the inherent EDLC [4].

It was found that pseudocapacitance arises from reversible redox reactions between oxygen-containing groups and -OH ions. Some researcheres have recommended that in order to achieve a high capacitance, it is preferable to use an H^+ -rich solution, e.g. H_2SO_4 , as the electrolyte when GOs are used as electrodes [4]. Some investigators also believe that only carbonyl (-C=O) and hydroxyl (-C-OH) functional groups offer a good pseudocapacitance

performance in comparison with the other oxygen functional groups on graphene. It was also found that graphene which is subjected to treatment in concentrated KOH solution also gained some increase in pseudocapacitance, this perhaps originated from the residual oxygen groups [28].

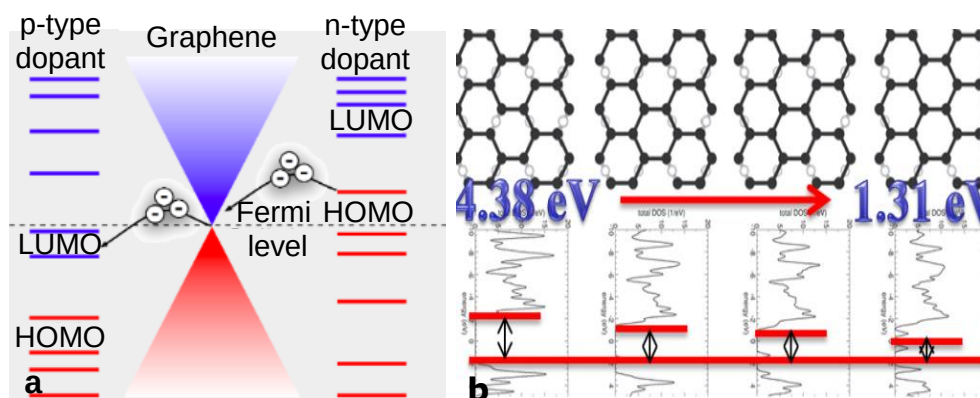


Figure 1-35. (a) Graphene's energy band and dopants' energy molecular orbital structures and possibilities of doping [153], (b) Atomic structure of graphene oxides with different amount of extraction of oxygen atoms and the evolution of total density of states [177].

Furthermore, the influence of oxygen functional groups on the electronic and energy band structure of GO has been realised and have been studied widely from the standpoint of theoretical modelling and simulations. Some authors believed that gap opening effects should be introduced in the energy band gap of graphene [178]. Others opine that p/n-type doping may play a part in the evolution of energy band structure and the variation of DOS of electrons [177]. Figure 1-35a showed some possible p/n-type doping in graphene, and 1-35b presents the theoretical study on the evolution of energy gap in GOs.

1.1.3.3 Nitrogen-doped Graphene (NG)

Investigators have known for a long time that ammonia activation not only increases both Brunauer–Emmett–Teller (BET) surface area and pore volume of porous carbon materials but also incorporates nitrogen atom into the carbon framework in the forms of pyridinic-, pyrrolic-, quaternary-N, and N-oxides of pyridinic-N [179,180]. Nitrogen doping can improve the wettability of mesoporous carbons to the electrolyte solution, and in turn, increase its electrochemical activity [181].

Some activation has been carried out on graphene to form N-contaminating derivatives. Marked improvements in the specific capacitance can be found in the N-modified graphene species. Furthermore, the contribution to pseudocapacitance has also been considered in these nitrogen doping sites. Qiu and Zhang [22] obtained a nitrogen-doped graphene product by means of a two steps route, during which graphene oxide was firstly reduced by hydrazine, then by a thermal reduction in an atmosphere of NH_3 gas, and consequently a specific capacitance of 144.9 F/g was achieved in the conventional organic solvent-based electrolyte. The authors reported that their N-doped graphene electrode has high conductivity of about 1000 to 3000 S/m and 0 to 4 V operating voltages in electrochemical capacitors. Jeong and Lee [20] employed a plasma-enhanced CVD process to treat dried GOs which was prepared through a modified Hummer's method. The final electrochemical testing indicated a 280 F/g specific capacitance in the electrolyte of 6 M KOH in comparison with the very poor capacitance of pristine graphene as shown in Figure 1-36.

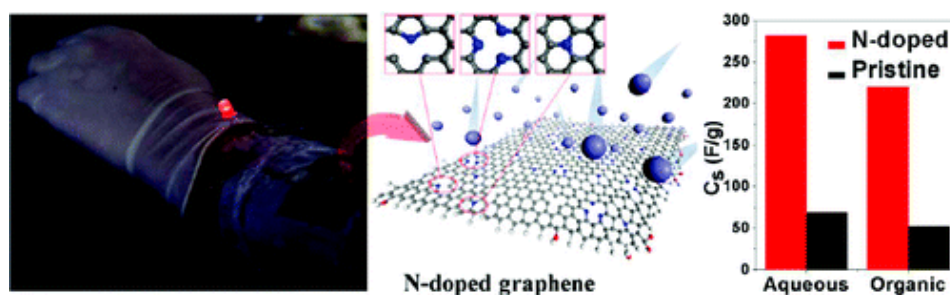


Figure 1-36. Nitrogen-doped graphene by the plasma enhancement. A schematic illustration of the plasma doping process. By the plasma process with physical momentum, nitrogen atoms replace the existing carbon atoms [20].

Remarkably, the researchers further conducted theoretical calculation with the aid of first-principles DFT to examine the binding energy between potassium ions and different N-doping configurations. Their results revealed that the possible origin of the improved capacitance is a certain N-configuration at basal planes of graphene. In addition, a series of excellent operating performance such as long cycle life (>200000 charge/discharge cycles), high

power capability, and compatibility with flexible substrates were also ascertained in this work.

It is necessary to point out that DFT is a very useful bottom-up modelling approach, and has been widely utilised in quantum chemistry, solid state physics, molecular dynamics, electronics and material sciences to investigate the target materials based on their atomic configuration, crystal lattice and electronic structure. It enables researchers to reveal the nature of many physical and chemical features of materials. Sun [25] adopted a one-step hydrothermal reaction using urea to synthesise reduced N-doped GOs. Wen [47] used a chemical and annealing route to achieve a similar product of NG. Both of them obtained NG with a relatively high nitrogen-doping level. Comparably high specific capacitance: 326 F/g and 302 F/g were achieved in their work respectively. All these studies not only prepared NG with high level of nitrogen-doping but also achieved promising specific capacitance in their prototype supercapacitors.

1.1.4 Electron delocalisation (ED) in materials

Electron delocalisation (ED) as a specific electronic structure originates from the delocalised electrons in matter. Different from localised electrons that are constricted or localised on only one atom or a single orbital, delocalised electrons are not associated with or localised on a single atom or a covalent bond. Delocalised electrons are shared by at least two or more atoms in matters [182]. This unique electronic structure broadly exists in some molecules, ions or solid materials including carbon, metals, metal oxides, non-metals and electronically conducting polymers. Different fields present ED slightly different, such as in organic chemistry ED refers to the resonance in conjugated systems and aromatic compounds, in solid-state physics free electrons has an extremely high degree of ED, and in quantum chemistry the phenomenon of molecular orbital extension over several adjacent atoms is also a kind of ED.

1.1.4.1 Electron delocalisation in carbon materials

The ED in carbon materials mainly originates from the unique π -conjugated system and aromatic rings. Adjacent atoms within the conjugated

system share the delocalised electrons forming a special orbital extension. The most classic example is benzene rings as shown in Figure 1-37.

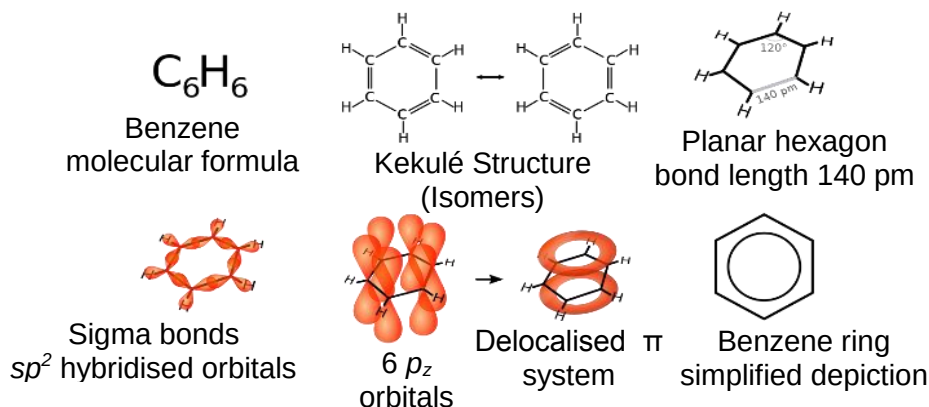


Figure 1-37. The various representations of benzene [183]

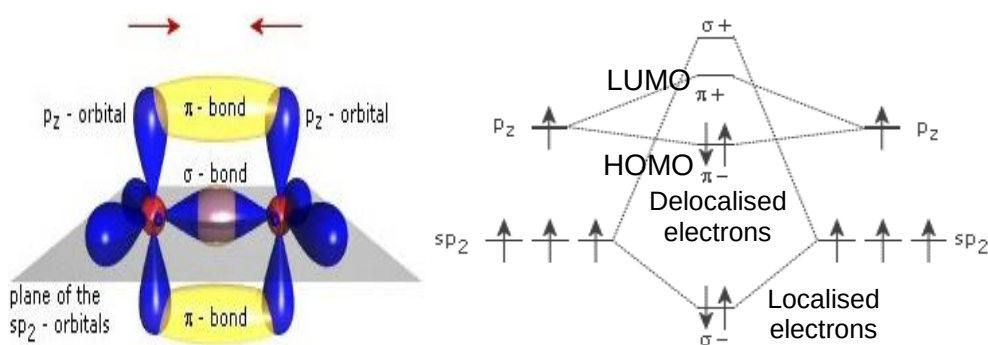


Figure 1-38. Scheme of the orbitals and bonds for two sp^2 -hybridised carbon atoms, modified from Ref. [184].

Specifically, the resonant ED in benzene originates from the π -electrons on the p_z -orbital of carbon atoms. This is based on the unusual properties of the carbon atom: among other configurations of electronic orbitals, carbon atoms can form the so-called sp^2 -hybridisations where the sp^2 -orbitals form a regular triangle within a plane and the p_z -orbitals of carbon atoms are perpendicular to the triangular plane, as shown in Figure 1-38. An σ -bond between two carbons can then be formed by formation of an orbital overlap of two sp^2 -orbitals. While two π -bonds can further be formed by sharing the electrons from the p_z -orbitals between the two neighbouring carbon atoms. The energy difference ($\Delta E_{\sigma\text{-bond}} =$

$|\sigma^+ - \sigma^-|$) between the occupied binding orbitals and the unoccupied anti-binding orbitals is quite large as shown on the right panel of Figure 1-38.

Correspondingly, longer chains of σ -bond carbon atoms would have a large gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), leading to insulating properties.

However, in sp^2 -hybridisation, the p_z -orbitals form additional π -bonds. These bonds have much smaller energetic difference between difference ($\Delta E_{\pi-bond} = |\pi^+ - \pi^-|$) the HOMO and LUMO, leading to semiconducting properties.

As one of the simplest examples, ED exists in the conjugate system of the benzene ring in which six un-bonding π electrons are contributed by six carbon atoms, and these electrons are in turn shared by all the carbon atoms, therefore, this conjugate structure is often drawn by a circle in the centre of the hex-ring as shown in Figure 1-39. Again the equality of the six carbon-carbon bonding length is one direct proof of the existence of ED. Furthermore, this delocalisation structure in benzene can be described as a kind of resonance structure according to valence bond theory [185].

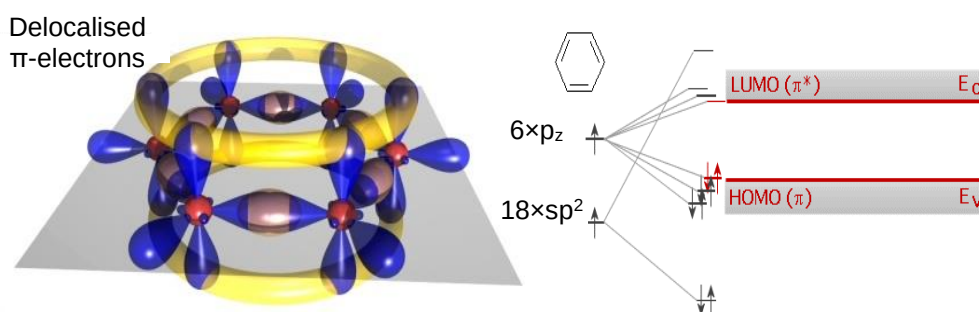


Figure 1-39. Scheme of a benzene ring (top) and the energy structure of small-molecule organics, modified from Ref. [184].

If carbon atoms form larger molecules, typically with benzene rings as the basic unit, the π -bonds become delocalised further and form a larger π -system which often has extensions from the molecule. The gap between occupied and empty states in these π -systems becomes smaller with increasing degree of delocalisation, leading to absorption and fluorescence in the visible spectra. These substances can be prepared as molecular single crystals. Due

to the close coupling of the π -systems of the molecules in these crystals, their pure forms display remarkable transport properties including band transport up to room temperature [185].

If a longer chain or larger area of sp^2 -hybridised carbon atoms is formed, corresponding to the case of electronically conducting polymers or graphene respectively, the π -bonds become delocalised along the chain or the whole basal plane and form a one-dimensional (1D) or two-dimensional (2D) conjugated system. The 1D-conjugated electronic system has a considerable band width (on the scale of an eV), i.e., this results in a 1D semiconductor with a filled valence band originating from the HOMOs and an empty conduction band originating from the LUMOs as shown in Figure 1-40. The transport properties of such molecules are usually determined by defects in the 1D-chains or by hopping from chain to chain. Therefore, the samples do not show band transport, but thermally activated hopping. Whilst, in 2D case of graphene, the 2D-conjugated electronic system of this specific carbon specie forms a zero band gap as the electronic energy band structure shown in Figure 1-33 (with conduction band and valence band touching each other at the Dirac corner). The transport properties of graphene is characterised by excellent ballistic transport or by hopping from region to region if defects exist in the 2D-layers.

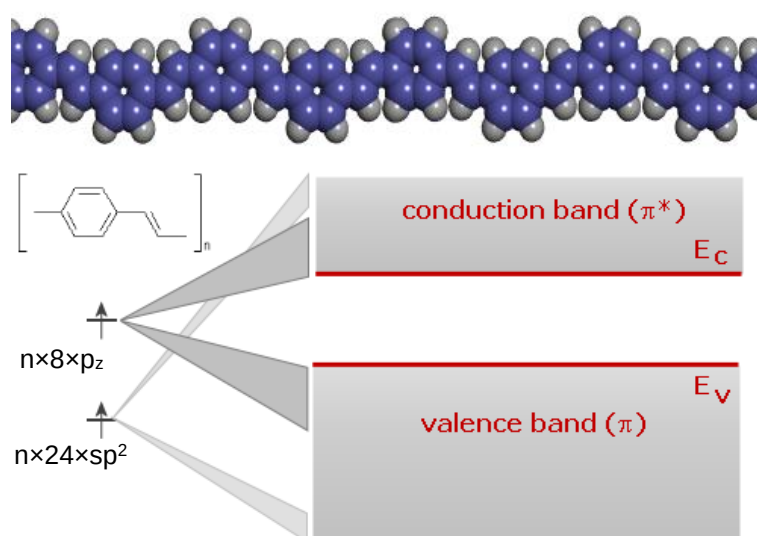


Figure 1-40. Scheme of a polymer subunit (top right) and the energy structure of polymer organics [184].

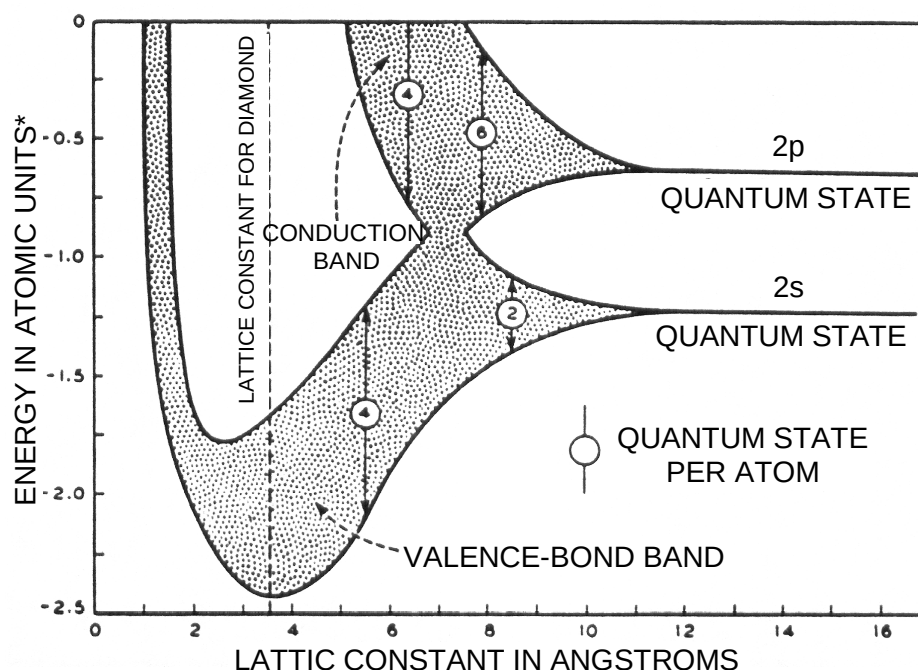


Figure 1-41. Representation of the energy levels for diamond as a function of inter-atomic distance [186]

From another aspect, in a full covalent bonding system, such as diamond (Figure 1-41), all outer shell electrons are bonded or 'localised' between the carbon atoms because of the sp^3 -hybridisation. No electronic orbitals have extension over several atoms. The energy level of the highest occupied orbitals and that of the lowest unoccupied orbitals are split so wide that valence electrons cannot jump between these two energy bands due to the large energy band gap ($E_g = \Delta E_{HOMO-LUMO} = |E_c - E_v|$) of about 5.6 eV. As a result, the electrons' mobility is restricted in diamond resulting in optical transparency and electrical insulating properties.

1.1.4.2 Electron delocalisation in metals

The metallic crystal is an extreme case of ED because of its fully delocalised valence level electrons. The outmost s-shell electrons of metals in Group IA and IIA in the periodic table (p -shell for Group IIIA and VIA metals, d -subshell for Group IB and VIIIB metals and f -subshell for Lanthanide and Actinide series) all display this extreme case of ED in the metal crystal lattice.

This extreme ED makes the metal crystal lattice look like many core of positive ions immerse in a delocalised electrons 'sea' or 'electron soup'. Schematics of the energy band structure of typical metals are shown in Figure 1-42. It can be seen that the Fermi level of typical metals is immersed in the overlapping region of the conduction band and valence band. Therefore, the electrons are shared by all metal atoms and can move freely throughout the whole crystal structure resulting in excellent conductivity.

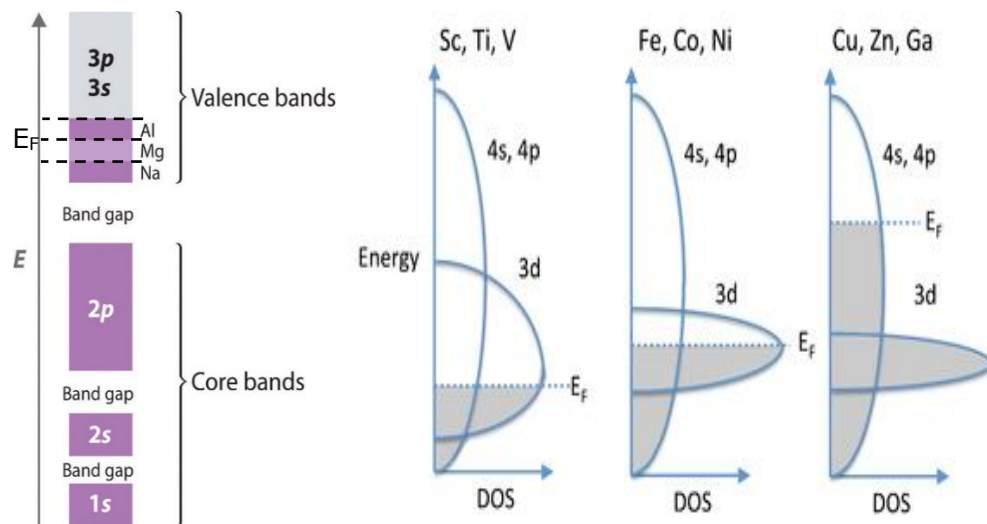


Figure 1-42. Typical Energy band structure of metals: (Left panel) The Band Structures of the Period 3 Metals Na, Mg, and Al, the 3s and 3p valence bands overlap in energy to form a continuous set of energy levels that can hold a maximum of eight electrons per atom, modified from [187]. (Right panel) Progressive filling of the 3d and 4s, 4p bands going across the periodic table from Sc to Ga, modified from [188].

It has to be mentioned that if no oxidation or discharge of metal happens as an external voltage is applied on the metal the Fermi level cannot vary significantly away from the average thermodynamic level. For example, the copper wire conduction shows that the mean free path of electrons in a copper wire at room temperature is about 40 nm. Therefore, the energy given to an electron by the electric field by 100 V applied to a 1 meter copper wire would be on the order of $W = e \times E \times d = 100 \text{ volts} \times 40 \text{ nm} = 0.000004 \text{ eV}$. Such an amount of energy cannot be absorbed by most of the electrons because there is no available energy level that is close to their energy [189].

1.1.4.3 Electron delocalisation in metal oxides

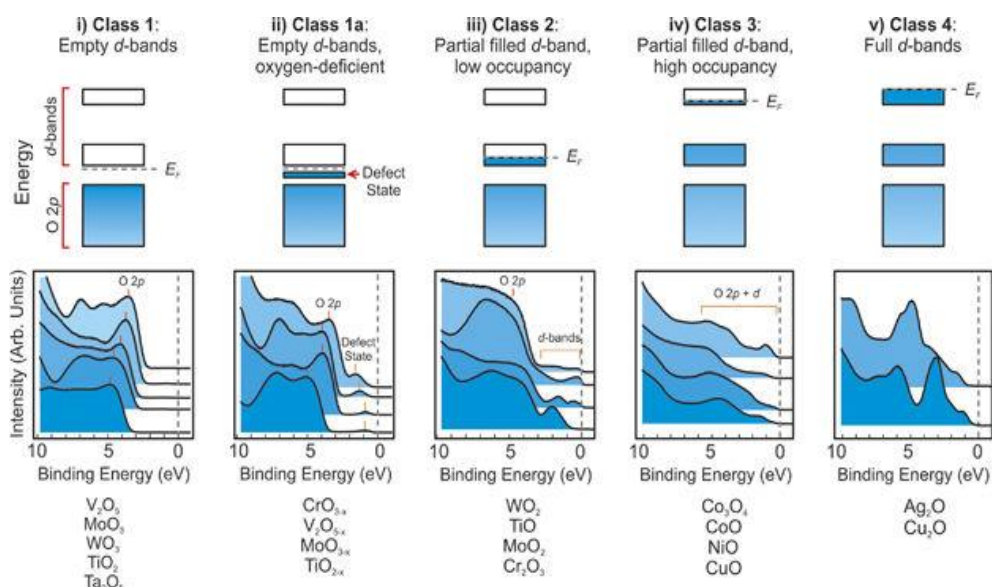


Figure 1-43. Schematic energy band diagrams and valence band photoemission spectra of various transition metal-oxide classes [190].

Metal oxides are normally characterised as insulators because most of them have relatively wide energy gap (E_g) with the Fermi level lying in between the conduction band (E_c) and the valence band (E_v) as shown in Figure 2-43 and 2-44. In the vast majority of cases, electrons are all localised in the valence band and cannot freely transfer within the solids, indicating completely localised electrons.

However, there are still some important exceptions, such as the following d -band species: Ag_2O , Cu_2O , partially filled d -bands species: Co_3O_4 , CoO , NiO , CuO , WO_2 , TiO , MoO_2 , Cr_2O_3 , oxygen-deficient states in CrO_3 , V_2O_5 , MoO_3 and TiO_2 and some complex oxides: $Tb_2Ti_2S_2O_5$, $Dy(Y)ZnPO$, $Rb_2Sn_2O_3$, Ca_4As_2O , $CaNb_2O_4$, $NaNbO_2$, $LiNbO_2$, $Ti_4V_2O_7$, $FeTeFO_3$ as shown in Figure 1-43 and 1-44.

Obviously, these simple and complex metal oxides are characterised by unique metallic conductance because of the delocalised valence electrons in their crystal lattice. These delocalised valence electrons exist around the Fermi level within the fully filled or half-filled d -shell of the metal elements, or even the oxygen-deficient states.

Furthermore, First-principles density functional theory (DFT) calculation reveals that RuO₂, IrO₂ and OsO₂ are also a class of very special metallic conductors [192]. As shown in Figure 1-45, in these TMOs, electronic states

crowded around the Fermi level have a relatively large population of DOS. These electronic states originate from highly delocalised electrons in *4d*-orbitals of Ru, Ir and Os atoms. Hereinto, RuO₂, as reviewed in Section 1.1.1.3, and IrO₂ show unique pseudocapacitive behaviour. The author of this thesis believes that the special ED in these TMOs may play a significant role in their pseudocapacitive behaviour. This is because, to the best of my knowledge, there is still lack of understanding on the correlation between the pseudocapacitive behaviour and the electronic structure of electrode materials. Therefore, investigating the pseudocapacitive behaviour from the viewpoint of the electronic structure of electrode materials is one of the novelties of this study.

1.2 Motivation

Based on the above literature review, it can be seen that pseudocapacitive electrode materials have both high charge storage capacity and fast charging/discharging capability. On the other hand, the excellent capacitive performance of graphene related materials have been experimentally proven to be originated from both large EDL capacitance and pseudocapacitance. However, the lack of comprehensive understanding of the origin of pseudocapacitance in these nanostructured carbon materials, especially at a level of electronic structure, has hindered the development and application of this capacitive faradaic charge storage. Therefore, a strong motivation was developed in this study to correlate pseudocapacitance with the electronic structure of nanostructured carbon materials.

1.3 Aim and objectives

The aim of this study is to correlate the pseudocapacitive charge storage behaviour with the delocalisation of valence electrons in nanostructured carbon materials with an expectation to contribute to the better understanding of the origin of pseudocapacitance.

In order to achieve this aim, several objectives have been identified as follows:

- A nanostructured carbon material with well-defined atomic configuration and electronic structure will be chosen as a proper object of study;

- Various techniques will be used to characterise the microstructure, spectroscopic properties, the charge storage capacity and the electronic structure, especially the degree of electron delocalisation (DED) of as-selected materials. Spectroscopic methods will be used to monitor the DED in samples;
- Electrochemical approaches will be used to modify the DED and monitor the pseudocapacitive charge storage in samples;
- The DED of samples will be correlated with the pseudocapacitance based on the characterisation and electrochemical measurement results;
- Representative material models will be established to reflect the atomic configuration and different DED; then the electronic structure of these models will be modelled with the aid of the First-principles density of theory (DFT);
- Finally, by comparison between experimental observations and theoretical predictions, the pseudocapacitive charge storage will be correlated with the corresponding DED in samples.

1.4 Scope of thesis

Chapter 1 starts with a comprehensive literature review on the fundamental background and the most recent progressing of the as-concerned field. Based on these, the research motivation, aim and objectives of this study are established, followed by the scope of this thesis.

The general methodology of research is proposed at the beginning of **Chapter 2** followed by details on the materials and instruments used in this research. A detailed synthesis process of graphene oxide (GO), the fabrication of working electrode and the electrochemical cell are described. Materials characterisations by microscopic, spectroscopic and electrochemical techniques employed in this research are briefly introduced, followed by a discussion on repeatability and reproducibility. In the last section of this chapter, a brief introduction is given on the theoretical calculation tool of CASTEP and the basic aspects of DFT.

The microscopic, spectroscopic and electrochemical characterisations of the as-prepared GOs are presented in **Chapter 3**. These characterisations include the optic microscope, scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), Raman spectroscopy, UV-Vis spectroscopy and X-ray photoelectrons spectroscopy (XPS). An empirical equation was established to semi-quantitatively evaluate the degree of electron delocalisation (DED) in the GO samples based on the deconvolution of the C 1s peak in the XPS. Electrochemical measurements including CV and EIS were utilised to analyse the charge storage in GO electrodes.

In **Chapter 4**, results and discussion are presented on electrochemical reduction (ECR) through potential cycling, i.e. CV to vary and control the DED of GO electrodes. The discussion is aided by Raman and XPS analyses for the detection of the DED variation in the electrochemically reduced GOs. Electrochemical characterisations (ECCs), including CV and EIS, are used as the indicator of the charge storage of the electrochemically reduced GO samples, i.e. POGs, with different DED. The influence of experimental variables, such as the reduction potential range, numbers of ECR cycle and electrolytes, is discussed in detail. The equivalent circuit simulation based on the EIS is established to identify the pseudocapacitive contribution in the total charge storage. The relationship between the pseudocapacitance and DED of POGs is finally established. Based on these results and discussions, a three-branch charge storage model is proposed to illustrate all the three charge storage processes in the GO electrode interfacing with the aqueous electrolyte.

The investigation of the structural, spectroscopic and capacitive charge storage properties of a commercial polycrystalline monolayer graphene (PMG) sample is reported in **Chapter 5**. The deconvolution of the C 1s peak in the XPS is used again to estimate the DED of the PMG. Also, results from CV and EIS are used to determine the pseudocapacitive contribution to the total charge storage in the PMG electrode interfacing with aqueous electrolytes.

A series of representative partially oxidised graphene (POG) models with different DED are established and optimised in **Chapter 6**. The electronic structures of these models are presented according to calculations aided by the

first-principles density functional theory (DFT). The relationship between the electronic structure and the DED of these POG models is discussed in detail. A specific charge density which reflects the charge storage capacity in the states of delocalised valence electrons is extracted and correlated with the DED. Finally, by combining previous experimental results in Chapter 3, 4 and 5, the correlation between the DED and pseudocapacitance in GOs is finally established. The foundation of pseudocapacitance and the critical influential factors are also illustrated at the end of this chapter.

The key achievements of this study and its contributions to advancement of knowledge are summarised in **Chapter 7** together with the conclusions on the related research findings. Recommendations for future work are also provided at the end of this chapter.

Chapter 2 Methodology

2.1 General strategy

In the following Figure 2-1 a general research route with four main steps and some key points is established specifically for this study:

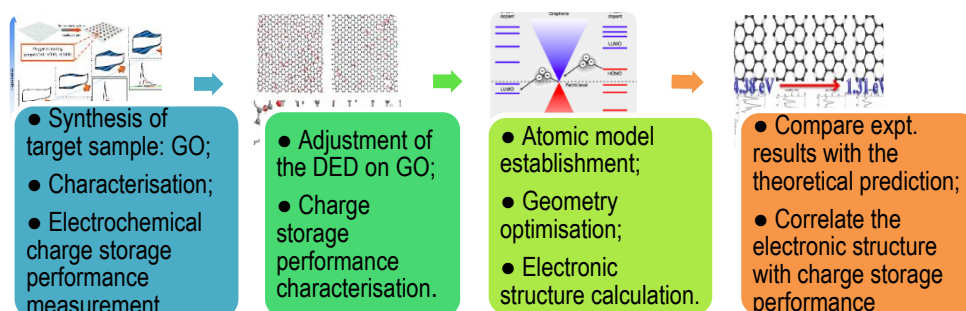


Figure 2-1. General research route for this study (The background figures cited and modified from references: [3,153,177,193])

In the first step, one of the target materials, i.e. GO, was synthesised followed by characterisation and observation of the electrochemical charge storage performance on the GO fabricated electrode. The relationship between the DED of GO and its oxidation degree was correlated based on the characterisation results. Capacitive charge storage performance observed on the original GO was taken as a starting point or reference point. The next step, the DED of GO was adjusted through electrochemical methods, e.g. potential cycling of electrochemical reduction (ECR). Capacitive charge storage of ECR-treated GO was monitored through immediately ECC after a certain step of ECR treatment. Spectroscopic characterisation on ECR-treated GO further correlated the charge storage performance with the DED of samples. In the third step, representative GO models were established and geometrically optimised based on the first-principles DFT followed by the calculation of electronic structures on the optimised GO structures. Electronic structures of GO, including the energy band structure and DOS, were calculated and analysed in detail. With these theoretical analysis and experimental results obtained in previous steps, the electronic structure of GO was correlated with the capacitive

charge storage, especially the pseudocapacitance of the GO electrode at the final stage.

2.2 Chemicals and materials

Table 2-1. *Materials used in this research*

Items	Grade	Supplier	States	Other inf.
Graphene Flakes (GF)	N/A	Sigma-Aldrich	as received	Raw materials
CVD Monolayer Graphene on Quartz (CVD MNG)	10X10 mm ²	PI-KEM Ltd	as received	Raw materials
Concentrated nitric acid (HNO ₃)	69 wt% aqueous solution	VWR BDH Prolabo	as received	Oxidant
Concentrated sulphuric acid (H ₂ SO ₄)	97-99 wt% aqueous solution	Parmacos	as received	Oxidant
Concentrated hydrochloric acid (HCl)	37 wt% aqueous solution	Sigma-Aldrich	as received	Cleaning agent
Concentrated phosphoric acid (H ₃ PO ₄)	85 wt% aqueous solution	Sigma-Aldrich	as received	Reactant
Potassium hydroxide (KOH)	Pure solid	Sigma-Aldrich	as received	Modifying agent
Potassium permanganate (KMnO ₄)	Pure solid	Sigma-Aldrich	as received	Oxidant
Hydrogen peroxide (H ₂ O ₂)	Liquid phase	Sigma-Aldrich	as received	Oxidant
Potassium Chloride (KCl)	Pure solid	Sigma-Aldrich	as received	Electrolyte
Deionised water	Liquid phase	self-product in lab	as prepared	Solvent
Silver conductive paint	Paint	RS Components	as received	Making electrical connections

2.3 Apparatus and instruments

Table 2-2. *Equipment used in this research*

Equipment	Model	Supplier	Accuracy and resolution
For characterisation			
Potentiostat	Autolab PGSTAT30	Ecochemie	E (V): $\pm 0.2\%$, 150 μV (applied potential resolution) and 300, 150 or 30 μV (measured potential resolution) I (A): $\pm 0.2\%$, 0.03% of current range (applied current resolution), 0.0003% of current range (measured current resolution) EIS resolution: 0.025%
Scanning electron microscope (SEM)	FEI-ESEM QUANTA 600	FEI Company	/
Transmission electron microscope (TEM)	JOEL 2000 FX TEM	JEOL	/
X-ray photoelectron spectrometer (XPS)	Kratos Axis Ultra DLD	Kratos	Binding energy (eV): ± 0.02 Atomic percentage (%): ± 0.1
UV-Visible spectrophotometer	Libra S22		/
Raman Spectrophotometer	LabRAM300	RS	/
For sample fabrication			
Sample drying oven	OP100	LTE Scientific	/
Freeze dryer	Modulyo 1305	Edwards	/
Electronic Pipette	EDP3	Rainin	/
Balance	AEA-220A	ADAM	(Max. 220 g, d = 0.1 mg)
Precision balance	Sartorius ME36S	Sartorius AE Germany	(Max. 31 g, d = 0.001 mg)
Titanium plate (1 mm thickness)	99.9 % pure	Good fellow Cambridge Ltd	/
Platinum Working Electrode	2 mm in diameter	CH Instruments	/
Ag/AgCl Reference Electrode	with the electrolyte of 3.0 M KCl	CH Instruments	/
Separator	-	Separator	/

2.4 Synthesis and preparation

2.4.1 Synthesis of GO following modified Hummers' route

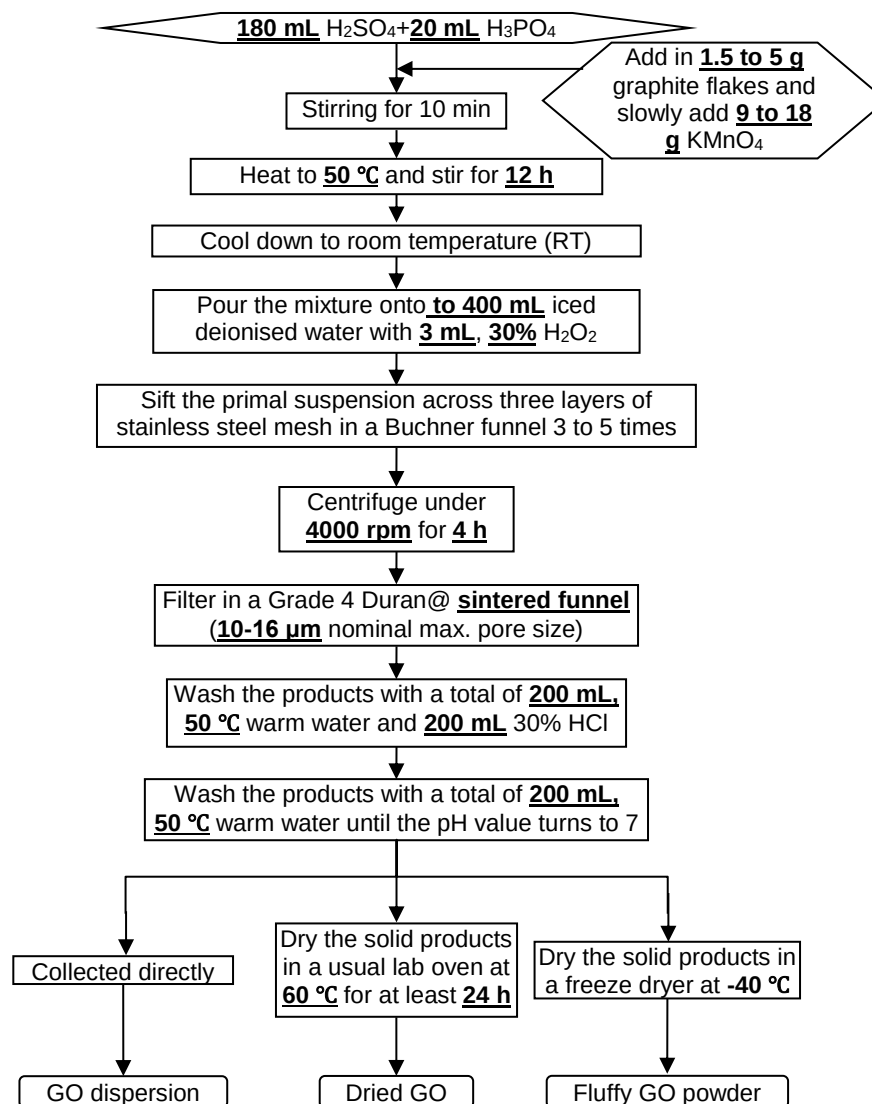


Figure 2-2. Preparation of graphene oxides

In order to obtain as-required GO samples, a Hummers' route was followed with partial modifications on such as reactants, procedures and sample collection ways. The detailed synthesis procedure can be found in Ref. [173]. A flow chart shown in Figure 2-2 presented the details on the synthesis procedure of GO. Depending on different requirements for sample storage and

characterisation, the GO products were collected in three different ways at the final step. For example, for the usual storage of GO, directly drying in a lab oven is the most convenient way to obtain long storable dried samples. However, this kind of sample is not suitable for microscopic characterisation because the GO fragments tend to form a compact structure through stacking with each other, especially when the GO is dried from a dispersion which has a high concentration. Thus, a freeze dryer was used to obtain a fluffy and stable GO samples based on critical point sublimation technology. GO dispersed in aqueous environment is easily to be used in spectroscopic characterisations and the fabrication of the GO electrode through the 'casting-drying' method.

2.4.2 Working electrode (WE) and electrochemical cells

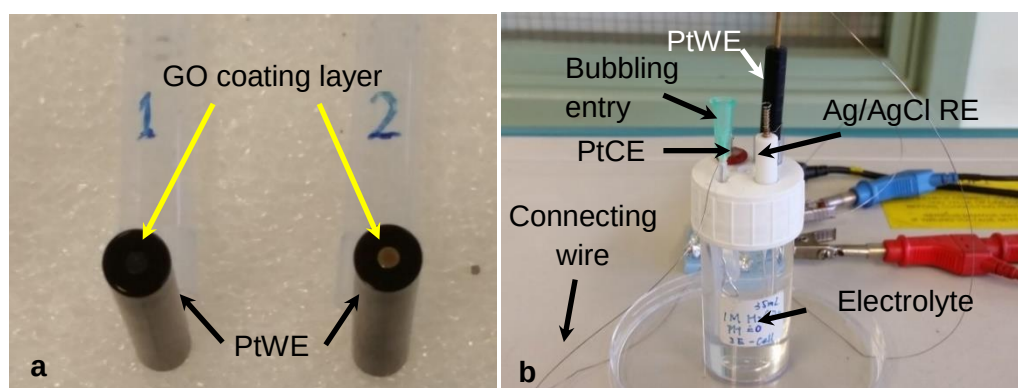


Figure 2-3. Graphene oxides coated Pt working electrode (a) and a typical tri-electrode cell (b) with Pt wire or graphite rod as a counter electrode, Ag/AgCl (3.0 M KCl) as a reference electrode and supporting electrolytes e.g. 3.0 M KCl or 1.0 M H_2SO_4 solution for electrochemical measurements.

In this study, three types of working electrodes were used in a traditional tri-electrode electrochemical cell. The first one was the platinum disk working electrode (PtWE) with 2 mm diameter coated with GO as shown in Figure 2-3a.

The second one was a home-made polished titanium plate with a dimension of $1 \times 1 \text{ cm}^2$, 1 mm in thickness and R_a : ca. $1 \mu\text{m}$, coated with GO and encapsulated in a specifically designed holder 3D-printed with clear photopolymer resin in a Form 2 3D printer supported by the manufacturer: Formlabs. This photopolymer resin is suitable for the ECC because of its insulating nature, inert chemical and electrochemical property. The entire

fixtures were shown in Figure 2-4a to d. The reason why the 3D-printing technology was hired to make the working electrode holder in this study is that, on the one hand, this special designed WE can load more amounts of GO in contrast with the traditional PtWE with on 2 mm diameter, thus facilitating the weighing procedure for deciding the actual loading mass of active materials, on the other hand, the O-ring fixture makes sure an consistent exposure surface of GO coating into the electrolyte, hence achieving more reliable and reproducible testing results than traditional ways.

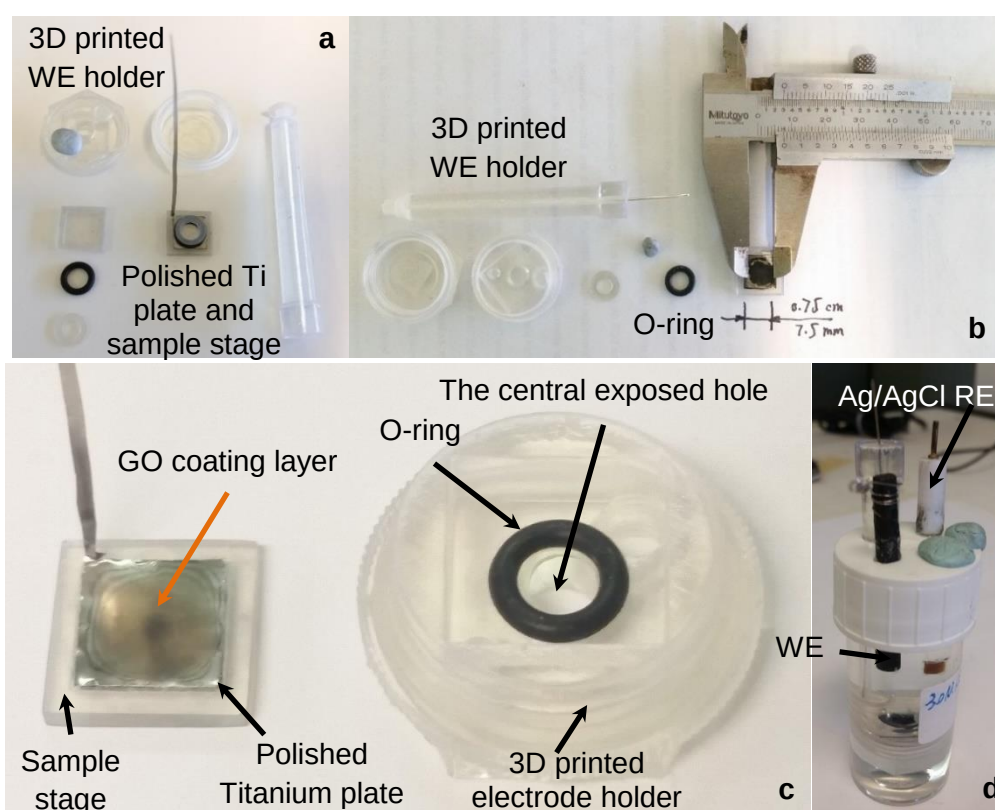


Figure 2-4. Graphene oxides coated a home-made polished titanium (R_a ca. $1\mu\text{m}$) working electrode and all parts of a 3D printed electrode holder before and after assembly (a) and a typical tri-electrode cell (b) with Pt wire or graphite rod as counter electrode, Ag/AgCl (3.0 M KCl) as reference electrode and a certain volume of electrolyte.

In addition, this set-up of working electrode is enabled to conduct a series of electrochemical treatments directly on the titanium plate with more convenience. As-prepared GO suspension was dropped and dried on the Pt or

TiWE under room temperature (RT) in a common lab situation to build up working electrode samples. Only a very small volume of GO suspension i.e. 2.5-5 μL , was dropped on the surface of 2 mm platinum disk, which can cover the disk properly and completely to achieve a good contact. In the case of Ti plate, the volume can achieve 25 μL , hence obtain a proper loading mass of GO. The third type of working electrode was specifically made for holding a $1\times 1\text{ cm}^2$ quartz plate covered with CVD monolayer graphene. This monolayer graphene was synthesised through traditional CVD procedure and transferred onto the $1\times 1\text{ cm}^2$ quartz plate by the manufacture (PI-KEM Limited). The working electrode was fabricated by partially capsuling the sample plate with epoxy resin. The exposed area of graphene in the electrolyte can be easily controlled in this specially designed WE. The detail structure of this kind of working electrode will be introduced in Section 5.2, Chapter 5.

To achieve higher stability and reliability in all electrochemical measurements a classic three-electrode cell was constructed for this study. Figure 2-3b and 3-4d showed the prototype of this homemade electrochemical cell which consisted of a working electrode, a reference electrode and a counter electrode immersed in the specific electrolyte. Before every routine testing, the whole cell was bubbled for at least 15 min with argon (Ar) gas to eliminate the influence of dissolved oxygen and the other gas.

2.4.3 Determination of the loading mass of a GO electrode

The accurate loading mass of active materials on the WE must be determined if a specific capacitance (C_m) needs to be calculated. However, it is not easy to know the actual mass of dried GO on the top of a 2 mm PtWE because of the small loading amounts. Thus, in this section, the mass of active materials was determined based on the determination of the mass concentration of GO dispersion. The detailed procedures were stated as follow.

Round aluminium plates with 13 mm in diameter were cut out from a large aluminium sheet by a puncher (Model: T07) and weighed before loading on a Sartorius ME36S balance. As-synthesised GO dispersion was treated in an ultrasonic bath at least 15 min to obtain a homogeneous suspension. Then a certain volume of GO dispersion, i.e. 10 or 20 μL , was dropped on an

aluminium plate. All plates were placed in a common lab oven under RT. The following day, aluminium plates loaded with dried GO were weighed again to obtain the actual mass of the dried GO by subtracting the mass of aluminium plates. The concentration of mass versus volume, $C_{w/v}$ in g/L, or mg/mL, can be determined by dividing the dried mass of GO by the volume of dispersion drop.

Considering the accuracy, arithmetic mean of five separate plates were weighed to determine the final concentration of as-synthesised GO dispersion.

For the GO coated titanium WE, the above procedures were modified by weighing the titanium plates directly before and after loading with GO. In this way, the actual loading mass of GO on Ti plates can be conveniently determined for further calculation of specific capacitance in ECC.

2.5 Characterisations

2.5.1 Microscopy and spectroscopy

AFM, SEM and TEM were also used to characterise the micromorphology of as-prepared GO. Depending on different requirements of specific devices, the sample preparation are also various as shown in Figure 2-5.



Figure 2-5. Samples for various electron microscopic techniques, (a) SEM samples obtained by casting way, (b) SEM samples prepared by freeze dry and (c) TEM sample grid [194]

For the SEM, either the GO dispersion was dropped and dried on the tag (Figure 2-5 a), or using freeze drier to obtain fluffier samples (Figure 2-5b). For the TEM, GO dispersion was dropped on a copper grid (Figure 2-5c) with amorphous carbon film as the supporting substrate and dried under atmosphere condition.

The optical bandgap of as-prepared GO was estimated from the UV-Vis absorption spectra based on the Tauc's empirical theory [195,196]. A Libra S22

UV-Visible spectrophotometer (detail information shown in Table 2-2) was used to collect the absorption spectra of GO homogeneous solution with different concentrations.

Chemical-state analysis with XPS has been widely used for the element carbon. In addition, the chemical state analysis for carbon in graphene species is enabling to directly extract the ratio of sp^2/sp^3 because of the distinguishable difference of binding energy between sp^2 (284.5 eV) and sp^3 (285 eV) hybridisation of carbon atoms [197]. In this study, through analysis and peak fitting of the XPS spectra of graphene species, the chemical states of carbon atoms, functional groups and even the DED of the sample can be investigated. The XPS equipment used in this study is a Kratos Axis Ultra DLD. The excitation source is a Mono (Al (Mono)) (120 W) anode, and the analyser is the hemispherical type. The binding energy range for the wide scan is set between 0 to 1400 eV. The binding energy step for high resolution scan is set to 0.1 eV. Other experimental parameters are under standard conditions.

Raman spectroscopy was also used to detect the possible variation of graphitic area and defects concentration in GO samples. Raman spectrum was acquired under room temperature on a Raman Spectrophotometer (Horiba LabRAM HR) armed with a green laser excitation source of 532 nm wavelength.

2.5.2 Electrochemical techniques

2.5.2.1 Cyclic voltammetry (CV)

CV is a classic electrochemical technology based on potentiodynamic electrochemical measurement. It has become an important and widely used electroanalytical technique in electrochemical research to study such as the electrochemical properties of an analyte in solution, the electrochemical properties of electrochemical capacitor [6], a variety of redox processes, determining the stability of reaction products, the presence of intermediates in redox reactions [198], electron transfer kinetics [199] and the reversibility of a reaction [200]. In the research field of capacitance materials, CV is helpful as a quick screening procedure to identify potential capacitor materials. The experimental procedure involves potential cycling between two voltage values (potential range) preselected for a given electrolyte [6]. Therefore, this

technology was adopted to characterise the electrochemical features of GO samples in traditional three-electrode cells.

In a CV experiment, a set potential is applied to the working electrode step-by-step under certain constant of sweeping speed or scan rate, meaning the potential to be ramped linearly versus time. When the set potential is reached, the working electrode's potential is converted to the opposite direction to return to the initial value. These cycles of sweepings in potential can be repeated as many times as desired.

Different electrochemical systems display various and distinct cyclic voltammograms (CVs). Two main types of CV are commonly observed in experiments. One is the typical redox system with apparent redox faradaic currents (see Figure 2-6a). The second one is in a capacitance system (see Figure 2-6b) with characteristic rectangular CV shape. The CV trace (black) in Figure 2-6c, undoubtedly, is a combination between these two types of feature indicating a unique pseudocapacitance in the as-concerned electrode material.

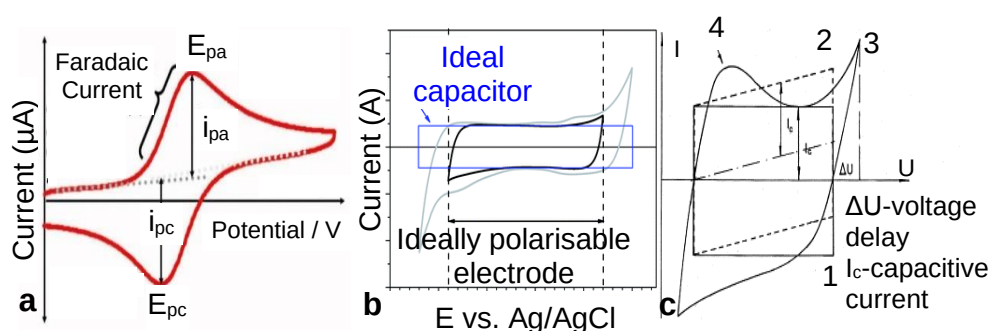


Figure 2-6. Different types of CV, (a) typical peak shaped CV of faradaic process [201], (b) typical rectangular CV of ideal capacitor and ideally polarisable electrode [202], and (c) typical semi-rectangular CVs in carbonaceous electrode materials [203], 1-ideal capacitor; 2-capacitor with resistivity; 3-capacitor with carbon material and 4-influence of redox reactions.

A standard CV experiment uses a reference electrode, working electrode and counter or auxiliary electrode. This combination is sometimes referred to three-electrode cells. The electrolyte is usually added to the sample solution to ensure sufficient conductivity. The solvent, or the electrolyte, and material composition of the working electrode will determine the potential range

that can be accessed during the experiment. A typical three-electrode setup arrangement is shown in Figure 2-7.

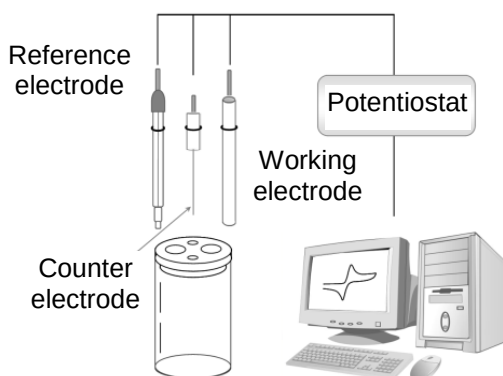


Figure 2-7. Typical three-electrode set-up [204]

2.5.2.2 Electrochemical impedance spectroscopy (EIS)

The frequency-response characteristics of the electrode material and its equivalent series resistance (ESR) are two important features in the evaluation of capacitive materials [6]. Impedance measurements are more useful for evaluating capacitor behaviour because the capacitance component of the impedance is the main quantity of interest and is directly determinable as in equation: $1/(2\pi fC)$. In addition, the combination of capacitance with any resistance can be easily evaluated and the role of porous-electrode behaviour readily perceived from the frequency-response behaviour of the impedance. Furthermore, when pseudocapacitance arises, it can often be distinguishably evaluated [6].

Nyquist plot in EIS measurement is commonly used to display Z_{im} vs. Z_{Re} relationship under different values of ω , the angular frequency of alternating current, in the complex plane. Figure 2-8 shows some typical Nyquist frequency responses of different electrode component configurations. Different dynamic processes on the electrode correspond to various and distinctive impedance Nyquist plot. These informative frequency responses can be further used in analysis and explanation of specific electrode processes.

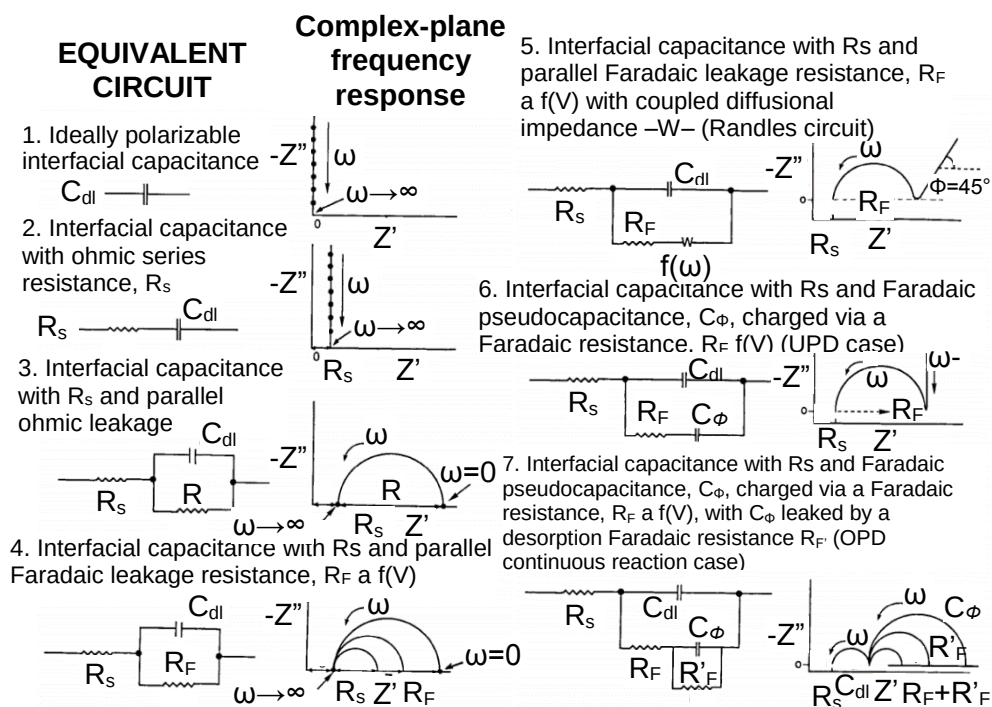


Figure 2-8. Typical Nyquist frequency responses and corresponding equivalent circuits. $-Z''$ is Z_{Im} and Z' is Z_{Re} [6]

In a general sense, an electrochemical cell can be simply considered as an impedance to a small sinusoidal excitation; hence one ought to be able to represent its performance by an equivalent circuit of resistors and capacitors that pass current with the same amplitude and phase angle that the real cell does under a given excitation.

A frequently used circuit to simulate the electrode process is called the Randles equivalent circuit shown in Figure 2-9 [11]. In practice, a chief objective of an impedance experiment in EIS is to discover the frequency dependencies of R_s and C_s and finally using theory to transform these functions into chemical information, including kinetic parameters of electrode process, pseudocapacitance component and the relative magnitudes of each element, etc. One of the most commonly observed frequency response impedance diagrams for high specific areas carbon electrode is shown in Figure 2-10, which have an equivalent circuit the same as shown in Figure 2-9.

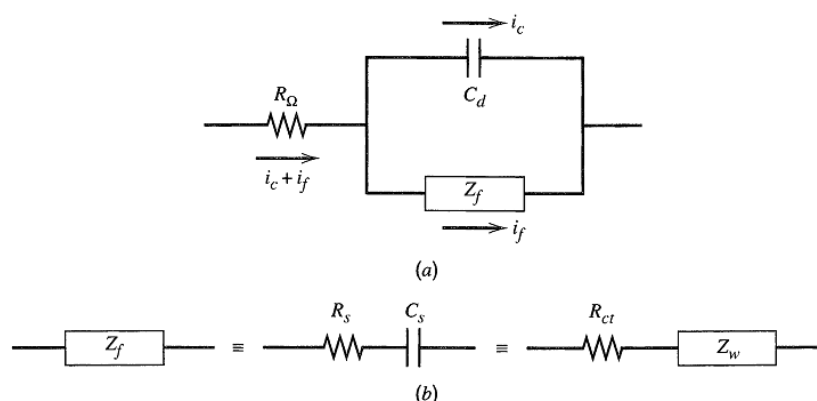


Figure 2-9. Randles equivalent circuit, (a) Equivalent circuit of an electrochemical cell, (b) Subdivision of Z_f into R_s and C_s , or into R_{ct} and Z_w . Where R_s , C_s , R_{ct} and Z_w represents the series resistance, the pseudocapacity, the charge-transfer resistance and the Warburg impedance respectively [11].

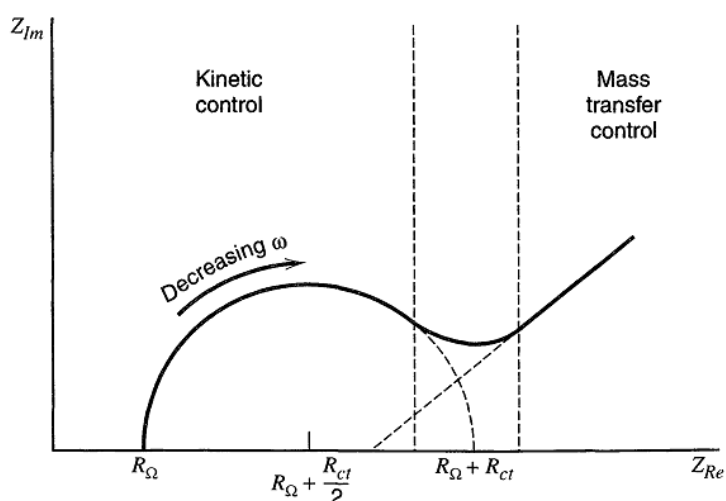


Figure 2-10. Typical Impedance plot for an electrochemical system. Regions of mass-transfer and kinetic control are found at low and high frequencies, respectively. Here, R_Ω is ESR; R_{ct} is the charge transfer resistance [11].

In this study, all electrochemical measurements were carried out using an Autolab PGSTAT30 potentiostat (Ecochemie), equipped with a FRA32 impedance module. CV was collected in a PC using the General Purpose Electrochemical System software (GPES). EIS data were collected in the same PC using the Frequency Response Analyser (FRA) software. The frequency range used for most measurements was 100 kHz to 10 mHz. The amplitude of the sinusoidal alternating current (AC) signal was 10 mV. EIS data analyses

were carried out in the software of FRA_V1.7 and the Fit-and-simulation tool in Nova application (version 2.1.3) supplied by Metrohm Autolab B.V. Electrochemical testing were carried out in traditional three-electrode cells with a 5 mm graphite rod or platinum wire as the counter electrode and an Ag/AgCl in 3.0 M KCl as the reference electrode.

2.6 Repeatability and reproducibility of results

The accumulation and analysis of experimental experiences were paid much attention in this study in order to obtain more rational and reliable experiential results. In the meantime, experimental experiences were also referred to guide the optimisation of experimental procedures during all laboratory work. For example, considering the sensibility of electrochemical measurements to the situation of electrode materials, in all electrochemical measurements, at least three samples were used for repetition to guarantee the repeatability and reproducibility of data. Besides, if abnormal or doubtful data were observed one more sample would be used to do the repetition. Otherwise, only arithmetic mean values were adopted and reported in the results and discussion part of this study.

2.7 Theoretical calculation of electronic structure

In order to correlate the ED of GO with its pseudocapacitive behaviour, theoretical calculations on the electronic structures of GO with various degrees of ED were carried out in Chapter 6 based on the first-principles DFT. In the following two sections, a brief modelling method and the basis of DFT were given for a general purpose. More details and parameters will be introduced in Section 6.2 of Chapter 6.

2.7.1 Modelling

The physiochemical properties of materials are depended on their atomic, molecular and phase structure to a great extent. That is to say, knowing the true structure of the as-concerned material plays a significant part in understanding materials' actual properties. Therefore, building up a well-defined structure model is indispensable before doing any theoretical computing and property expectations. There is no exception for the research on graphene oxides and its electronic structures. A series of simple but representative GO

models were built up to simulate the true structures of pure graphene, fully oxidised graphene and partially reduced/oxidised graphene species by referring previous reports. These models simply include a monolayer graphene segregated by different coverages of epoxy groups. By adjusting the coverage of these epoxy groups on the basal plane of graphene various degrees of ED can be achieved and controlled. All the modelling was done in the interface environment of Materials Studio 5.0. Geometrical optimisations, e.g. the adjustment of the bond length and bond angle, were carried out on all models to minimise their total energy, hence to obtain the most possible stable structures. Consequently, a series of representative models with optimised geometrical structures, especially for the partially reduced/oxidised graphene with various DED, can be obtained for further electronic structure calculation.

2.7.2 Density functional theory (DFT)

The density functional theory [205] is based on a hypothesis which believes that all ground-state properties of the material are functionals of the charge density of ρ [206]. Specifically, the total energy, E_{total} , can be written as:

$$E_{\text{total}}[\rho] = T[\rho] + U[\rho] + E_{\text{xc}}[\rho] \quad \text{Equation 2-1}$$

where $T[\rho]$ is the kinetic energy of a system of non-interacting particles of density ρ , $U[\rho]$ the classic electrostatic energy due to Coulombic interactions, and $E_{\text{xc}}[\rho]$ includes all many-body contributions to the total energy.

The charge density of ρ can be written as:

$$\rho(\mathbf{r}) = \sum_i^N |\phi_i(\mathbf{r})|^2 \quad \text{Equation 2-2}$$

where the sum is over all occupied molecular orbitals (MOs).

Based on this hypothesis, the ground state properties of materials can be described as different functionals of charge density. The charge density is the distribution of electrons in materials. That means if one can obtain the density of distribution of electrons in a well-defined structure model by solving the Schrodinger equation, ground state properties of this material can be predicted based on the geometrical structure and electronic structure. In actual calculation based on the DFT, a series of plane wave basis set [207] and pseudopotential [208,209] which are used to express the atomic and electronic

orbital function and their potential energy should be carefully chosen; electronic exchange and correlation effects must be also considered and described within special approximation using various functionals.

According to the DFT, the electronic structure can be obtained by solving the Schrodinger equation on the as-established material model. Thereby, the energy band structure and electron density of states can be further extracted from the results of the calculation.

In this study, the DFT calculations were performed by the academic CASTEP package version 7.0.3 in Materials Studio 5.0 as the interface and visualizer. The CASTEP is a quantum mechanics-based program, which employs the DFT and plane-wave pseudopotential method [210]. The electronic exchange and correlation effects were described within the generalized gradient approximation (GGA) using the Perdew Burke Ernherzhof functional [211] which is the most popular functional in GGA and has been widely used in theoretical prediction of the electronic structure for graphene and its derivatives [177,212-214].

Chapter 3 Synthesis and Characterisation of GO

3.1 Introduction

The focus of this chapter will be mainly put on the characterisation of the as-prepared GO products to inspect their quality, micromorphology and spectroscopic features. These characterisations include optical microscopy (OM), scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), UV-Vis spectroscopy, Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). Important spectroscopic information, energy band gap, elemental composition and chemical states information were obtained. Thereafter, the electrochemical capacitance and impedance spectrum behaviours of the GO working electrode were investigated through a series of ECC, such as CV and EIS. Standard study procedures were established for the charge storage analysis, which can be further used in the subsequent investigation on the electrochemical modified GO and CVD monolayer graphene in the next two chapters.

3.2 Products of graphene oxides (GO)

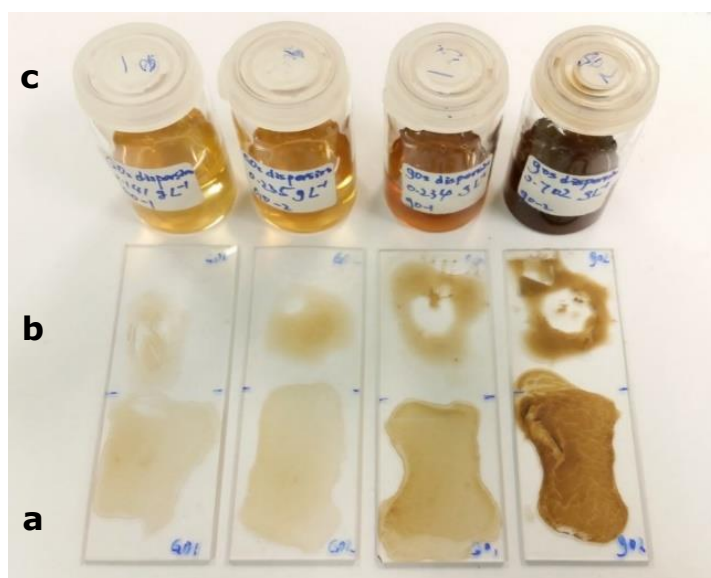


Figure 3-1. Final GO products obtained from Hummers' route, (a) directly dried GO samples on glass plates, (b) freeze dried GO samples, and (c) GO suspension with different concentrations

At the final stage of the GO synthesis, a brown-yellowish GO suspension with high homogeneity was obtained, as shown in Figure 3-1.

3.3 Basic property characterisation

Before the synthesis of GO, SEM, Raman spectroscopy and XPS were also used to characterise the raw material: graphite flakes. This part of data was collected in Appendix A to B. The following characterisations were mainly focused on the as-synthesised GO products.

3.3.1 Morphological and microscopic structure of GO

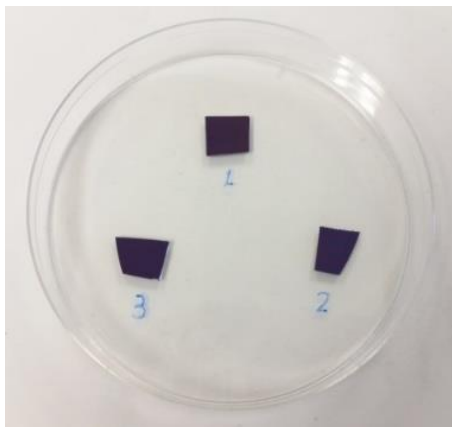


Figure 3-2. GO on the SiO₂/Si wafer

GO was first observed under an optical microscope (OM) to learn its micromorphology. As shown in Figure 3-2, a drop of very dilute GO dispersion (<1 g/L) was dried under RT on a Si wafer with a SiO₂ layer (300 nm thick). This type of SiO₂/Si wafer shows a special purple colour under sunlight. The surface of the SiO₂/Si wafer was slightly etched by a concentrated sodium hydroxide solution to improve its wettability. In this way, GO fragments can freely lay on the surface of the SiO₂. Layer-like structure and various layer numbers of graphene fragments can be observed directly under the OM. This is because graphene with different ranges of thickness can exhibit different colours on this kind of SiO₂/Si wafer [215].

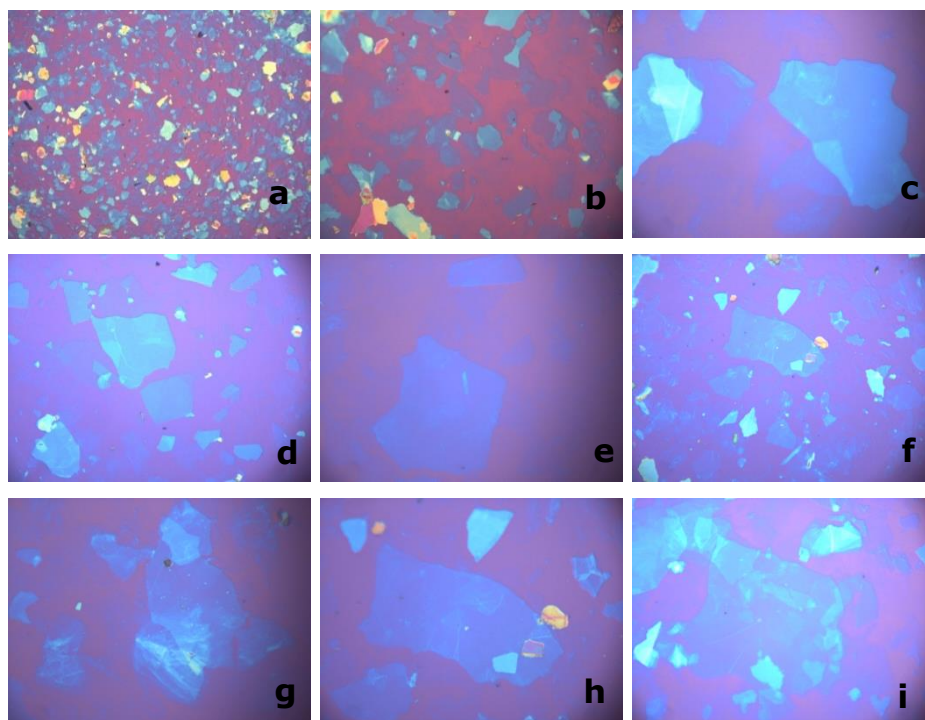


Figure 3-3. Optical microscope photos of GO on the SiO_2/Si wafer under various magnifications. a) 50X, b) 100X c) 400X, d) 200X, e) 400X, f) 200X, g) 400X, h) 400X, i) 400X

As can be seen in Figure 3-3a to i, the layer-like GO fragments show different shapes. The particle size and the number of layers are quite heterogeneous. Wrinkles and edges are the main types of defect. Such kind of micromorphology is expected due to the violent synthetic conditions with strong oxidants and high temperature. Strong oxidants grafted large amounts of oxygen-containing groups on the edge and basal plane of graphene. The high temperature and persistent stir established violent reaction circumstances leading to a robust exfoliation to the graphite flakes. GO fragments were split layer-by-layer from the graphite flakes in such a violent atmosphere, resulting in a wide distribution in particle size.

The same SiO_2/Si wafer was used in the AFM observation. Figure 3-4a to f showed representative observation results. Singular and folded structures can be clearly seen in these images with more details, such as edges (indexed by No. 1 in Figure 3-4c and e), wrinkles (indexed by 3), folds (indexed by 2) and fractures (indexed by 4).

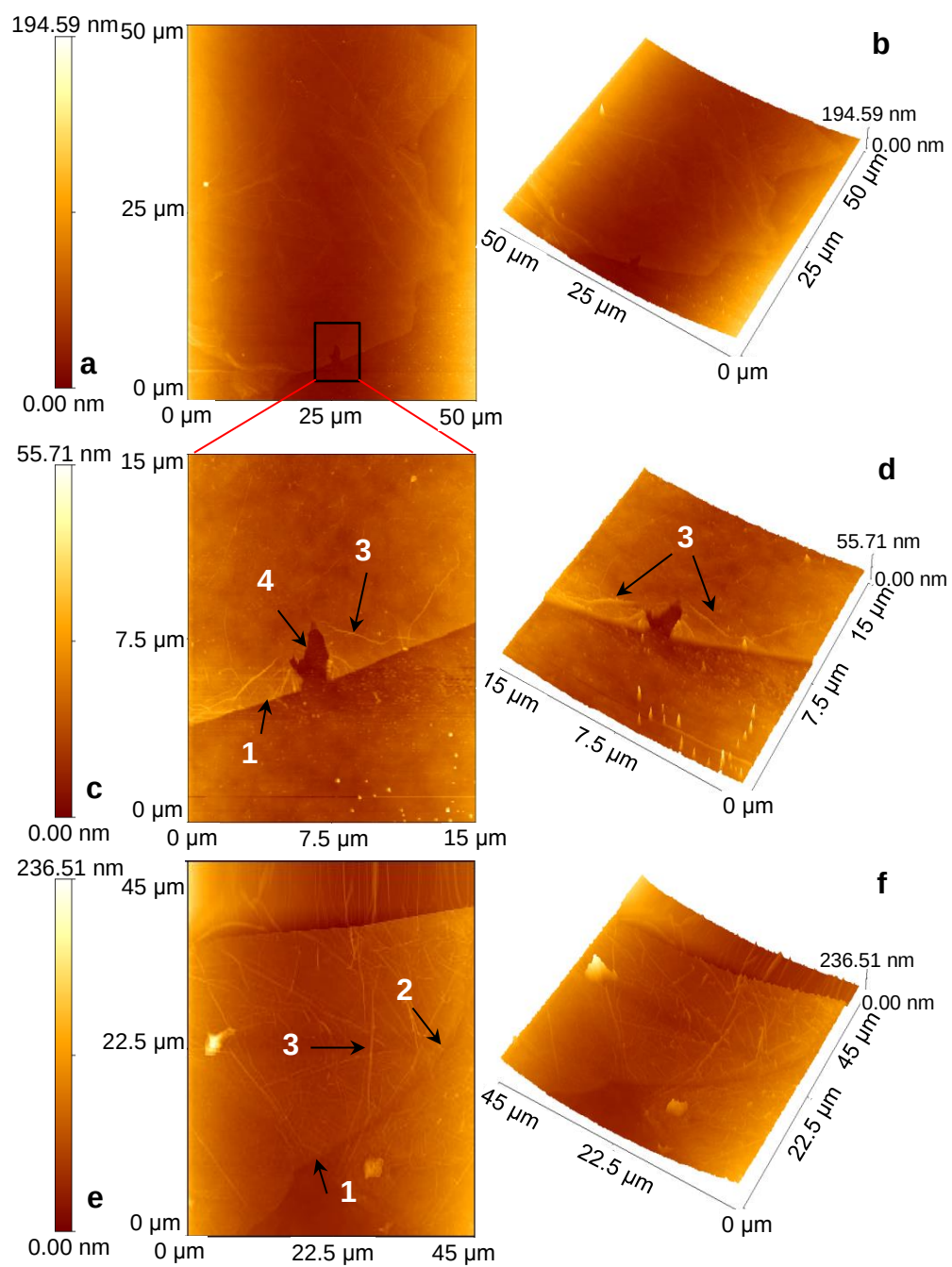


Figure 3-4. AFM images of GO fragments

The thickness measurement shown in Figure 3-5a and b indicated that the thickness of GO fragment is about 2.6 to 8.6 nm which agrees well with the theoretical prediction of about 3.5 to 7 nm and other published data [173].

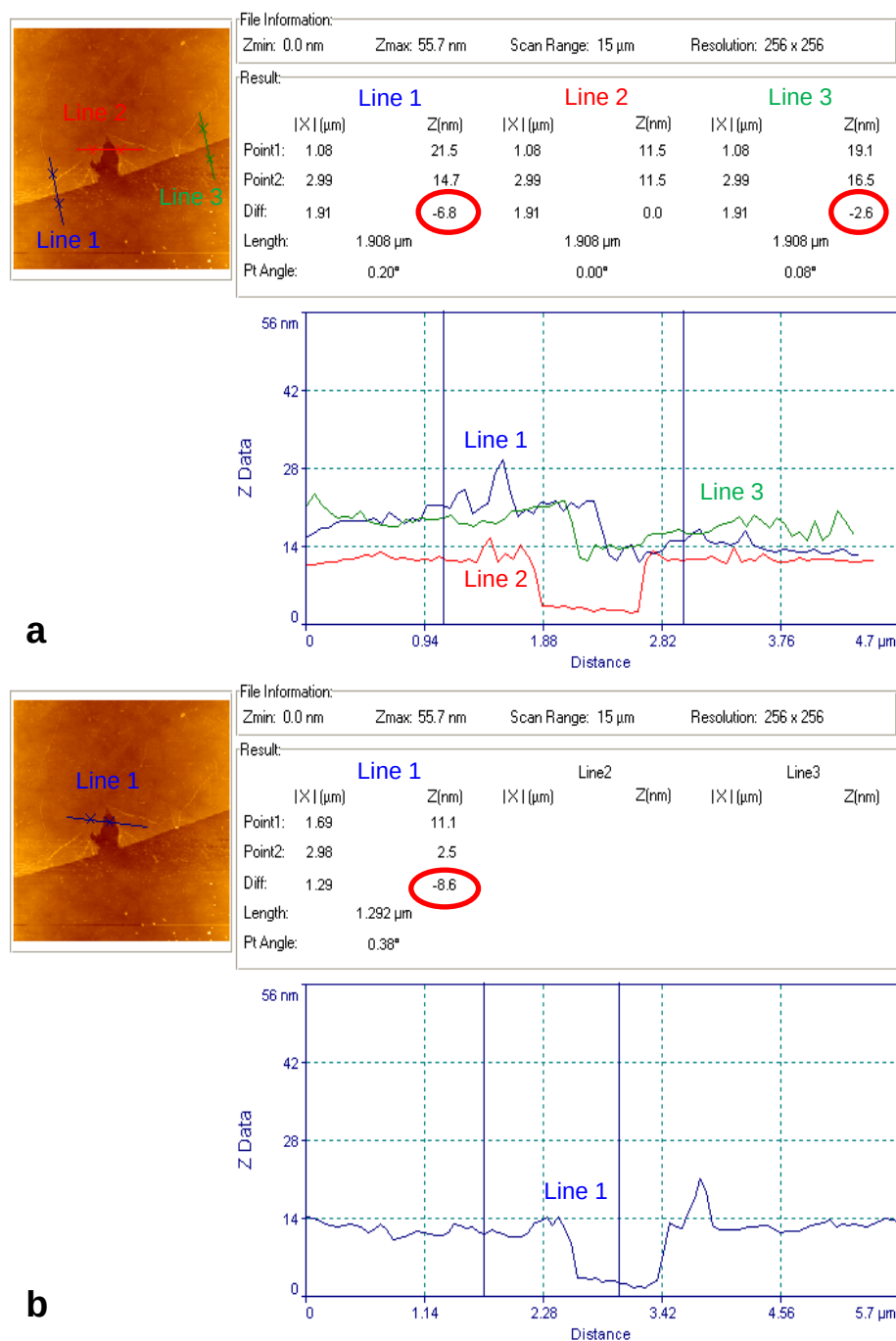


Figure 3-5. AFM thickness measurement on GO fragments

Two different sample preparations mentioned in Figure 2-5, Section 2.5.1 were used in SEM characterisation. Representative images under

different magnifications were shown in the following Figure 3-6 and 3-7 respectively.

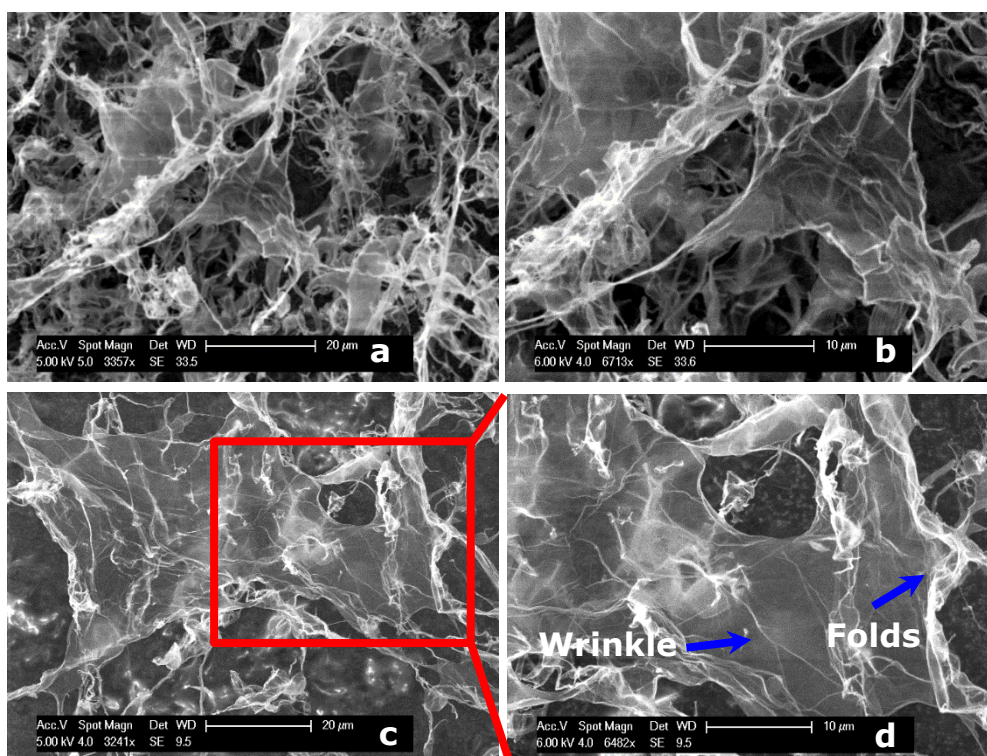


Figure 3-6. Freeze-dried GO on a conductive carbon tag.

During the violent reaction condition of Hummers' route, highly effective exfoliation accompanying with a strong oxidising environment can anchor great numbers of hydrophilic oxygen-containing groups on the graphene sheets, especially on the basal and edge plane of graphene sheets. These oxygen-containing groups can further expand the interlayer spaces of graphene sheets twice larger or more than the interlayer distance of 0.335 nm in graphite [216]. The violent reaction conditions, in the meantime, brought many wrinkles and other defects onto GO fragments. On the other hand, trapped water molecules in between the two layers of graphene can further enlarge the interlayer space, especially in aqueous solution. Direct dropping and drying GO suspension on the surface of substance resulted in severe aggregation of GO fragments because of the evaporation of water molecules. However, the freeze-drying technique based on a low temperature dehydration process can remove the ice

by sublimation. GO fragments cannot freely move in the iced solution, thus resulting in a dried but fluffy GO framework without severe aggregations. After sublimation of the solvent, a good dispersion state of GO fragments can be achieved. Consequently, very good microscopic images can be obtained clearly reflecting the layer-like feature and the in-situ status of each GO fragments. As can be seen in Figure 3-6, rather curly and wrinkled GO fragments with wide distribution of sheet size dominated in the micromorphology of the freeze-drying GO. Many publications [173,217] proved that these wrinkles are quite common and intrinsic microstructural features of GO obtained through the Hummers' route.

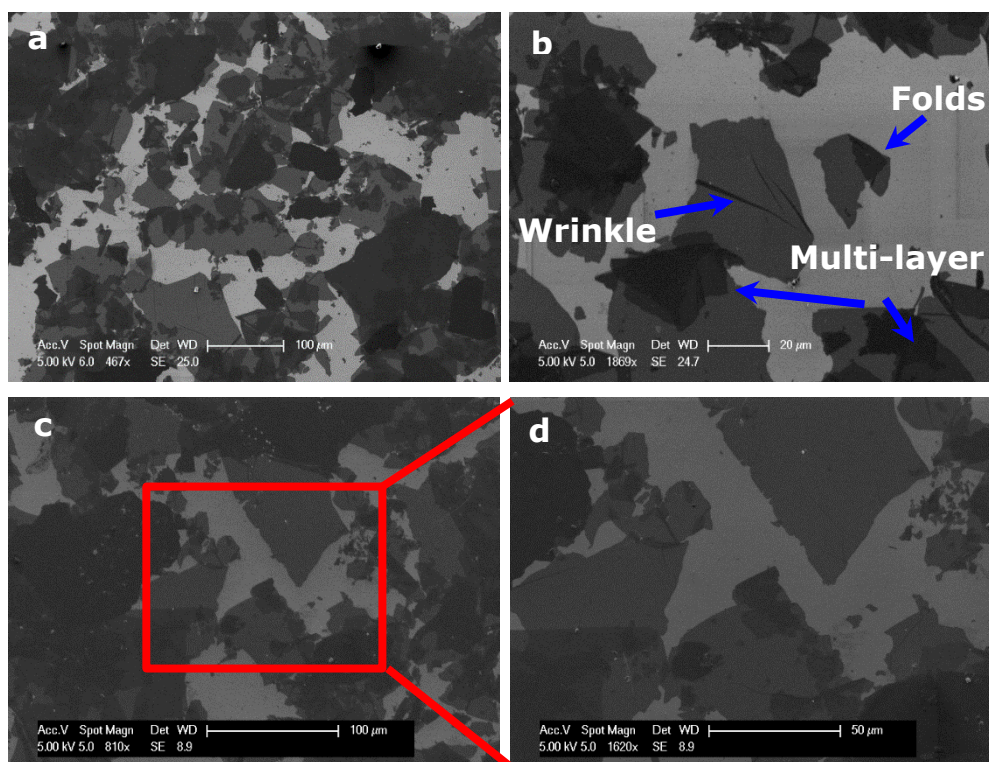


Figure 3-7. GO fragments freely lay on the Si/SiO₂ wafer

In comparison, GO fragments dried on the SiO₂/Si wafer, as displayed in Figure 3-7, showed less curly and wrinkled microstructures. This may be resulted from the joint action between the super smooth surface of the SiO₂/Si wafer and the surface tension of GO suspension during the drying process.

Layer-like fragments with less curly morphologies can be clearly seen under this condition of sample preparation. Therefore, it is more convenient for observing and characterising the dimension of the GO layers than the freeze-drying way. As can be seen, GO sheets have a very wide distribution of particle size from about 10 to 200 μm . This can be attributed to two facts. The one is that the practical crystal particle size of the single layer graphene in the raw graphite flakes is non-uniform in essence because of crystallographic defects. The other one is that violent and heterogeneous reaction conditions broke the GO sheets further.

The TEM photos in Figure 3-8 show that silk-like thin sheets cover one of the holes on the copper grid with a layer of the amorphous carbon film as the substrate. In addition, many wrinkles and folds marked by black arrows can be observed on this sheet. These microstructural features are quite similar with those observation in the SEM. It is quite difficult to differentiate this sheet from the substrate because of the extremely thin layer and almost transparent feature under the electron beam. In order to determine the true nature of the sheet, selected area electron diffraction (SAED) was conducted on the centre region (red dash line circled area) of the sheet. An apparent six-fold symmetric diffraction pattern (highlight in white circles) indicated a hexagonal reciprocal space. This hexagonal symmetry reflects a characteristic crystal lattice of graphene. This further confirmed that the as-observed object is indeed a sheet of graphene species.

It is worth to note that the diffraction patterns inserted in Figure 3-8 b are slightly different from that in 3-8 d with apparent halo ring to some extent. This can be attributed to either the contribution of the amorphous carbon substrate or a few GO layers stacking each other with different orientations. The former can bring continues and uniform diffraction rings, but the latter can result some degrees of deviation to the diffraction pattern in contrast with the first layer of GO. Certainly, the intrinsic non-uniform structure originated from the oxygen-containing groups on the GO sheet also contributes these fuzzy diffraction rings. All the above results indicated that this GO sample has a good hexagonal crystal lattice.

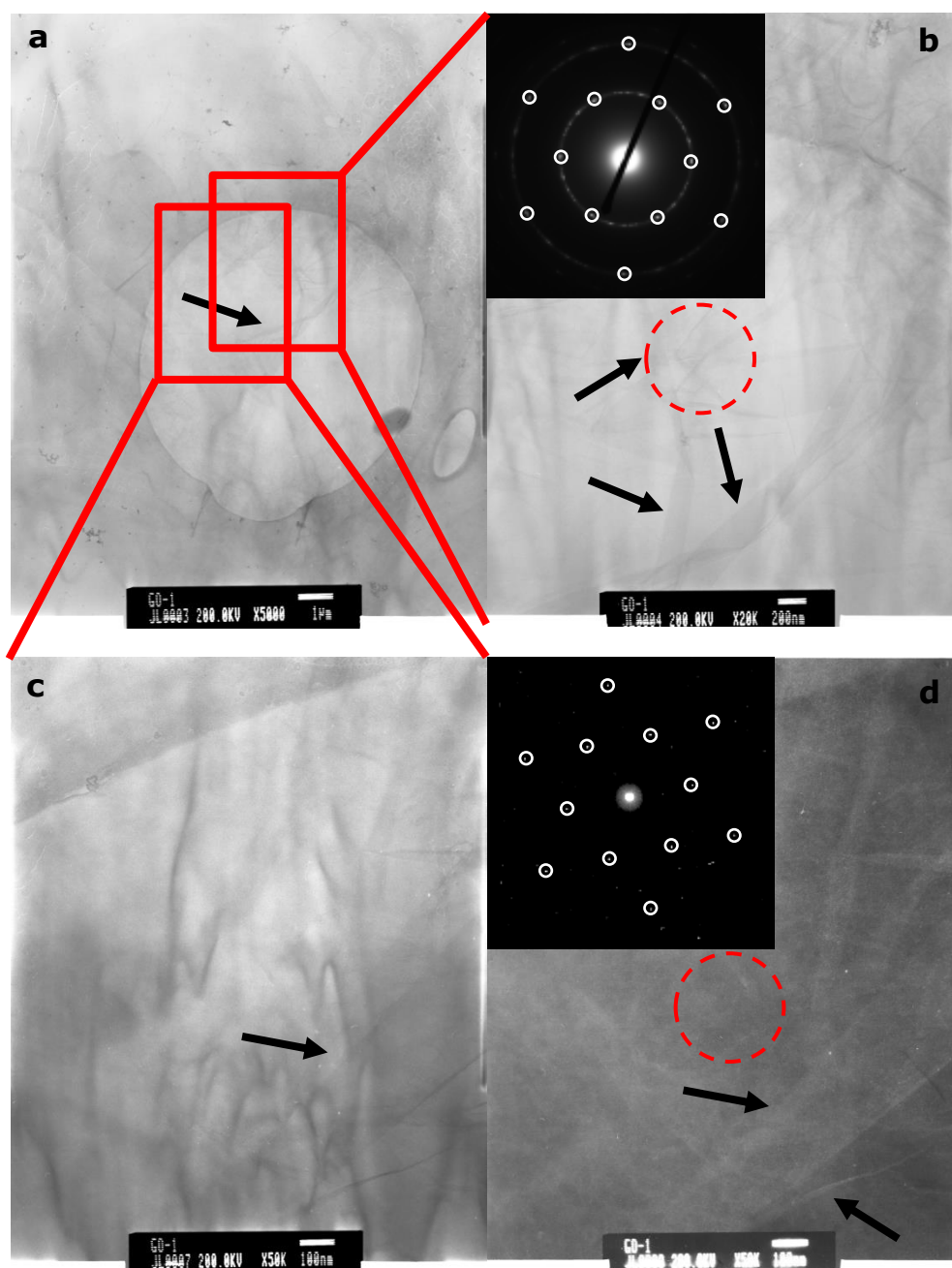


Figure 3-8. TEM images and selected area electron diffraction pattern (SAEP) of a GO sheet

3.3.2 Spectroscopic characterisation

Raman spectrum of the raw material (graphite flakes) were collected in Appendix B. Here attention was only paid on the as-synthesised GO. A certain volumes of GO suspension were dropped on the Ti plate and dried at RT. Raman spectrum was collected under an optic microscope with an objective

lens of 50X magnification. Representative point and spectrum were shown in Figure 3-9.

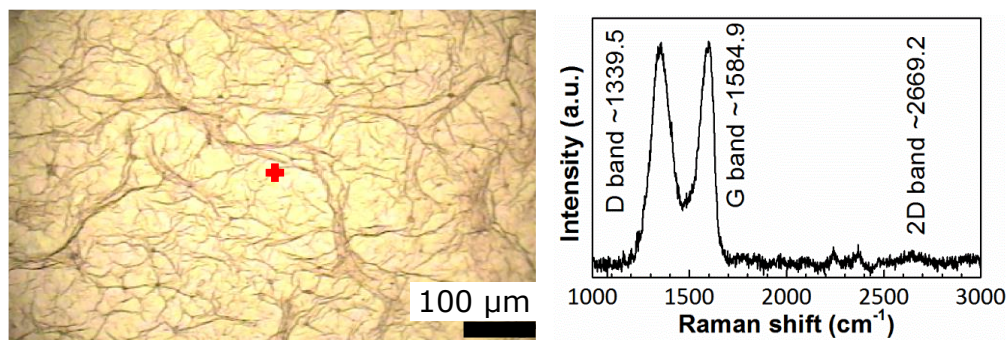


Figure 3-9. Typical Raman spectrum of GO on a representative point

Two characteristic scattering bands or peaks were observed at around 1339.5 cm^{-1} and 1584.9 cm^{-1} , corresponding to the D and G bands respectively. Several weak scatterings around 2669.2 cm^{-1} just detectable were originated from the 2D band. One of the most apparent features of the Raman spectrum of GO is two broadening G and D bands. This broadening G band can be attributed to the appearance of a D' band at 1610 cm^{-1} [218] and a series of high-intensity new bands [219,220]. It is agree well with publications that the G peak has a slightly higher intensity than the D peak in GO [221]. Comparing the Raman spectrum of GO with that of graphite flakes, obviously variations can be observed as shown Figure 3-10.

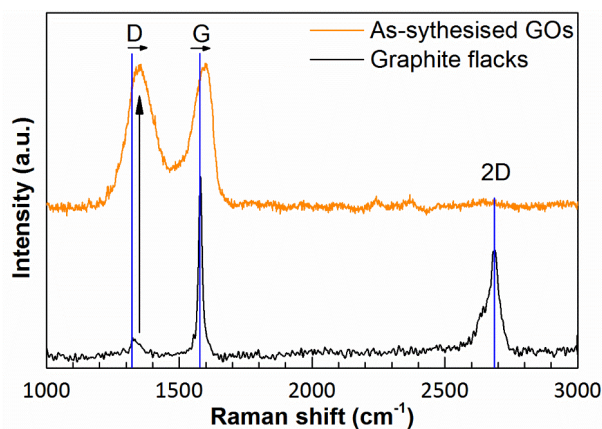


Figure 3-10. Raman spectra of graphite flakes (black line) and GO (orange line)

As can be seen, except the apparent broadening, the D and G bands of GO have a slight blue shift in contrast to the corresponding bands of graphite flacks. This broadening can be attributed to a great deal of structural defects, such as hydroxyl and epoxy groups, introduced by the violent oxidation and exfoliation during the synthesis procedure [219]. The intensity of D band climbed up quite a lot relative to the G band also indicating the existence of large amounts of defect in GO. From Figure 3-10, a more apparent transformation can be found by simply comparing the intensity of specific bands, e.g. D and G. The I_D/I_G ratio increased from 0.16 in GF to 0.99 in GO. Whilst, the ratio of I_{2D}/I_G reduced from 0.37 in GF to 0.08 in GO as collected in Table 3-1. These results were also consistent with other publications [217].

Table 3-1. Relative intensity ratio of specific Raman peaks

Samples	Ratio between specific peaks	
	I_D / I_G	I_{2D} / I_G
GF	0.16	0.37
GO	0.99	0.08

These variations not only can be attributed to a sharp increase of defects' concentration. It is also reasonable to believe that defects such as edges, vacancies, heteroatoms and functional groups can also bring comparable extent influence on the electronic structure of GO, such as bandgap opening or defect energy levels [222-224]. These effects on the electronic structure can vary the DED of GO further through different ways, e.g. the transformation of sp^3 to sp^2 hybridisation due to the bonding with oxygen atoms, vacancy defects which break the continuity of π -conjugated system. That is to say, to some extent, these spectroscopic variations can reflect the corresponding change on the electronic structure of GO or even the variation of the DED. Therefore, through observing this variation it is possible to acquire the relationship between the DED and other physiochemical properties of GO, such as the charge storage performance of GO based electrode.

UV-Vis absorbance spectra were collected on the aqueous GO dispersion of two different concentrations. Results were presented in Figure 3-

11. Two characteristic absorbance bands were observed: one shoulder band at ca. 310 nm of wavelength originated from the electronic transition of $n \rightarrow \pi^*$ [225] and the other one at ca. 230 nm which can be attributed to the electronic transition of $\pi \rightarrow \pi^*$ [225].

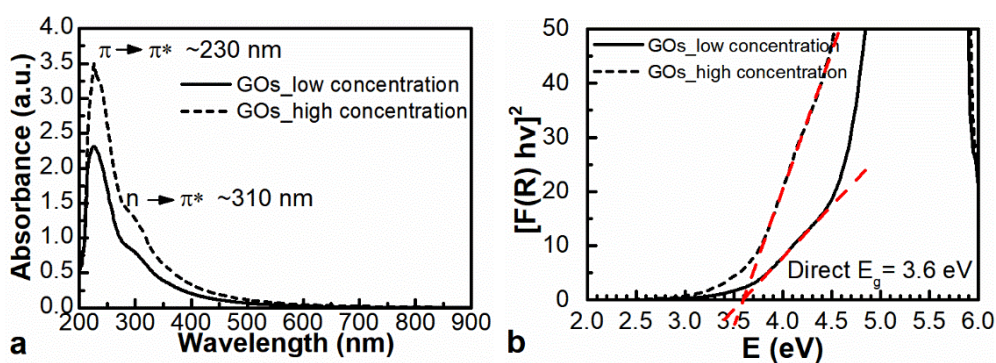


Figure 3-11. Representative UV-Vis absorbance spectra (a) and the corresponding Tauc Plot (b) of GO dispersion under two different concentrations

The intensity of these two absorption bands increases under high concentration of GO. These data agree well with other reports [225,226] on the UV-Vis spectroscopy of GO. The Tauc plot was converted from the UV-Vis spectrum based on the Tauc's empirical theory [195,196] and displayed in Figure 3-11b. In the fitting region (red dashed line) of the Tauc plots, only $n = 1/2$ gives the best linear correlation between the absorption coefficient $(\alpha h\nu)^{1/2}$ and incident photon energy $h\nu$, indicating a direct-allowed optical transition since the HOMO and LUMO. The direct-allowed energy band gap can be extracted from the intercept of the linear fit with the abscissa, i.e. absorption edges. The intercepts under both low and high concentration of GO have the same value. It indicated that the GO synthesised in this study has a direct band gap ca. 3.6 eV characterising a typical insulator. This result is expected because large amounts of oxygen-contaminating groups, such as epoxy, hydroxyl, carbonyl and carboxyl, exist on the edge or basal plane of every graphene fragment. These functional groups connected with carbon atoms of graphene through covalent bonds which further transform the orbital hybridisation of carbon from sp^2 to sp^3 , thus decreased the degree of ED of the entire conjugated system. Therefore, it can be seen that there is a probability to control

the DED and electronic structures of GO by simply adjusting the amounts of oxygen-containing groups, for example through electrochemical reduction or oxidation.

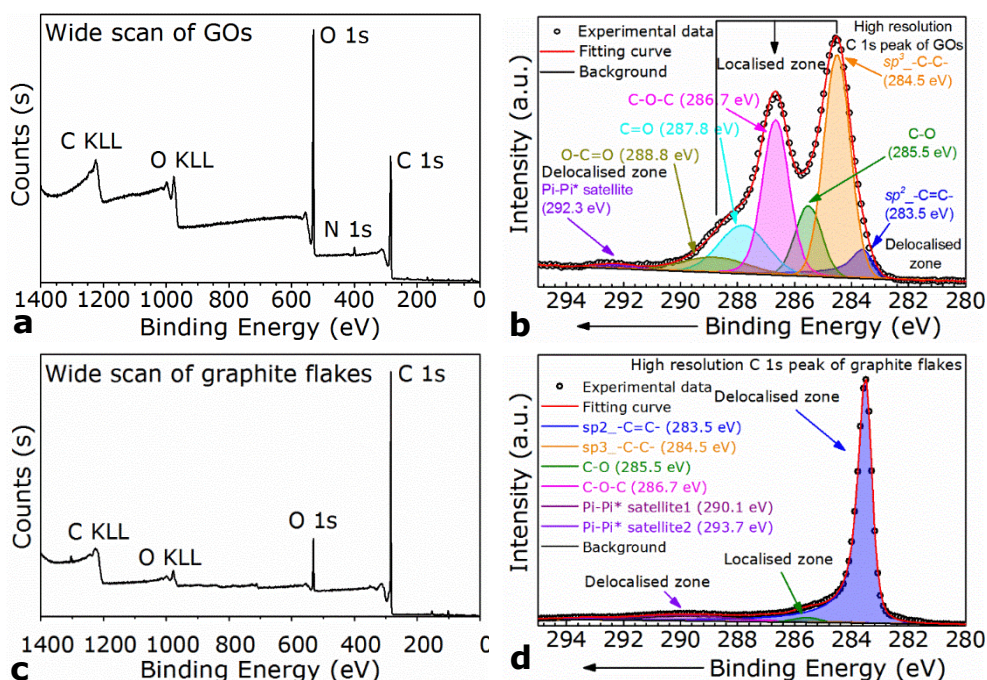


Figure 3-12. Representative XPS spectra for GO coating layer (a) wide scanning spectra (b) high-resolution C 1s spectra, and for graphite flakes raw materials (c) wide scanning spectra (d) high-resolution C 1s spectra

XPS spectra of GO coating layer were collected through the method introduced in Section 2.5.1, Chapter 2. Figures 3-12a and b showed the wide scan and the high resolution spectra of GO respectively. The XPS of graphite flakes was also measured as a control and shown in Figure 3-12c and d. These data not only can be used to examine the element ratio between the carbon and the oxygen but also to extract information about the sp^2 component from the complex C 1s peak through peak fit and deconvolution. In the wide scan spectrum of original graphite flakes (Figure 3-12c) the oxygen element was also detectable because in practice the oxygen contamination is inevitable especially on the edge plane of the graphite. The ratio of C/O is about 90.59 atom%:7.30 atom% ≈ 12.4 according to the quantitative analysis of characteristic peaks for each component. Very small amounts of silicon ca. 2.11 atom% were detected.

The existing oxygen can be attributed, on the one hand, to absorbent oxygen and oxygen-containing molecules.

On the other hand, some oxygen-containing functionalities resided on the surface of graphite flakes can also contribute to photoelectrons in the spectrum. The percentage of silicon is agreed with the certificate of the composition of the raw product. The high resolution C 1s peak of graphite flakes (Figure 3-12d) shows an asymmetric single peak at ca. 283.5 eV with a narrower full wave at half maximum (FWHM) ca. 0.6 eV. It indicated that one chemical state of carbon element predominate in graphite flakes. This major chemical state can be attributed to the sp^2 -conjugated region of graphite flakes. Two apparent π - π^* satellites shake-up also proved the existence of the large delocalised region in the raw material. A very small portion of C-O and C-O-C contributions can still be deconvolved in the C 1s envelop by considering the presence of oxygen-related functionalities.

In the case of GO, the peaks detected at 285 eV and 530 eV in the wide scan correspond to the C1s and O1s spectrum respectively. A very weak N 1s peak can also be detected at ca. 396.8 eV. The high intensity oxygen peak indicated a very high oxygen concentration in GO in contrast to that in graphite flakes and implied a high degree of oxidation of GO. No other impure peaks were detected means that almost all by-products during Hummer's synthesis procedure have been washed away properly. A relatively high quality of GO was obtained. The weak N 1s peak can be explained by the nitrogen absorption in GO fragments during and/or after synthesis.

By quantification of the peak area of each element, the carbon to oxygen ratio is ca. 2.57. This value is slightly higher than a theoretical prediction (C:O = 2) of the fully oxidised graphene but still falls into the wide range of C:O reported in literature [227]. This result included two aspects of fact: the first, the degree of oxidation on graphite/graphene depends greatly on experimental parameters, such as raw materials, the practical synthetic process and conditions. These variables make the carbon to oxygen ratio to vary in a very wide range, therefore, the above C:O ratio can only reflect an achievement in this study's experiment. The second, it can be seen that even under a strong oxidation condition of Hummer's method fully oxidised graphene (FOG) cannot

not be obtained.

The high-resolution C1s peak of GO is composed of two main peaks with ca. 2 eV chemical shift in contrast with the single C1s peak of graphite flakes. One peak at ca. 284.5 eV is a mixture peak originated from sp^2 - and sp^3 -hybridised carbons. The other one at ca. 286.7 eV is originated from the carbon atoms bonded with epoxy groups (C-O-C). The deconvolution of C 1s peak also showed there are other oxygen-containing groups in the GO.

Theoretically, the discrepancy of the adjacent chemical environment resulted in the dominating chemical shift for the C 1s peak. If the carbon bonds with a hetero-atom which has a higher electronegativity the photoelectrons of the carbon will have a larger binding energy. The double bond oxygen causes a stronger energy shift than the single bond oxygen. More hetero-atoms bonded with the central atom lead to higher chemical shift. More complicated configurations result in a wider FWHM for the sub-peak of the corresponding component.

Therefore, considering about the most possible oxygen functional groups existing in GO, the envelope of C 1s can be deconvoluted into seven components: a dominating peak of sp^3 -C-C- at ca. 284.5 eV, a secondary weak peak assigned to sp^2 -C=C- about 1 eV lower than sp^3 -C-C-, a -C-O sited at ca. 285.5 eV, a secondary intensive peak corresponding the epoxy (-C-O-C-)/ether at about 286.7 eV, a ketone (-C=O) at ca. 287.8 eV, a carbonyl (O-C=O) at ca. 288.8 eV and a shake-up broad band corresponding to the π - π^* satellite photoelectrons at ca. 292.3 eV.

Through peak fitting based on the above deconvolution, it can be seen that the synthetic curve for C 1s (solid red line) had a high consistency with the experimental data (black circle line). It indicated that epoxy (-C-O-C-)/ether is the major component of oxygen-containing functional groups in contrast with the other functional groups in the GO. It agreed well with previous experimental and theoretical reports [228,229]. In the true structure of GO [230], except oxygen-modified region and other intrinsic defect regions the rest of regions on the basal plane of GO are simply pure graphitic area with well-preserved double bonds. This fact was revealed under the observation of high resolution TEM in

Ref. [230].

Based on these findings, seeing from an atomic level, the sp^2 -hybridised region can be strictly distinguished from the sp^3 -hybridised region on the basal plane of GO because of the well-defined boundary between these two regions. Therefore, the origin of photoelectrons can also be separated into two classes of source. The one is originated from the localised region in which sp^3 -hybridised predominates the atomic configuration, and the other one is delocalised region in which sp^2 -hybridised is the only configuration. It is very important to make this discrimination, especially for this study, because the electronic localised region and delocalised region can be easily distinguished in the high-resolution C 1s peak.

According to this, the DED of GO can further be estimated and correlated with the spectroscopic composition of C 1s peak. In practice, the component of the C 1s peak can be classified into two main groups: the first, delocalised zone includes only the sp^2 -C=C- contribution and its shake-up band, the second group contains the contributions originated from the sp^3 -C-C- and all other oxygen-containing components. If the DED is defined as a ratio between the sp^2 contribution and the sum of sp^2 and sp^3 contributions, corresponding to the delocalised (D) and localised (L) region respectively. The following Equation 3-1 can be established to correlate the DED of GO with the peak area of sp^2 and sp^3 subcomponents in the C 1s envelop.

Regarding the deconvolution of the C 1s peak, the sp^2 component should be fitted with asymmetric shape (preferably derived from a real graphite or graphene sample). Here, in this study it was derived from the high resolution C 1s peak of graphite flakes and CVD monolayer graphene. The sp^3 carbon and functionalised carbon should be fitted with symmetric peak shapes. The sp^3 carbon peak should be 1 eV to the higher binding energy side of the sp^2 component [231]. Therefore, as long as both the sp^2 and sp^3 subcomponents can be fitted and separated through a proper deconvolution, the DED of samples can be semi-qualitatively describe as:

$$\text{DED (\%)} = \frac{sp^2}{sp^2 + sp^3} \times 100\% =$$

$$\frac{D}{D+L} = \frac{\text{Peak area (sp}^2 \text{ contributions)} \times 100}{\text{Peak area (sp}^2 \text{ contributions)} + \text{Peak Area (sp}^3 \text{ contributions)}} \% \quad \text{Equation 3-1}$$

where Peak area (sp² contributions)=Peak Area (sp²-C=C-),

Peak Area (sp³ contributions)=Peak Area (sp³-C-C-).

Thus, the DED of newly synthesised GO can be roughly approximated to be about 6.16% : (6.16 + 35.57)%, i.e. $sp^2/(sp^2+sp^3) \approx 14.76\%$. While the DED of graphite flake is about 86.01% : (86.01 + 0.46)% = 99.47%.

The above Equation 3-1 is named as '*DED equation*' for the convenient citation in this dissertation. This equation will be used as a key indicator to evaluate the DED of all GO samples in this study.

It has to mention that the deconvolution of high-resolution C 1s peak is not sufficient for the identification the sp^2/sp^3 ratio properly because of the arbitrary assignment during the deconvolution for solving the accurate concentration of sp^2 and sp^3 subcomponents. Therefore, in this research, another method was used to acquire a semi-quantitative estimation of the sp^2/sp^3 ratio, i.e. the DED. This method is the so-called '*D-parameter*' which was established by Lascovich and co-authors through the investigation in amorphous carbon structures [232]. This method utilises the C KLL Auger peaks which are originated from the relaxation phenomena of photoelectrons from the L shell to K shell of carbon atoms around the kinetic energy from 220 to 290 eV or the binding energy from 1197 to 1267 eV. The D-parameter denotes the distance between the most positive maximum and the most negative minimum of the first derivative curve of the C KLL peaks [232].

The D-parameter of a pure diamond sample, i.e. ideal sp^3 -hybridisation, equals to ca. 13 to 14.2 eV. Whereas, this parameter increases to ca. 21 to 22 eV in the highly oriented pyrolytic graphite (HOPG), i.e. pure sp^2 -hybridisation. It was found that the relative concentration between sp^2 and sp^3 -hybridisation in amorphous carbon is linearly related to the D-parameter [232].

Figure 3-13 showed the first derivative of X-ray induced C KLL spectra from graphite flacks and as-synthesised GO as well as their corresponding D-parameters. As can be seen that the D-parameter of graphite flakes reaches

around 20 eV, indicating a higher percentage of sp^2 hybridisation or a higher DED. While the D-parameter of as-synthesised GO is only 14 eV. That means plenty of sp^2 -hybridisation bonded carbons were transferred into sp^3 -hybridisation in GO, therefore, the percentage of sp^2 , i.e. the DED, declined. If the D-parameters of pure diamond (13 eV) and HOPG (21 eV) in references [232,233] were taken as the two extreme cases of the sp^2 concentration, i.e. 0% and 100%, respectively, then the D-parameters of the graphite flakes and GO can be used to estimate the actual sp^2/sp^3 ratio, i.e. the DED in these samples through a linear interpolation based on the relationship of $DED\% = sp^2\% = (D_i - 13)/(21 - 13) \times 100\%$, where D_i denotes to the D-parameter of the specific sample. Thus, the DED ($sp^2\%$) of graphite flakes is about 87.5%, and it is 12.5% for the as-synthesised GO. These estimations are only slightly lower than those DED% estimated from the deconvolution analysis.

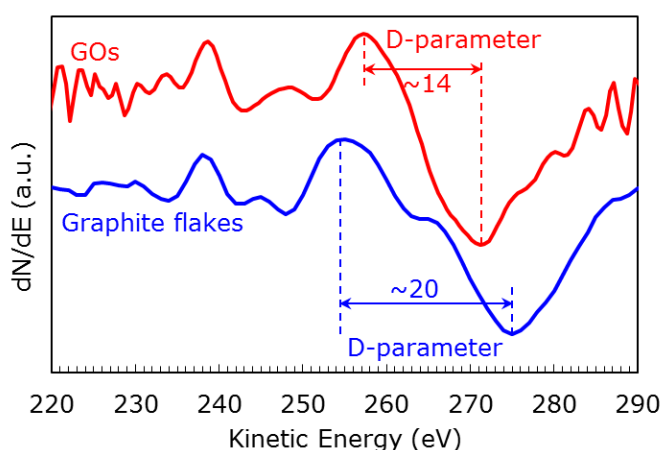


Figure 3-13. The first derivative of C KLL spectra of raw material: graphite flakes (solid blue line) and GO (solid red line) and corresponding D-parameters

3.4 Electrochemical behaviour and capacitance of GO electrode

In order to investigate the electrochemical properties, especially the capacitive charge storage of GO as promising electrode materials, ECCs were carried out on the GO working electrode which was fabricated by the method introduced in Section 2.4.2, Chapter 2. The effective capacitive potential range (CPR) and the electrochemical redox window of GO were investigated in the following sections. These information facilitate to find a proper reduction

potential for the next step of adjustment to the DED of GO through modifying its oxidation degree. In addition, impedance behaviour was also included to provide supporting information of the charge storage mechanism of GO electrodes.

3.4.1 GO on platinum working electrode

A series of CV measurements were carried on GO coated PtWE in the electrolyte of 3.0 M KCl and 1.0 M H₂SO₄ respectively. Representative experiment data were shown in Figure 3-14a and b. Bare PtWE was scanned firstly as a control in both electrolytes to learn its background current. Pronounced difference was observed on the CVs in the two electrolytes.

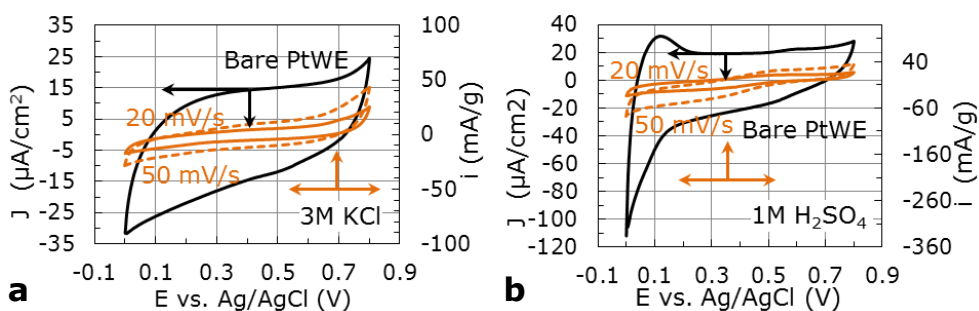


Figure 3-14. Representative CVs of GO coated Pt working electrode of 2 mm in diameter, CE: graphite rod. Data was collected in 3.0 M KCl (a) and 1.0 M H₂SO₄ (b) respectively. The black solid line is bare PtWE at a scan rate of 20 mV/s. The current density is normalised by the projected area of PtWE to the left side and the actual loading mass of GO to the right side.

In 3.0 M KCl, bare PtWE has a hysteretic current response showing a depressed shape. It can be attributed to a typical EDLC in series with a certain values of intrinsic resistance in the potential range of 0.0-0.8 V vs. Ag/AgCl. The charging and discharging current density at scan rate of 20 mV/s is about $\pm 15 \mu\text{A}/\text{cm}^2$. After coated with GO, the total current response on the WE was heavily suppressed to only ca. $\pm 2 \mu\text{A}/\text{cm}^2$, at 20 mV/s and less than $\pm 5 \mu\text{A}/\text{cm}^2$, at 50 mV/s. It indicated an extremely high resistance of the coating layer which can be attributed to the insulator nature of GO coating layer which conceals, or precisely blocks the current response originated from the Pt substrate. At the negative and positive potential boundaries, slightly rising cathodic and anodic

currents may be originated from the adsorption of protons and anions or even anodic oxidation processes respectively.

In 1.0 M H₂SO₄, apparent cathodic and anodic waves can be observed in bare PtWE approaching the left border of the CV, which can be attributed to the hydrogen adsorption and desorption respectively because of the proton-rich environment. Especially the hydrogen desorption peak appearing at ca. 0.127 V vs. Ag/AgCl is in good agreement with previous reports [234]. The charging and discharging current density from 0.2 V to 0.8 V is about $\pm 20 \mu\text{A}/\text{cm}^2$, at 20 mV/s. When the WE was coated with GO the total current response diminished to about $\pm 5 \mu\text{A}/\text{cm}^2$, at 20 mV/s and ca. $\pm 7 \mu\text{A}/\text{cm}^2$, at 50 mV/s respectively. It is noteworthy that the hydrogen desorption and adsorption were also dramatically depressed when PtWE was coated with GO in this electrolyte.

If the Equation 1-13 introduced in Section 1.1.1.2, Chapter 1 is employed, the area-specific capacitance of GO coated electrode can be roughly estimated to ca. $100 \mu\text{F}/\text{cm}^2$ in 3.0 M KCl and $250 \mu\text{F}/\text{cm}^2$ 1.0 M H₂SO₄ respectively. The area-specific capacitance of bare PtWE can also be estimated in this way showing about $750 \mu\text{F}/\text{cm}^2$ in 3.0 M KCl and $1000 \mu\text{F}/\text{cm}^2$ in 1.0 M H₂SO₄ respectively. These two values exceeded at least two orders magnitude of the common metallic electrode ($20\text{--}50 \mu\text{F}/\text{cm}^2$) and the bright platinum ($17 \pm 1 \mu\text{F}/\text{cm}^2$) [234]. This may be because some contributions of the pseudocapacitance originated from the absorption/desorption of protons on the platinum surface to the apparent capacitance in this experimental condition. Therefore, it can be seen that the platinum may not be a good choice as the current collector for investigating the electrochemical property of carbon-based electrode materials, especially in the proton-rich electrolyte.

The actual loading mass of GO in the electrode can be determined as introduced in Section 2.4.3, Chapter 2. Thus, the specific capacitance of GO coated PtWE can also be roughly estimated at ca. 0.25-0.40 F/g from the average current response. Another way to estimate the capacitance is using the charging/discharging read from the Autolab and following Equation 3-2.

$$C = \frac{Q_+ + Q_-}{2U} \quad \text{Equation 3-2}$$

where Q_+ is the charge stored during the charging process, Q_- the charge released during discharging process, and U the potential range of CV (here, 0.8 V). Then again specific capacitance (C_m) can be obtained in both electrolytes at various scan rates and shown in Table 3-2. The total interfacial capacitance which can further show a good agreement with the former method using Equation 1-13.

Figure 3-15 plotted the trend of measured capacitance and specific capacitance of GO coated on PtWE vs. the scan rate in both electrolytes based on the results shown in Table 3-2. Firstly, capacitance obtained in 1.0 M H_2SO_4 is always higher than that in 3.0 M KCl. This can be ascribed to part of contribution from the pseudocapacitance originated from protons in H_2SO_4 , while such a pseudocapacitance is relatively low in KCl because of a lower proton activity. Secondly, both capacitance values in two electrolytes decrease gradually as the scan rate increases. It indicated a common phenomenon that under higher charging-discharging rate counter ions cannot fully enter or release from some porous channel as fast as enough along with the sweep speed of potential. From another aspect, the pseudocapacitance can also be restrained at a higher charging/discharging speed because of its nature of faradaic charge storage. This is also the reason when the scan rate increases the capacitance in 1.0 M H_2SO_4 gradually approaches that in 3.0 M KCl. All of these results indicated that GO is definitely an insulator in nature, which has a very poor conductance and capacitive performance. This also supports the findings of the UV-Vis spectroscopic characterisation in Section 3.3.2.

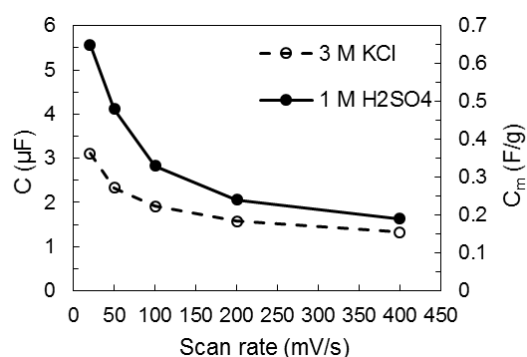


Figure 3-15. Capacitance performance of GO coated PtWE vs. scan rate in 3.0 M KCl (dash line) and 1.0 M H_2SO_4 (solid line) electrolyte

Table 3-2. Actual measured capacitance (C) and specific capacitance (C_m) derived from instrumental reading charging/discharging data on GO coated PtWE

Scan rate (mV/s)		20	50	100	200	400
C (μF)	3.0 M KCl	3.1	2.3	1.9	1.6	1.3
	1.0 M H_2SO_4	5.9	4.3	3.0	2.2	1.7
C_m^* (F/g)	3.0 M KCl	0.35	0.26	0.21	0.17	0.15
	1.0 M H_2SO_4	0.65	0.48	0.33	0.24	0.19

* The mass of coating GO is around $10\text{ }\mu\text{g}$ determined by means of the methodology in Section 2.4.3, chapter 2.

3.4.2 GO on polished titanium working electrode

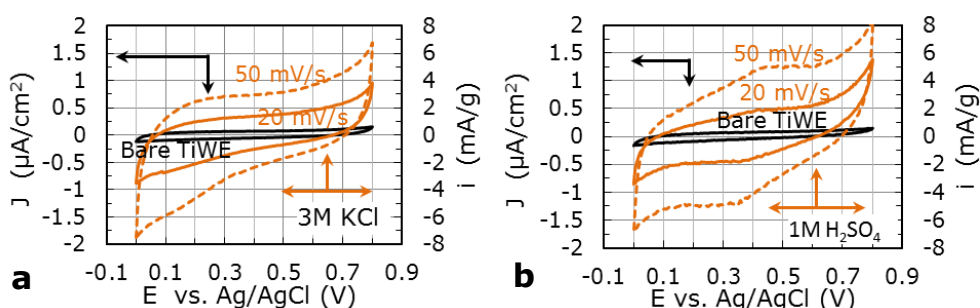


Figure 3-16. Representative CVs of GO coated titanium working electrode with a practical exposure area of ca. 0.4418 cm^2 , CE: graphite rod. Data was tested in the electrolyte of 3.0 M KCl (a) and 1.0 M H_2SO_4 (b) respectively. The black line is bare TiWE at 20 mV/s. The current density is normalised by the projected area of TiWE to the left side and the actual loading mass of GO to the right side.

The good catalysis of platinum for the reduction of protons has been known for a long time [235,236], especially under negatively polarisation and in acidic media. This also leads to a relatively small exchange-current density of hydrogen evolution on platinum (ca. 3.1 amp/cm^2) in H_2SO_4 [237]. The aqueous electrolyte can partially penetrate the GO coating layer and contact with the substrate of platinum. If hydrogen evolution occurs the accumulation of hydrogen bubbles will be inevitable. This may cause bad affects to the GO coating layer, e.g. the stripping of GO off the platinum substrate, especially during a long-term negative polarisation. This is undesirable and can further introduce unexpected impedance, such as the equivalent resistance ESR and/or charge transfer resistance R_{ct} , to the electrode, hence resulting in unreliable observation and analysis about the true electrode behaviour of GO.

Considering these issues, a titanium substrate was utilised in subsequent experiments to substitute for the platinum WE because of its relative larger exchange-current density for hydrogen evolution (ca. 8.2 A/cm^2) in H_2SO_4 , i.e. poor catalytic activation for hydrogen evolution [237]. CV characterisations on the home-made GO working electrodes were further conducted to investigate the electrode behaviour. Experimental results were collected in both 3.0 M KCl and 1.0 M H_2SO_4 electrolytes and plotted in Figure 3-16a and b.

Bare TiWE was scanned beforehand as a control in both two electrolytes to ascertain the background current response shown as the black solid line in Figure 3-16a and b. As is expected, a quite low background current response was barely detected on bare titanium WE within the potential range of 0.0 - 0.8 V. This potential range has been found in many studies [163,168] to be an effective capacitive potential range of GO electrode material vs. the Ag/AgCl. Therefore, the current response in this potential range was paid more attention in this study.

The current density at 20 mV/s in both electrolytes is ca. $0.05 - 0.08 \mu\text{A/cm}^2$, corresponding to the area capacitance ca. $2.5 - 4.0 \mu\text{F/cm}^2$. In contrast with the highly depressed CVs of the GO coated PtWE, the CVs of GO coated TiWE exhibit more features of GO itself rather than the background current response coming from the current collector.

In the meantime, the shape of CVs is distinguishable in two electrolytes. In 3.0 M KCl, CVs show some extent of depressed rectangular shape with slightly rising anodic and cathodic currents at the two boundaries of the potential range. The charging and discharging current density at 20 and 50 mV/s scan rate are ca. ± 0.35 and $\pm 0.75 \mu\text{A/cm}^2$ respectively, which are almost ten times higher than the background response of bare TiWE. The depressed shape of CVs indicates a very high resistance of the GO coating. Slightly rising current responses are originated from the adsorption of protons and anodic oxidation process respectively.

On the other side, in 1.0 M H_2SO_4 , a lean parallelogram CV with a pair of weak current waves at around 0.4 V was observed within the potential range. The average charging/discharging current densities, in this case, are ca. ± 0.5

and $\pm 1.0 \mu\text{A}/\text{cm}^2$, at 20 and 50 mV/s respectively. Noteworthy, the pair of weak current waves are enhanced as the scan rate goes up. This pair of current waves may originate from a charge storage behaviour relative to oxygen-containing functional groups and H^+ ions [3,4] following the reaction shown in Equation 3-3.



The same as in KCl, apparent rising of anodic and cathodic current can be observed in 1.0 M H_2SO_4 on the positive and negative boundaries of the potential range because of the hydrogen evolution to the left and oxidative process to the right respectively. It can be seen, so far, that titanium has a very weak background interference to the current response of GO in contrast with the platinum. That is to say, when the titanium is coated with GO, the current response mainly reflects the i-E performance of the loaded materials (GO).

Using Equation 1-13, the area-specific capacitance (C_a) of GO working electrode can be roughly estimated to ca. $16 \mu\text{F}/\text{cm}^2$ in 3.0 M KCl and $23 \mu\text{F}/\text{cm}^2$ 1.0 M H_2SO_4 respectively. The area-specific capacitance of bare Ti substrate can also be estimated in this way ca. $2.5 - 4.0 \mu\text{F}/\text{cm}^2$ in both two electrolytes. It can be seen that the area-specific capacitance of GO WE is at least two orders of larger than the background value. In conclusion, in comparison with platinum, titanium as a current collector may be a better choice for investigation the electrochemical performance of carbon-based electrode materials, especially in the proton-rich electrolyte.

Table 3-3. Actual measured capacitance (C) and specific capacitance (C_m) derived from instrumental reading charging/discharging data on GO coated TiWE.

Scan rate (mV/s)		2	5	10	20	50	100
C (μF)	3.0 M KCl	22.6	16.4	13.9	10.0	8.9	7.3
	1.0 M H_2SO_4	35.2	18.1	12.3	9.4	8.3	7.2
C_m^* (F/g)	3.0 M KCl	0.19	0.14	0.12	0.09	0.08	0.06
	1.0 M H_2SO_4	0.31	0.16	0.11	0.08	0.07	0.06

* The mass of coated GO was weighed directly on the $1 \times 1 \text{ cm}^2$ titanium plate. The average value is about $100 \pm 10 \mu\text{g}$ for a $25 \mu\text{L}$ GO dispersion with a concentration ca. $4 \pm 0.4 \text{ g/L}$.

The specific capacitance of GO coated TiWE can be roughly estimated about 0.1 ± 0.05 F/g. Another way to estimate the practical capacitance is using the charge storage obtained from the Autolab and Equation 3-2. Thus specific capacitance can be calculated at various scan rates and shown in Table 3-3, which showed good agreement with the previous roughly estimation.

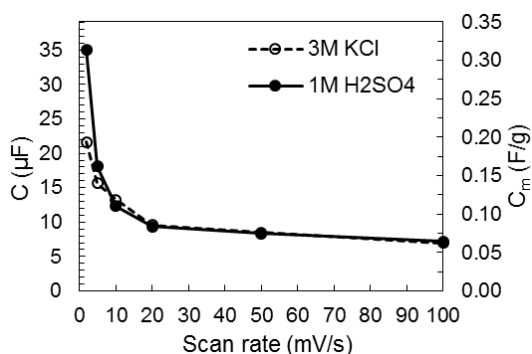


Figure 3-17. Capacitance performance of GO coated TiWE vs. scan rate in 3.0 M KCl (dash line) and 1.0 M H₂SO₄ (solid line)

Figure 3-17 plots out the trend of area- and mass-specific capacitance of GO coated TiWE as a function of scan rate in two electrolytes based on the data shown in Table 3-3. The greatest distinction between Figure 3-17 and Figure 3-15 in which Pt as the current collector is that the total capacitance on the titanium current collector in both electrolytes is closer to each other, especially at scan rate higher than 20 mV/s.

As discussed in the previous Section 3.4.1, the relatively large background current of Pt contributes a great part of the total capacitance. This portion of capacitive contribution is, in essence, a pseudocapacitance originated from the adsorptive protons, which covers up the weak capacitive current response originated from the GO. While this is not the case when the Ti is the current collector because of its lower background current. In the meantime, at a higher charging/discharging speed the pseudocapacitance also decreases because of its faradaic nature. Therefore, the total interfacial capacitance in 1.0 M H₂SO₄ gradually approaches that of in 3.0 M KCl as the scan rate increases.

In addition, the specific capacitance in both electrolytes are closer to each other in the case of Ti than that in the case of Pt.

Electrochemical impedance spectra were further studied to provide more information about the capacitive and electrode behaviour of GO electrode. Firstly, the frequency-distribution of the interfacial capacitance vs. the stand-by potential applied on bare TiWE within the effective capacitive potential range was observed at eight specific frequencies. The as-concerned interfacial capacitance (C_f) at a given frequency (f) and stand-by potential (p) was estimated from the Equation 3-4:

$$C_f^p = -\frac{1}{2\pi f Z''} \Big|_p \quad \text{Equation 3-4}$$

where Z'' is the imaginary part of the impedance recorded by the instrument.

Representative potential dependency of capacitance (C-E plots) of GO working electrode were displayed in Figure 3-18a and b. The interfacial capacitance distribution at different frequencies and stand-by potentials revealed the practical charge storage performance at the interface of the GO coated TiWE.

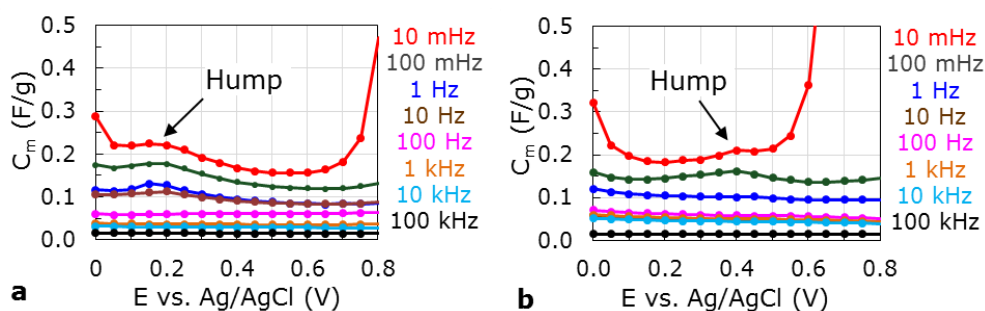


Figure 3-18. Representative potential dependency of capacitance of the GO electrode in 3.0 M KCl (a) and 1.0 M H_2SO_4 (b). Capacitance is normalised by the actual loading mass of GO.

In most of the potential region GO had almost a constant capacitance. Great deviations away this constant value were only observed at the two potential boundaries approaching 0.0 V and 0.7 V in both two electrolytes. This increase of capacitance can be attributed to the decrease of imaginary impedance (Z'') because of the adsorption of protons at the negative side and

oxidation of chloride and/or hydroxyl ions at the positive side. Therefore, these boundary deviation phenomena cannot account for the capacitive behaviour.

Noteworthy, as the specific frequency lower than 100 Hz, a very weak hump structure (black arrowed) emerged in the C-E distribution at ca. 0.15 V in 3.0 M KCl and ca. 0.4 V in 1.0 M H₂SO₄ respectively. These hump structures became more and more extruding as the frequency went down. It is coincidentally corresponding to the location of the broad current waves observed in CVs as shown in Figure 3-16. However, this feature has not been observed in the bare titanium background. Therefore, it is reasonable to account this feature to be originated from GO. By now, the origin of these humps can only be attributed to the charge storage mechanism originated from the interfacial reaction shown in Equation 3-3 between adsorptive hydrogen ions (H_{ads}) and oxygen-related functional groups. The positive shift of the hump in H₂SO₄ may be related to a higher activity of H⁺ ions in H₂SO₄ than in KCl.

Based on the above investigation of the C-E distribution, representative stand-by potentials were selected to carry out further full-spectrum scanning from 100 kHz to 10 mHz. Representative Nyquist and Bode plots were shown in Figure 3-19a to d.

Different from the pure capacitive behaviour of bare titanium substrate, the GO electrode showed more features in its EIS spectra. Firstly, the ESR which was estimated from the intercept of the impedance distribution on the abscissa axis in Nyquist plots maintained at ca. 20 Ohm and 16 Ohm in 3.0 M KCl and 1.0 M H₂SO₄ respectively. It indicated that a thin layer of GO did not contribute too much resistance on the overall ESR of the cell used in this experiment. Secondly, more variations can be observed on the phase angle-frequency profile from the medium 1000 Hz to low frequency limit in contrast with the pure capacitance of bare TiWE which has almost a constant phase angle approaching to -90° in the same frequency region. This is evidently relative to the interfacial properties of the GO electrode. Thirdly, in 1.0 M H₂SO₄, at more positively stand-by potential the real part of impedance (Z') increased faster than the imaginary part (Z'') resulting to a non-linear relationship in the low frequency region. It can be attributed to the electrochemical oxidation of GO and increased charge transfer resistance at the GO | electrolyte interface.

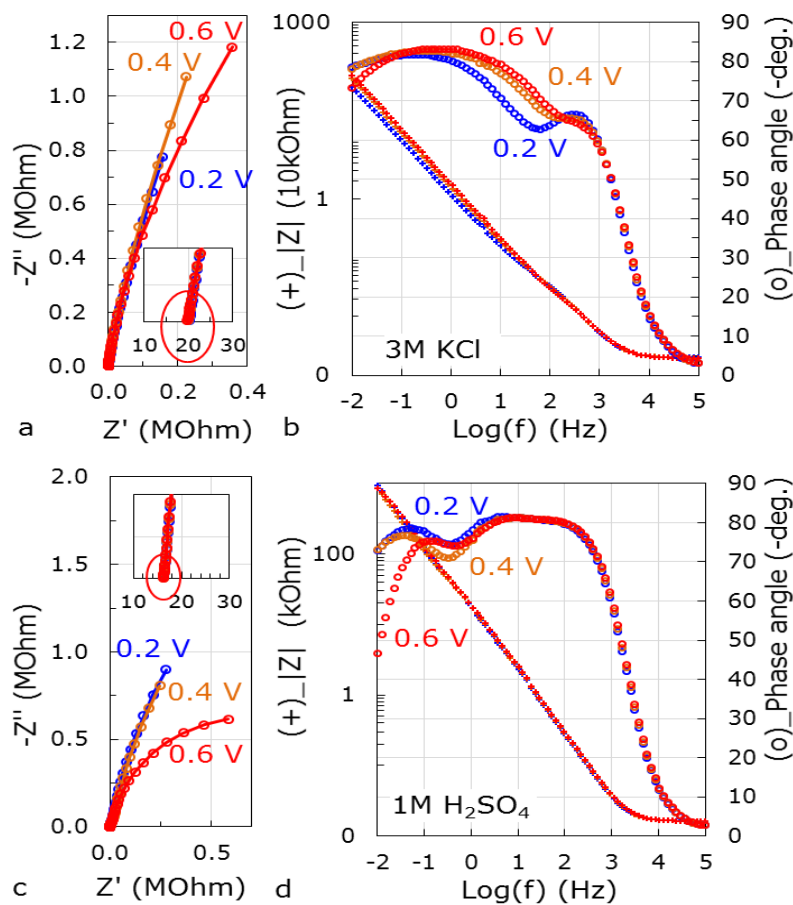


Figure 3-19. Representative EIS of GO coated TiWE with a practical exposure area of 0.4418 cm², CE: graphite rod. Data was collected in 3.0 M KCl. (a) Nyquist plot and (b) Bode plot; in 1.0 M H₂SO₄. (c) Nyquist plot and (d) Bode plot respectively.

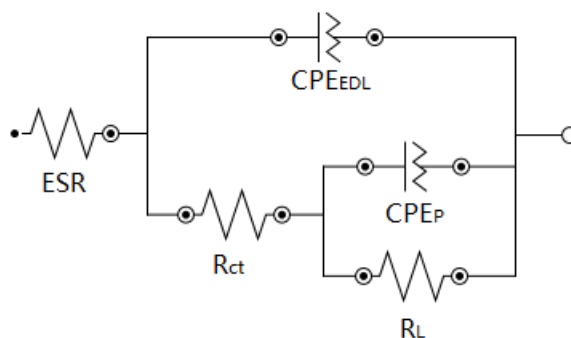


Figure 3-20. The most optimised equivalent circuit used to simulating the GO coated titanium electrode in both 3.0 M KCl and 1.0 M H₂SO₄. The CPE_{EDL} represents the EDLC, CPE_P the pseudocapacitance, R_{ct} the charge transfer resistance and R_L the leakage resistance.

Fitting and simulation of EIS data were conducted further to give more informative details of the GO electrode. According to the most optimised fitting results, an equivalent circuit shown in Figure 3-20 was used to represent the GO electrode in both electrolytes of 3.0 M KCl and 1.0 M H₂SO₄. The fitting data at different stand-by potentials were also collected in Table 3-4 and 3-5.

Table 3-4. Fitting values for components in the equivalent circuit of Figure 3-20 in 3.0 M KCl

Components	GO coated titanium WE in 3.0 M KCl				
Stand-by potential (V)	0.2	0.3	0.4	0.5	0.6
ESR (Ω)	19.8	19.8	19.7	19.5	19.6
CPE _{EDL} ($\mu\text{S}\cdot\text{s}^n$)	6.92	6.79	6.51	6.32	6.20
Frequency power n_{EDL}	0.918	0.919	0.922	0.924	0.925
R _{ct} (Ω)	968	866	745	658	586
CPE _p ($\mu\text{S}\cdot\text{s}^n$)	8.74	6.55	5.08	4.35	4.03
Frequency power n_p	0.899	0.904	0.917	0.927	0.930
R _L ($M\Omega$)	15.1	11.6	13.1	9.41	6.47

Table 3-5. Fitting values for components in the equivalent circuit of Figure 3-20 in 1.0 M H₂SO₄

Components	GO coated titanium WE in 1.0 M H ₂ SO ₄		
Stand-by potential (V)	0.2	0.4	0.6
ESR (Ω)	16.1	16.1	16.0
CPE _{EDL} ($\mu\text{S}\cdot\text{s}^n$)	8.77	8.31	8.10
Frequency power n_{EDL}	0.936	0.939	0.938
R _{ct} ($k\Omega$)	114	92.4	102
CPE _p ($\mu\text{S}\cdot\text{s}^n$)	4.87	6.61	4.63
Frequency power n_p	0.938	0.909	0.978
R _L ($M\Omega$)	4.85	5.25	1.23

As can be seen from these fitting results, the ESR in both electrolytes and at different stand-by potentials maintains almost a constant value which is consistent with that is shown in Nyquist plots (inserts in Figure 3-19a and c). The other electric components in 3.0 M KCl decline in value slightly as the stand-by potential goes more positively. This can be attributed to the variation of the counter ion species in the EDL on the electrolyte side under different stand-by potentials, such as from K⁺ to Cl⁻ ions. In 1.0 M H₂SO₄, the general tendency for each electric component was the same as that observed in 3.0 M KCl, while noteworthy, charge transfer related pseudocapacitance (CPE_p) showed a

higher value at the stand-by potential of 0.4 V in contrast with those at 0.2 V and 0.6 V. This was consistent with the current waves observed in CVs (Figure 3-16b).

Generally speaking, the total interfacial capacitance of GO electrode in both electrolytes can be separated into two parts: the one is EDLC, and the other one is charge transfer-related pseudocapacitance. The pseudocapacitance and its accompanying charge transfer resistance (R_{ct}) varied a lot in contrast with the EDLC (CPE_{EDL}) under different stand-by potentials. This finding in EIS of GO electrode may offer an opportunity to study the pseudocapacitance and its nature in GO electrode materials through the EIS analysis. It has to mention that the reason why this study chose KCl and H_2SO_4 as the electrolyte. Not only because they are the most commonly used aqueous electrolytes in research and commercial supercapacitor devices but also the difference of the activity of H^+ ions in these two electrolytes. As reviewed in Section 1.1.1.3, Chapter 1, the proton-rich atmosphere enables outstanding pseudocapacitance in most of classical pseudocapacitive materials, e.g. RuO_2 , $\alpha-MnO_2$, activated carbonaceous and graphene species. That is to say, in KCl the interfacial capacitance is dominated by the EDLC with only a slight portion of pseudocapacitance, while in H_2SO_4 the pseudocapacitance takes the major part in the total interfacial capacitance because of the higher activity of H^+ ions. Therefore, H_2SO_4 as a proton-rich electrolyte is a good media for this study to observe the pseudocapacitive charge storage of GO electrodes.

3.5 Summary

Optic microscopy, SEM, TEM and AFM were employed to characterise the as-synthesised GO in this chapter. Fairly curly and folded single layer and/or few layers were confirmed as the main morphology of the dried GO. SAED armed TEM characterisation further determined the crystal lattice of GO. These results indicated a successful preparation of this major target material.

Raman spectroscopy analysis uncovered large amounts of in-layer and edge defect existing in GO. UV-Vis spectroscopy revealed that GO is an insulator in nature with a direct energy gap of ca. 3.6 eV because of the very high degree of oxidation. XPS characterisation found different hybridisation

states of carbon and several types of oxygen-related functional group existing in GO. Based on the bounding state of electrons in functional groups and conjugated structure, the high resolution C 1s peak of GO can be further classified into two groups i.e. the localised and delocalised groups through proper peak fit and deconvolution. More significantly, a useful '*DED Equation*' was established based on the deconvolution result, which can further correlate the as-concerned DED of GO with the peak area of sp^2 and sp^3 -hybridisation. D-parameter was extracted from the C KLL Auger electron spectrum of GO and graphite flakes. This parameter, as a supplement of deconvolution analysis, can be used as another semi-quantitative way to estimate the DED of GO.

Electrochemical charge storage performance of GO coated Pt and TiWE were investigated by CV and EIS. CV results indicated that the extremely high resistance of GO arising from its insulating nature blocks almost all current flowing into or out from the working electrode resulting in a very weak current response and poor capacitive charge storage. A larger background current of platinum in contrast with that of titanium covers up the electrode behaviour of GO. Therefore, it was determined that the titanium is a better substrate in contrast with the platinum for this research.

Furthermore, EIS analyses revealed more detailed impedance behaviour and the interfacial capacitance distribution of the GO working electrode at various operating frequencies and stand-by potentials. An equivalent circuit with paralleled EDLC and pseudocapacitance was obtained from fitting and simulation the EIS data to represent the interfacial behaviour of the GO electrode. It was proposed at the end of this chapter that the EIS analysis may offer a good opportunity to learn the charge storage mechanism of the GO electrode materials.

Chapter 4 Control of the DED on GO through Electrochemical Reduction

4.1 Introduction

Based on the investigation in Chapter 3, on the one hand, Raman spectroscopy and XPS can be used to characterise the defects concentration and the chemical states of carbons in GO respectively. An important empirical equation - *DED equation* - was established to correlate the DED of GO with the spectrum composition of the C 1s envelop successfully. On the other hand, the titanium plate was confirmed to be a better substrate than platinum for investigation of the electrode behaviour of GO coating layer within the as-concerned potential range (0.0 to 0.8 V) because of its extremely low background current interference. Therefore, the interfacial capacitive behaviour including EDL capacitance and pseudocapacitance of GO can be investigated without the interference originating from the substrate.

The oxidation degree of actual GO products, in real preparation practice, distributes widely from batches to batches because of different synthesis processes and conditions. There is no exception for the GO synthesised through Hummers' way. The final GO products have an extremely wide distribution of its oxidation-degree because of several uncontrollable factors, such as the origin of raw materials, synthetic temperature, degree of reaction during the exfoliation of graphite flakes. Regarding these, in the subsequent experiments, using the GO product synthesised in the same batch is compulsory to eliminate the aforementioned inconsistencies. On the other hand, it was found in many studies [227,238] that GO can be properly reduced aiding with proper wet chemical or electrochemical processes, for example using reductants, e.g. the hydrazine [239] or hydrogen accompanying with post-annealing under high vacuum and high temperature [227]. Inspiring by this, an electrochemical reduction (ECR) way, i.e. potential cycling, was employed in this chapter to reduce GO resulting in an adjustment of the degree of oxidation and even the DED of the GO without using hazard toxic substances and other high demanding experimental parameters. In addition, electrochemical techniques, e.g. CV and EIS, were also used to characterise the GO before and

after the ECR treatment. The adjustment of the DED of GO was achieved technically by controlling the redox degree of GO, in essence, by adjusting the population of oxygen-containing groups in GO through the ECR treatment. Due to the reduction, the graphitic area, i.e. the electron delocalisation region, on the basal and edge planes of graphene can recover to some extent, resulting in the variation of the DED of GO [3]. On the one side, this variation of DED can be detected and characterised by Raman and XPS. Thus parameters and conditions of ECR treatment can be correlated with the DED of samples. On the other side, CV and EIS characterisations can give the actual performance of interfacial charge storage on each ECR-treated sample. By combining these two aspects, the DED and the interfacial charge storage or even the pseudocapacitance of GO can finally be correlated.

In this chapter, GO coated titanium plates ($1 \times 1 \text{ cm}^2$, pre-polished to Ra: ca. $1 \text{ }\mu\text{m}$) served as the only working electrode during all ECR treatments and characterisations. ECR treatments conducted in 3.0 M KCl within three negative potential windows on the GO coated TiWE. The redox degree of the GO coating layer was adjusted under various ECR parameters, such as the cycling numbers from 10 to 1000 and different polarisation windows. Key experimental parameters on specific reduction potential ranges and cycling numbers were listed in Table 4-1.

Table 4-1. Experimental parameters of the electrochemical reduction of GO

Sample index: Sij	Potential range	/	-1.0 to 0.0 V	-1.1 to -0.5 V	-1.15 to -0.5 V
ECR cycles	(i)-(j)	0	1	2	3
0	0	S00*	/	/	/
10	1	/	S11	S21	S31
20	2	/	S12	S22	S32
40	3	/	S13	S23	S33
80	4	/	S14	S24	S34
100	5	/	S15	S25	S35
300	6	/	S16	S26	S36
500	7	/	S17	S27	S37
1000	8	/	S18	S28	S38

*S00 is a control sample without any treatment. The average loading mass is about $100 \pm 20 \text{ }\mu\text{g}$ determined through the methodology introduced in Section 2.4.3, Chapter 2.

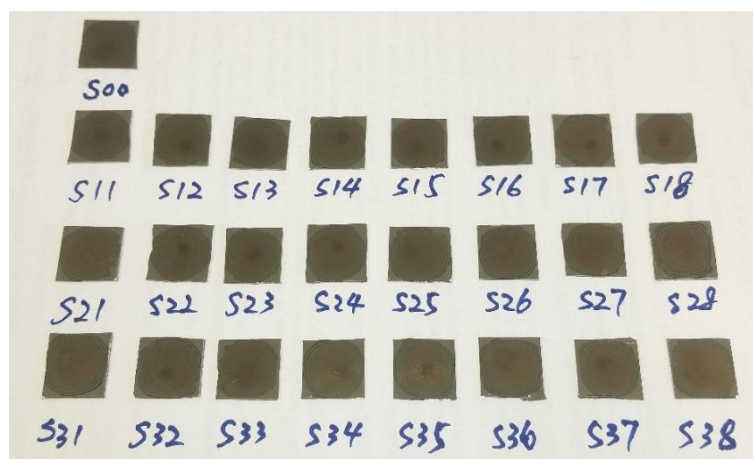


Figure 4-1. Samples of GO coated titanium plates before ECR

Samples of GO coated titanium plates before ECR treatment were shown in Figure 4-1. The sample preparation and the determination of the actual loading mass of GO followed the methodology introduced in Chapter 2. Specifically, on the sample preparation, 25 μL GO suspension (ca. 4 ± 0.4 g/L) was dropped and dried on a Ti plate. This volume was determined by considering the actual size (1×1 cm²) of the Ti plates because too much volume of GO suspension will be beyond the capacity of the Ti plate. Too much loading mass also resulted in a thicker GO coating layer. The thick coating layer can block the penetration of electrolyte into the inner-layer of GO, hence hinders the occurrence of the charge storage and electrochemical reduction. Thus, it would be better for the GO coating layer as thin as possible. However, too less volume of GO suspension resulted in a very non-uniform GO coating layer formed on the Ti plate. On the other hand, the coverage area of GO layer may be smaller than the inner-diameter of the O-ring (see Figure 2-4a to c) which was used in the electrode holder for sealing, thus a part of bare titanium may be exposed resulting in a non-uniform distribution of electric field on the electrode | electrolyte interface. A proper loading mass of GO was explored and optimised based on the experimental experience. This part of lab work was collected in Appendix C for reference.

The freshly prepared GO coating layer, as can be seen in Figure 4-1, shows a golden yellow colour on the polished titanium plates. It has to mention

that the dried GO coating layer is composed of large amounts of GO fragments stacking randomly rather than a monolayer GO sheet. Curly, folded and entangled fragments with high defects concentration are predominant micro features in the GO coating layer just as confirmed in the SEM characterisation in Section 3.3.2, Chapter 3. According to the SEM characterisation shown in Figure 3-7, a schematic of the actual structure of GO coated Ti plate can be drawn out in following Figure 4-2.

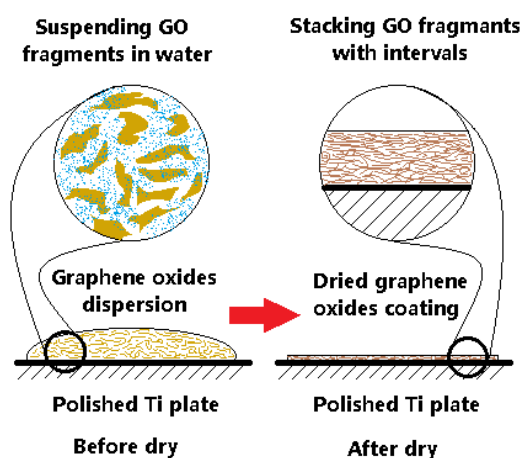


Figure 4-2. Schematic of the structure of GO coated titanium plates before ECR

4.2 Electrochemical reduction of GO

Before ECR treatment, the CV and EIS characterisations were carried out on every GO electrode only in 3.0 M KCl for the purpose of checking the consistency between each sample. The interfacial capacitance recorded at this step was used as a starting point for the subsequent comparative studies with the ECR-treated samples. Figure 4-3 collected the specific capacitance (C_m) of 24 samples from S11 to S38 before the ECR. The specific capacitance was calculated from the CV data using Equation 3-2 in a function of scan rates. Power type trend lines were used to reflect the variation trend of the specific capacitance versus the scan rate. As can be seen that the specific capacitance distributed in a range from 0.02 to 0.16 F/g at the scan rate from 100 mV/s to 5 mV/s. The higher the scan rate is, the lower the specific capacitance was observed. Most values of the capacitance at a specific scan rate were roughly

proximate, except three individual deviations. These results agree well with the previous characterisation results in Section 3.4.2, Chapter 3. Statistical analysis gave the average values and standard deviation under the corresponding scan rate as shown with the red 'X' and error bar respectively in Figure 4-3. It indicated that the specific capacitance decreases from ca. 0.095 ± 0.022 to 0.055 ± 0.022 F/g as the scan rate increases from 5 mV/s to 100 mV/s. This decline can be attributed to the typical interfacial capacitance behaviour which discussed and explained in Section 3.4.1.

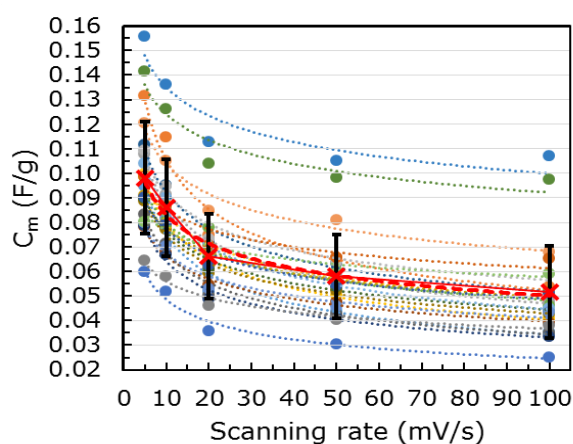


Figure 4-3. Distribution of the specific capacitance of 24 samples of GO coated TiWE before ECR in the electrolyte of 3.0 M KCl versus different CV scan rates. Red crosses with trend line (red dash line) and standard deviation error bars (black) are the average value of all 24 samples at corresponding scanning rate.

Samples underwent different degrees of ECR are shown in Figure 4-4. The detailed treatment procedures are recorded in Appendix F. The typical procedure includes a series of ECC before and after ECR treatments, i.e. CV and EIS. Experimental parameters were summarised in Table 4-1. A full procedure of ECR treatment plus ECCs on each sample took at least 6 to 8 hours. According to the previous experiences, a long-term immersion in aqueous electrolyte seriously affected the stability of GO coating layer and relevant measurements, especially during the full frequency EIS scan after ECR treatments which may result in the delamination between the GO coating layer and titanium substrate. This is partly because of the absence of a binder. Currently, most of the binders, such as polytetrafluoroethylene (PTFE), are

insulating. Considering the poor conductivity of GO itself, therefore, the binder-free coating was deliberate to avoid additional resistance to be introduced in the working electrode. Meanwhile, it was tried all the best to complete a full procedure of ECR treatment plus ECCs within a duration as short as possible to avoid the aforementioned side effects. In addition, at least three samples for each series number (Sij, in Table 4-1) were used to guarantee the repeatability and reproducibility of the results. If sample failure was found or abnormal or doubtful data appeared one more sample will be used to do a repetition. Representative results are shown in Figure 4-4. As can be seen, from left to right, the golden yellow colour of reduced GO became darker and darker as the cycles of ECR are increased from 10 to 1000. The ECR potential range resulted in the similar influence on these samples as it was dragged more negatively.

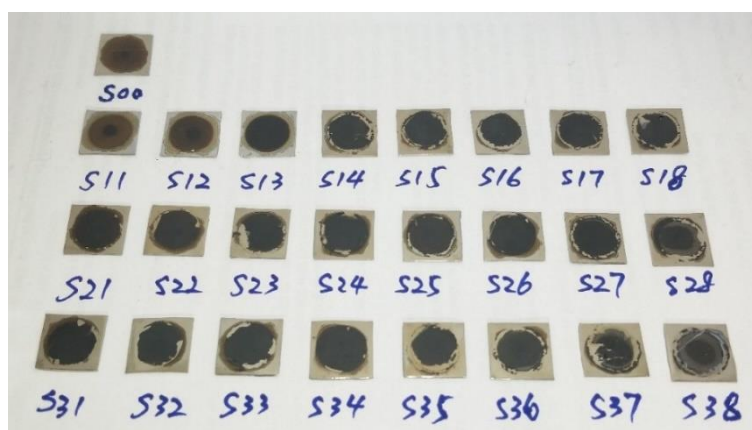


Figure 4-4. Representative GO samples underwent different degrees of ECR

The reduction of GO in aqueous electrolytes was attributed to the reduction of surficial oxygen functionalities by active hydrogen atoms (H^*) formed under negative polarisation of the electrode, resulting in the recovery of graphitic region on the GO sheet to some extent [27]. This may be the very reason the DED of GO increases gradually during the electrochemical reduction. The improvement of the DED of GO as the ECR is progressing is one of the crucial arguments in this research. Only based on this, the adjustment or control of the DED of GO through ECR treatment can be achieved. Therefore, it is

rational to believe that the above samples underwent different degrees of ECR have various DED.

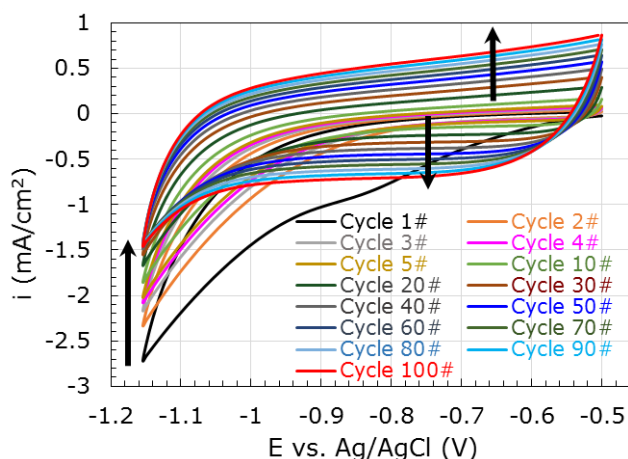


Figure 4-5. Representative CVs of the ECR treatment on GO (e.g. S35 listed in Table 4-1). Reduction potential range is -1.15 to -0.5 V with 100 cycles of CV. The current density is normalised by the projected area of the exposed surface of 0.4188 cm². The scan rate is 200 mV/s. Only representative cycles are shown in this plot.

Figure 4-5 displayed the representative CVs recorded during the ECR treatment on GO working electrode, e.g. S35 in Table 4-1. A weak current wave always arose in the first cycle at the potential around -0.75 to -0.9 V vs. Ag/AgCl, while disappeared in the subsequent CVs. It may be originated from desorption of oxygen-related contaminants, adsorbates or other electrochemical activities on the surface of the GO electrode. As long as a certain potential is applied across the electrode | electrolyte interface the surface of electrode will be polarised by the excessive charge, immediately an electric field will be established. Electrostatic force then propels counter ions to migrate and accumulate at the electrode | electrolyte interface, cations such as H⁺, K⁺ to the cathode, anions such as Cl⁻, OH⁻, SO₄²⁻ to the anode, resulting in the establishment of the EDL including the inner and outer Helmholtz layer (IHP and OHP) as introduced in Section 1.1.1.2.

As the potential of the electrode is dragged more negatively an over-potential will be established between the applied potential and the possible redox electrode potential (here, the reduction of H⁺). When the over-potential

exceeds the reduction potential of protons and the surficial oxygen-containing functionalities, charge transfer occurs at the surface of GO electrode with the pronounced climbing-up cathodic current. Before the bulk reduction of the hydrogen, large amounts of active hydrogen atoms (H^*) will first form with strong activity readily to attack oxygen-containing functionalities. The reduction of GO and the recovery of ED region can occur under this reduction process. It should be mentioned that the scan rate used in all ECR treatment was 200 mV/s. This high scan rate can restrict the degree of polarisation on the electrode, in other words limited the magnitude of the over-potential, thereby newly formed H^* had no enough time to form hydrogen molecules because the second step of H_2 formation is a relatively slow electrode process [237].

Thus, in practice, the evolution of hydrogen gas was very limited during the ECR treatment of GO, although small amounts of H^* combination is inevitable, particularly when the potential was dragged too negatively and a long-term ECR procedure were carried out. This may damage the GO coating layer because of the accumulation of H_2 bubbles, and lead to a poor connection i.e. an increasing resistance to the entire electrode.

The gradually decreased cathodic current response at the negative limit of the CVs during the ECR treatment indicated a gradually declined amounts of oxygen functionalities in the GO. On the other side of the CVs window, nearly symmetrical current response gradually increased as the ECR treatment was progressing. This symmetrical current response corresponds to a typical capacitance behaviour. This improvement of capacitive current response indicated a gradually increasing interfacial capacitance in GO coating layer during the ECR treatment.

In order to correlate this improved interfacial capacitance with the DED of GO, Raman and XPS spectroscopic characterisations were carried out again on the ECR-treated samples in the following two sections.

4.3 Variation of the DED investigated through Raman spectroscopy

Before and after ECR, Raman spectra of all GO samples were recorded in order to detect the possible variation of the DED in the GO sample. Wide spectrum scans from 1000 to 3000 cm^{-1} were carried out to determine the

location of possible characteristic peaks and bands of samples. The results indicated that only the D and G bands between 1000 and 1800 cm^{-1} are detectable, informative and worth to further analysis. Thus, all spectra data exhibited in this section were only focused on this range of Raman shift.

Representative spectra of ECR-treated samples were plotted in Figure 4-6a to c. All spectra were normalised by the D band. The spectrum of untreated GO did not plotted in these figures to avoid possible misleading because it was found that the intensity of the D band is lower than that of the G band in the case of untreated sample as found in Section 3.3.2.

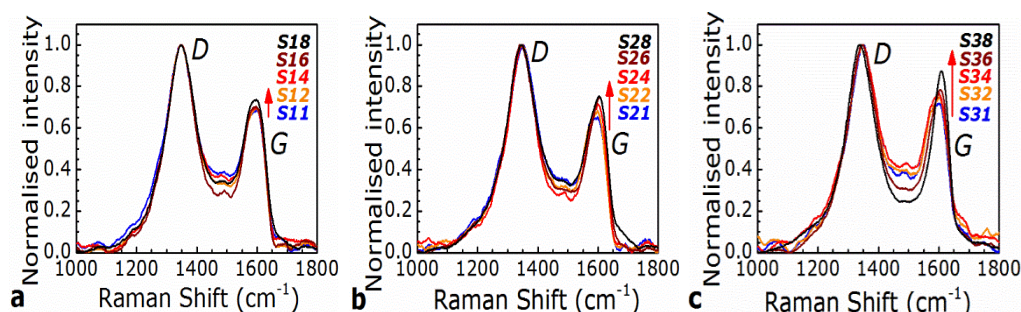


Figure 4-6. Raman spectra of representative GO samples reduced in: (a) -1.0 to 0.0 V, (b) -1.1 to -0.5 V and (c) -1.15 to -0.5 V vs. Ag/AgCl respectively. The corresponding sample series numbers and experimental parameters listed in Table 4-1.

Within the as-concerned range of Raman shift, two major bands correspond to the disorder-induced D band at around 1200-1400 cm^{-1} and the G band at around 1587-1620 cm^{-1} respectively. Spectra of three groups of sample reduced in different potential ranges are very similar in shape. Noteworthy, the relative intensity of the G band increased gradually versus the D band in all three groups of sample a, b and c with slightly different extents. In most cases, discussing the absolute intensity of any specific peak is pointless in Raman analysis. The peak ratio between specific bands is more informative to learn the variation tendency of as-concerned features, such as the degree of defects, the layer numbers and crystallise size, especially in investigating graphene species. Based on existing knowledge [221,240,241], the I_D/I_G ratio is one of the well-known indexes which not only can reflect the degree of disorder but also the degree of sp^2 preservation. Therefore, the I_D/I_G ratio was utilised to

explore the possible variation of these intrinsic features of GO before and after ECR treatment. At least three points on each sample were inspected and the average value of the I_D/I_G ratio was reported in Figure 4-7.

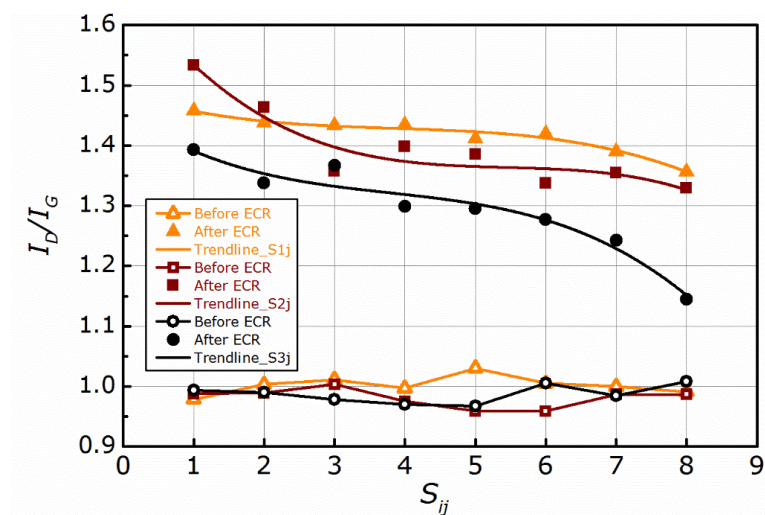


Figure 4-7. Variation tendency of the I_D/I_G ratio of GO samples before and after different degrees of ECR treatment. S_{ij} corresponds to the sample series number listed in Table 4-1. Series S1j, S2j and S3j denote the three ECR potential ranges: -1.0 to 0.0V, -1.1 to -0.5 V and -1.15 to -0.5 V vs. Ag/AgCl respectively.

As can be seen, before the ECR treatment, the I_D/I_G ratio maintains ca. 0.95 - 1.03 in all GO samples, while it distributes in a wider range from 1.55 to 1.10 in the ECR-treated samples, indicating a violent variation of the I_D/I_G ratio after ECR treatment. This sharp increase of the defects-induced D band versus the G band after ECR treatment can be attributed to the decrease in the average size of the sp^2 domains upon reduction of the exfoliated GO [242], and can be explained if new graphitic domains were created that are smaller in size to the ones present in GO before reduction, but more numerous in number [243]. However, as long as the samples have been ECR treated, the D band intensity does not change violently anymore, in contrast, as shown in Figure 4-7a to c, the G band begin to increase versus the D band as the ECR cycles increase and the reduction potential range is more negative. This can be evidently attributed to a recovery of the sp^2 graphitic region in GO, meaning an increasing DED. When the ECR cycles are constantly increasing, the I_D/I_G ratio decreases

gradually within all three reduce potential ranges just in different extents. As shown, the decline of the I_D/I_G ratio become greater and steeper when the reduction potential range was more negative. It has to be mentioned that, in this research, the ECR potential range was restricted only within -1.15 to 0.0 V, and the number of CV cycles was set to no more than 1000 cycles in order to avoid the severe accumulation of hydrogen bubbles in the GO coating layer.

As introduced in Section 2.4.2, Chapter 2 and in Figure 4-2, the GO working electrode is a stable thin layer formed by large amounts of GO fragments coated on the polished titanium surface. The ECR treatment on the GO coating layer is a relatively mild process without any violent chemical reaction which may affect the framework of GO coating layer. Therefore, it is reasonable to assume that the GO coating layer maintained a relatively static state because of all GO fragments staying in the same position with no lateral movement and further reconfiguration during the whole ECR treatment. Hence, the layer-number sensitive G band cannot vary too much for any other reason except for the intrinsic structure transformation of GO during the treatment including preceding ECC and ECR. That is to say, the variation tendency of the I_D/I_G ratio of ECR-treated samples can be evidently attributed to the recovery of the sp^2 region in GO fragments. This recovery directly leads to the increasing intensity of G band. Obviously, this conclusion is reasonable as the reduction process occurs in the GO coating layer. Although the true structure of GO at an atomic level is extremely complicated [230]. The intrinsic structure of GO can still be defined as a combination of two types of region on GO the sheet. The one is a delocalised π -conjugation region with the pure graphitic plane, and the other one is localised region with sp^3 carbon bonded with oxygen-related functionalities. In terms of the oxygen functionalities, it may include epoxy, hydroxyl, carbonyl and carboxyl, etc. [230]. Hereinto, the two major basal-plane-populated functionalities: epoxy and hydroxyl and one of the edge-plane-populated groups: carboxyl can all be reduced during ECR treatment. Especially the reduction or removal of the basal plane groups, i.e. epoxy and hydroxyl, it can undoubtedly bring some degrees of recovery of the graphitic region (sp^2 region). Hence this gain definitely increases the DED in GO after the ECR treatment.

However, it is still very hard to say exactly how much of the graphitic regions can be recovered during the ECR treatment and to what extent if only the Raman analysis is relied on. That is to say, at this stage, the Raman observation can only give a qualitative result about an increasing of DED in ECR-treated samples. Therefore, a conclusion can be drawn out that as the ECR cycle increased and reduction potential range was polarised more negatively, the DED of GO was gradually improved. GO transformed to the partially oxidised or reduced graphene (POG) with a relatively lower degree of oxidation, i.e. higher DED, than that of the original sample. In order to obtain more supporting evidence qualitatively or even quantitatively, XPS characterisation and analyses were carried out on the same batch of GO and POG samples. These results will be presented and discussed in the next section.

4.4 XPS evidence of the various DED in ECR-treated GO

All samples listed in Table 4-1 were submitted to XPS characterisation. Sample S00 represents the original status of GO without ECR treatment. Three randomly selected points on the exposed area of each sample were shone by X-ray in a high vacuum chamber to collect the photoemission electrons. As investigated in the Section 3.3.2 of spectroscopic characterisation, Chapter 3, the integral area of the specific photoelectron peak gives the relative content of the specific element. Representative wide scan spectra were plotted in Figure 4-8a, b and c, corresponding to the three ECR potential ranges respectively.

As can be seen in the figure, only three elements' 1s peaks and their KLL photoelectrons were detected, including two principal elements: carbon (C) and oxygen (O), one trace element of nitrogen (N). Hereinto, peak at ca. 530 eV corresponds to the O 1s, ca. 284.5 eV the C 1s and ca. 399 eV the N 1s peak. The trace N may be originated from the adsorptive N₂ in samples. All samples showed quite similar wide scan spectrum only with slightly different intensity ratio between the two principal elements of carbon and oxygen. As black arrowed in Figure 4-8, the O 1s peak gradually declines when the reduction cycles increases.

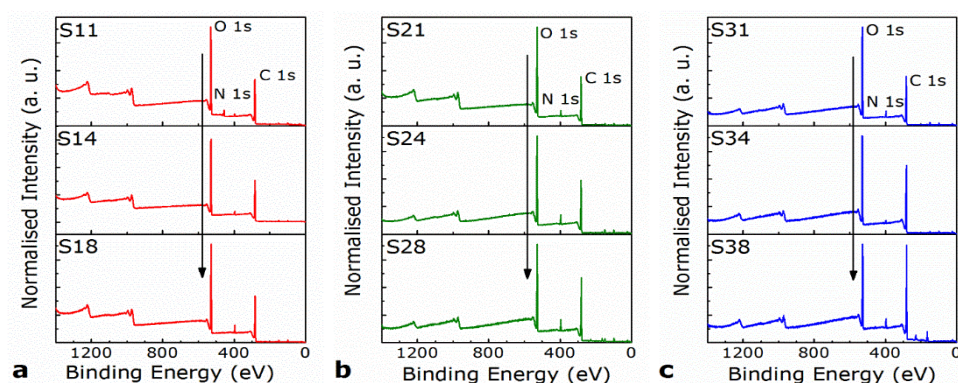


Figure 4-8. Representative XPS wide spectra of GO treated under various degrees of ECR, Data are normalised by the O 1s peak. Reduction potential range in (a) is -1.0 to 0.0 V, (b) -1.1 to -0.5 V and (c) -1.15 to -0.5 V

More accurate carbon to oxygen ratio can be obtained by the integral area ratio between C 1s and O 1s peak. Average values of C:O were calculated from three wide scan spectra on each sample then plotted in Figure 4-9 versus the sample series number.

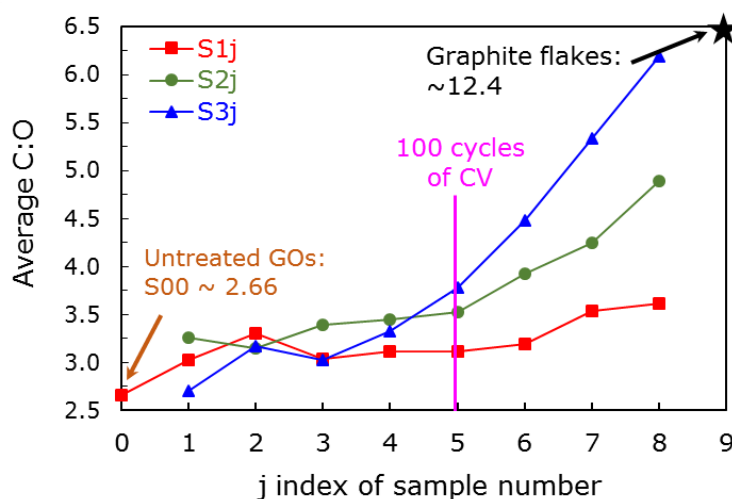


Figure 4-9. Average C:O extracted from the integral area ratio between the 1s peak of carbon and oxygen, series S1j, S2j and S3j denote the three ECR potential ranges: -1.0 to 0.0 V, -1.1 to -0.5 V and -1.15 to -0.5 V vs. Ag/AgCl respectively.

It shows that when the ECR cycles are lower than 100 cycles, from sample (S00) to (Si4), the variation of C:O is not remarkable in all three ECR potential ranges. While after 100 cycles of ECR, the increase of C:O ratio

predominates in the reduction potential ranges of -1.1 to -0.5 V and -1.15 to -0.5 V, but still not so pronounced for the first potential range. Undoubtedly, this increasing C:O can be attributed to the reduction of GO coating layer. A part of oxygen-related functionalities in the basal plane and/or on the edge of GO were removed during the reduction of GO, which resulted in a part of conjugated double bonds in GO were recovered. Obviously, the more negatively the reduction potential is polarised, the steeper the C:O ratio climbed up.

The C:O of samples treated in the potential range of -1.0 to 0.0 V increased slightly from 3.0 to around 3.5, from 3.0 to 4.75 for samples reduced in the potential range of -1.1 to -0.5 V and from 2.7 to beyond 6.0 for samples reduced in the potential range of -1.1 to -0.5 V. Only rely on the C:O ratio, it was still very hard to demonstrate the improvement of the DED in GO during the ECR procedures because, in actual, only the removal of those oxygen functionalities which resided on the basal plane of GO leads to the recovery of the graphitic region, hence resulting in the variation of DED. Base on the XPS study in Section 3.3.2, the analysis on the high resolution C 1s peak can give a good supplement about the implication of ECR treatment on the DED of GO. The GO before ECR treatment have a C 1s envelop with double peaks. One of the peaks located at around 283 - 285 eV is a combination of emission photoelectrons originated from those 1s shell of carbon atoms with pure single and double bonds, i.e. (sp^3 -C-C-) and (sp^2 -C=C-). Another peak, more precisely a broad band ranging from 285.5 to 290 eV can be assigned to the 1s shell photoelectrons emission originated from carbon atoms bonded with various oxygen-related functionalities. The second band is the typical chemical shift of carbon atoms in GO. Different bond configurations between carbon atoms and oxygen functional groups results in different degrees of chemical shift. For example the peak of carboxyl (O-C=O) stands at a higher binding energy (ca. 289 eV) than that of carbon atoms linked with hydroxyl (-C-OH, ca. 285.5-286 eV), epoxy (C-O-C, ca. 286-287 eV) and carbonyl (-C=O, ca. 288 eV) because the 1s electrons of carbon in carboxyl groups are attracted by the two more electronegative oxygen atoms. Thus, the main C 1s peak can be decomposed by a symmetrical component corresponding to the sp^3 -C-C- at ca. 285 eV and asymmetrical component corresponding to the sp^2 -C=C- with 1 eV lower binding

energy than that of sp^3 -C-C- peak. Again, all distinguishable components can be classified into two groups, one 'localised zone' and one 'delocalised zone'.

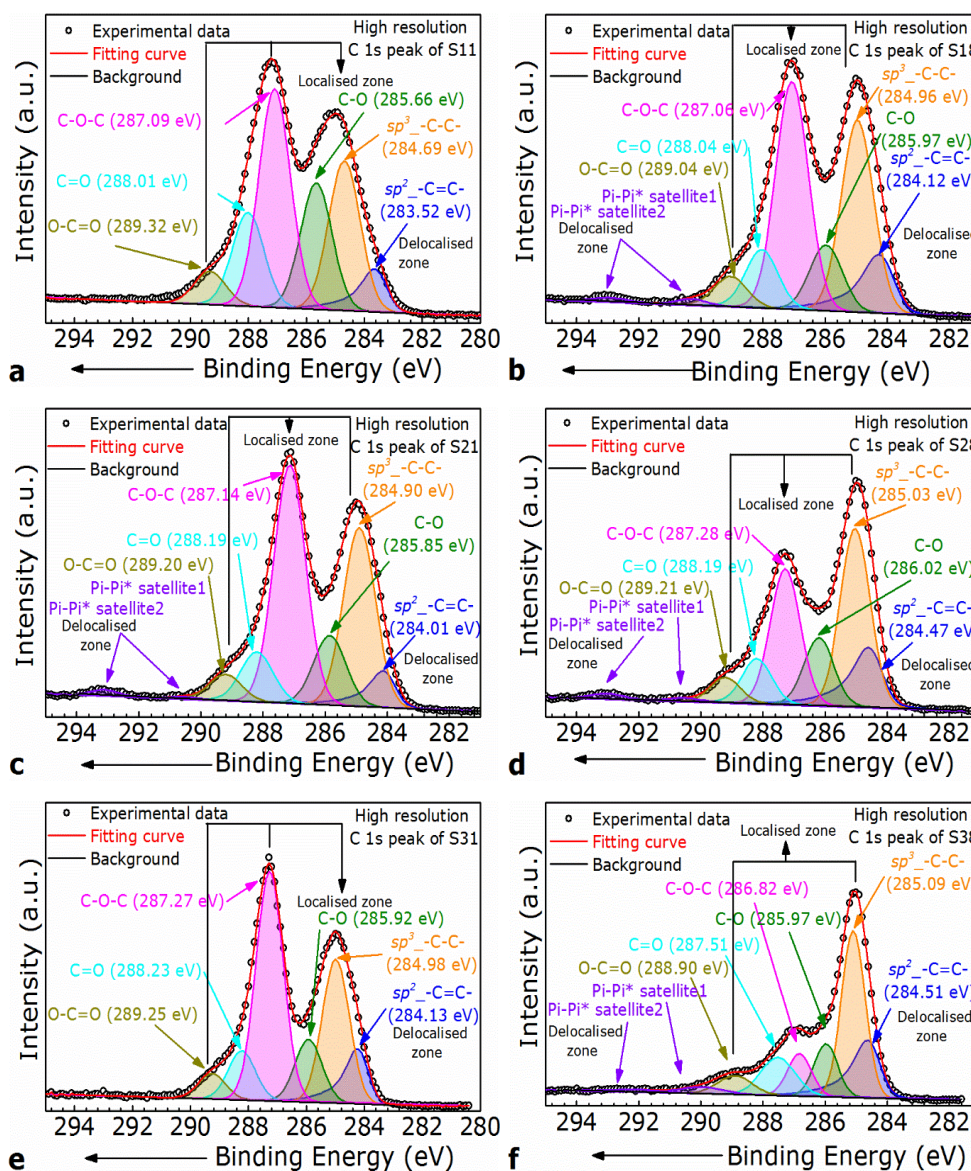


Figure 4-10. Representative high resolution C 1s spectra of GO with various degrees of ECR, the C 1s peak is charge corrected to 285 eV when doing deconvolution. (a) and (b) corresponds to the series of sample reduced under -1.0 to 0 V for 10 and 1000 cycles of CV scanning; (c) and (d): -1.1 to -0.5 V, (e) and (f): -1.15 to -0.5 V.

Representative high resolution C 1s envelopes and their deconvolution results are shown in Figure 4-10a to f. The results indicated that these C 1s band of the GO can be de-convoluted into seven components originated from

sp^2 -C=C-, sp^3 -C-C-, C-O, C-O-C, C=O, O-C=O and Pi-Pi* satellite respectively in an increasing order of binding energy. It can be found that in the GO sample underwent fewer cycles of ECR, e.g. 10 cycles of CV for example S11, S21 and S31, the major photoelectrons contribution comes from the carbon atoms bonded with epoxy groups (C-O-C). This is understandable because these samples still have a relatively high degree of oxidation and the functional groups, such as (-C-OH) hydroxyl and (-COOH) carbonyl, do not contribute more photoelectrons than epoxy groups (C-O-C). According to the relative integral area of each component, the amount of each functionality follows the order of C-O-C > C-O > C=O > O-C=O. A low fitting error and residual (R^2) indicated that good deconvolution and fit were obtained for all these C 1s high resolution peaks. The FWHM of all components is around 1.1-1.2 eV, which is very proper for a typical FWHM of carbon 1s peak. Peak locations of all components have a good agreement with those results reported in publications [228,229] again implying the rationality and reliability of the fit and deconvolution. The major variation was found on the intensity ratio between the epoxy peak and the sp^3 -C-C-/ sp^2 -C-C- peak. From 10 to 1000 cycles of ECR this ratio reversed in all three ECR potential ranges. In fact, the true process is that when the ECR cycles increased the photoelectron contribution originated from C-O-C component and other oxygen-containing components gradually declined till lower than the contribution of the sp^3 -C-C-/ sp^2 -C-C- component.

That is to say, as the ECR treatment progressed oxygen-containing functionalities were gradually reduced and removed from the GO matrix. More significantly, the asymmetric sp^2 -C=C- component gained the intensity following the same order, meaning the DED was improved gradually either. This deduction can be further explicated by the quantitative analysis on these components aiding with the DED Equation 3-1. For the rest samples in Table 4-1, the corresponding deconvolution results on the high resolution C 1s envelop were collected in Table 4-2.

It is noteworthy to point out that samples under fewer cycles of ECR showed no notable Pi-Pi* shake-ups resulting in an approximately zero % atomic concentration. As the ECR cycle went up, the Pi-Pi* shake-ups became more and more detectable but still in a negligible level, although two more

components were introduced in fitting these shake-ups. Therefore, this part of contribution did not show in Table 4-2. However, as long as the Pi-Pi* shake-ups became detectable their integral area were also counted in the entire contribution of ED zone.

Table 4-2. Component concentration and the DED of GO underwent various degrees of ECR treatment

S.N.	sp^2 - C=C- (a)	sp^3 - C-C- (a)	C-O (a)	C-O-C (a)	C=O (a)	O-C=O (a)	DED (b)	D- para. (c)	DED (d)
S00	6.09	24.47	16.51	44.1	6.14	2.68	19.9 %	14.00	12.50 %
S11	6.6	22.51	19.02	32.83	14.09	4.95	22.7 %	14.00	12.50 %
S12	6.9	21.95	15.33	33.44	15.34	7.04	23.9 %	14.50	18.75 %
S13	8.58	26.03	16.56	28.19	14.52	6.12	24.8 %	14.50	18.75 %
S14	9.37	28.52	16.85	26.98	13.38	4.9	24.7 %	14.50	18.75 %
S15	9.21	26.05	16.32	29.89	13.86	4.66	26.1 %	15.00	25.00 %
S16	9.62	25.5	17.98	28.08	12.15	5.05	27.4 %	15.00	25.00 %
S17	11.27	29.09	9.47	36.8	7.79	4.45	27.9 %	15.50	31.25 %
S18	12.01	28.7	9.78	34.81	8.9	4.55	29.5 %	16.00	37.50 %
S21	8.7	27.82	10.9	39.28	8.17	4.29	23.8 %	14.00	12.50 %
S22	8.48	24.59	12.32	37.58	11.17	4.57	25.6 %	14.30	16.25 %
S23	9.89	28.63	10.31	40.88	6.42	3.24	25.7 %	14.40	17.50 %
S24	10.58	26.86	12.27	36.32	8.91	3.83	28.3 %	14.80	22.50 %
S25	12.62	29.22	11.29	33.32	7.72	4.3	30.2 %	15.20	27.50 %
S26	14.77	30.47	11.59	28.06	8.37	4.83	32.7 %	15.50	31.25 %
S27	17.11	31.67	8.67	29.46	6.71	5.04	35.1 %	16.00	37.50 %
S28	18.24	29.86	12.08	24.58	8.8	4.82	37.9 %	17.00	50.00 %
S31	9.94	25.31	11.07	40.53	8.67	4.48	28.2 %	14.33	16.67 %
S32	12.21	27.36	11.27	35.99	8.82	4.34	30.9 %	14.50	18.75 %
S33	12.71	26.18	9.81	36.74	8.98	4.79	32.7 %	14.70	21.25 %
S34	16.32	29.63	7.68	34.17	6.87	4.49	35.5 %	15.17	27.13 %
S35	15.94	23.76	9.06	35.01	8.55	4.99	40.2 %	15.67	33.33 %
S36	16.99	24.11	9.01	33.79	8.94	4.98	41.3 %	16.33	41.67 %
S37	17.06	22.85	10.17	34.29	7.99	5.05	42.7 %	17.00	50.00 %
S38	27.8	31.22	10.07	8.45	12.54	6.11	47.1 %	17.83	60.42 %

(a) Components are counted in % Atomic Concentration;

(b) DED values are calculated by Equation 3-1 established in Section 3.3.2, Chapter 3 based on the component percentage of sp^2 -C=C- and sp^3 -C-C-;

(c) D-parameters are extracted from the corresponding C KLL Auger peak of each sample following Ref. [232] as introduced in Section 3.3.2, Chapter 3;

(d) These DED values equal to the sp^2 percentage estimated by a linear interpolation between D values of 13 eV (diamond, 100% sp^3) and 21 eV (graphite, 100% sp^2) Ref. [232].

Furthermore, if we plot the DED versus the sample numbers in Figure 4-11, the relationship between DED of GO samples and different degrees of ECR can be seen more clearly.

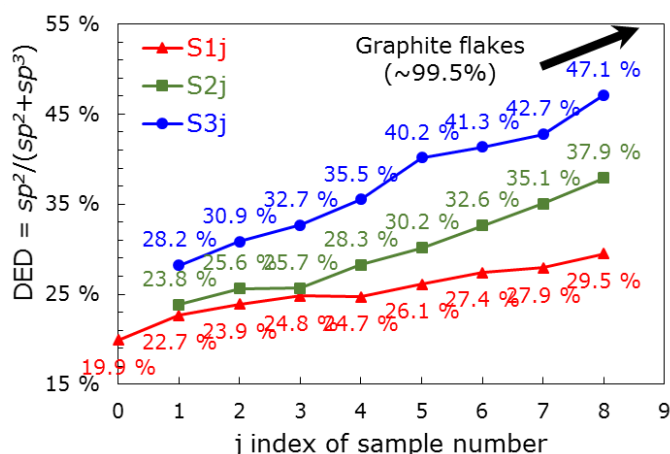


Figure 4-11. Variation of the DED versus the sample series number. Series S1j, S2j and S3j ($j = 1$ to 8) denote the three ECR potential ranges: -1.0 to 0.0 V, -1.1 to -0.5 V and -1.15 to -0.5 V vs. Ag/AgCl respectively.

As can be seen in Figure 4-11, the DED of GO in all three ECR potential ranges climbs up gradually as the CV cycle increases from 10 to 1000. The increase of DED becomes more pronounced when the sample is reduced in a more negative potential range. When the ECR potential range is -1.1 to 0.0 V, the DED increases from ca. 22% to ca. 30%; from ca. 23% to ca. 38% for the range of -1.1 to -0.5 V and from ca. 28% to ca. 48% for the range of -1.15 to -0.5 V. These tendency are consistent with the variation of C:O ratio reported in the previous section. This phenomenon is also expectable considering the removal of oxygen-containing functional groups which leads to the recovery of the graphitic region. It can be seen that, differing from the C:O shown in Figure 4-10, the increase of DED% is not so prominent in this analysis. This is understandable that, except oxygen-containing groups, hydroxyl, epoxy, etc., existing on the basal plane of GO, large numbers of other oxygen-related groups are populated on the edge side of GO fragments, e.g. the carbonyl, carboxyl and hydroxyl, the reduction of these edge-side functionalities does not contribute too many improvements to the DED in GO except forming a great

deal of dangling bonds or defects. That is to say, even though lots of oxygen-containing groups were removed during the ECR treatment resulting in a sharp increase of C:O ratio, the actual DED of GO would not be improved to a great value. From another aspect, during the ECR treatment, the resistance between GO fragments, and even the overall GO coating, can be decreased to some extent because of the removal of edge-side functionalities. Besides, it can also be seen that all the DED of partially reduced GO listed in Table 4-2 are still far lower than that of the raw material: graphite flakes ca. 99.5% as shown in Figure 3-12d, Section 3.3.2. The maximum DED is not beyond 50%. That is to say, more than half areas of GO fragments are still in sp^3 hybridisation based on this half-quantitative estimation from the deconvolution analyses of C 1s peak.

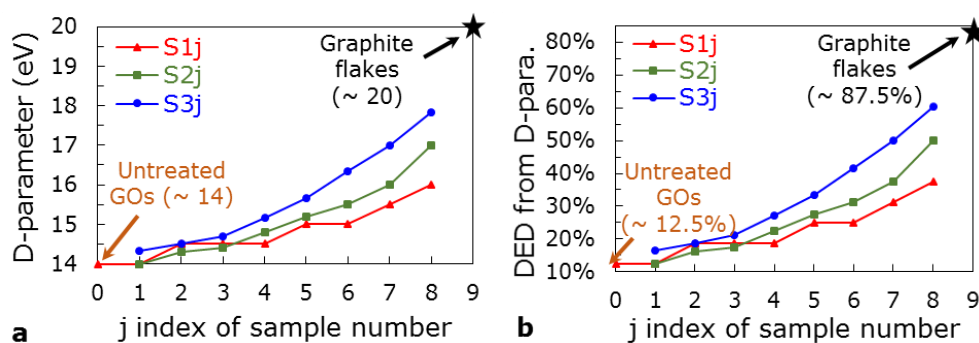


Figure 4-12. (a) D-parameters extracted from X-ray induced C KLL and (b) DED ($sp^2\%$) estimated by a linear interpolation of the corresponding D-parameters of samples from S00 to S38. The D-parameter and DED of graphite flakes are marked by a black star on the top right corner. Series S1j, S2j and S3j denote three ECR potential ranges: -1.0 to 0.0 V, -1.1 to -0.5 V and -1.15 to -0.5 V vs. Ag/AgCl respectively.

D-parameter was utilised again to evaluate the DED of the GO. The values of D-parameter obtained from the first derivative of X-ray induced C KLL peaks following the same method introduced in Section 3.3.2 and listed in Table 4-2 as well. Then the DED% of all GO samples can be estimated by means of the linear interpolation in relating to the extreme conditions in the case of diamond and graphite. Figure 4-12a and b showed the D-parameter and the estimated DED of all GO in three ECR potential ranges. As can be seen that DED values in three reduction potential ranges showed a consistent tendency in comparison with the previous results obtained from the deconvolution of the

C 1s peak. Generally, the DED values estimated from D-parameters are lower than those obtained from the deconvolution. Untreated GO (e.g. S00) stands the lowest DED ca. 12.5%, and the graphite flakes stands the highest DED of ca. 87.5%. The DED of the rest GO gradually improves from 15% to 60% in the order of the corresponding degree of ECR. Such a lower estimation in contrast with the DED obtained from the deconvolution of C 1s peak may either because of an arbitrary assignment of the percentage for each sp^2 and sp^3 components when doing the deconvolution or the scan step setting in collecting the C KLL spectra. Nevertheless, the overall trend is still consistent between these two methods.

4.5 Interfacial charge storage of ECR-treated GO electrode through CV analysis

Raman and XPS analyses in Section 4.3 and 4.4 correlated the DED of GO with its degree of ECR. In the following sections, attention will be paid on the interfacial charge storage on these ECR-treated GO electrodes aiding with two major electrochemical technologies: CV in this section and EIS in the next section. From this section, the ECR-treated GO will be noted as partial oxidised graphene (POG) for convenience. Neutral 3.0 M KCl and acidic 1.0 M H_2SO_4 solutions were used as the supporting electrolyte. The operating potential range (OPR) of POG electrode was restricted only within 0.0 to 0.8 V vs. Ag/AgCl because it was broadly found in both published studies and the preliminary experimental observation in this study that this potential range covers the major capacitive potential range (CPR) of graphene-based electrode materials in these two electrolytes.

Cyclic voltammetry is one of the most straightforward characterisation techniques for screening capacitive electrode materials because the capacitive behaviour shows typical rectangular cyclic voltammogram (CV) within a capacitive potential range (CPR). The existence of resistance in electrode, such as the connecting resistance or charge transfer resistance (R_{ct}), only leads to a hysteretic current response, but does not affect the characteristic capacitive CV, e.g. just resulting in a depressed CV to some extent.

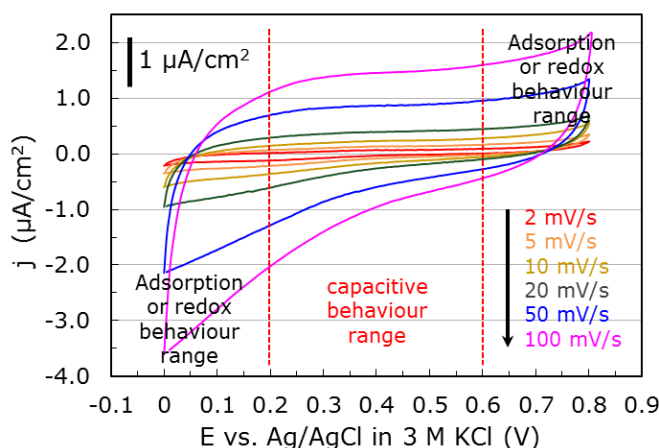


Figure 4-13. Representative CVs of GO coated TiWE (sample S00)

Electrochemical features of GO before ECR treatment, especially the capacitive CV had been investigated in Section 3.4.2, Chapter 3 with some preliminary discussions. Representative CVs of GO without ECR treatment are presented in Figure 4-13 for further discussion and analyses. It can be seen that, as a typical insulator, GO have a relatively narrow CPR around only 0.2 to 0.6 V approximated from the water-level region of current response in CVs (in between the two vertical red-dash lines). Beyond this range, a slight anodic (i_A) and cathodic current (i_C) waves originated from adsorption and/or redox processes gradually arose up approaching the positive and negative potential limits respectively. In each region, the current response has completely different relationships with the scan rate (i - u). As reviewed in Section 1.1, Chapter 1, there are two distinguishable i - u relationships existing in the usual electrode process: one is a linear relationship between the current (i) and the scan rate (u), the other one is a linear relationship between the current (i) and $\sqrt{u}$. It can be found that the current response of untreated GO is dominated by a capacitive behaviour with very small contributions originated from the adsorption or redox processes. Therefore, the estimation of the interfacial capacitance performance of GO working electrode within the potential range from 0.0 to 0.8 V vs. Ag/AgCl still give reliable results. Thus the specific capacitance of POG electrodes is calculated within the same potential range, i.e. 0.0 to 0.8 V, and recorded in following Table 4-3. In all cases, the capacitance was estimated using the

Equation 3-2. A projected electrode area of 0.4418 cm^2 exposed in the electrolyte rather than the actual contact area was used to normalise the area-specific capacitance ($C_a / \mu\text{F}\cdot\text{cm}^{-2}$). The specific capacitance ($C_m / \text{F}\cdot\text{g}^{-1}$) was normalised by the actual loading mass of GO on Ti plates.

As can be seen in Table 4-3, firstly, the average loading mass of GO is about $104 \pm 8.9 \mu\text{g}$. Secondly, the mean values of C_a and C_m gradually decrease from 33.23 to $16.73 \mu\text{F}/\text{cm}^2$ and from 0.15 to 0.08 F/g respectively as the scan rate increases from 5 mV/s to 100 mV/s. The standard deviations of C_a are larger than that of C_m possibly because the projected area was used in the calculation of C_a rather than the true area. This substitution neglected the difference between the projected area and the actual accessible surface area with the electrolyte. Although it can assume that the accessible surface area would not change violently during the entire ECR treatment, the actual specific surface area still distributes a slightly wide among these samples.

Table 4-3. Area and mass specific capacitance of 24 GO samples before ECR treatment

S.N.	Mass * (μg)	Scan rate (mV/s)									
		5		10		20		50		100	
		C_a	C_m	C_a	C_m	C_a	C_m	C_a	C_m	C_a	C_m
S11	112	32.69	0.13	28.18	0.11	17.86	0.07	15.09	0.06	2.90	0.03
S12	101	45.20	0.20	39.47	0.17	25.78	0.11	22.68	0.10	18.61	0.08
S13	108	37.12	0.14	21.41	0.12	22.61	0.09	20.04	0.08	16.51	0.06
S14	118	22.99	0.18	29.23	0.16	20.53	0.11	17.45	0.09	14.16	0.08
S15	103	20.69	0.14	17.92	0.12	12.41	0.09	10.62	0.07	8.68	0.06
S16	95	30.76	0.21	26.88	0.19	20.86	0.14	19.12	0.13	15.99	0.11
S17	88	38.47	0.16	32.76	0.14	24.76	0.11	21.90	0.09	17.92	0.08
S18	101	27.00	0.17	23.26	0.15	18.81	0.12	16.49	0.11	13.61	0.09
S21	106	28.74	0.11	24.68	0.10	17.40	0.07	14.80	0.06	12.10	0.05
S22	119	30.50	0.15	26.60	0.13	20.55	0.10	9.36	0.04	14.75	0.07
S23	103	27.17	0.13	23.05	0.11	16.81	0.08	14.22	0.07	11.60	0.05
S24	108	30.95	0.13	27.23	0.12	21.10	0.09	18.54	0.08	15.33	0.07
S25	108	35.78	0.16	31.01	0.14	22.38	0.10	19.07	0.09	15.55	0.07
S26	99	41.39	0.17	36.24	0.15	29.25	0.12	27.91	0.12	23.46	0.10
S27	105	37.66	0.17	32.61	0.15	25.29	0.11	21.99	0.10	20.42	0.09
S28	94	34.32	0.13	30.03	0.12	22.30	0.09	19.19	0.07	17.86	0.07
S31	100	27.58	0.12	24.22	0.10	18.35	0.08	15.85	0.07	15.04	0.07
S32	99	27.59	0.12	29.17	0.13	23.33	0.10	20.83	0.09	20.44	0.09

S33	110	53.58	0.23	46.88	0.20	38.76	0.17	36.22	0.16	36.81	0.16
S34	98	34.01	0.15	29.84	0.13	24.30	0.11	22.64	0.10	22.46	0.10
S35	105	22.25	0.10	20.06	0.09	15.94	0.07	14.01	0.06	13.20	0.06
S36	106	31.33	0.14	27.57	0.12	21.73	0.09	18.95	0.08	17.90	0.08
S37	101	31.11	0.13	27.40	0.12	21.59	0.09	18.71	0.08	17.69	0.08
S38	115	48.69	0.21	43.42	0.19	35.85	0.16	22.68	0.10	18.61	0.08
Mean	104	33.23	0.15	29.13	0.14	22.44	0.10	19.10	0.09	16.73	0.08
Std. Dev.	8.9	8.083	0.034	6.951	0.029	5.842	0.026	5.519	0.026	6.129	0.025

** This is the actual loading mass of GO on the 1×1 cm² titanium plate weighted directly after the coating layer is dried. All above capacitance calculated from Equation 3-2 with charge values obtained from the Autolab. CVs were carried out in 3.0 M KCl only with Ag/AgCl as a reference electrode.*

In spite of these variation and deviation on these untreated GO electrodes, the variation trend of the C_a and C_m versus the ECR treatment on POG, as will be seen in the following sections, is still pronounced. Therefore, there is still chance for this study to extract a reliable tendency between the capacitive performance of GO and ECR parameters from the experimental data.

A series of CV testing was carried out in 3.0 M KCl immediately after the gradient ECR treatment in the same electrolyte followed by EIS testing. Then the working electrode was took out from the 3.0 M KCl, washed with deionised water 3 to 5 times, and then washed with the 1.0 M H₂SO₄ 3 to 5 times, thereafter immersed in the 1.0 M H₂SO₄ 3-5 min before doing the subsequent CV and EIS characterisations in the electrolyte of 1.0 M H₂SO₄.

4.5.1 Interfacial charge storage of POG electrodes in 3.0 M KCl

Figure 4-14a to f presented representative CVs (only at 5 and 50 mV/s of scan rate) of all 24 POG electrodes. As can be seen, in 3.0 M KCl, slight different CV shapes were observed at low and high scan rate respectively. At 5 mV/s shown in Figure 4-14a, c and e, capacitive current responses start almost from the very beginning of the CPR (0.0 V) up to ca. 0.5 V. Then it climbs up sharply and keep increasing till the positive boundary of the CPR (0.8 V). This is because at relatively low scan rate the capacitive current response is lower than the other current responses originated from adsorption or redox processes. This is not the case on the cathodic side towards 0.0 V because it is only a very early stage of hydrogen adsorption without any decent reduction process. When

the scan rate is improved from 5 mV/s to 50 mV/s, the capacitive current contribution, i_c , becomes comparable or even exceeding those adsorption or redox current contributions resulting in a better capacitive CVs than those at low scan rate. This is because of the different current to scan rate relationships. Therefore, the capacitive current response increases faster than redox-originated current response.

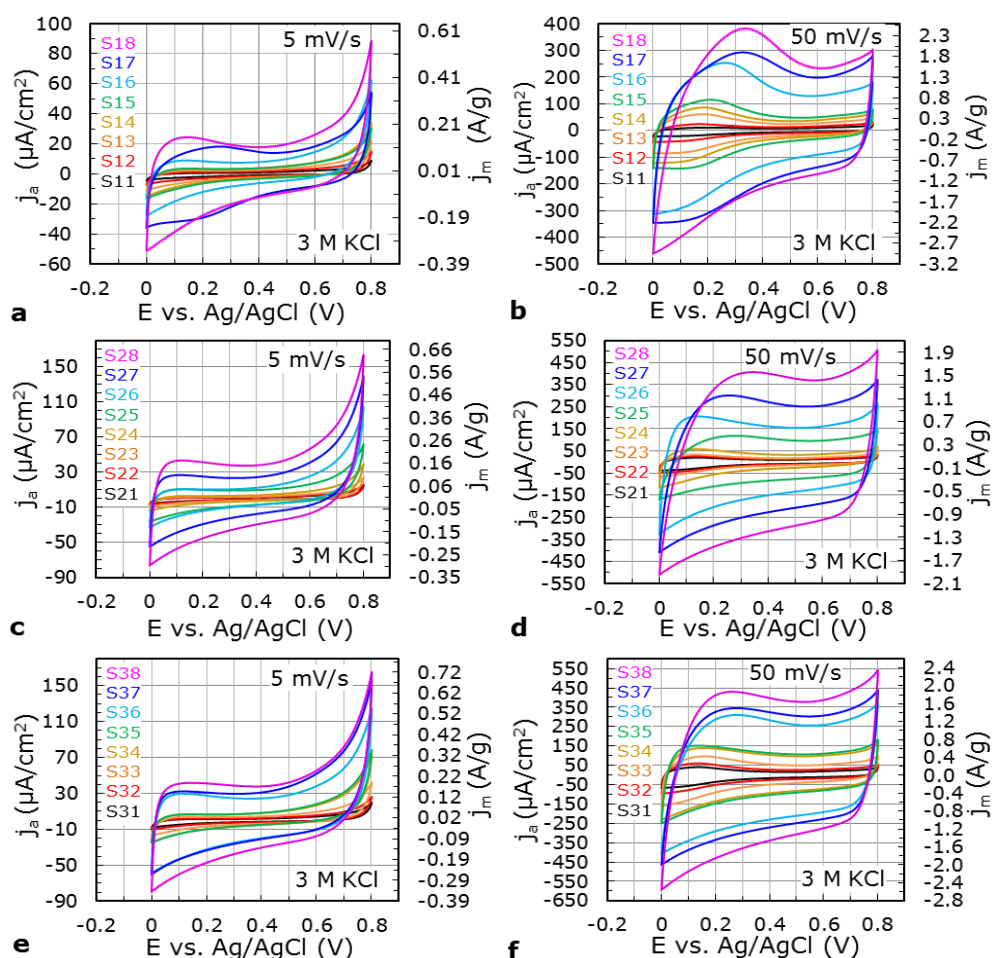


Figure 4-14. Cyclic voltammograms of POG electrodes tested in 3.0 M KCl. (a) and (b) were GO reduced within -1.0 to 0.0 V potential range, (c) and (d) reduced within: -1.1 to -0.5 V and (e) and (f) reduced within: -1.15 to -0.5 V

In some cases, e.g. in Figure 4-14a, a pair of current waves originated from the protons' adsorption/desorption can be observed around 0.0 to 0.2 V vs. Ag/AgCl, especially in samples (S1j, j = 1 to 8) reduced in -1.0 to 0.0 V ECR potential range. It can be attributed to large amounts of oxygen-containing

functionalities still exist in these POGs with a relatively low degree of reduction. Thus the surficial restricted redox of these oxygen-related functional groups contribute the pair of current response. This phenomenon can be further proved in Figure 4-14b, the same series of samples at a higher scan rate because the pair of current responses show the same improving speed as the capacitive current response. In the case of 50 mV/s, CVs were closer to rectangular shape, especially when samples were reduced in a more negative potential range (S2j and S3j), indicating a better capacitive behaviour.

4.5.2 Interfacial charge storage of POG electrodes in 1.0 M H₂SO₄

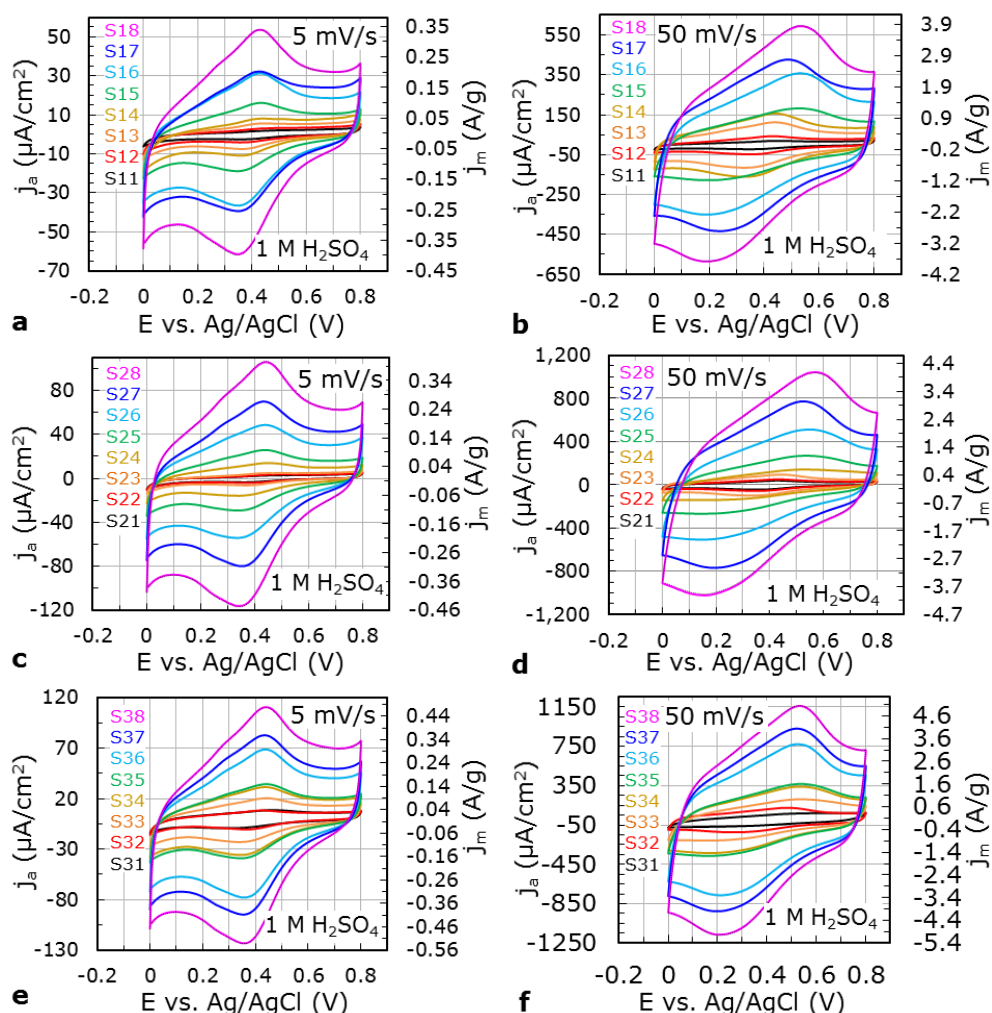


Figure 4-15. Cyclic voltammograms of POG tested in 1.0 M H₂SO₄. (a) and (b) are GO reduced within -1.0 to 0.0 V potential range, (c) and (d) reduced within: -1.1 to -0.5 V, (e) and (f) reduced within: -1.15 to -0.5 V

Furthermore, the same batch of POG electrodes were interfaced in 1.0 M H_2SO_4 to carry out the CV characterisation. Completely different voltammograms were observed in this type of electrolyte. Representative results are shown in Figure 4-15.

As exhibited in Figure 4-15a to f, a pair of broad current waves centred at ca. 0.4 V were observed in all cases of CV. It can be seen that as the degree of ECR increased, from Si1 (10 cycles of ECR) to Si8 (1000 cycles), $i = 1, 2$ and 3, the current response was gradually improved and showed an apparent variation in shape. The CVs of samples that have relatively fewer cycles of ECR, such as 10, 20 and 40 cycles, show current wave pairs but not so pronounced in comparison with the capacitive background current. While the pair of current waves becomes relatively pronounced in samples which have the ECR treatment more than 80 cycles. The covering area beneath the pair of current waves becomes even comparable with that area below the capacitive background current. It indicated that the charge storage relative to this pair of waves becomes comparable with the capacitive portion. At a low scan rate (5 mV/s), the broad anodic current wave rises up almost from the very beginning of potential range (0.0 V) up to 0.65 V with a maximum at ca. 0.43 V (denoted as E_{pa} , anodic peak potential).

In reversed current response the broad cathodic wave rises up from 0.6 to 0.1 V and peaks at ca. 0.35 V (denoted as E_{pc} , cathodic peak potential). The peak-to-peak separation ($\Delta E_{peak} = E_{pa} - E_{pc}$) is around 80 mV and $(E_{pa} + E_{pc})/2 =$ ca. 0.39 V. However, at a higher scan rate, e.g. 50 mV/s, the maximum anodic wave positively shifts to ca. 0.53 V and the cathodic wave peak negatively shifts to ca. 0.19 V, thus the ΔE_{peak} expands to ca. 340 mV, but the $(E_{pa} + E_{pc})/2$ is at ca. 0.36 V.

As is known, a reversible redox reaction on the electrode has a $\Delta E_{peak} = 59/n$ mV, where $n (\geq 1)$ is the stoichiometric number of electrons consumed or transferred in the electrode reaction. Hence, the ΔE_{peak} would always ≤ 59 mV especially at a very low scan rate and sufficient diffusion. These observations indicated that the charge storage relative to this pair of current waves is not a typical diffusion-controlled redox process.

On the one hand, the surface-restricted thin layer redox normally shows a mirror symmetrical current peaks as reviewed in Figure 1-8, Section 1.1.1 because of the absence of diffusion control. If, however, the process of electron transfer is a control step the peak-to-peak separation can be increased under a high speed scan rate. Regarding these, this charge storage process can be related to a slow electron transfer.

On the other hand, as discussed in Section 3.4.2, Chapter 3, this pair of current wave is most likely originated from a surficial redox process of oxygen-related functional groups on the POG and the adsorption of H^+ ions [3,4] following the reaction: $C_xO + H^+ + e^- \leftrightarrow C_xOH$. Noteworthy, this redox reaction can also be seen as the redox of GO itself. That is to say, the electrons in relation to this process are stored into the GO matrix and balanced by the adsorptive protons.

In conclusion, the charge storage in relative to this pair of current waves can be attributed to the surficial redox of oxygen-related groups accompanying with a slow electron transfer. This type of charge storage has the same essence as the pseudocapacitive behaviour in RuO_2 and MnO_2 as reviewed in the literature review of Section 1.1.1.3. Therefore, it can be attributed to the pseudocapacitance of the POG electrode.

4.5.3 Correlation of interfacial charge storage with the DED of POG

As discussed in the last two sections, generally, the charge storage current responses of all POG in KCl (Figure 4-14) and H_2SO_4 (Figure 4-15) improve to different extent in contrast with the untreated GO electrode (Figure 4-13). Both EDLC and pseudocapacitance are gradually improved as the ECR cycle increases from 10 (Si1) to 1000 (Si8) of CVs, $i = 1$ to 3, cf. Table 4-1. This improvement can also be observed in samples reduced in more negative ECR potential range following the same order from S1j to S3j, $j = 1$ to 8. All these indicated that the improvement of interfacial charge storage is originated from the reduction of GO.

Aiding with Equation 3-2 in Chapter 3, the interfacial charge storage of POG electrode in two electrolytes can be calculated. The results are presented in Figure 4-16a to d. It has to mention that the interfacial charge storage includes

both the EDLC and pseudocapacitance two parts of contribution. For clarity, only the results calculated at scan rates of 5 and 50 mV/s are displayed in these Figures. Samples reduced in three ECR potential ranges are plotted in the same panel of Figure 4-16.

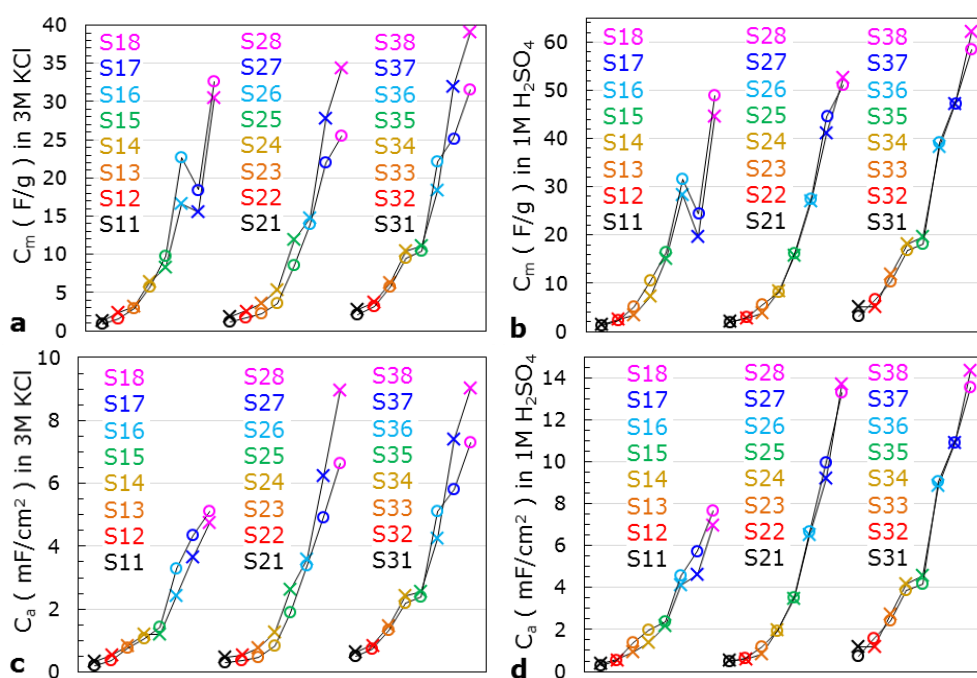


Figure 4-16. Specific capacitance of POG with gradient degrees of ECR: (a) and (b) the specific capacitance C_m in 3.0 M KCl and 1.0 M H_2SO_4 respectively; (c) and (d) the area-specific capacitance C_a in 3.0 M KCl and 1.0 M H_2SO_4 respectively. The surface area refers to the projected area of working electrode, 0.4418 cm^2 . Samples denoted by S1j ($j = 1$ to 8) are reduced within -1.0 to 0.0 V , S2j: -1.1 to -0.5 V and S3j: -1.15 to -0.5 V vs. Ag/AgCl. Index $j = 1$ to 8 refers to the ECR cycles from 10 to 1000 listed in Table 4-1. Circles (o) data are collected at 50 mV/s and crosses (x) data at 5 mV/s.

As assumed in Section 4.2 that the GO fragments always stay at the same place during the whole ECR treatment, hence the actual variation of the specific surface area is negligible. That is to say, the rise of area-specific capacitance can only be attributed to the improvement of the interfacial charge storage of POG rather than the variation of specific surface area. From another aspect, the mass-specific capacitance also improves very sharply within the same ECR potential range as the cycles of ECR increases. Furthermore, as samples were reduced in a more negative ECR potential, e.g. S3j, $j = 1$ to 8, their specific capacitance gained more than those samples which were reduced

within less negative potential range under the same cycles of ECR. In the proton-rich electrolyte, 1.0 M H_2SO_4 , the interfacial charge storage of POG treated under the same ECR conditions always have almost 1.5 to 2 times higher value in contrast with those POGs in 3.0 M KCl.

Several reasons resulted in the improvement of the interfacial charge storage through gradient ECR treatment on GO. The first reason, also the most intuitionistic one, is the decreased resistance of the GO coating layer after ECR treatment improves the EDLC by benefiting the flow and accumulation of electrons and holes in the GO coating layer. This is achieved through the removal of oxygen-containing functionalities on both basal plane and edge side of GO fragments, especially the carbonyl. Hence more excessive charge can accumulate on the electrode side, resulting in more counter ions are attracted and accumulate on the electrolyte side to balance these excessive charges. The second reason is the improvement of the pseudocapacitance contribution. During the ECR treatment more and more basal plane regions which are covered by oxygen functionalities are reduced to form many relatively small oxygen functionalised regions. These regions are segregated or surrounded by the recovered graphitic regions. This process can lead to the improvement of the redox activity of GO when it was reduced to POG, therefore, benefits the interfacial charge storage in the manners of pseudocapacitance, especially when proton-rich electrolyte is used.

Combining all these results with the Raman and XPS characterisation results, it can be found that the higher the DED was achieved in POG the better interfacial charge storage can be obtained in POG electrode.

4.6 Interfacial charge storage of ECR-treated GO electrode through EIS analyses

4.6.1 Entire ECR treatment carried on the same sample

As is known, the impedance spectroscopy technique [244-246] is highly sensitive to many internal and external factors, such as the surface roughness, heterogeneity, intrinsic structure, interfacial properties of as-examined electrode and experimental parameters. Experimental experiences tell that any existence of inconsistency in relation to above factors may result in chaotic, incomparable

or even unexplainable data. As shown in Figure 2-3 in Section 2.4.2, Chapter 2, the traditional tri-electrode cell used in this study innately has many shortcomings that may introduce inconsistency if more than one cells are used, for example the electric connections, the state of current collector, interfacial states of GO coating, reference electrode, counter electrode and electrolyte in-use. Therefore, considering these trivial problems, plenty of lab work were carried out to decrease or even eliminate these possible interferences originated from the above factors. One of the simplest strategy is to fix the above variables as much as possible during an entire ECR treatment procedure and all relevant ECCs by using only one cell and fewer samples. This can be easily achieved by using only one sample for the entire ECR treatment. Typical ECR and ECC procedures were collected in the Appendix D. In this section, only three samples were used for three different ECR potential ranges but for the entire ECR treatment from 10 cycles to 1000 cycles of reduction as denoted in following Table 4-4. Impedance spectroscopy behaviours were characterised before and after the whole ECR treatment.

Table 4-4. Experimental parameters for investigation the influence of ECR on the EIS of POG electrodes

Reduction Potential Window	-1.0 to 0.0 V	-1.1 to -0.5 V	-1.15 to -0.5 V
Sample number	S1	S2	S3
ECR cycles*	from 0 to 1000	from 0 to 1000	from 0 to 1000

* These ECR cycle steps follow the same intervals as shown in Table 4-1 from Si1 to Si8, $i = 1$ to 3. Sample preparation is the same as introduced in Section 3.1.

The complex-plane impedance (Nyquist plots), Bode plots and the capacitance-frequency distribution of the three samples are shown in Figure 4-17a to g. These EIS data were collected only in 3.0 M KCl at only one stand-by potential of +0.4 V vs. Ag/AgCl. The stand-by potential at 0.4 V is just the midpoint of the capacitive potential range (CPR) of POG. All these characterisation settings are set to reduce the immersion time of the electrode in the electrolyte, hence to avoid as many as side effects mentioned in Section 3.4.2. Experimental experiences told that relatively high quality and repeatable EIS data can be obtained by fixing most of influencing factors.

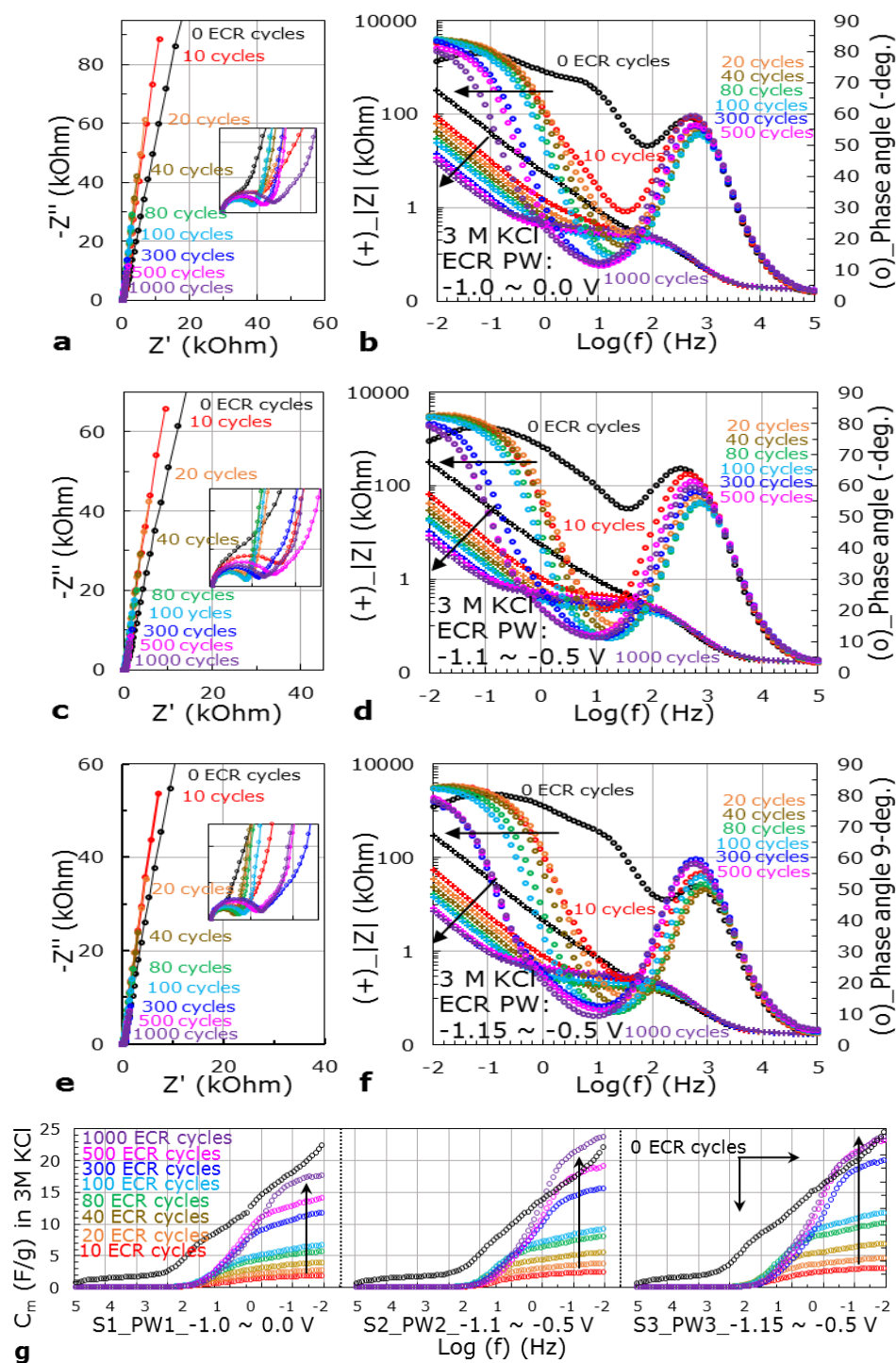


Figure 4-17. Nyquist (a, c and e), Bode plot (b, d and f) and the capacitance-frequency dependency (g) of GO treated with different cycles of ECR within three reduction potentials vs. Ag/AgCl in 3.0 M KCl. For each reduction potential range, ECR treatments were carried out on the same sample.

It can be seen that both the Nyquist and Bode plot can be divided into three frequency regions. The first is the high-frequency region from 1×10^5 to 1×10^2 Hz. As zoomed out and inserted in (a, c and e), in this region a pronounced semicircle of Z'' - Z' relationship shows in all ECR-treated samples but not in untreated samples, which corresponds to the first phase angle peak in the Bode plots. It was found that the diameter of the semicircle did not vary monotonously. It decreases as the ECR cycles increase from 10 to 80 or even 100, then enlarges from 300 to 1000. As introduced in Section 2.5.2.2, Chapter 2, the high frequency limit of the semicircle to the left hand side denotes the ESR, and the minimum value at the right hand side of the semicircle denotes the sum of the ESR and a charge transfer resistance (R_{ct}). It can be seen that the values of ESR are nearly invariable in all cycles of ECR. This indicated that only the R_{ct} is responsible to the variation of the diameter as the sample is reduced during the ECR treatment.

However, during the reduction of GO there is no reason to have an increased R_{ct} . Therefore, the possible reason for this abnormal increase of R_{ct} may be attributed to some extent of the separation between the POG layer and the titanium plate because of the accumulation of hydrogen bubbles especially after too many cycles (>300) of ECR treatment. This separation obviously weakens the contact between the POG and the titanium plate. This phenomenon has also been noticed in previous CV characterisation. When the ECR treatment beyond 300 cycles relatively depressed CVs can be observed.

The second is the medium frequency region from 1×10^2 to 1 Hz. It corresponds to the frequency region around the keen frequency in Nyquist plot and a valley-like phase angle in Bode plot. This region can be observed in all GO and POG samples. The valley-like phase angle is originated from a transform of the electrode property from a capacitive to a resistive feature corresponding to an almost 0° of phase angle. Noteworthy, the untreated GO shows a shallower valley of phase angle than that of ECR-treated samples. This is one of the main distinctions between the untreated and the ECR-treated GO, or POG electrode. The medium frequency region in the Bode plots (Figure 4-17b, d and f) just corresponds to the R_{ct} i.e. the second plateau on the $|Z|$ -f plot.

Again it shows no monotonous decline as the ECR cycles increase, thus this is consistent with the variation of the semicircle's diameter.

The third is the low frequency region below 1 Hz. In this region capacitive feature predominated the electrode behaviour again with the phase angle close to -85° . As can be seen in Nyquist plots (Figure 4-17a, c and e) the Z'' - Z' shows a perfect linear relationship in the low frequency region. Both imaginary and real part of impedance at the last frequency point (10 mHz) gradually decline to lower and lower values as the ECR cycles increase, indicating the improvement of total capacitance. This can be further proved by the capacitance-frequency distribution shown in Figure 4-17g.

Thereafter, EIS fit and simulation were carried out in order to analyses possible mechanism of the charge storage on these POG electrodes. According to the simulation experience obtained on untreated GO samples in Section 3.4.2, an analogue equivalent circuit shown in Figure 3-20 was used as a start point of data fit. However, no matter how the electric components were adjusted the fitting results still showed no satisfactory χ^2 and the error percentage of each component. Satisfactory fit and simulation should have χ^2 -values within or lower than the order of 10^{-4} and the error percentage of each component less than 10%. This failure indicated that a possible intrinsic transformation may exist in these POGs. Thus a new electric circuit should be considered to fit the present EIS data of POG electrode. In practice, EIS fit and simulation should follow the problem-solving principle of Occam's razor [247] and try all best to use an empirical circuit as simple as possible and introduce a new component with solid physical basis. In our case, the necessity to introduce a new component or branch is originated from a consideration of whether there is an intrinsic modification or variation of the GO after the ECR treatment. The reduction of GO through ECR treatment brings in a relatively limited variation to the sample. Thus the variation of a new electric circuit should be limited and comparable with the precedent one.

By re-examining the impedance spectrum and reconsidering the possible electrode process, including EDLC, adsorption/desorption and pseudocapacitance during the charge storage, several candidates were tried to acquire the optimised accuracy without losing rational physical explanation. It

has to emphasise that any newly introduced component cannot be arbitrary without considering its basis of existence. Although more components may give a higher fitting accuracy, overfitting can also rise and has to be avoided. That is to say, one can always get a good looking fit by adding more and more circuit elements to a model intentionally. Unfortunately, these elements have no basis in physics for the as-concerned system. Empirical models are sometimes worthy studying to optimise circuit. In addition, actually, there is not a unique equivalent circuit that describes the whole spectrum. One cannot assume that an equivalent circuit that produces a good fit to a data set represents an accurate physical model of the as-concerned cell [248].

Finally, an equivalent circuit shown in Figure 4-18, was confirmed as the best candidate with satisfactory χ^2 value ($< 4 \times 10^{-4}$) and the error ($< 10\%$) of all relevant components for all EIS data of POG. This circuit just has one more R-Q serial branch in contrast with the initial circuit (Figure 3-20) used to fit the untreated GO. The entire circuit is still capacitive in essence without the leakage resistance. If one more, two more or even three more such branches are introduced the candidate circuit shows no a better fitting accuracy, for example a lower the χ^2 value. It indicated that this circuit already achieved the optimised simulation comparing with other candidates.

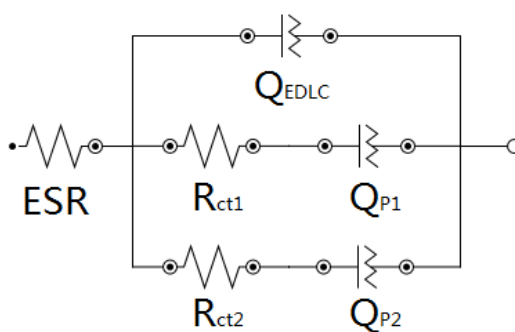


Figure 4-18. The optimised equivalent circuit used to simulate the impedance behaviour of POG electrode. ESR represents electrolyte resistance and other connection resistances. Q_{EDLC} is a constant phase element used to replace the EDLC. Two parallel branches with a serial R_{ct} and a Q_P are used to represent two charge transfer related capacitive components.

The most prominent feature of this circuit is no bypass of leakage resistance. In fact, if there is a leakage resistance the entire circuit will become

resistive feature, especially at the low-frequency limit. However, the almost -85° phase angle at all low frequency limit in the Bode plots (Figure 4-17b, d and f) showed no evidence of a resistive transformation in all POG electrode. Thus, the capacitive feature is a more rational prediction. Furthermore, the constant phase element (Q or CPE) gives the whole fit at least one order of magnitude lower value of χ^2 , meaning a higher accuracy. In practice, if just three pure capacitance are used in the simulation, fitting results with a relatively lower error but high value of χ^2 (around 10^{-3}) are obtained. It was also found that if we replace the two paralleled R-Q branches by a single R-Q branch, both χ^2 -value and error percentage will become out of control and lose all reliability, although theoretically a sum of $(R_{ct1}+R_{ct2})$ and $(Q_{P1}+Q_{P2})$ are the same in essence with the values of single R_{ct} and Q_P . The truth is that the two constant phase elements have different frequency constants (n-values). It may be attributed to two different charge storage mechanisms. These two constant phase elements Q_{P1} and Q_{P2} implied that there must be pseudocapacitance related charge storage contribution in the POG electrode. One of the representative fitting results is shown in Figure 4-19.

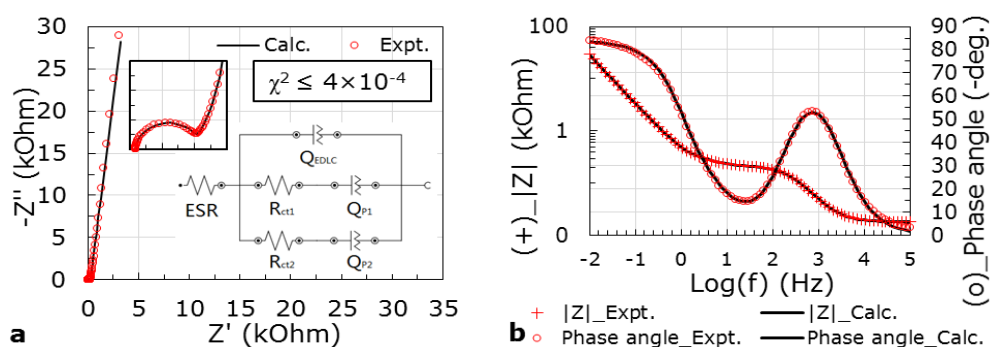


Figure 4-19. Representative simulation results (red circles) and experimental data (black solid line) based on the optimised equivalent circuit in Figure 4-18. (a) Nyquist plot inserted with χ^2 value and equivalent circuit, (b) the corresponding Bode plot.

As can be seen from the above fitting results, in the present case, the proposed circuit achieved a very high fitting accuracy with the χ^2 lower than 4×10^{-4} and no apparent deviation between the experimental data and simulated points in the whole range of frequency. During further simulation studies of all other POG samples it was found that the same high level of fitting accuracy can

be achieved by just a small adjustment on the value of each component in this circuit. The result circuit can cover all POG samples treated by an entire ECR treatment from 10 to 1000 cycles of CV scan.

The complete simulation results regarding to each electric component for all three samples in Table 4-4 are collected in Table A.1, Appendix E. Significant variation trend of each electric element versus the ECR cycles within the three ECR potential ranges are extracted from these results and plotted in Figures 4-20a to f. These results facilitate this study to learn the possible charge storage mechanism on the POG electrode and to correlate the degree of ECR or even the DED of POG with the variation of the interfacial charge storage.

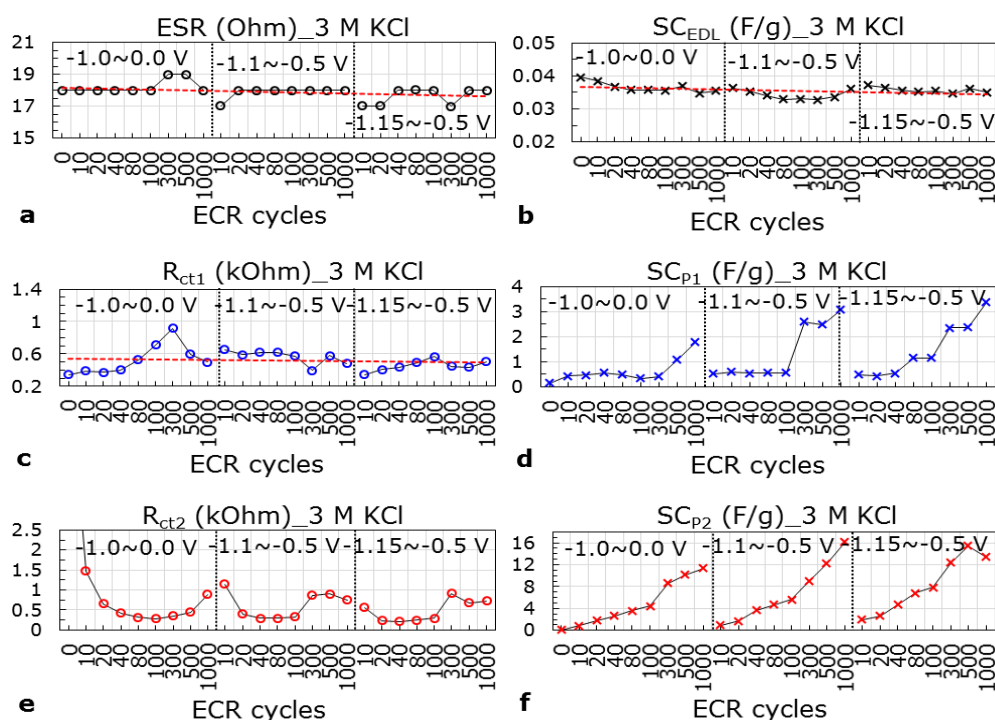


Figure 4-20. Crucial electric components of Figure 4-18 and their variation versus the ECR cycles from 0 to 1000 in three ECR potential ranges. Detailed data are collected in Table A.1, Appendix E. The effective specific capacitance (SC) are calculated from the equation of $C_{EFF} = (R_{ct} \times Q)^{1/n} / R_{ct}$, for a series connection of the CPE and R branch cf. [244]. The mass of active material is the actual loading of POG on the titanium plate determined through the way introduced in Section 2.4.3. 3.0 M KCl is the supporting electrolyte.

Firstly, it can be seen from Figure 4-20a as the ECR cycles increase from 10 to 1000 the ESR maintains at almost a constant of ca. 18 Ohm in all three ECR potential ranges. It indicated that the reduction of GO during the ECR

treatment has no apparent effect on the ESR of the testing cell. However the other two charge transfer resistance R_{ct} s (c and e) show a relatively violent variation during the ECR treatment. As can be seen that the first charge transfer resistor (R_{ct1}) varies its value around ca. 0.55 kOhm. No apparent tendency can be observed. The second charge transfer resistor (R_{ct2}) declines gradually from the 0 cycle of ECR to 100, then has a slight climbing up from 100 to 1000 cycles of ECR. Actually, this variation implied some intrinsic transformations of POG during the ECR treatment because all these charge transfer s are in nature relative to the process of electron transfer.

Hence, the variation of these R_{ct} s may reflect some information about electrode processes including charge storage and even the variation of the electronic structure of electrode materials. That is to say, it is possible to study the influence of the ECR treatment on the charge storage performance of electrode materials through examining the variation of these charge transfer related resistors. However, so far, it is still hard to make any clear deduction for these variations. One of the possible explanations is that as the ECR treatment is progressing, oxygen-containing functionalities on both the basal and the edge plane of GO fragments are reduced and removed to some extent just as confirmed in XPS characterisations in Section 4.4. This reduction declines the resistance of entire GO coating layer, hence benefits the charge storage in the GO side. The reduction of GO is more beneficial for the mobility of electrons and holes, hence results an improvement of the charge density on the electrode side.

Secondly, in regards to the capacitive components in the equivalent circuit it was found that the specific EDLC (SC_{EDL}) in Figure 4-20b barely changes, similar as the ESR, with a value of ca. 0.036 F/g (red dash line denoted) during the entire ECR treatment in three reduction potential ranges. It has to emphasise that simulation values of the specific EDLC do not completely represent the actual EDLC of GO electrode. The reason is not all the surfaces of GO fragment are accessible for counter ions of the electrolyte because most of the GO fragments or sheets are entangled with each other or stacked layer by layer as shown in the SEM characterisation in Section 3.3.1 on the true microstructure of the GO coating layer. In other words, the GO coating layer

formed by the '*casting-drying*' way directly on the Ti plates is not so porous. This resulted in that the actual capacitance of the GO electrode may be far lower than the true value of capacitance. In fact, it is not the aim of this study to improve or optimise the capacitance of GO. Thereby, the absolute values of these specific capacitance are not so important to consider, but the relative values and the overall variation tendency versus the ECR treatment is the crucial information for this research.

Different from the EDLC, the two charge transfer related capacitors, Q_{P1} and Q_{P2} gain a pronounced improvement as the ECR cycles increase from 10 to 1000. The values of these two capacitors are more than 2 to 3 orders of magnitude larger than those of the EDLC. It indicated that the improvement of the interfacial charge storage of POG during the ECR treatment is in fact originated from these two charge transfer related capacitors rather than from the EDLC term. From another aspect, as the ECR potential range is shifted more negative, the improvement of these two capacitive components become more pronounced. So far, it can be said that the improvement of charge transfer related capacitances may have special relationship with the ECR treatment on GO. Seeing from the electrolyte side towards the GO coating interface, the accumulation of counter ions towards the electrode interface contributes the charge density at the interface. This is the fundamental of charge storage mechanism in the EDL on the electrolyte side. However, based on the above fitting results, the ECR treatment does not improve the EDL capacitance, but in turn boosts charge transfer related capacitors (Q_{P1} and Q_{P2}), i.e. pseudocapacitance terms. However, the real reason on the improvement of the pseudocapacitance is still not so clear at this stage. Therefore, more experimental facts are necessary, especially the correlation between the variation of these pseudocapacitance terms and the electronic structure of POG during the ECR treatment.

4.6.2 ECR treatment carried on separate samples

As mentioned in the last section, too many cycles of ECR treatment may bring some side effects to the GO electrode, such as the excessive accumulation of hydrogen bubbles and separation between GO coating layer and the Ti substrate. Therefore, shorten the duration of the ECR treatment is

essential to diminish or even eliminate these side effects. On the other hand, as can be seen in the last section, the EIS characterisation after each step of ECR treatment can only be carried out in the same electrolyte (3.0 M KCl) because of the experimental design. Thereby no other characterisation steps, such as the Raman or XPS, can be introduced during the ECR treatment to monitor the possible variation which occurred on the ECR treated POG only when the entire ECR procedure is finished. Even though, the improvement of the charge transfer related pseudocapacitance was still observed in the POG electrode. Apparently, these data are still not enough to correlate the improvement of pseudocapacitance with the DED of POG. Therefore, the entire ECR treatment procedure from 10 to 1000 cycles of ECR on the single sample was split onto separate samples and in different electrolytes both 3.0 M KCl and 1.0 M H₂SO₄ in order to monitor the possible variation of the DED in POG versus the improved pseudocapacitance but in a relatively shorter test time. This way not only can shorten the ECR treatment duration to no more than 6 hours on each individual sample but also provides separate samples to conduct further spectroscopic characterisation. These Raman and XPS characterisation results have been presented in Section 4.3 and 4.4. Other ECR conditions were kept identical with those in the last section. The ECR parameters are listed in Table 4-1 for each individual sample.

EIS characterisation on the above separate samples includes the potential dependency of capacitance (E-C) from 0.0 V to 0.8 V with the interval of 0.05 V at only eight specific frequencies and the wide frequency spectrum scan from 10 kHz to 10 mHz at only +0.4 V vs. Ag/AgCl in 3.0 M KCl and 1.0 M H₂SO₄ for further analysis through equivalent circuit simulation. The detailed testing procedures on individual sample were compiled in Appendix F.

Representative potential dependency of capacitance of the POG electrode is shown in Figure 4-21a and b.

Apparent difference can be observed by comparison these distribution with those of untreated GO shown in Figure 3-18. The interfacial charge storage of POG, in this case, was improved at least 100 times higher than that of untreated GO at the corresponding specific frequency. For the other POGs which have a lower reduction degree, the improvement is of course less than

this case to some extent. At the frequency higher than 10 Hz, capacitance distributes almost constantly versus the stand-by potential from 0.0 to 0.8 V around only 2.5 to 4 F/g in this case. When the frequency lower than 10 Hz, a pronounced 'hump' structure was observed in both 3.0 M KCl and 1.0 M H₂SO₄ but located at the different stand-by potentials. The hump structure was always observed at ca. +0.1 V vs. Ag/AgCl in 3.0 M KCl, but at ca. +0.4 V vs. Ag/AgCl in 1.0 M H₂SO₄ accompanying with a weak shoulder at ca. +0.3 V vs. Ag/AgCl. If these hump structures are deducted from the baseline at these specific frequency an almost constant background capacitance can be approximated within the as-examined stand-by potential range as denoted by the dash lines shown in Figure 4-21. It indicated that when frequency lower than 10 Hz the interfacial charge storage on the POG electrode is indeed a hybrid mechanism including at least two terms. The one must be the traditional EDLC, and the other one is the pseudocapacitance contribution. If the CVs of POG investigated in Section 4.5 are recalled one can immediately aware that these hump structures are just the position at which a broad current wave was observed in both two electrolytes. Therefore, they must be originated from the same charge storage mechanism relative to the pseudocapacitance behaviour relative to protons as explained in previous Section 4.5.

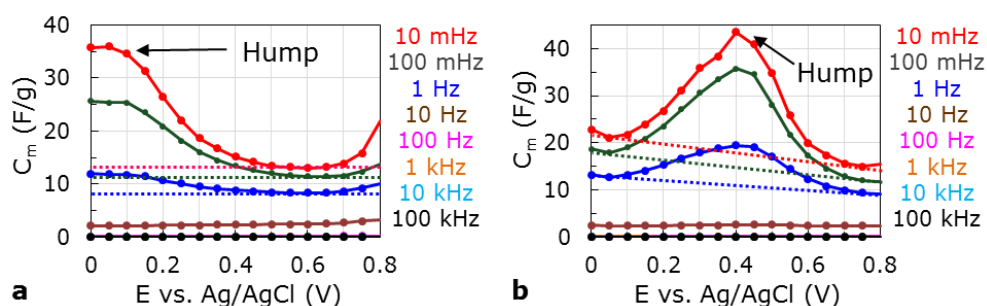


Figure 4-21. Representative potential dependency of capacitance of the POG electrode in 3.0 M KCl (a) and 1.0 M H₂SO₄ (b). Capacitance is normalised by the actual loading mass of POG. The dash lines sketched the possible background capacitance by deducting the hump structure, which is almost invariable versus the stand-by potential.

Interesting information can be further observed if we examine the variation of frequency-dependent capacitance of all POG samples versus their degree of ECR. Three representative frequency points at low (10 mHz), medium

(10 Hz) and high (1 kHz) frequency region were selected to extract the specific capacitance of POG and plotted in Figure 4-22a to f. Specific capacitance (C_m) is estimated based on the relationship between Z'' -C, i.e. $C = -1/2\pi fZ''$, at the selected frequency point.

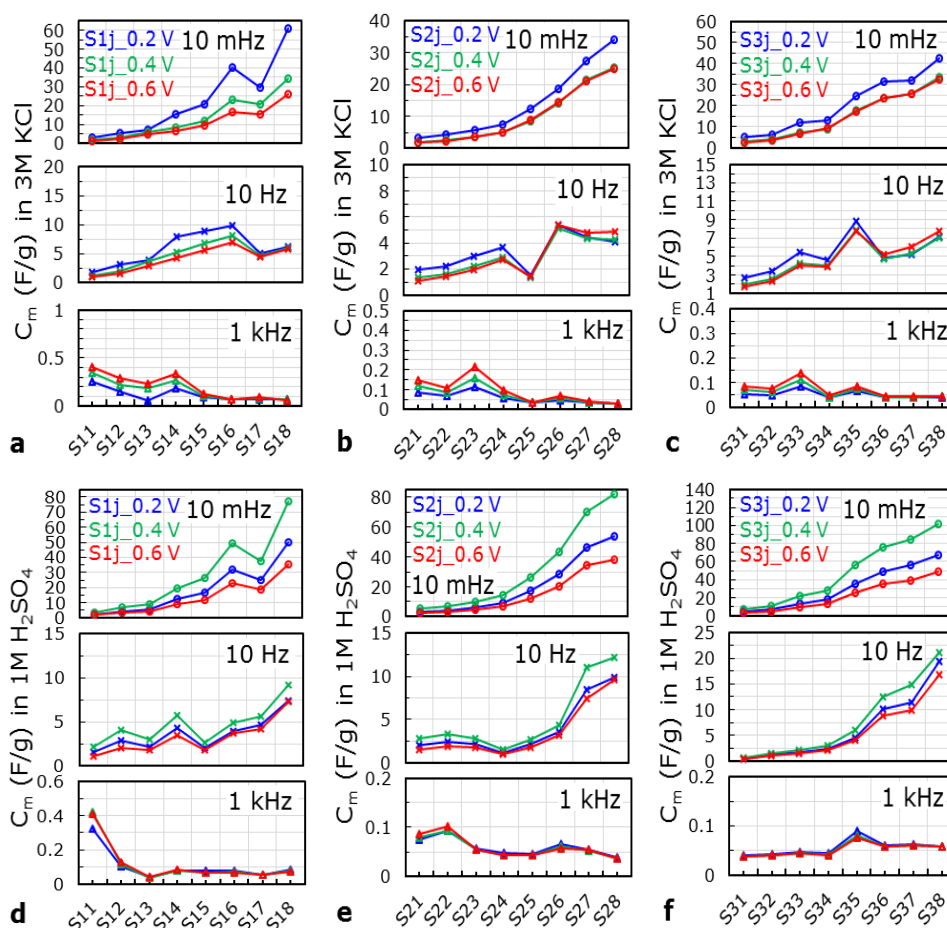


Figure 4-22. Frequency dependent capacitance of all 24 POG samples at three representative frequencies (1 kHz in high frequency, 10 Hz in medium frequency and 10 mHz in low frequency) and three stand-by potentials applied on electrode: 0.2, 0.4, 0.6 V vs. Ag/AgCl. Specific capacitance (C_m) is estimated from the relationship of Z'' -C, i.e. $C = -1/2\pi fZ''$ at selected frequency point. All capacitance are normalised with the actual loading mass of POG. Data were tested in 3.0 M KCl (a) to (c) and 1.0 M H_2SO_4 (d) to (f) respectively.

It can be seen that in both two electrolytes the specific capacitance of POG varies quite differently at the three specific frequency points as the ECR cycles increased from 10 to 1000 which correspond to the sample series number from Si1 to Si8. When the frequency was set to 1 kHz, the specific capacitance varied within a very narrow range ca. 0.1 ± 0.05 F/g no matter how

the ECR degree of the sample varied from Si1 to Si8. However, when the frequency was at 10 Hz or 10 mHz, a pronounced climbing-up was observed following the same order of the increasing ECR cycles. This variation trend is also consistent with the capacitance obtained from the CV analyses in Section 4.5. It can also be seen that as the frequency becomes lower the specific capacitance increases more sharply, for example, the variation range at 10 Hz is from 0 to 20 F/g, while it becomes 0 to 100 F/g at 10 mHz (Figure 4-22f) from the lowest degree of ECR to the highest one. Specific capacitance is improved higher when the GO was treated in the more negative ECR potential range, although it is still not the case at the frequency of 1 kHz.

In addition, obvious deviations of the specific capacitance at three stand-by potentials (0.2, 0.4 and 0.6 V) were observed especially at 10 mHz but not too pronounced at 10 Hz and 1 kHz. It indicated that the possible charge storage mechanism is more sensitive to the stand-by potential applied on the electrode at low frequency than at high frequency.

As reviewed in Section 1.1.1, capacitive charge storage mainly includes two mechanisms: EDL capacitance and pseudocapacitance. Apparently, different mechanisms characterise unique electrode kinetic process, hence have distinguishable electrode behaviour. For example, the EDLC originated from the pure electrostatic adsorption of counter ions without any charge transfer process, thus this type of capacitance has a relatively fast response time during charging and discharging courses.

However, the pseudocapacitance should have a relatively longer response time than the EDLC because of its faradaic mechanism. This difference on the response time can be readily detected through frequency related EIS techniques [6]. Therefore, the capacitive behaviour observed in high frequency region mainly reflects the EDLC. While the pseudocapacitance should be properly reflected in the medium and even low frequency region in which the response time can be matched. Based on this, the interesting phenomena observed in Figure 4-22 can be explained from two aspects. The one is that the EDLC of POG is not so sensitive to the ECR treatment, hence varied in a narrow range. The other one, the pseudocapacitance may very sensitive to the ECR treatment on the POG electrode, resulting in an increasing

tendency as the degree of ECR was improved from Si1 to Si8. According to the Raman and XPS characterisation on these POGs in Section 4.3 and 4.4, the experimental parameters of ECR treatment have been successfully correlated with the DED of POG. Thereby, the DED of POG can now be properly correlated with the interfacial charge storage of the POG electrode at this stage. This draws out a conclusion that the EDLC of POG is not so sensitive to the variation of the DED in POG; while, the pseudocapacitance may very sensitive to the variation of the DED, resulting in an increasing specific capacitance as the DED was improved from Si1 to Si8.

The wide frequency (from 10 kHz to 10 mHz) scan of all 24 POG samples listed in Table 4-1 in 3.0 M KCl and 1.0 M H₂SO₄ are shown in the following Figure 4-23 and 4-24 respectively. These Figures show all Nyquist and Bode plots of POG prepared within the three ECR potential ranges of -1.0 to 0.0 V (a and b), -1.1 to -0.5 V (c and d), and -1.15 to -0.5 V (e and f) respectively.

As can be seen that these EIS are very similar with those displayed in Figure 4-17. The second plateau in $f-|Z|$ plots and the diameter of semicircle in Nyquist plots do not show any pronounced variation trend versus the increasing degree of ECR. The first phase angle peak of some samples in the Bode plots are higher than -45° , while the others lower than this value. A phase angle with a value greater than the -45° indicates a characteristic of higher reversible kinetic process [244]. The variation of the phase angle peak is more violent than that was observed in Figure 4-17. It was found that samples had slight separation between the GO coating layer and the Ti plate if a long-term ECR treatment was carried out, particularly for those have 300 cycles or more cycles of ECR, although there is no crack and falling off from the current collector because of the restriction of the O-ring in the working electrode holder. This side effect has been attributed to the accumulation of hydrogen bubbles during the long-term ECR treatment.

In additional, the ECR procedure was split onto separate 24 samples in this section, and this experimental design resulted in the difference of the contact quality between the GO coating layer and Ti substrate in individual sample is definitely larger than that in the single sample used in the last section. This is another reason why a more violent deviation of the first phase-angle

peak was observed in these samples. It indicated that the phase angle in high frequency region is highly sensitive to the contact quality between the GO coating and the current collector.

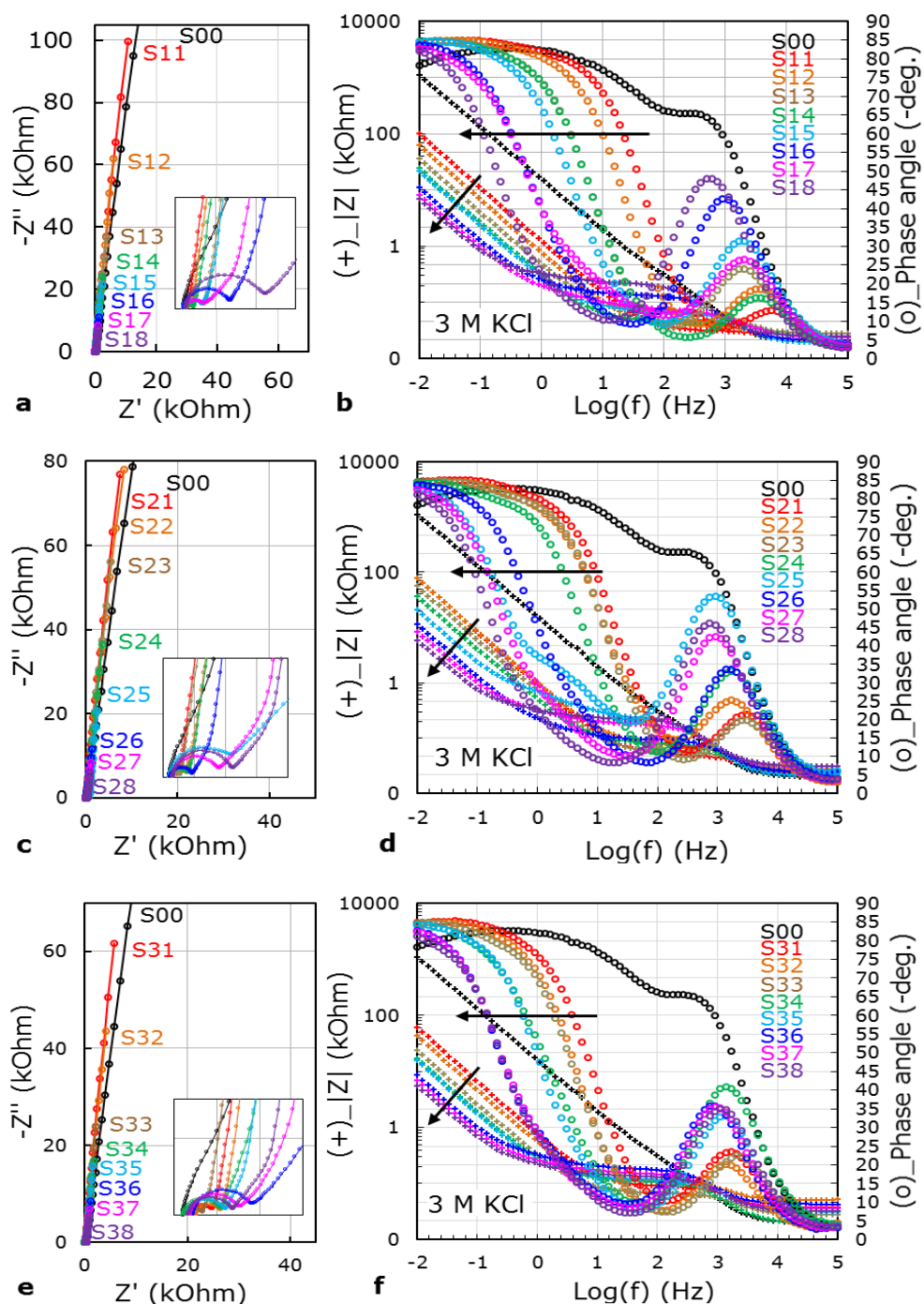


Figure 4-23. Nyquist and Bode plots of 24 POG from S11 to S38 collected in 3.0 M KCl at the stand-by potential: 0.4 V

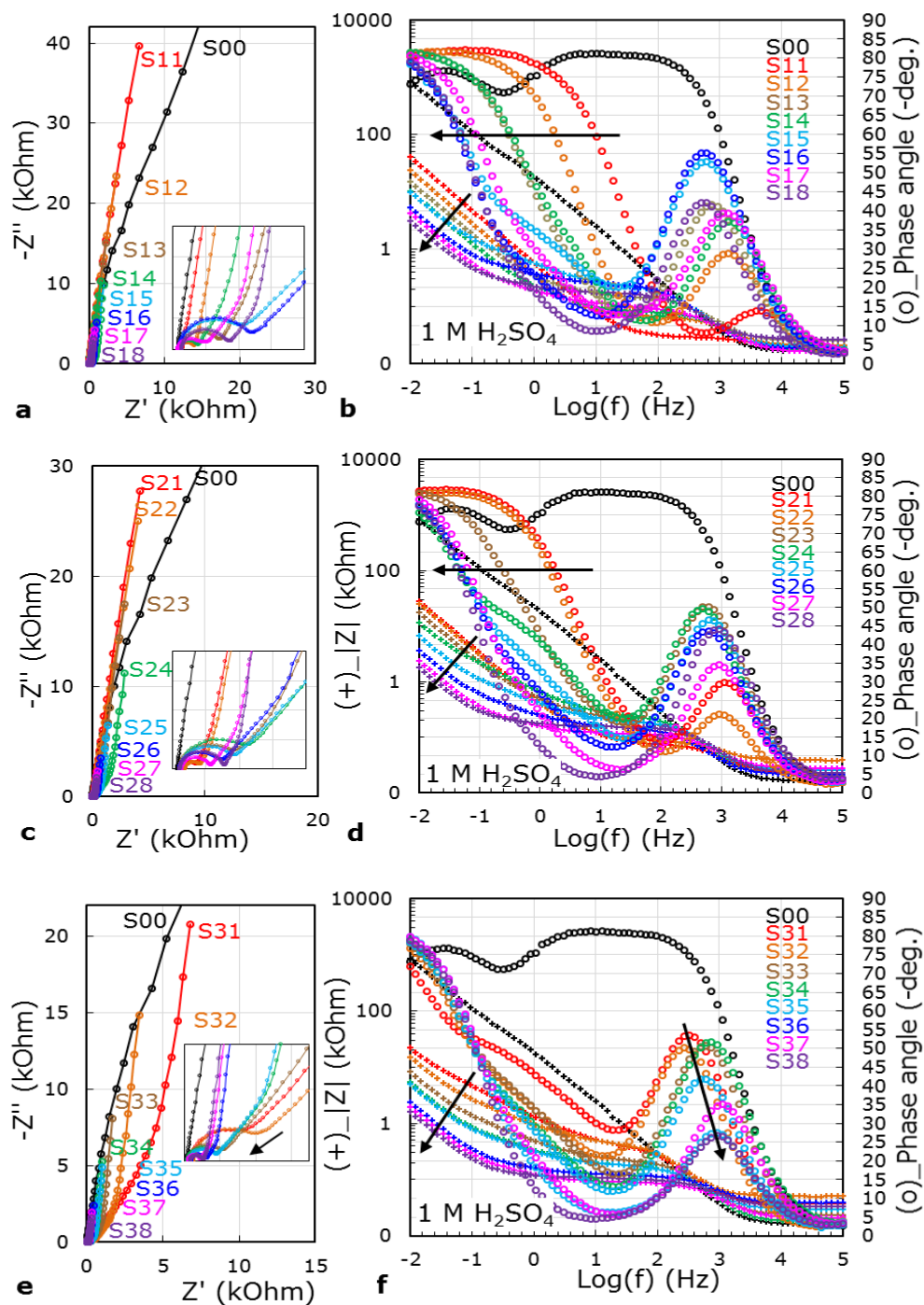


Figure 4-24. Nyquist and Bode plots of 24 POG from S11 to S38 collected in 1.0 M H_2SO_4 at the stand-by potential: 0.4 V

Thereafter, equivalent circuit simulations based on the EIS fit were conducted again on all 24 POG samples as analogue as that was done in the

last section. The same equivalent circuit shown in Figure 4-18 was used to conduct the simulation. It was found, the same, a lower χ^2 value within 10^{-4} and acceptable error percentage for each component indicated satisfactory fit results.

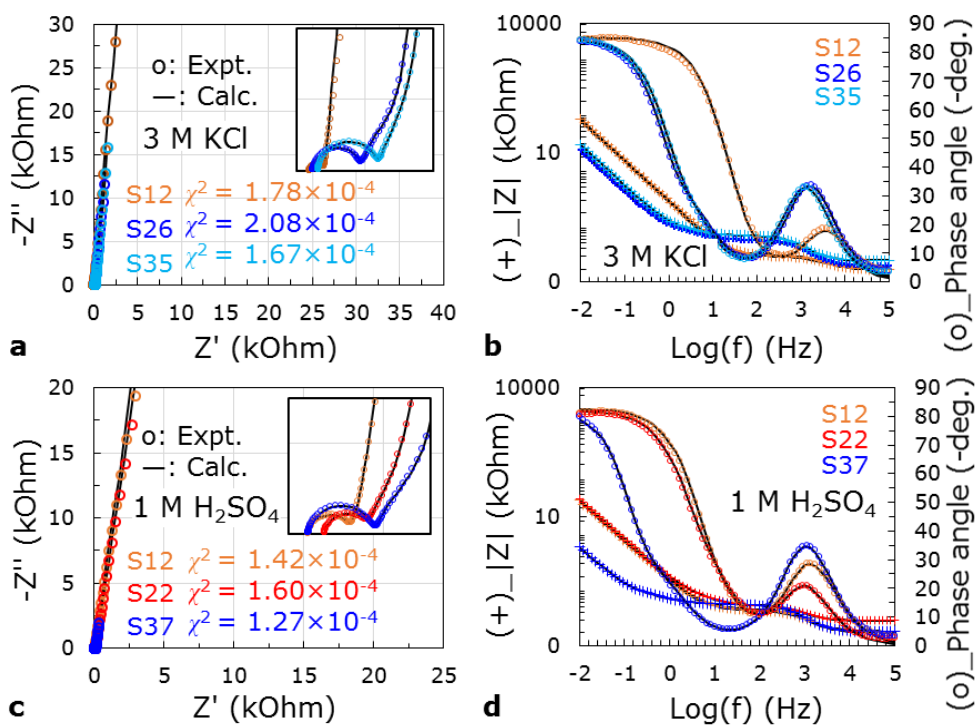


Figure 4-25. Representative simulation results (coloured circles) and experimental data (black solid line) based on the optimised equivalent circuit in Figure 4-18. (a) and (b) Nyquist and corresponding Bode plots in 3.0 M KCl, (c) and (d) in 1.0 M H₂SO₄.

It has to be noted that, due to the experimental design, more deviations on the fitting results are expected because more variables were introduced into the system, such as contact quality, connecting resistance, surface states of the GO coating layer. These variables were apparently different from sample to sample, although it was tried all best to keep the consistency during the samples and electrodes preparation. Theoretically, the ECR treatment caused the GO coating layer irreversible modification from the initial state to the final state. That is to say, the ECR varied the essence of GO so much that leading to variation on the practical values of components in the simulation electrical circuit. The detailed fitting results and values of each electrical components were collected in Table A.2 and A.3 of Appendix G for 3.0 M KCl and 1.0 M H₂SO₄ respectively.

Representative fitting curves in and the corresponding experimental data in two electrolytes were displayed in Figure 4-25a to d. The χ^2 -values indicated a good fit in both two electrolytes.

The crucial electric components of the 25 samples listed in Table 4-1, including the untreated sample S00, were extracted from the fitting results and plotted in Figure 4-26a to f for 3.0 M KCl and 4-27a to f for 1.0 M H₂SO₄ respectively.

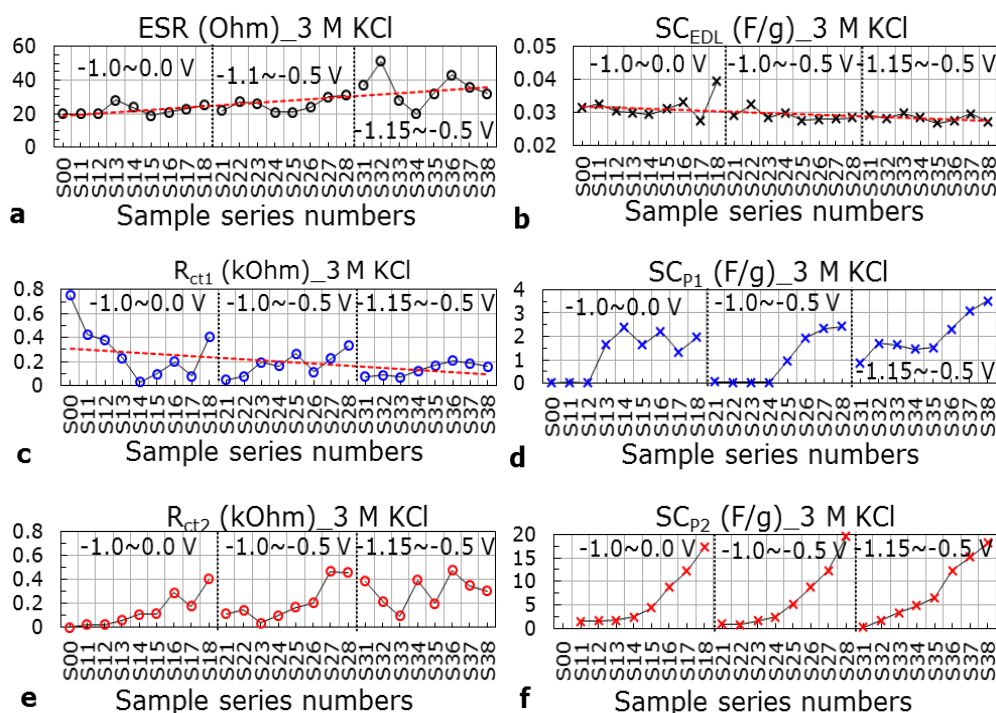


Figure 4-26. Crucial electric components of Figure 4-18 and their variation versus the sample series number. Sample series numbers are the same as those listed in Table 4-1. Detailed data are collected in Table A.2, Appendix G. 3.0 M KCl is the supporting electrolyte.

Firstly, the ESR did not show apparent change from the sample S00 to S38 in both two electrolytes. Few exceptions can be attributed to the individual difference between samples. The other two charge transfer resistances varied more violently than the ESR without apparent tendency.

Secondly, the specific EDLC (SC_{EDL}) maintained almost at a constant level ca. 0.03 F/g in 3.0 M KCl and ca. 0.04 F/g in 1.0 M H₂SO₄. It has to mention that the ECCs in 1.0 M H₂SO₄ were carried out after completion those in 3.0 M

KCl. The sample has to be washed carefully and rinsed with 1.0 M H_2SO_4 before further measurements. All these operations may affect the stability of the POG coating layer obtained through ECR in 3.0 M KCl, especially for those samples already had long-term ECR treatment, e.g. hundreds cycles of ECR. Therefore, fitting results may have a more violent vibration, for example the SC_{EDL} in Figure 4-27b for 1.0 M H_2SO_4 . In spite of this most of the fitting results are still around a constant level at ca. 0.04 F/g. That is to say, in fact, the ECR treatment on these samples did not change their EDLC very much. Only the newly formed wrinkles and folds in the POG coating layer introduced by the accumulation of hydrogen bubbles lead to some extent of surficial modification, hence improve the EDLC by means of enlarging the SSA of the layer. Obviously, this effect is very limited in a small amount, thus the influence on EDLC is also very limited.

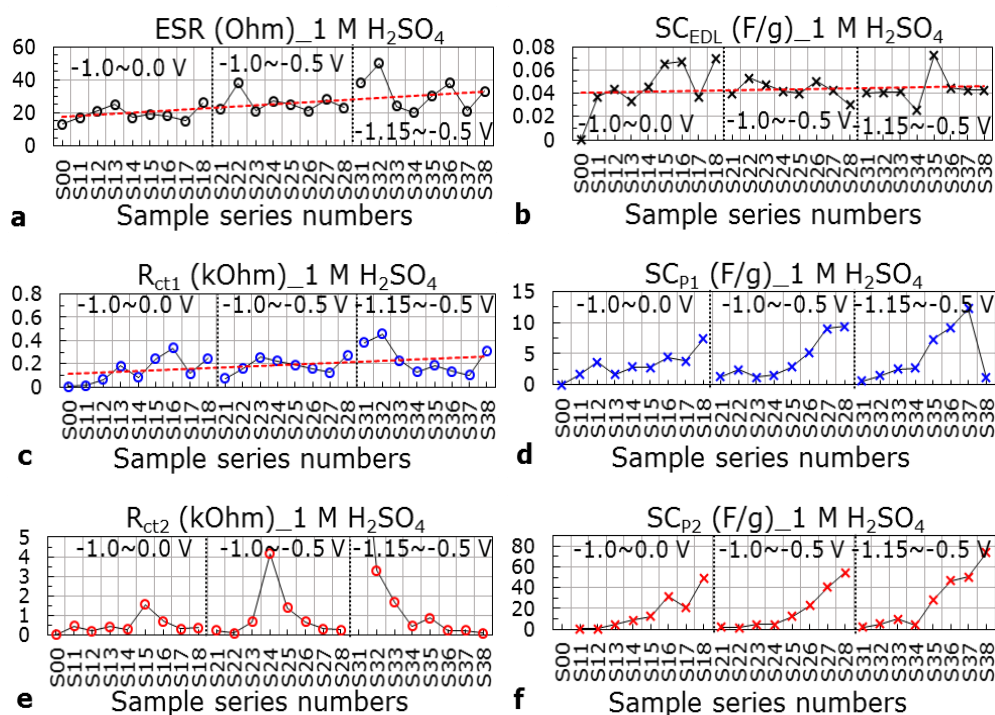


Figure 4-27. Crucial electric components of Figure 4-18 and their variation versus the sample series number. Sample series numbers are the same as those listed in Table 4-1. Detailed data are collected in Table A.3, Appendix G. 1.0 M H_2SO_4 is the supporting electrolyte.

These results revealed again an improvement of the two charge transfer related capacitances due to the ECR treatment and showed very good consistency with the results in the last section. It was noted that there is a

sudden decrease for the second capacitance term of S38 in 1.0 M H_2SO_4 . The possible reason for this may be some failure on this sample. This sample has been treated with 1000 cycles of ECR under the polarised potential approaching the decomposition limit of the electrolyte. Therefore, stripping-off or separation failures because of the large amounts of hydrogen accumulation may occur and introduce many side effects to this sample, hence the EIS characterisation suffered. However, this single exception still did not affect the general variation tendency in this series of results.

Based on the Raman and XPS characterisation in Section 4.3 and 4.4, the degree of ECR treatment was already correlated with the DED of POG. Now the above information can be explained properly. Firstly, the EDLC of POG electrode did not vary too much by the improved degree of ECR, i.e. the improved DED of POG. Secondly, the two charge transfer related capacitances were promoted as the DED of POG was improved. That is to say, the improvement of interfacial charge storage on POG electrode was originated from the two charge transfer related. These two charge transfer related capacitance may be originated from pseudocapacitance but definitely not from the EDLC.

Based on the above electrode behaviour in terms of a tree-branch circuit (Figure 4-18), there is necessity to reconsider the actual microstructure of the POG | electrolyte interface and relevant charge storage mechanisms.

The following Figure 4-28 sketched the possible interfacial configuration of the POG electrode.

It can be seen that, in the OHL, traditional EDL counter ions approach the electrode interface to balance a portion of excessive charge bearing on the electrode side. While, in reality, the charge density in the EDL is relatively low only about 0.18 electrons per atom stored as a double-layer charge at a 1 V cell if a common charge densities of the double layer (about 16 to 50 $\mu\text{C}/\text{cm}^2$) at plane electrodes are used and take an average capacitance of 30 $\mu\text{F}/\text{cm}^2$, and an atom density of about 10^{15} cm^{-2} at a smooth electrode surface for instance [6]. There are still lots of spare space on the electrode surface accessible for other types of charge storage.

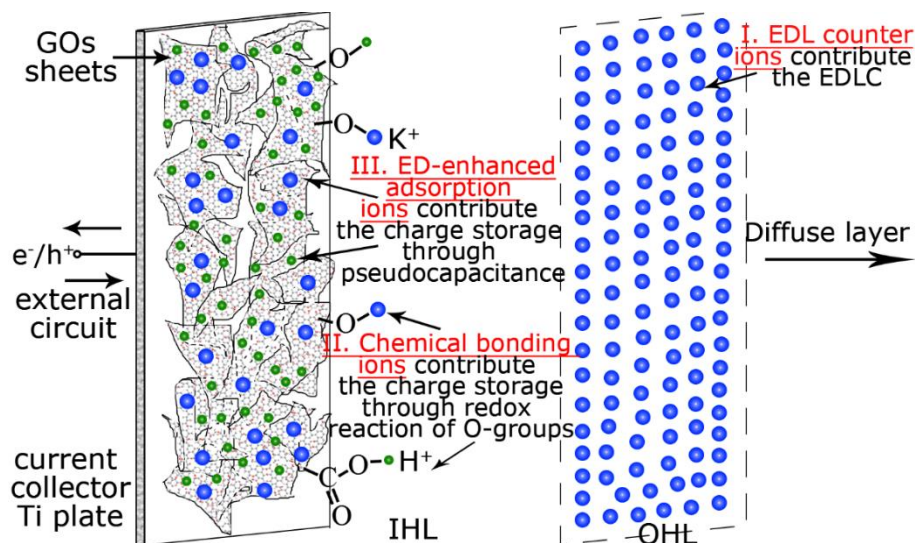


Figure 4-28. Schematic of three major charge storage mechanisms at the POG electrode | electrolyte interface: I for traditional EDLC, II for surface-restricted redox charge storage and III for pseudocapacitance. The EDL and oxygen-containing functional groups are exaggerated to clarify the details on the interfacial. IHL and OHL refer to the inner and outer Helmholtz layer respectively. The distance between the POG sheets and the EDL counter ions is also exaggerated to leave more space for illustration. Only cations are shown. All solvent molecules and anions are neglected.

In order to balance the rest excessive charge on the POG sheets, two other types of charge storage mechanisms may take into account. The first one is the chemical adsorption or precisely, chemical bonding originated from the redox reaction of oxygen-containing functionalities on either the basal or the edge plane of POG sheets as depicted by the charge storage mechanism (II) in Figure 4-28. This charge storage mechanism is accompanied by a charge transfer from the electrode to the localised valence states in the oxygen functional groups. The second one may be the so-called ED-enhanced adsorption, denoted by the charge storage mechanism (III) in Figure 4-28, through which the counter ions approach closer to the surface of the POG sheets. This charge storage mechanism is proposed as the pseudocapacitance because it is related to the redox of POG and the charge storage in the delocalised electron states. A partially charge transfer during this charge storage may occur in the partial electron delocalisation states in the POG. This argument will be further studied in Chapter 6 through a theoretical calculation

of the electronic structure of POG. Based on the EIS analyses, it was believed that the three branches equivalent circuit (Figure 4-28) used to simulate the POG electrode behaviour may be originated from the above three types of charge storage mechanism, i.e. one common EDLC and two charge transfer related branches. As shown in the experimental facts, the latter two branches of charge storage mechanism can be improved by the ECR treatment on the POG. Raman and XPS characterisation in Section 4.3 and 4.4 proved that the promoted ECR treatment brought the higher DED in the GO and turned it into partially reduced GO, i.e. POG. Therefore, it is rational to deduce that a higher DED may cause higher interfacial charge storage. However, the common metal electrodes with extremely high DED only have limited interfacial capacitance ca. 16 to 50 $\mu\text{F}/\text{cm}^2$ originated from the traditional EDLC without any pseudocapacitance contribution. Whether this is the same case for graphene and its derivatives when they achieve a higher DED? Thus more experimental facts are necessary to carry out, especially focusing on graphene species which have a higher DED than POG studied in this chapter. The electronic structure basis of the pseudocapacitance in POG is still not clear at this stage. Why does the partially reduced GO gain an improvement on its pseudocapacitance as its DED is improved? How does this improvement relate to the electronic structure of POG through the variation of the DED? This research proposes that there must be some fundamental reasons relative to the electronic structure which plays a key role in beneficial the pseudocapacitance of POG electrode. Therefore, more experimental investigations and theoretical explanations will be carried out in the next two chapters.

4.7 Summary

In this chapter electrochemical reduction (ECR) way, i.e. potential cycling, was employed to control the DED of GO in three negatively polarised potential ranges, resulting in a series of POG species with different DED. The reduction process on GO can be attributed to the reduction and removal of the oxygen-containing functional groups on the basal and edge plane of the GO sheets.

The gradually decreased I_D/I_G ratio in Raman studies of POG indicated that the graphitic region on POG sheets was gradually recovered as the degree

of the ECR treatment was improved. XPS characterisation on these POGs uncovered a decreasing amounts of oxygen-containing functionalities and an improvement of the DED through the deconvolution of high resolution C 1s peak and the D-parameter method. Aiding with the *DED equation* established in Chapter 3, the experimental parameters of ECR treatment were correlated with the DED of POG.

ECCs, including CV and EIS, on the POG electrode revealed that as the degree of ECR on the GO was increased the interfacial charge storage of the POG electrode was also improved.

Through EIS fit and the equivalent circuit simulation, it was found that there are at least three charge storage mechanisms existing on the POG electrode. The one is the traditional EDLC and the other two are charge transfer related interfacial charge storage. Significantly, results showed that the improvement of the interfacial charge storage on the POG electrode is not originated from the EDLC but from the two charge transfer related contributions. Aiding with the *DED equation* again the improvement of the interfacial charge storage on the POG electrode was finally correlated with the DED of POG. At the end, based on all of the investigation results in this chapter, a three-branch charge storage model was proposed to represent the interfacial charge storage behaviour of the POG electrode.

Chapter 5 Electrochemical Charge Storage of Polycrystalline Monolayer Graphene

5.1 Background

Whether a higher interfacial charge storage can be achieved by simply increasing the DED of graphene? This is a simple but interesting question that one may immediately ask based on the improving capacitance observed in the POG in Chapter 4. In fact, further ECR treatment on the POG through CVs in aqueous electrolyte may cause a series of failures, including strip off, hump up and even exfoliation, to the coating layer because of the excessive accumulation of hydrogen originated from the decomposition of the aqueous electrolyte. These failures hindered the POG working electrode to achieve its higher DED through such a simple ECR treatment in the aqueous environment.

In practise, many other processes can bring higher DED in POG. For example through wet chemical reduction or further anneal in the reductive atmosphere e.g. H_2 and/or NH_3 . However, it undoubtedly varies the microstructure of the GO coating layer heavily, which may introduce more variables in experimental investigation, hence losing the comparability with the results observed during the ECR treatment.

Therefore, in this chapter the author turns to samples of the commercial CVD polycrystalline monolayer graphene (PMG) on quartz as the substitute of graphene species with higher DED in contrast with the POG. This PMG is a continuous graphene film coalesced by many monolayer graphene crystal flakes with different lattice orientations [249]. Raman and XPS spectroscopy were employed to characterise the nature of PMG and to trace its DED. Electrochemical charge storage and impedance behaviours were investigated through the CV and EIS techniques. The results revealed an unusual interfacial charge storage behaviour on these PMGs in contrast with that observed in POG.

5.2 CVD polycrystalline monolayer graphene (PMG) working electrode and experimental set-up

The PMG Working electrode (WE) was fabricated by partially capsuling the sample of PMG on the quartz plate with epoxy resin (ER) as schematically

shown in Figure 5-1. The exposed area of graphene in the electrolyte can be easily controlled in this specially designed PMG WE.

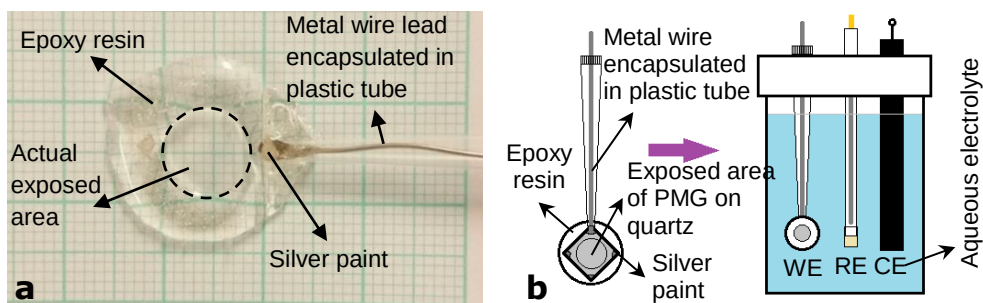


Figure 5-1. (a) Photograph of the polycrystalline monolayer graphene (PMG) working electrode (WE) placed on a graph paper for estimation of the exposed PMG area. (b) Schematic illustrations of (left of b) the construction of the PMG WE, and (right of b) the three-electrode cell with the PMG WE, the Ag/AgCl reference electrode (RE), and a graphite rod counter electrode (CE) in an aqueous electrolyte.

The silver paint was used to make the electric connection from the PMG WE to the metal wire lead. Four tiny droplets of the silver paint were carefully coated on the four corners of the PMG coated quartz plate. One of the corners was further connected with metal wire for the external connection, the diagonal corner was left unsealed by epoxy resin as a checking point for electrical connection before transferring the WE into the electrolyte. After curing of the epoxy resin, the PMG WE was ready for use in electrochemical testing. The resistance the PMG between the checking point and the metal wire lead was measured by a multi-meter to ensure a good quality of connections. Thereafter, the checking point was sealed properly by epoxy resin to avoid any contact between the silver paint and the electrolyte and the possible resulting interferences. To recheck the electric connection after uses, a small drop of deionised water was placed onto the exposed PMG area, then the resistance of the PMG between the water drop and metal wire lead was measured as illustrated in Figure 5-2. This electric connection check through the water drop contact, which is termed as ‘water check’ for the convenience of discussion later in this paper, could prevent secondary damage to the fragile PMG of single atomic thickness.

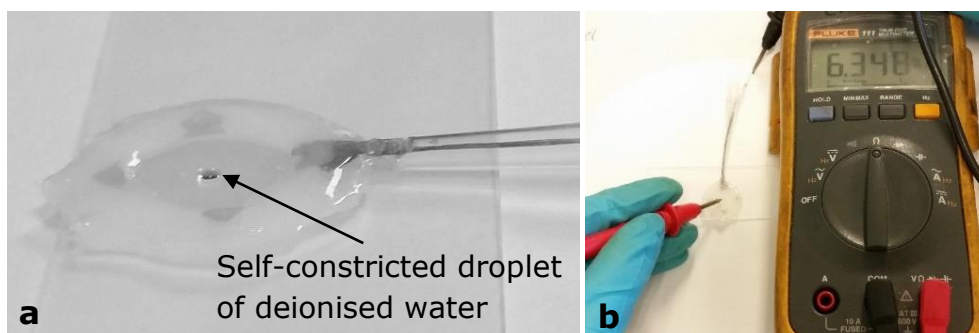


Figure 5-2. Water check. (a) Photograph showing a self-constricted water droplet on the exposed PMG area. (b) Manual check of the electric connection between the exposed PMG area and the metal wire lead via the water droplet.

Cyclic voltammograms (CVs) were recorded, mainly focusing on identification of the capacitive potential range (CPR). The overall bonding between the PMG and the substrate was expected to be weak because there was only one layer of carbon atoms on the quartz substrate. Indeed, it was observed that gas evolution on the WE could lead to exfoliation of the PMG from the quartz substrate. Hence, the CPR was explored by extending the potential scan in small steps e.g. ± 0.05 V or ± 0.10 V, starting from a narrow range of 0.20 V around the open circuit potential (OCP). In addition, the single atomic layer feature of this PMG sample makes it unnecessary to carry out any pre-treatment in several hundreds of break-in potential cycles. EIS was carried out immediately after recording all the CVs. To enable quick analysis, specific frequency points were selected for EIS analysis during the potential scan within the CPR without invoking any redox responses. Then a few bias potentials within and near the CPR were selected for the frequency scan from 100 kHz to 10 mHz.

5.3 Raman inspection of CVD monolayer graphene

A typical optical microscopic image of the PMG on quartz is shown in Figure 5-2a, revealing clearly grain boundaries (white lines indicated by the black arrows) as expected for a polycrystalline material. The grain shapes, sizes and orientations varied widely and irregularly. Many white spots appear randomly in the image, likely resulting from ripples or bubbles formed during the

transfer process, or adsorptive impurities on both the quartz substrate and the graphene layer itself [250].

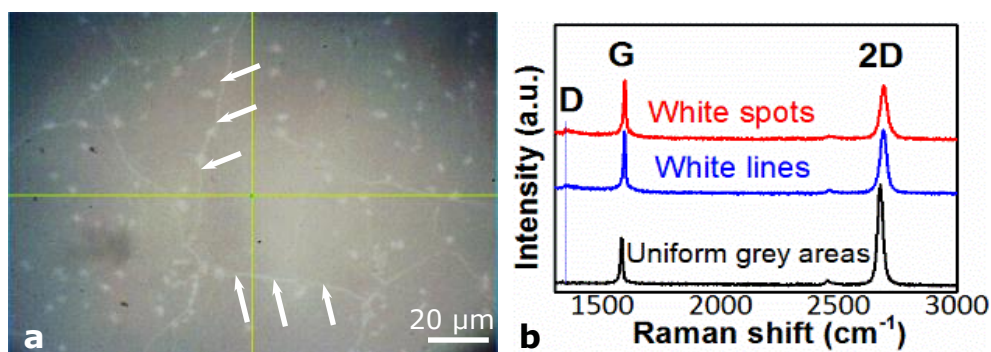


Figure 5-3. (a) A typical optical microscopic image (100X) of PMG on quartz showing three features: white lines indicated by the arrows (grain boundaries), white spots (ripples or bubbles) and uniform grey areas (monolayer graphene)). (b) Typical Raman spectra recorded on the uniform grey area (bottom black line), white lines (middle blue line) and white spots (top red line) as shown in (a).

Raman spectra were collected from the PMG sample as exemplified in Figure 5-3b. The three spectra correspond to the three features in Figure 5-3a. The 2D bands with the maximum intensity at ca. 2670 cm^{-1} and the G bands at ca. 1600 cm^{-1} confirm the monolayer feature of the PMG sample. Here the 2D band is the overtone of the D band, and the G band originates from the in-plane breath vibration mode of sp^2 carbon atoms. The I_{2D}/I_G ratio approached to 1.97 at the perfect single layer region. The absence of the D band on the bottom spectrum indicates a low concentration of defects in the uniform grey area in contrast with that in the areas of white spots and lines. On the upper two spectra of the white lines and spots, the I_{2D}/I_G ratio reduced to 0.93, and the D band also emerged, indicating partial twists and localised disorder of carbon lattices [241].

5.4 XPS inspection of CVD monolayer graphene

Figure 5-4a presents a high resolution C1s peak on the XPS of the PMG sample. The main peak of C1s at 283.4 eV has an asymmetric shape, implying the sp^2 bond ($-C=C-$) to be dominant in this sample. Deconvolution also gave traces of epoxy ($-C-O-C-$) at 285.5 eV, ketone ($-C=O$) at 287.9 eV and two broad $\pi-\pi^*$ satellite shake ups at 290.0 and 293.5 eV. Based on the XPS in Figure 5-

4a and the optical image in Figure 5-3a, it is reasonable to assume that these oxygen-containing groups (OCGs) may randomly decorate on the graphene surface in very small amounts. The composition of these OCGs is less than 20% by summing up all the contributions from epoxy (-C-O-C-), ketone (-C=O) and carbonyl (O-C=O) groups.

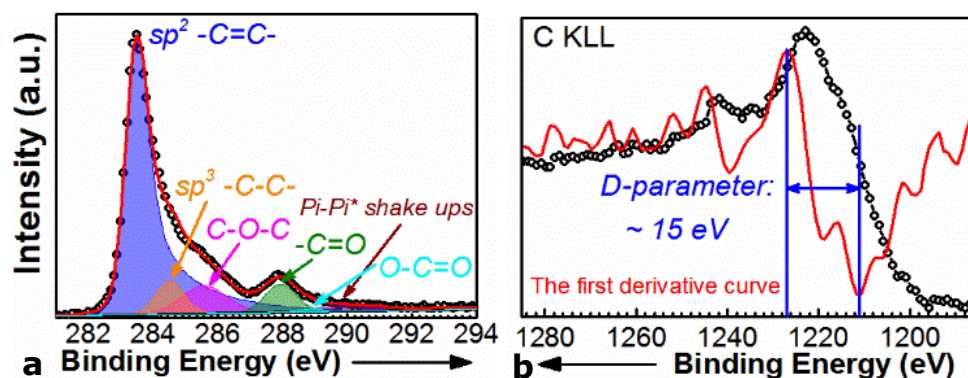


Figure 5-4. Representative XPS of PMG on quartz: (a) deconvolution of the high resolution C 1s peak. Black circles denote the experimental data, red solid line the fitting curve, and (b) the C KLL Auger spectrum (black circle) and its first derivative trace (red solid line).

The carbon KLL Auger electron spectrum of the PMG as shown in Figure 5-4b was used to extract the D-parameter which denotes the distance (double arrowed in Figure 5-4b) between the maximum peak and minimum valley on the first derivative of C KLL curve. This D-parameter is supposed to vary linearly with the sp^2/sp^3 ratio in common carbonaceous materials [232]. Its value should range in 12-13 eV for materials with extreme sp^3 -hybirdisation (e.g. diamond), and in 22-23 eV for those with extreme sp^2 -hybirdisation (e.g. graphite). Other carbon species with mixed sp^2 and sp^3 hybridisations should have D values between 12 and 23 eV. According to Figure 5-4a, the deconvolution of the high resolution C 1s peak of PMG suggests that the PMG has a high fraction of sp^2 component in contrast with the sp^3 component. That is to say, the D-parameter of this sample should be closer to 23 eV. However, the measured D-parameter is only ca. 15 eV. This contradiction was also observed in other studies and attributed to the interaction between graphene and the SiO₂ in the quartz substrate [233]. Therefore, it is impossible to evaluate the DED of this type of PMG based on the value of D-parameter.

5.5 Charge storage performance from CV analyses

In order to observe the capacitive charge storage in the PMG WE, CVs were recorded in different potential ranges, starting from -0.15 to 0.15 V vs. Ag/AgCl, for example, in the neutral 3.0 M KCl at a scan rate of 100 mV/s. This was denoted by CV1 in Figure 5-5a. It can be seen that on the negative potential side near -0.15 V, a very weak cathodic current was detected, and it should be attributed to the reduction of H^+ to adsorbed H. Thereafter, CVs at lower scan rates were recorded and labelled as CV2: 50 mV/s, CV3: 20 mV/s and CV4: 10 mV/s. No pronounced differences could be observed except a linear decrease of the current.

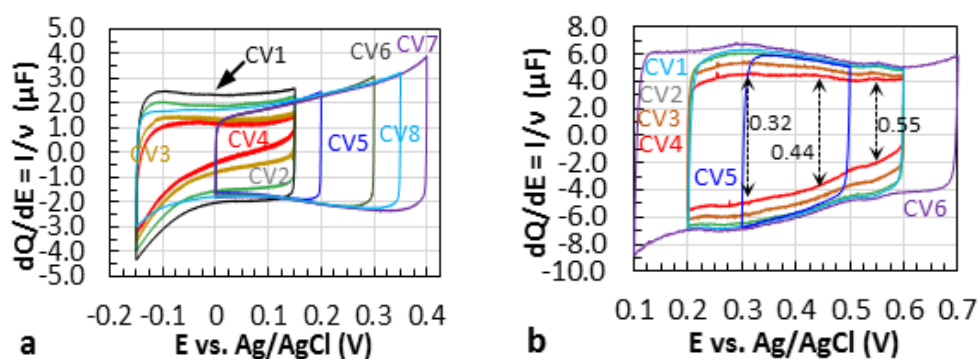


Figure 5-5. CVs of the PMG WE in (a) 3.0 M KCl and (b) 3 M HCl. Note that the y-axis is the scan rate normalised current i.e. the differential capacitance, $dQ/dE = I/v$.

Positive potential scan commenced from the range of 0 to 0.20 V (CV5), 0 to 0.30 V (CV6), and then 0 to 0.40 V (CV7) at a rate of 100 mV/s. It can be noticed that when the positive potential limit is shifted to more positive values, the current near the positive limit gradually increased, suggesting oxidation of the PMG. This oxidation is expected to cause irreversible damage because of the monolayer nature of the PMG. This is evidenced by CV8 which was recorded after recording CV7 in a wide potential range from -0.15 to 0.35 V. It can be seen that the currents between -0.15 and 0.15 V on CV8 are notably smaller than that on CV1 although both CVs were recorded at the same scan rate of 100 mV/s. In summary, the CVs in Figure 5-5a confirm a dominant capacitive charge storage mechanism in the PMG WE. Reduction of H^+ occurs at potentials more negative than -0.05 V, whilst oxidation of the PMG almost

starts from the very beginning of the positive potential vs. Ag/AgCl. According to these CVs, the CPR can be estimated in between -0.05 and 0.35 V.

Table 5-1. Capacitances calculated from CVs in Figure 5-5.

Electrolytes		3.0 M KCl		3 M HCl		
Exposed area*		0.50 (cm ²)		0.54 (cm ²)		
Potential range (V)	Scan rate (mV/s)	C _a (μF/cm ²)	C _m (F/g)	Potential range (V)	C _a (μF/cm ²)	C _m (F/g)
−0.15 to 0.15	10	3.7	24.4	0.20 to 0.60	7.5	49.5
	20	4.2	28.0		9.0	59.4
	50	4.9	32.4		10.1	66.7
	100	4.7	31.2		10.3	68.0
0 to 0.20	100	3.5	23.3	0.30 to 0.50	10.1	66.7
0 to 0.30	100	3.9	26.1	0.10 to 0.70	10.8	71.3
0 to 0.40	100	4.4	28.7	/	/	/
−0.15 to 0.35	100	4.2	27.2	/	/	/

*The actual exposed area in the electrolyte was measured with a graph paper (cf. Figure 5-1a) on each sample to 0.50 ± 0.05 cm², and the load mass of graphene in μg was calculated based on the monolayer assumption and the actual exposed area.

In the acidic electrolyte of 3 M HCl, as Figure 5-5b displays, the CPR was found to be between 0.15 and 0.65 V. The scan rates from CV1 to CV4 in Figure 5-5b correspond to 100, 50, 20 and 10 mV/s, respectively. When the potential range was extended in both directions i.e. between 0.10 and 0.70 V, weak cathodic and anodic currents resulting from H⁺ reduction and PMG oxidation, respectively, could be detected. Different from those CVs obtained in KCl, several very broad current waves were observed to superimpose on the supposedly rectangular background CVs in HCl. As can be seen in Figure 5-5b, the broad cathodic and anodic waves are both centred at ca. 0.30 V, which suggests adsorption and desorption as the origins. However, they were absent on the CVs recorded in KCl, therefore the broad waves may be attributed to the interaction between H⁺ and the PMG surface, particularly the small number of OCGs. The simplest interaction between H⁺ and OCGs is protonation which neutralises negatively charged OCGs, or making neutral OCGs positively charged. These changes, in turn, make it easier for reduction or more difficult for oxidation, leading to a positive shift of the potential for charge transfer

reactions. In addition, the specific capacitance (and hence the specific charge capacity) of the PMG WE was found to be 4 to 5 times higher in 3 M HCl than in 3.0 M KCl as summarised in Table 5-1. The higher capacitance in HCl could be highly likely due to the much smaller size but the higher mobility of the H^+ ion in comparison with the K^+ ion. As a result, more H^+ ions could access and accumulate on the PMG WE, and hence higher charge capacity or capacitance.

It is worth mentioning that the non-oxidative HCl was chosen as the acidic electrolyte in this work because the PMG on quartz was found to be vulnerable to oxidation in the oxidative acid of 1.0 M H_2SO_4 in which only a few cycles of potential scan could lead to distorted CVs. In line with the CV findings, it was also observed under the optical microscope that corrosion occurred to the PMG at grain boundaries and defects even at the very beginning of the potential scan. Meanwhile, if positively shifting the positive potential limit, over-oxidation became more serious, leaving many broken holes randomly distributed in the PMG coating as revealed by the water check, and optical microscopic inspection. Figure 5-6 presents the evidence.

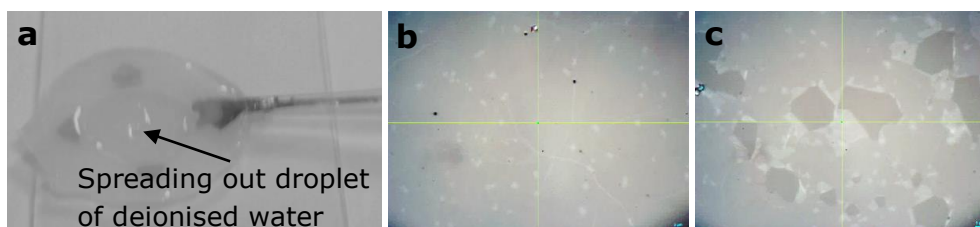


Figure 5-6. (a) Water check of the damaged sample. (b, c) Optical microscopy evidence of PMG before (b) and after (c) the damage caused by slight oxidation.

In a newly assembling PMG WE, a small droplet of deionised water can be self-constricted into a finite volume, (relatively small contact angle) on the PMG surface because of the hydrophobicity of pure graphene, as shown in Figure 5-2a. However, when the PMG is damaged or broken, the water droplet would spread out on the surface due to the hydrophilicity of the quartz substrate, as shown in Figure 5-6a. The optic micrographs in Figure 5-6b and 5-6c compare the surface of the newly assembled PMG WE and that with broken holes because of over-oxidation and/or other harsh electrochemical treatments.

These holes not only introduced inhomogeneous edge defects but also caused the graphene to exfoliate from the quartz substrate. The holes could have allowed components of the electrolyte to enter between the PMG coating and the quartz substrate which are held together by the weak Van der Waals force. This scenario could particularly develop if H₂O molecules and/or H⁺ ions formed the stronger hydrogen bonds with the oxygen-containing groups at the edges of the holes.

As discussed above, it can be established from the CVs in Figure 5-5 that the CPR of the PMG in 3.0 M KCl is approximately from –0.05 to 0.35 V, but in 3 M HCl it becomes wider and positively shifted, from 0.15 to 0.65 V. With these fairly rectangular CVs, the capacitance of the PMG WE can be estimated from Equation 3-2 as mentioned in Section 3.4.1, Chapter 3.

Calculation results under different experimental conditions are summarised in Table 5-1. It can be seen that the area normalised capacitance (i.e. areal capacitance), C_a , of the PMG is from 4 to 5 $\mu\text{F}/\text{cm}^2$ in 3.0 M KCl and from 8 to 10 $\mu\text{F}/\text{cm}^2$ in 3 M HCl. These values are well in line with the literature on the EDL capacitance, C_d , of carbonaceous materials. For example, the interfacial capacitance of highly orientated pyrolytic graphite (HOPG) was reported to be 3 to 4 $\mu\text{F}/\text{cm}^2$, especially at the potential of zero charge (PZC) [251,252]. However, interestingly, the C_a value of the PMG obtained in this work in 3 M HCl is about twice higher than the extremely low value of 3 to 4 $\mu\text{F}/\text{cm}^2$. In other words, in 3 M HCl, there was about 50% or more of the measured capacitance that was not from C_d . As it can be seen in Figure 5-5b, CVs in 3 M HCl were not perfectly rectangular in shape. There at least three broad current couples visible at around 0.32, 0.44 and 0.55 V, even at high scan rates. In spite of the few oxygen-containing groups in the PMG as detected by the XPS in Figure 5-3a, it is not reasonable to attribute more than 50% of the measured capacitance completely to the redox reactions of these oxygen-containing groups. This extra capacitance could be a sum of a minor contribution from the redox reactions of the OCGs (1 to 5% as estimated from the CVs), but a major part (> 45%) from the transfer of partially delocalised valence electrons in the PMG as previously explained as the intrinsic origin of pseudocapacitance [253].

The specific capacitance of the PMG varied slightly from 11 to 32 F/g in 3.0 M KCl, and from 50 to 70 F/g in 3 M HCl, both of which are slightly higher than the results obtained from organic and ionic liquid electrolytes in which only the C_d could be observed [254]. In this work, it was noticed that even when a small damage occurred on the PMG, the decline of charge storage performance could be probed by the CV variations in terms of either or both of the current and shape. The damage on the PMG could be further verified through the ‘*water check*’ as described in the experimental section. If there were a damage on the sample, it could be detected electrically between the surface of the PMG and the metal wire lead as long as a small water drop was placed on the damaged area. Figure 5-2 and 6-6 show the difference when doing the ‘*water check*’ between the as-assembled PMG WE and that with a damaged region within the exposed area.

As revealed by the optical microscopic and spectroscopic analyses discussed above, the PMG used in this work had various defects at both macro- and microscopic levels. The observed humps or bents, de-bonding and peeling off from the substrate, broken holes, cracks and folds are macroscale defects and may all hinder counter ions from accessing and accumulating on the PMG surface, and hence depress the surface charge storage. On the other hands, defects at atomic and molecular scales such as grain boundaries and OCGs, particularly when protonated in acidic electrolytes, may introduce additional electronic states in graphene that could benefit to increasing the charge storage capacity as predicted by DFT modelling [253]. The benefit quantification of the specific defects is out of the interest of this study, and this part of work can be put into the future work.

5.6 Charge storage performance and equivalent circuit

EIS measurements were carried out immediately after recording the CVs, starting with checking the potential influence on the impedance in a small potential range within the CPR i.e. -0.10 to 0.20 V in 3.0 M KCl and 0.20 to 0.60 V in 3 M HCl. During the potentiostatic experiments, EIS was recorded at 7 selected frequencies. The imaginary component of the impedance, Z'' , was used to estimate the capacitance according to $C = 1/(2fZ'')$ where f is frequency. It is acknowledged that, strictly speaking, the $1/(2fZ'')$ values are only equivalent

to capacitance if the frequencies are sufficiently low, and the EIS data can be simulated by a simple serial RC circuit. As a first approximation and also for the convenience of discussion, in this paper, the plot of the value of $C = 1/(2fZ'')$ versus the potential, E , is referred as the 'C – E profile'. Figure 5-7a and 5-7b show the C – E profiles of the PMG WE in the electrolytes of KCl and HCl, respectively.

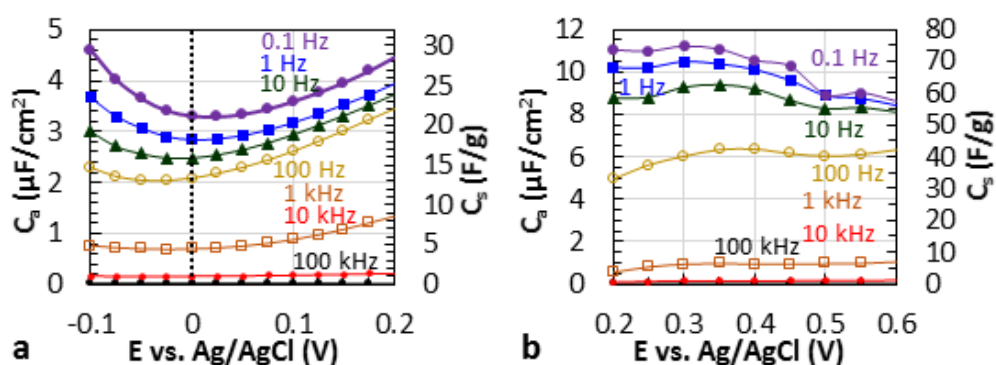


Figure 5-7. Representative capacitance – potential profiles of PMG at indicated frequencies in (a) 3.0 M KCl and (b) 3 M HCl. The areal and specific capacitances were calculated according to $C = 1/(-2\pi fZ'')$ at the indicated frequencies and normalised by the actual exposed PMG area (C_a) and the calculated PMG load mass (C_s).

Firstly in the neutral KCl, when the frequency was higher than 1 kHz, the C – E profile remained almost flat, indicating an insignificant potential influence. This is understandable because Z'' is less related to the capacitance at high frequencies. At frequencies of 1 kHz or lower, valley-like profiles were observed at every frequency. The valley resides approximately at 0 V vs. Ag/AgCl. This phenomenon has been broadly observed on HOPG in both aqueous and non-aqueous electrolytes [251,252], but is rarely reported on monolayer graphene. Possible reasons include the difficulty in obtaining reproducible samples, relatively narrow decomposition potential window for aqueous electrolytes and the fragility of monolayer graphene.

As can be seen Figure 5-7a, the C – E profile gradually moved upwards from almost zero to 4~5 $\mu\text{F}/\text{cm}^2$ (or 25~30 F/g) as the frequency declined from 100 kHz to 100 mHz. The low frequency C – E profiles at 10 to 0.1 Hz are consistent with the CV characterisations. It can also be seen that the variation

trends or shape of the $C - E$ profiles are generally similar from 100 Hz to 100 mHz. Completely different $C - E$ profiles were observed in 3 M HCl as shown in Figure 5-7b, in spite of the increasing trend following the decreasing frequency. The most pronounced difference was that the $C - E$ profiles were not valley shaped. Instead, within the applied potential window, several humps appeared, especially at low frequencies (10 to 0.1 Hz). These features also correspond to the three current waves on the CVs in Figure 5b. With lowering the frequency, the $C - E$ profiles moved upwards from 8 to 12 $\mu\text{F}/\text{cm}^2$ (or 55 to 70 F/g). Again, the low frequency $C - E$ profile is consistent with the CVs in capacitance.

Thereafter, frequency scans from 10^5 to 10^{-2} Hz at fixed potentials were performed to create the Nyquist and the Bode plots as exemplified in Figure 5-8a to 5-8d. Three representative potentials were chosen i.e. -0.10 , 0 and 0.05 V in 3.0 M KCl, while 0.30 , 0.40 and 0.50 V in 3 M HCl. From both the Nyquist and Bode plots, in the two electrolytes, the impedance of the PMG can be separated into (I) a high frequency region from 10^5 to 10^2 Hz, (II) a medium frequency region from 10^2 to 10^{-1} Hz, and (III) a low frequency region from 10^{-1} to 10^{-2} Hz.

Figure 5-8a presents typical Nyquist plots of the PMG WE in the KCl. It can be seen that at 0 and 0.05 V, the Nyquist plot is dominated by a tilted and slightly curved line that may be seen as a capacitive feature, or a portion of a large semicircle. At -0.10 V, the plot was clearly a fractional semicircle. According to the CVs in Figure 6-5a, 0 and 0.05 V are within the CPR, which means the tilted lines in Figure 5-8a should be capacitive in nature. However, -0.10 V is just outside the negative end of the CPR and can cause H^+ reduction, which agrees with the observed fractional semicircle on the Nyquist plots. For a further verification, the relation between Z'' and f was analysed. As shown in Figure 5-8e, when lowering the frequency, the value of $C = 1/(-2\pi fZ'')$ remains fairly constant at 0 and 0.05 V, but increases significantly at -0.10 V. Figure 5-8g plots Z'' versus $1/f$, showing satisfactory linear relations at 0 and 0.05 V, but not at -0.10 V. Thus, it is reasonable to attribute the tilted lines in the Nyquist plot at 0 and 0.05 V are dominated by capacitive contributions. The capacitance

derived from the slopes of the fitted straight lines is $4.0 \mu\text{F}/\text{cm}^2$ which is in good agreement with the CV result.

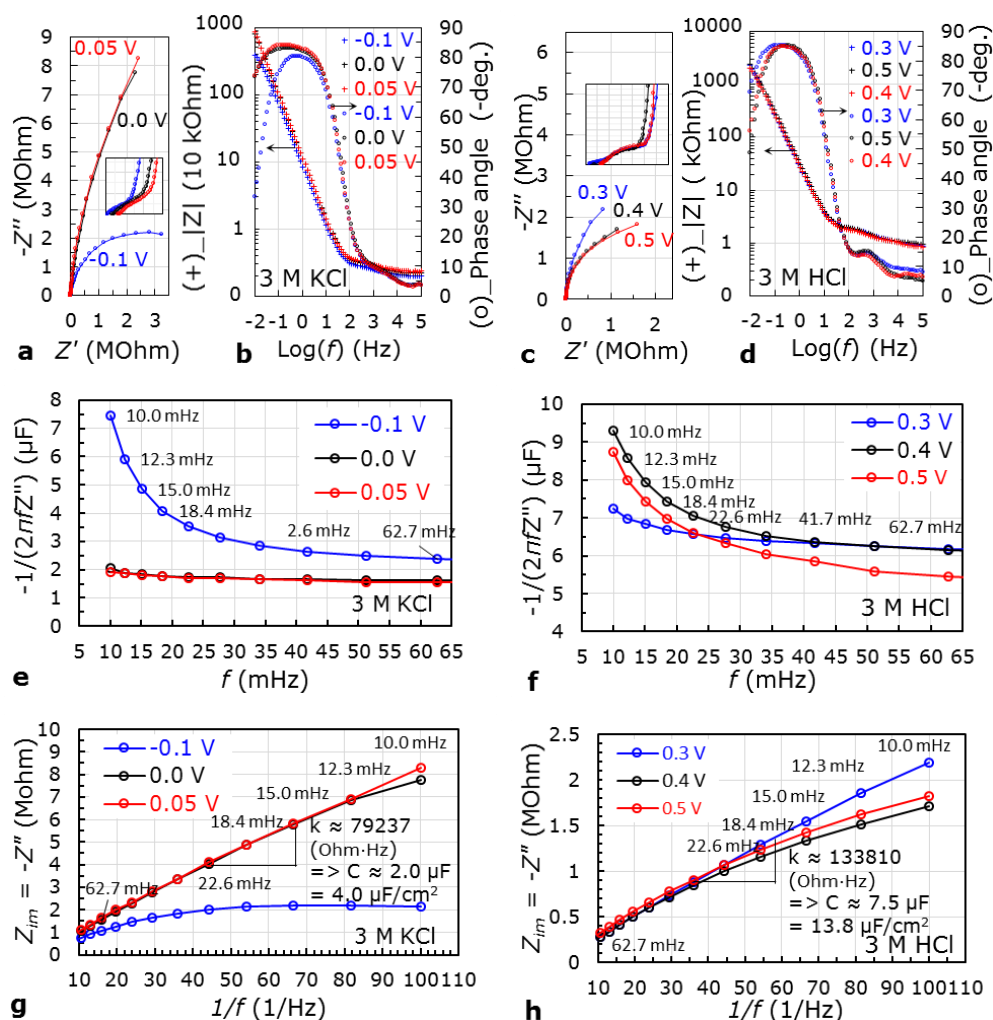


Figure 5-8. EIS of PMG in (a,b) 3.0 M KCl and (c,d) 3 M HCl, presented in format of (a,c) the Nyquist plot and (b,d) the Bode plot. Apparent capacitances of PMG calculated from the last ten imaginaries ($-Z''$) of impedance to the low frequency limits in (e) 3.0 M KCl and (f) 3 M HCl. Dependence of the impedance Z_{im} on the frequency for PMG WE in (g) 3.0 M KCl and (h) 3 M HCl.

As shown in the inset of Figure 5-8a, at high frequencies, the Nyquist plots are featured by a small fractional semicircle at all potentials. This small semicircle appears also at -0.10 V, its origin is interesting to explore if the large semicircle is attributed to H^+ reduction. More analyses and discussions will be

given on the small semicircle later based on findings from equivalent circuit simulations.

In 3 M HCl, all the Nyquist plots in Figure 5-8c presented a large fractional semicircle at low to medium frequencies and a small fractional semicircle at high frequencies as shown by the inset. The three applied potentials i.e. 0.30, 0.40 and 0.50 V, were all within the CPR as identified by the CVs in Figure 5-5b. However, it is worth mentioning that unlike in KCl, the CVs in HCl showed small but recognisable current waves for redox reactions within the CPR, which could be responsible for the observed large semicircles in Figure 5-8c. Nonetheless, in Figure 5-8f and 5-8h, the capacitive contribution is still fairly dominant at 0.30 V on the relations between Z'' and f , but becomes insignificant at 0.40 and 0.50 V. The capacitance derived from the more linear plot in Figure 5-8h is $13.8 \mu\text{F}/\text{cm}^2$ which is consistent with the CV findings. Again, if the large semicircles in Figure 5-8c are attributed to the redox reactions, the origin for the small semicircles on the Nyquist plots at high frequencies deserve further analysis which will be given later on the basis of equivalent circuit simulation.

The Bode plots in both Figure 5-8b and 5-8d reveal more interesting information. The main features are very similar to all the Bode plots recorded in both electrolytes of KCl and HCl, except for that recorded at -0.10 V in KCl. With lowering the frequency to below 100 Hz, the impedance modulus, $|Z| = \sqrt{Z'^2 + Z''^2}$ increases linearly with a slope close to -1 (on the logarithm scales). This indicates that the PMG WE was comparable with a serial RC circuit at low frequencies. The exception is that at -0.10 V in KCl, the increase of the modulus at frequencies below 100 mHz became slower, indicating a leaking serial RC circuit. The current leakage can be reasonably attributed to H^+ reduction on the PMG WE. On the other side, when increasing the frequency beyond 100 Hz, the impedance modulus decreases slowly but not in a perfect linear manner, indicating a complex combination of serial and parallel RC elements. (In ideal cases, at high frequencies, the serial RC circuit has a constant modulus equal to R , whilst the parallel RC circuit shows a linearly decreasing modulus with the slope being -1 on the logarithm scale).

The non-ideal and complex features of the modulus plots are better resolved and more pronounced on the phase angle plots at high frequencies. The small peak or wave on the phase angle plots between 100 and 10k Hz can be reasonably related to the small fractional semicircle on the Nyquist plots. With decreasing the frequency to below 100 Hz, all the phase angle plots experienced a maximum plateau that varies between -83° and -85° which again verifies the dominant capacitive contribution. (An ideal capacitor corresponds to a phase angle of -90° .) However, unlike the modulus plots, it is interesting to note that at further and lower frequencies, the phase angle decreased again, indicating current leakage through the capacitive element(s). This behaviour is obviously related to the large fractional semicircle on the Nyquist plots. In particular, at -0.10 V in KCl, the phase angle plot showed a much faster decrease after the capacitive plateau than the other phase angle plots. This unique feature can be linked to the fact that H^+ reduction is dependent on the supply of H^+ from the aqueous electrolyte to the PMG WE. The non-capacitive behaviour of the PMG WE at very low frequencies is indicative of continuous charge transfer, which would be unlikely only resulting from the OCGs. This is because (1) the OCGs were confined on the surface of the PMG WE, (2) their number was limited, and hence (3) their redox changes would be eventually complete at a given potential for a long time or low frequency, giving rise to capacitive behaviour. Another possible cause is the small amount of redox active impurities in the aqueous electrolyte, but identification of such impurities goes beyond the scope of this work.

The qualitative analyses and discussion given above suggest that the PMG WE is electrically a complex combination of both resistive and capacitive elements. More interestingly, the presence of a large and a small fractional semicircle, respectively, at medium to low and high frequencies on the Nyquist plots suggests two different processes, each of which resulting from charge transfer crossing an interface or boundary between two condensed phases. To help better resolve the impedance plots of the PMG, an equivalent circuit was developed with reference to the provisional attribution of the EIS data. In other words, the equivalent circuit includes two capacitive elements of which each is in parallel with a resistive element. Several combinations were tested using the

FRA_V1.7 software to fit the EIS data, and the best fitting results were obtained from the equivalent circuit in Figure 5-9.

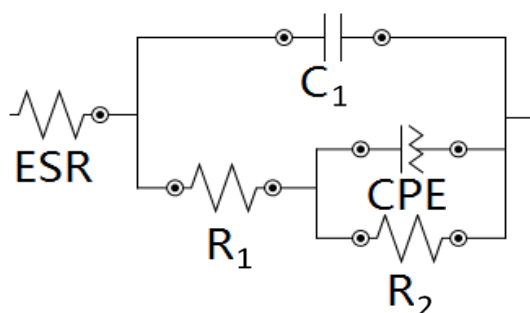


Figure 5-9. Equivalent circuit used to simulate the EIS data of the PMG WE. ESR: Equivalent series resistance. C_1 and R_1 : Capacitive and resistive elements for the high frequency semicircle. CPE and R_2 : Capacitive and resistive elements for the low to medium frequency semicircle. (cf. Figure 5-8)

In this circuit, the parallel C_1 and R_1 correspond to the small fractional semicircle at high frequencies, whilst CPE (constant phase element) and R_2 are for the large fractional semicircle at low to medium frequencies. The CPE was employed to reflect the fact that the dominant capacitive element represented by the plateau on each of the Bode plots at low to medium frequencies in Figure 5-8b and 5-8d had a phase angle between -83° and -85° , instead of -90° for an ideal capacitor. It is acknowledged that more complex equivalent circuits were used to simulate the EIS data of graphene-based materials [255], whilst the relatively simpler circuit in Figure 5-9 also needs refining in future work.

The final results from a simulation of the impedance data in Figure 5-8 are presented in Table 5-2. The validity of the equivalent circuit is firstly reflected by the very consistent and potential independent ESR values. On average, the ESR was $1.11 \pm 0.87 \text{ k}\Omega \cdot \text{cm}^2$ in KCl and $0.565 \pm 0.12 \text{ k}\Omega \cdot \text{cm}^2$ HCl, which agrees well with the greater mobility of H^+ ions than that of K^+ ions in water.

An unexpected result is the very small value of C_1 . It was only ca. $0.2 \text{ }\mu\text{F}/\text{cm}^2$ in 3M KCl, and 0.4 to $0.5 \text{ }\mu\text{F}/\text{cm}^2$ in 3 M HCl, and was almost independent of the applied potential. Such small capacitance was unlikely resulting from charging and discharging of the EDL on the PMG WE, but it could possibly be the collective reflection of the resistance to the current flow through

the grain boundaries in the PMG. This attribution also agrees with the values of R_1 being much smaller than those of R_2 because the former should be electronic in nature, but the latter reactive and/or ionic as discussed below.

Table 5-2. Results from equivalent circuit simulation of impedance data of the PMG electrode (cf. Figure 5-9).

Electrolytes	3.0 M KCl			3M HCl		
Exposed area*	0.50 (cm ²)			0.54 (cm ²)		
Potential vs. Ag/AgCl (V)	-0.1	0.0	+0.05	+0.3	+0.4	+0.5
ESR ($\Omega \cdot \text{cm}^2$)	1019	1125	1193	567	552	577
C_1 ($\mu\text{F}/\text{cm}^2$)	0.2(1)	0.2(1)	0.2(1)	0.4(0)	0.5(3)	0.5(2)
R_1 ($\Omega \cdot \text{cm}^2$)	387	475	484	473	422	480
CPE ($\mu\text{S} \cdot \text{s}^{-n}/\text{cm}^2$)	3.7(7)	2.7(9)	2.7(6)	10.5(9)	10.2(7)	8.9(8)
n	0.92	0.93	0.94	0.95	0.96	0.96
C_{CPE} ($\mu\text{F}/\text{cm}^2$)	4.6	3.9	3.6	12.8	11.8	10.0
R_2 ($\text{M}\Omega \cdot \text{cm}^2$)	2.5	23.7	22.8	5.0	2.2	2.1
χ^2	6.8×10^{-4}	3.4×10^{-4}	4.7×10^{-4}	4.2×10^{-3}	3.2×10^{-3}	2.3×10^{-3}
C_{total} ($\mu\text{F}/\text{cm}^2$)	4.8	4.1	3.8	13.2	12.3	10.5
$C_1\%$ in C_{total} (%)	4.4	5.1	5.4	3.1	4.3	4.9
$C_{\text{CPE}}\%$ in C_{total} (%)	95.6	94.9	94.6	96.9	95.7	95.1

* The exposed area in the electrolyte was measured to $0.50 \pm 0.05 \text{ cm}^2$ (cf Figure 5-1a). The effective capacitance of the CPE was calculated according to $C_{\text{EFF}} = (R_F \times Q)^{(1/n)}/R_F$ [244].

For the CPE, the n values were all very close to 1.0, suggesting the CPE to be dominantly capacitive. The variation of n was also fairly independent of the applied potential, and differed insignificantly between the neutral and acidic electrolytes. This fact indicates the CPE behaviour was intrinsic of the PMG. The values of effective capacitance of the CPE were also in good agreement with the capacitance values derived from CVs recorded in both the electrolytes of KCl and HCl, and also those derived from the low frequency Z'' data (cf. Figure 5-8g and 5-8h).

However, the value of R_2 varied significantly upon changing the potential and electrolyte. It was smaller at -0.10 V in KCl, and at all the applied potentials in HCl. It is known according to the CVs in Figure 5-5 that at these potentials, there were redox reactions on the PMG WE, namely electro-conversion

between H^+ and adsorbed H (H_{ads}) at -0.10 V in KCl, and the redox chemistry related to the OCGs on the PMG. Obviously, these electron transfer reactions helped the leakage of current through the capacitive elements (e.g. EDL) of the PMG, and reduced the value of R_2 . This understanding is supported by the fact that at both 0 and 0.05 V in KCl, R_2 was about an order of magnitude larger than at other potentials in either KCl or HCl. These two potentials are within the CPR of the PMG in KCl, thus no redox reaction could help leak the current, larger R_2 values are therefore expected.

Nevertheless, although the average value of R_2 was very large i.e. $23.25 \pm 0.45 \text{ M}\Omega \cdot \text{cm}^2$ at the two applied potentials within the CPR in KCl, it is sufficient to cause, at low frequencies, the large fractional semicircle on the Nyquist plots, and the decrease of phase angle on the Bode plot. In other words, the origin of R_2 in KCl at 0 and 0.05 V was still a charge transfer reaction. There may be two possible origins: the weaker redox activities of OCGs in the neutral electrolyte of KCl, and redox active impurities in the aqueous electrolyte, such as the trace amount of transition metal ions. It is worth noting that R_2 was an order of magnitude smaller at -0.10 V where H^+ reduction occurred in KCl in which the H^+ concentration should be at the level of 10^{-7} M which should be comparable with the activity (concentration) of impurity transition metal ions in aqueous electrolytes. For example, the Fe content in the commercial KCl used in this work was $\leq 0.0002\%$ (Sigma-Aldrich, CAS No. 7447-40-7) which is equivalent to a molar concentration of $\leq 8.0 \times 10^{-6}$ M in the 3.0 M KCl. Such low concentrations of transition metal impurities may not be detected on the CV as those in Figure 5-5, but could contribute to R_2 and be reflected in the Nyquist plot in Figure 5-8. Alternatively, in the neutral aqueous electrolyte of KCl, redox activities of the OCGs were also much lower, and hence may lead to a larger value of R_2 . Obviously, both the transition metal impurities and OCGs may contribute, and further work is needed for better clarification.

5.7 Summary

The structural and interfacial charge storage properties of commercial polycrystalline monolayer graphene (PMG) were investigated by optical microscopy, XPS and Auger electron spectroscopy, and also by CV and EIS in aqueous electrolytes with the assistance of equivalent circuit simulation.

The Raman characterisation indicated the existence of defects in this type of graphene species. The D-parameter value failed to evaluate the DED% in such a monolayer graphene with a quartz substrate. The deconvolution of C 1s peak gave an approximation ca. 95% of the DED% and the existence of low concentration (< 20%) of oxygen-containing groups.

The CV results showed that the mass-specific or area-specific capacitance of PMG is ca. 27.6 F/g or ca. 4.1 $\mu\text{F}/\text{cm}^2$ in 3.0 M KCl and ca. 63.6 F/g or ca. 9.6 $\mu\text{F}/\text{cm}^2$ in 3.0 M HCl. The EIS showed consistent results with the area-specific capacitance ca. 4.0 $\mu\text{F}/\text{cm}^2$ in 3.0 M KCl and ca. 13.8 $\mu\text{F}/\text{cm}^2$ in 3.0 M HCl.

These values of specific capacitance are just comparable with the maximum ones observed in POG species in Chapter 4 although this type of graphene species has almost 95% of the DED. EIS fitting and equivalent circuit simulation revealed that around 95% of the specific capacitance is contributed from the pseudocapacitance rather than EDLC. This is explained as the partial electron delocalisation introduced around the Fermi level of the PMG by structural defects, such as oxygen-containing groups, grain boundaries.

Chapter 6 Electronic Structure of GO with Partial ED and Its Implication on Pseudocapacitance

6.1 Background

After the long journey of experimental investigations, including the synthesis, characterisation and electrochemical investigation of GO and PMG from Chapter 3 to 5, here we come to the most significant part: theoretical study. In this chapter, as one of the biggest novelties of this study the electronic structure of graphene and its oxides will be studied to correlate the partial ED with the charge storage mechanism of pseudocapacitance. As a matter of fact, any electrochemical process has its own electronic fundamentals. To our best knowledge, this study is for the first time trying to correlate the pseudocapacitance with the electronic structure of electrode materials. Thus, an *ab initio* study assisted with DFT was used in the theoretical calculation of this chapter.

Undoubtedly, the electronic structures of graphene-based electrode materials play a significant role in its charge storage performance. Critically, the electronic property of graphene depends on the exact energy band structure and the surface situation. Hence it is desirable to investigate the possible correlation between the electronic structure, especially the ED in graphene-based electrode materials and the charge storage mechanism. However, current studies on laboratory-made GO have not yet revealed the well-defined atomic structures [256], which brings many obstacles to resolve the electronic structures. Further, oxygen in GO is known to only exist in a few forms e.g. hydroxyl, carbonyl, carboxyl, ether and epoxy [256]. Thus, GO may be modelled with one of such groups because, disregarding structural variation, they still share some common properties. Specifically, the commonality sought in this work is the segregation of the continuous ED in graphene by oxygenated groups into smaller zones where ED becomes restricted and partial.

In order to have a feasible theoretical calculation, a series of simple but new partially oxidised graphene (POG) models with gradually changed degrees of ED are established and optimised using the CASTEP programme that is based on the First-principles density functional theory (DFT) [210]. Energy

bands and density of states (DOS) are calculated on geometrically optimised POG structures. Projected DOS analyses were carried out. A discussion is given later, trying to correlate these extra bands with pseudocapacitance for electrochemical energy storage. It shall be emphasised that the modelled POGs are to demonstrate a theoretical example, instead of a full mimic of the true structure of laboratory-made GO. Although this modelling work may be very simple in the view of an experienced modelling expert, the reported findings are unprecedented and also important because pseudocapacitance as a common experimental observation has been predicted, for the first time, from theoretical models in a semi-quantitative manner.

6.2 Methodology and modelling

6.2.1 Methodology

First of all, all ab initio studies have to establish on a well-defined structure or model in regarding to as-concerned system to an atomic or molecular level. Then, the most fundamental principles and theories, such as molecular dynamics and quantum mechanics, were taken into account to formulate relevant force and energy field in the as-studied system. Some arbitrary but rational assumptions may be introduced to achieve actual feasibility and simplification for calculation. One of the examples is the famous Born-Oppenheimer approximation [257]. It assumes that the motion of atomic nuclei is negligible in contrast with that of electrons in a molecule or solid state materials. That means the wave function of electrons can be separated from that of nuclei, hence facilitating theoretical calculation. The other similar assumptions include the 'effective core potential' [209], periodic boundary condition [258], plane wave basis set [208] and the functional assumption between the basic physiochemical properties of materials and their charge density at ground state in First-principles density functional theory (DFT) [205,206].

Therefore, before calculation, a well-defined crystal structure of GO has to be established first not only can represent the partially oxidised or reduced GO with gradient DED, but also the gradient DED can be conveniently controlled and adjusted. Thus, considering the practical complexity, in our GO

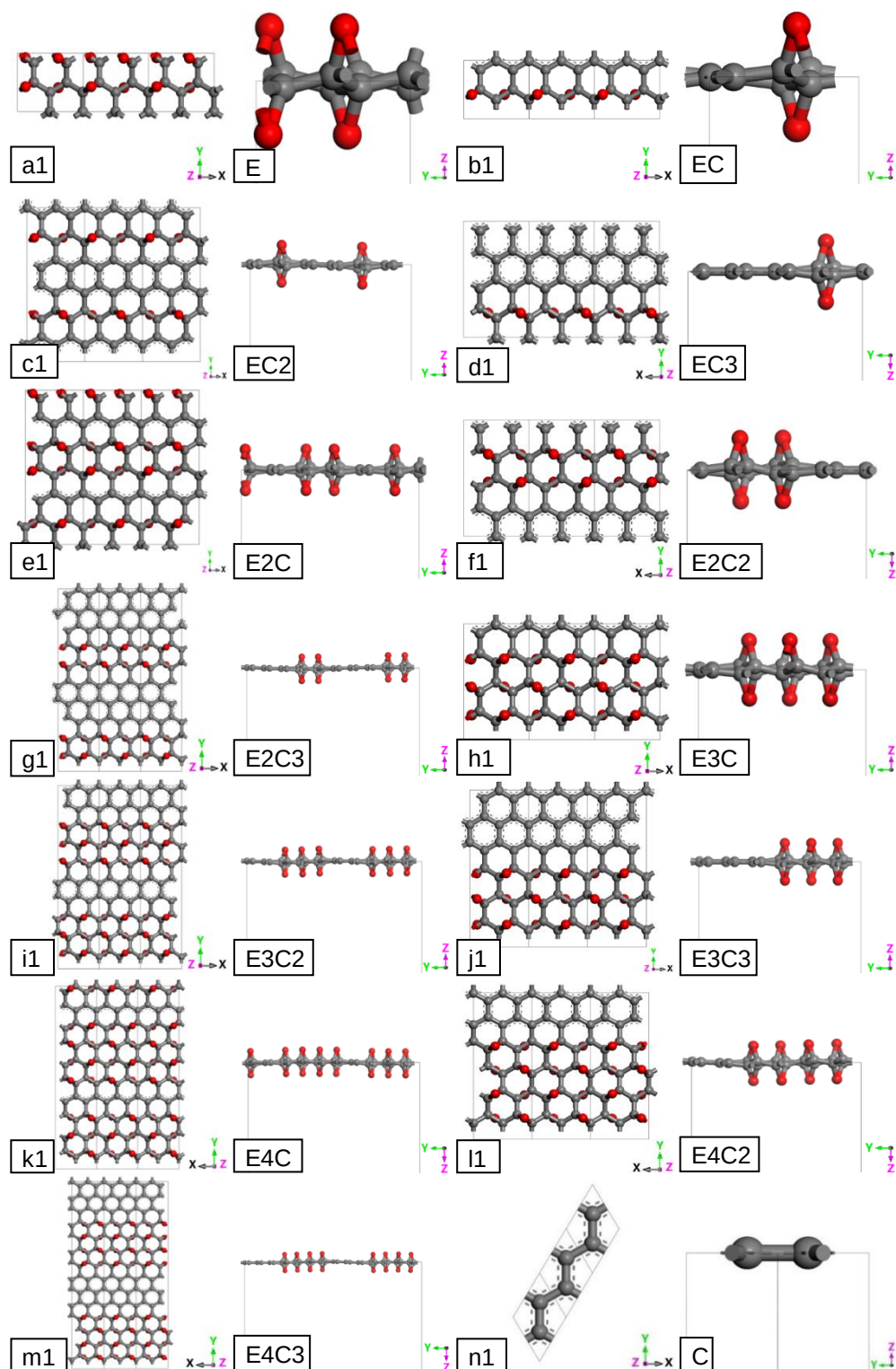


Figure 6-1. Fully optimised geometry structures of fully GO (a1), partially redox GO (b1 to m1), pure graphene (n1), and corresponding side views of each unit cell labelled in abbreviated forms. Detailed structural parameters were collected in Appendix I, Table A.4.

models, epoxy groups are considered as the only functionality to segment the ED region on the basal plane. By simply tuning their coverage on the basal plane of GO, both the degrees of oxidation/reduction and DED can be easily modified and controlled. Only the Type-II fully oxidised graphene (FOG) structure is considered since it has been theoretically proven to be the most stable configuration among all other.[178] Electron delocalisation areas (EDAs) are defined as the columns of π -conjugated double-bond around the carbon chains extending along the [010] direction in the unit cell of GO. These EDAs are separated by a certain width of the epoxy group covered areas. Details of established models are collected in Figure 6-1 (a1 to n1). Then the DFT calculations were performed on these GO models for geometric optimisation followed by electronic structure calculation based on optimised unit cell lattices.

Analysis on the electronic structure such as the energy band, the density of states (DOS) and projected DOS were carried out. Variations of the electronic structure, particularly the integral of DOS around the Fermi level, were sorted out to correlate with the change trend of the DED as well as the charge storage performance in these partially oxidised species. Details on the computational methodologies, parameter settings and criteria of calculation accuracy will be described further in the subsequent sections.

6.2.2 Modelling

The atomic structure of GO (GO) has been studied for over 80 years, since Hoffmann et al., proposed a structure in which the O atoms in graphite oxides are bound to the C atoms in the basal plane [259,260]. From these early work, hydroxyl groups are also present in graphite oxide.[260,261] Solid state ^{13}C NMR studies provided evidence for C–OH, C–O–C, and $>\text{C}=\text{C}<$ groups in graphite oxide [262] and [256]. In summary, The GO consist of a one-atom thick layer of graphene randomly decorated with oxygen-containing functional groups, such as carbonyl($>\text{C}=\text{O}$), hydroxyl ($>\text{C}-\text{OH}$ or $>\text{C}-\text{OH}$), epoxy ($>\text{C}-\text{O}-\text{C}<$ or $>\text{C}-\text{O}-\text{C}<$) and ether groups($>\text{C}-\text{O}-\text{R}'$ or $>\text{C}-\text{O}-\text{R}'$) [263]. Here, ' $>\text{C}-$ ' symbol, differed from ' $>\text{C}-$ ', is used to represent those in-plane carbon atoms of GO with sp^3 hybridisation by bonding with another heteroatom, and ' $>\text{C}-$ ' the edge carbon atoms. It is evident that carbonyl and ether groups normally arise on the edge of the GO layer as well as that of pore defects. Based on other publications

[212,230,264-266], the epoxy group (>C-O-C<) is identified as the most dominant species compared with the other three functionalities like bonding hydrogen (>C-H), hydroxyl (>C-OH) and peroxide (>C-O-O-C<) [264], which mainly resided on the basal plane of graphite and graphene rather than on edge. Moreover, atomic force microscopy (AFM) revealed that the GO sheets appear to have a thickness equal to integer multiples of ca. 6.7 Å [265], indicating that epoxy groups are likely to exist on both sides of the graphene layer [267]. Thus, in our GO models, only epoxy groups were considered to establish the target GO models without losing the representation, meanwhile achieving rational simplification. A periodic structure with parallel strips of epoxide and clean graphene ribbons was adopted in our modelling, and which has been proved to be more energetically favourable, namely a comparable stability [268]. The basal layer of all graphene and its oxides were placed in the x-y (a-b) plane and modelled in a hexagonal or rectangular supercell for the limitation of periodic boundary conditions in CASTEP calculation. The z (c) -axis constant was set to 20 Å between each layer in a unit cell to eliminate interactions between neighbouring GO sheets and thus to simulate a single layer of GO. Detailed geometry configurations and lattice parameters were exhibited in Figure 6-1 from a1 to n1 and Table A.4, in Appendix I. Furthermore, the carbon to oxygen ratio (C:O) can also be easily extracted from the unit cell structure and shown in the second column of Table A.4. More importantly, this simplified model enables to learn the DED directly by just comparing the area difference between the strips of epoxide and graphitic regions, namely sp^3 and sp^2 region. Thus the sp^2 to sp^3 ratio can be clearly defined in these models.

A specific ruler established in Figure 6-2 was used to scale the corresponding C:O and DED of all the above fourteen models from fully oxidised derivatives to pure graphene with expectation to represent the POGs synthesised and electrochemically modified in previous chapters.

It can be seen from these two rulers that all synthesised and electrochemically reduced GO distributed in the purple rectangular region, for C:O in between 2.5 and 6.25; DED from 12.5% to 60.5%. Detailed data were collected in Table A.4, Appendix I. GO models established for theoretical calculation covered almost the whole range of C:O and DED even beyond the

super-concerned purple region. That is to say, these models are highly representative in this study. The DED and C:O of the raw material of graphite flakes were also extracted from different ways and denoted on the ruler for reference. These values already close the upper limit of the DED of full sp^2 hybridisation.

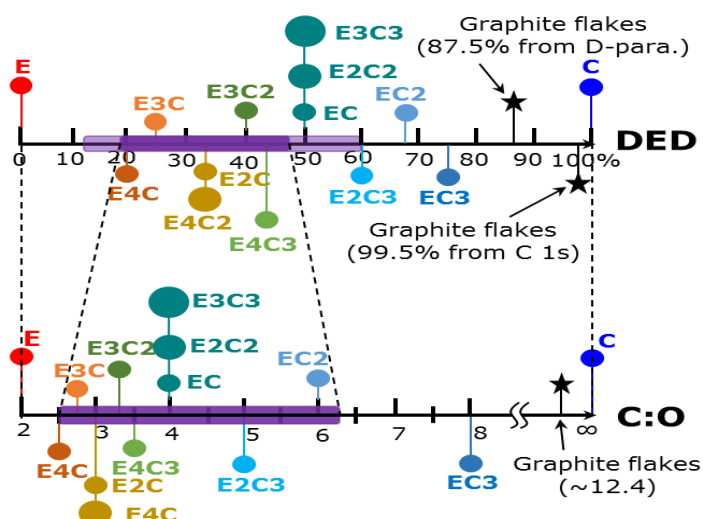


Figure 6-2. C:O and DED rulers used to scale the GO models in coloured bubbles to represent the as-synthesised and electrochemically reduced GO samples in purple highlighted region. Here, the letter E and C in formula E_iC_j denote epoxy covered sp^3 hybridised region and graphitic sp^2 hybridised region respectively. Two subscript numbers (i and j) denote the exact number of carbon chains in these two regions in a unit cell of corresponding models. The dark and light purple rectangular covered the range on the DED rulers represent the DED estimated from the D-parameter and the C 1s deconvolution of XPS respectively according to data cited from Section 4.4, Chapter 4.

6.2.3 Computational method

The First-principles DFT calculations were performed using the academic CASTEP package version 7.0.3 and using Materials Studio 5.0 (Accelrys) as the interface and visualizer. The CASTEP is a quantum mechanics-based program, which employs the DFT and plane-wave pseudopotential method [210]. The electronic exchange and correlation effects were described within the generalized gradient approximation (GGA) using the Perdew Burke Ernherzhof (PBE) functional [211], which has been widely used in theoretical predictions of the electronic structure for graphene and its

derivatives [177,212-214]. All calculations were carried out on the models shown in Figure 6-1 under the same ultra-fine energy cut-off (380 eV) for the plane wave basis set. This cut-off energy was determined by a forehand convergence testing. A desktop computer with a single Intel Core i3-4130 CPU @ 3.40GHz, 8.0 GB RAM memory and 1 T hard disk drive was used for all calculations. The Brillouin zone sampling was performed with three to four special Monkhorst–Pack k-points [269] as shown in Figure 6-3. Three k-points of Γ -K-M were assigned to pure graphene, and four k-points of Γ -K-M-B for GO depending on the shape of the reciprocal lattice and Brillouin zone. The k-points sampling followed a principle of computer resource saving without sacrificing the calculation accuracy. That is by using the minimum numbers of sampling in the Brillouin zone to achieve a proper Brillouin zone integration without losing too much accuracy with the energy band calculation. In fact, pre-calculation had been carried out by gradually increasing the number of k-points for all as-defined GO species. The results indicated that no apparent variations can be observed under a finer sampling, namely more k-points, especially for the fully oxidised graphene (FOG) because of its relatively wide energy gap. But this is not the case for POG species, theoretically, higher sampling density in the Brillouin zone means a higher resolution for the energy states and DOS, which is very critical for inspecting species with narrow energy gap and/or fine extra energy states fairly close to the Fermi level. Of course, denser sampling in the Brillouin zone again means higher demanding of the computing resource. Thus, based on our pre-calculation results, the k-points sampling was determined and shown in the last column of Table. A.4 in Appendix I. Only spin-paired setting was performed in all calculations since tests demonstrated negligible effects of spin-polarization. The geometry optimisations were carried out with Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm [270] and its quality was set to perform the calculation until the energy tolerance was below 2.0×10^{-5} eV/atom, atomic forces were below 0.05 eV/Å, maximum stress tolerance was below 0.1 GPa, and maximum displacement tolerance was below 0.002 Å. The self-consistent field (SCF) tolerance and k-point set of electronic structure calculations, including energy band and density of states, were set to a convergence threshold of 5×10^{-7} eV/atom (Ultra-Fine). The electronic structures of the above models were calculated in the first Brillouin zone (the grey zone

encircled by a dashed line) of each crystal structure following the path as shown in Figure 6-3 (a-c). A smearing integration method with a smearing width of 0.2 eV was used to obtain DOS diagram because this value is approximately equal to the thermodynamic fluctuation at room temperature.

In order to investigate the influence of different sizes and separations of EDAs, chains of epoxy groups were removed from GO leaving various degrees of the π -conjugated zone. These zones varied in width from one zigzag carbon chain to three, and the distance between each zone was controlled by the coverage of epoxy groups ranging from one to four columns. These structures can not only represent partially reduced or oxidised GO but also have distinguishable DED. The electronic structures of the above optimised models were calculated in the first Brillouin zone as shown in Figure 6-3 (a-c).

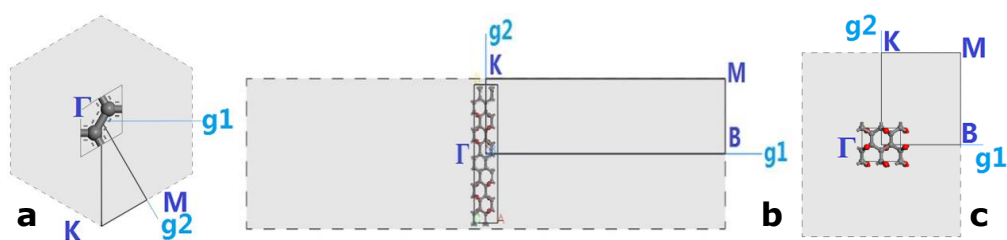


Figure 6-3. Brillouin zones of (a) pure graphene unit cell, (b) partially oxidised and (c) fully oxidised graphenes.

6.3 Energy band structure and DOS of GO with partial ED

Structural optimisation was first studied from fully oxidised graphene (FOG), via the above defined POGs, to PG with a gradually increased DED, aiming to select the optimal structures (cf. Figure 6-1 a1 to n1). PG has a 6/mmm unit cell for its characteristic hexagon symmetry, encapsulates only two carbon atoms in its unit cell with the a and b lattice constants being equal to 2.466 Å, and the C-C bond length reaching 1.4235 Å. These are consistent with both the experimental and theoretical studies [150]. Other unit cells of GO are degenerated to the primitive tetragonal lattice (P1) since the occupation of epoxy groups reduced the symmetry of these derivatives. Areas of carbon atoms bonded with epoxy groups show a periodically wrinkled structure along

the zigzag chain attributing to the transformation of hybridised orbitals from sp^2 to sp^3 . More details are collected in Table A.4, Appendix I.

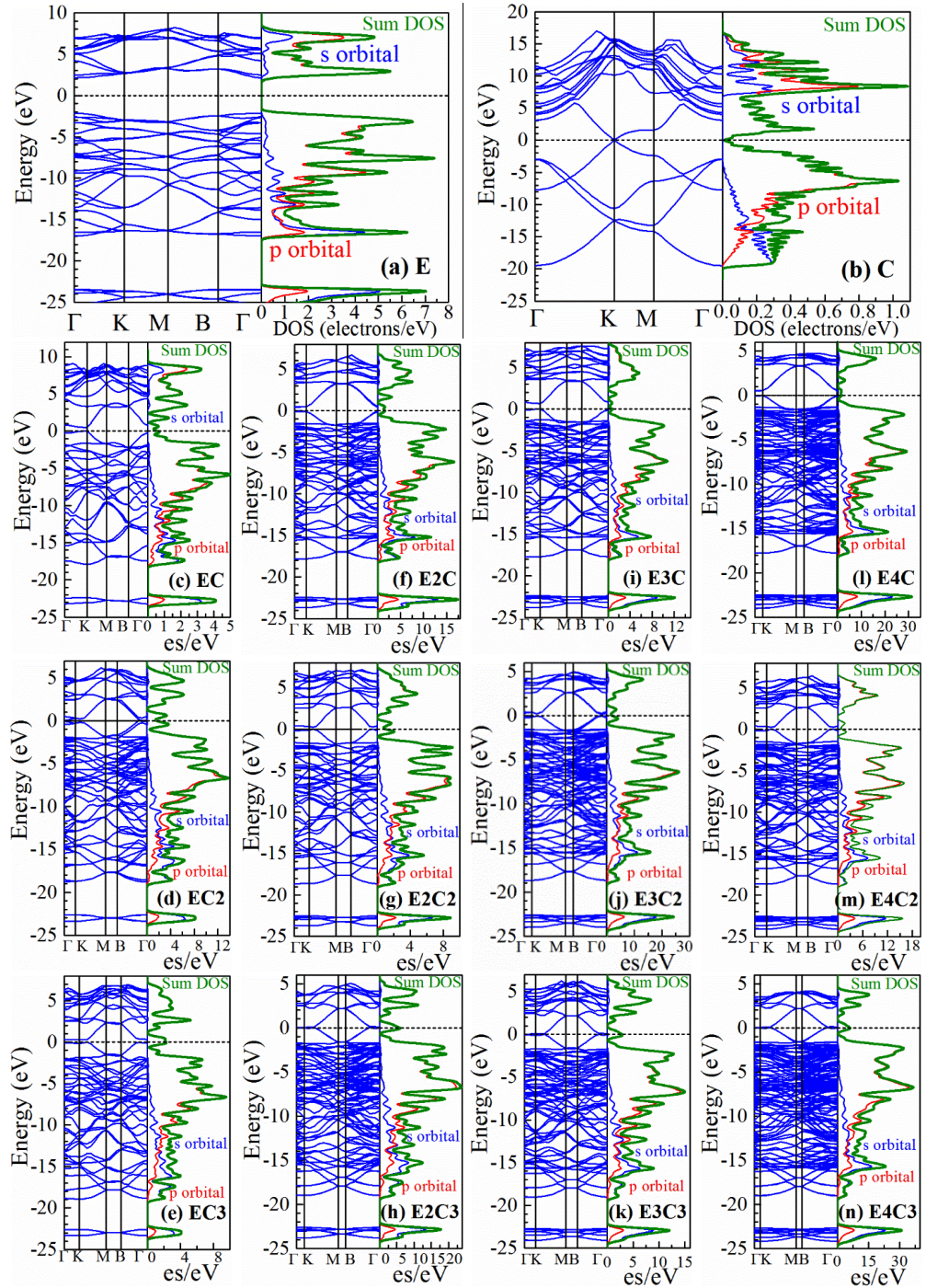


Figure 6-4. All calculation results of the energy band structures and density of states: (a) fully oxidised graphene, (b) pure graphene and (c-n) partially oxidised graphene

As shown by the results in Figure 6-4 (c-n), all the partially reduced or oxidised GO models have a very similar electronic band structure, especially around the Fermi level (E_F). In fact, the two closest energy levels, above and below the E_F , are derived from p_z orbital of carbon atoms and the $2p$ orbitals of oxygen atoms. Differing from the Dirac distribution at the K point of PG, a part of flat energy bands close the E_F , along Γ to K in POGs, extends wider in E-k space as EDAs increase. Significantly, these flat bands resulting in a higher electronic density of states (DOS) can enhance the electron confinement effect and the quantum capacitance which is directly correlated to the DOS [252,271], therefore can benefit the storage of electrons/holes within these delocalised states in some range of energy level, in other words, improving the ability of charge storage within these delocalised regions. In the first sequence of POG models (Figure 6-4 c, d and e), only one column of epoxy group separates two neighbouring EDAs which varied from one to three columns of zigzag carbon double-bonds. It was found that the energy gap (E_g) changed non-linearly from 0.496 eV, sharply decreased to 0.041 eV, and then increased to 0.289 eV. Since the thermal equilibrium fluctuation at 298 K is on the order of 0.1 eV, the second model in this sequence is almost a conductor for this thermal fluctuation owing to its narrow E_g . The second sequence of POGs, in Figure 6-4 f, g and h, had two columns of epoxy groups separating the neighbouring zones of ED which again increased from one to three zigzag chains of carbon double-bonds. E_g narrows down from 0.429 eV (semi-conductivity) to 0.182 eV, and then vanishes to 0.0 eV (full conductivity). In the following third (Figure 6-4 i, j and k) and fourth (Figure 6-4 l, m and n) sequences of POGs, E_g decreases in a similar trend from 0.666 eV to 0.145 eV, then to 0.027 eV and from 0.513 eV to 0.227 eV, then to 0.011 eV respectively. Again, the last structures in these two sequences were almost conductors. The origin of these narrow E_g s have been ascribed to both the breakdown of sub-lattice symmetry in graphene by the epoxy groups and the change in carbon hybridization from sp^2 to sp^3 due to strong covalent bonding between C and O [267]. In addition, it was proposed that the EDAs also play a role in the determination of these discretely narrow E_g s by interference with the epoxy group bonding areas. In terms of the DOS, all models, except FOG and PG, show very similar distributions. Peaks between -20 and -25 eV correspond mainly to the 2s orbital of O from the epoxy groups. Comparing

absolute DOS intensities between unit cells is of limited because the actual intensity of DOS is proportionated to the numbers of atoms within the unit cell. However, the intensity of DOS around the Fermi level, which can be considered as extra states originating from the p -orbitals of the carbon atoms, increases with increasing EDA (see through the same column of Figure 6-4 e.g. c to e or f to h), but decreases slightly with the extension of the epoxy group coverage (see through the same row of Figure 6-4 e.g. c to l or d to m).

Representative species are exhibited into Figure 6-5 extracted from Figure 6-4, including two extreme cases of FOG in a with a wide energy gap (E_g) of ca. 4.286 eV and PG in b with a gap of 0 eV. In between, electronic structures of POGs show similar but very interesting fine structures especially near each of the respective Fermi levels, highlighted in red oval rings.

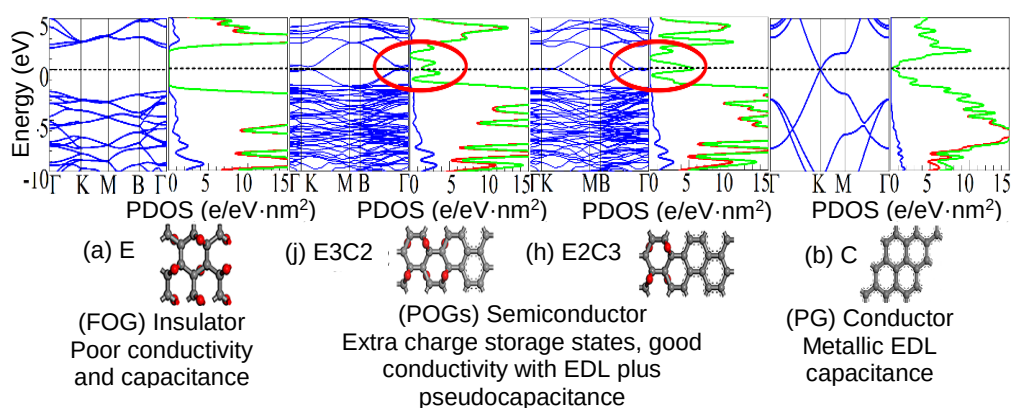


Figure 6-5. Representative energy band structures and DOS as well as the corresponding species: (a) fully oxidised graphene (FOG), (b) pure graphene (PG) and partially oxidised graphenes (POGs), corresponding to Figure 6-3 (j and h). In the middle, the dashed horizontal line denotes the Fermi level. In the DOS diagrams, the blue line denotes the s -orbital, red line the p -orbital and green line the sum.

The fine structures of the DOS of selected POG species are magnified in Figure 6-6. Table 6-1 lists the calculated values of the energy gaps, the maximum population densities of states, or DOS maximum, around the Fermi level and predicted properties of the FOG, POG and PG models.

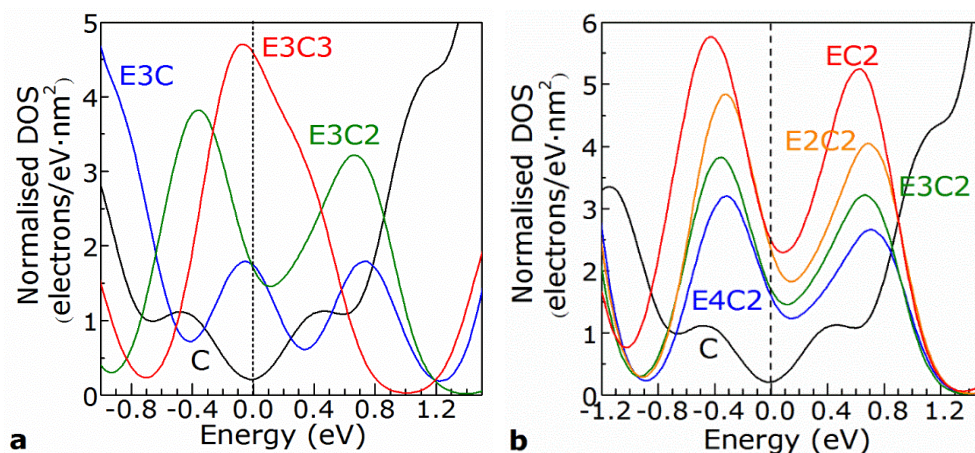


Figure 6-6. Representative DOS of POG species selected from Figure 6-3 and magnified regions (with 90° anticlockwise rotation) around the Fermi level. The Fermi level corresponds to the black dashed vertical line at 0.0 eV. The solid black C curves in both figures show the DOS of PG around the Fermi level. (a) The columns of the epoxy covered area were fixed to 3, the degree of ED goes up from E3C to E3C3; (b) the columns of π -conjugated double-bond carbon chains were fixed to 2. A smearing integration method in CASTEP with a width of 0.2 eV was used to obtain these DOS diagrams.

Table 6-1. Calculated values of E_g , comparison of DOS around the Fermi level for FOG, POG and PG models.

Class	Abb. form	UC area ($\text{\AA}^2$)	E_g (eV)	Width (eV) ^a	DOS Max. ^b	Predicted property ^c
FOG	E	21.05	4.286	N/A	0.0	I
POG	EC	21.05	0.496	1.6	3.3	S
	EC2	63.15	0.041	2.4	3.2	S-M
	EC3	42.10	0.289	1.9	5.4	S
	E2C	63.15	0.429	1.5	2.5	S
	E2C2	42.10	0.182	2.3	4.8	S
	E2C3	105.26	0.000	1.7	5.6	S-M
	E3C	42.10	0.666	1.6	1.8	S
	E3C2	105.26	0.145	2.3	3.8	S
	E3C3	63.15	0.027	1.7	4.7	S-M
	E4C	105.26	0.513	1.6	1.5	S
	E4C2	63.15	0.227	2.3	3.2	S
	E4C3	147.41	0.011	1.7	4.1	S-M
PG	C	5.28	0.000	1.2	1.1	M

a. These values of energy width were obtained from Figure 6-6, corresponding to the range between the first valleys after the peak towards negative and positive energy respectively.

b. Sample from as-concerned energy level range within the width around the Fermi level. The DOS maximum is normalised by the area projected in the direction of c-axis of each unit cell, see the third column, therefore in a unit of electrons/eV·nm².

c. I: Insulator; S: Semiconductor; S-M: Semi-Metal; M: Metal.

On one hand, the fully delocalised electrons endow PG with behaviour like that of the ordinary metal electrode offering typical electrical double layer capacitance (EDLC). However, the ideal specific area of PG is $2630 \text{ m}^2/\text{g}$, corresponding to the mass specific EDL capacitance of 526 F/g [132]. This means that the maximum charge density accumulated on the graphene sheet would be no more than $20 \text{ } \mu\text{C}/\text{cm}^2$ in a 1 V cell. On the other hand, as can be seen in the Figure 6-5 b, the DOS of PG decreases very quickly to almost zero when approaching the Fermi level (or the Dirac cone) [271]. Such a low DOS around the common stability range of aqueous electrolyte further reduces the interfacial capacitance of PG because of the vanished quantum capacitance [224,272,273]. For FOG, a wide forbidden gap blocks all current flowing through the fully localised framework. Therefore, only negligible capacitance due to polarisation as in a conventional dielectric material could be observed in FOGs.

Completely different landscapes showed up in the case of POGs. Two approaches were adopted in this study to examine the impact of various ED areas (EDAs) on the electronic structure. The first is to gradually increase the size of the π -conjugated column, denoted in Table 6-1 by C with a fixed number of epoxy groups denoted by E. The second is to maintain the size of the π -conjugated column with gradually increased areas of epoxy groups. Intriguingly, a bunch of extra energy states can be observed near the Fermi level in energy bands and DOS diagram of all POGs within the range of $\pm 3 \text{ eV}$. These extra states gain density and become more compact, as the EDA increases in the order of E3C, E3C2 and E3C3. However, when the EDA is fixed, the DOS maximum of each of these extra states decreases with the extension of the coverage of epoxy groups in the order of EC2, E2C2, E3C2 to E4C2. Representative DOS normalised by the c-direction area of the corresponding unit cell are shown in Figure 6-6. PG only has a very low value of DOS, especially around the Fermi level. However quite a large improvement in the DOS around this energy region showed in all POGs. Based on the normalised DOS curves, in some energy range, the charge capacity of these states can achieve 5 to 6 electrons/ $\text{eV} \cdot \text{nm}^2$, corresponding to 5 to 6 folds of that of PG (ca. $1.1 \text{ electrons}/\text{eV} \cdot \text{nm}^2$). Thus the charge density can achieve 80 ca. $96 \text{ } \mu\text{C}/\text{cm}^2$, corresponding to a true area specific differential capacitance about 80 to 96

$\mu\text{F}/\text{cm}^2$ in 1 V cell that is beyond four times higher than the common EDLC. Considering the extremely light of a single layer of graphene fragment, the specific capacitance can be further larger than the common values of EDLC.

Conclusive experimental revelation of the energy band structure and DOS in GO or POG is hampered by their complicated atomic configurations, but a few experimental results had offered some hope. A capacitive photocurrent spectroscopy technique was utilised to determine the electronic DOS for GO and partially reduced GO [27,28,230]. DOS diagrams were extracted from the capacitive photocurrent spectra, and showed a series of extra states. Three discrete transition states at about 0.7, 1.6 and 3.2 eV found in Refs. [224,273] were also observable in our DOS results of POGs, which are approximately aligned with those extra energy levels around the Fermi level in our study. Further, more additional states arise close to the Fermi level and become closer in energy space as the GO is reduced to a greater extent, again supporting our theoretical predictions.

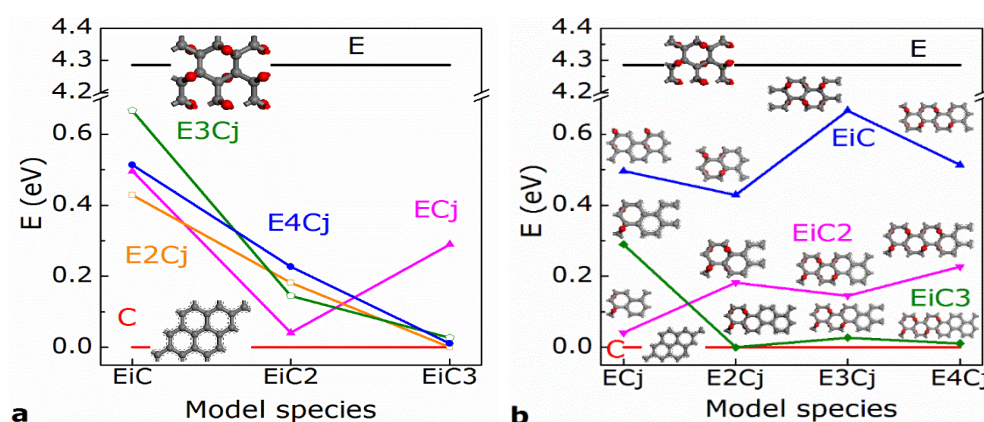


Figure 6-7. Effects of EDA and EPA on the energy band gap, E_g , of different POGs: (a) width of EDA, (b) size of EPA. Red and black horizontal lines represent PG with a band gap of 0 eV and FOG with a band gap of 4.286 eV, respectively.

Figure 6-7 further shows the variation of E_g as a function of the sizes of EDA and epoxy group columns. As the epoxy group column is fixed in Figure 6-7 a, E_g decreases with the expansion of the EDA. The exception is EC3 with an E_g value of 0.289 eV which is wider than those of the other three models. From Figure 6-7 b, it is hard to summarise a clear E_g trend of the effect from increasing

the epoxy group areas (EPAs) as the EDA is fixed, for the fluctuating data. Here, one may consider that increasing the EPA represents different distances between neighbouring EDAs. Hence the variation of EDA may play a greater influence on the electronic structure and E_g than that from the EPAs.

6.4 Projected DOS (PDOS) analyses

It is worth highlighting that different from other published studies, view in this study is the influence arising mainly from the variation of EDAs rather than the defects or functional groups. This is because these extra energy states originate from delocalised electrons in regions of limited sizes, rather than from localised electrons in the epoxy groups and those sp^3 carbons which bonded with. All these can be verified through a projected DOS (PDOS) analysis. Therefore, the PDOS analysis carrying out on two representative POGs shows apparent extra energy states near the Fermi level e.g. the species of E2C3 and E3C2.

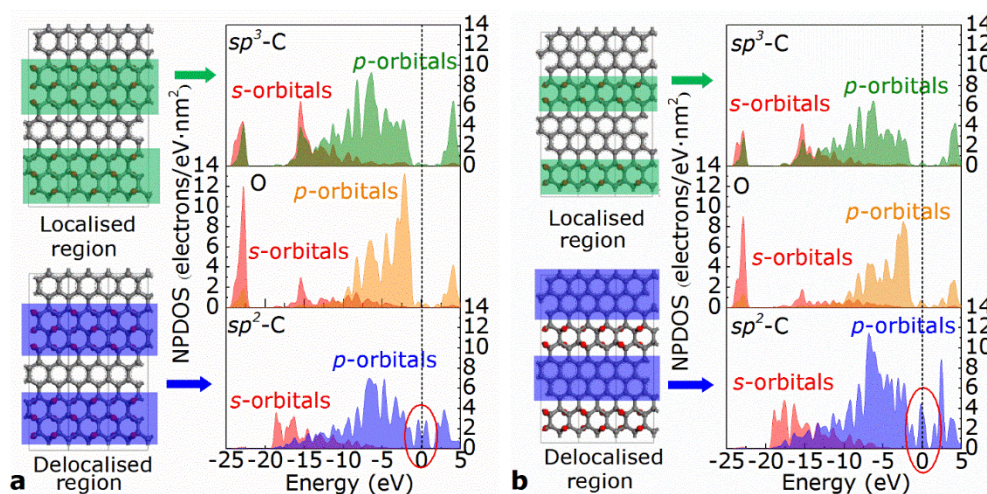


Figure 6-8. Normalised PDOS (NPDOS) analyses of two representative POGs: (a) E3C2 and (b) E2C3. The carbon atoms enclosed in the blue and green rectangles contain delocalised and localised electrons, respectively.

Carbon atoms in GO can be roughly classified into two groups. The one in which carbons completely bonding its four sp^3 orbitals with the neighbouring carbon atoms or oxygen atoms; the other one in which carbons maintained the π -conjugated double bonds. As shown in Figure 6-8 on left hand side, carbon

atoms within the sp^2 region (in blue rectangular), namely the ED region, contribute a major portion to the PDOS population densities of as-observed extra energy states near the Fermi level, especially from the p -orbital of those double bond carbon atoms. For fully-localised carbon and oxygen atoms, covering in green rectangular, they only contribute negligible parts in the PDOS. Thus, it is rational to assign those extra bands on the carbon atoms within the π -conjugated region rather than those carbon atoms sp^3 -bonded with oxygen atoms. Additionally, only this double bonded region is responsible for the transport of electrons/holes in graphene. Therefore, there is a reason to believe that these discrete extra energy states may play a big role in benefiting the charge storage in a manner of pseudocapacitance as long as they hold a proper distribution within the operating potential range of electrode materials.

6.5 Charge storage enhanced by partial ED states

As can be seen that the unit of the normalised DOS is in electrons/eV·nm². Hence an integration doing over the energy (eV) in a definite range results to a 'specific charge density' in a unit of electrons/nm². Considering electrons only, the so-called 'specific charge density' denotes the amount of electrons which can be stored in the energy states within the as-concerned energy region. Thus, a theoretical estimation of the charge capacity can be achieved by doing this integration over the normalised DOS against the energy around a certain range.

Considering the stable potential range of aqueous electrolytes, those energy states beyond ± 2 eV in the energy space are actually meaningless and useless in practical charging/discharging in aqueous electrolytes. Hence, the integration interval was set to [-1.0, +1.0] eV centred by the Fermi level. Thus the '*specific charge density*' is the underneath area of the normalised DOS curve between -1.0 and +1.0 eV. With this method, the charge storage capacity of all above 14 GO models and their corresponding DED can be correlated with the aid of rulers introduced in Figure 6-2, Section 6.2.2. The integration area for each GO models became one data point and was plotted versus the corresponding DED ($sp^2\%$) in Figure 6-9. Meanwhile, the DED distribution of 24 GO samples investigated in Chapter 4 was also represented in the regions covered by light and dark purple rectangular from ca. 12.5 to 60.5%. The light

and dark purple rectangular covered ranges represent the DED value estimated from the D-parameter and C 1s deconvolution of XPS respectively. A cubic polynomial trend line was used to fit the general tendency. It was intriguingly found that the 'specific charge density' is not monotonously increasing as the DED was improved whereas peaks at around 60 to 80% of the DED, and turns down thereafter to a relatively lower value till in the pure graphene. The possible locations of the interfacial charge storage for the raw material of graphite flakes based on different approximations of the DED were also black-star marked on the trend line. It indicated that even for graphite flakes with a high DED, the charge storage performance does not show the highest value.

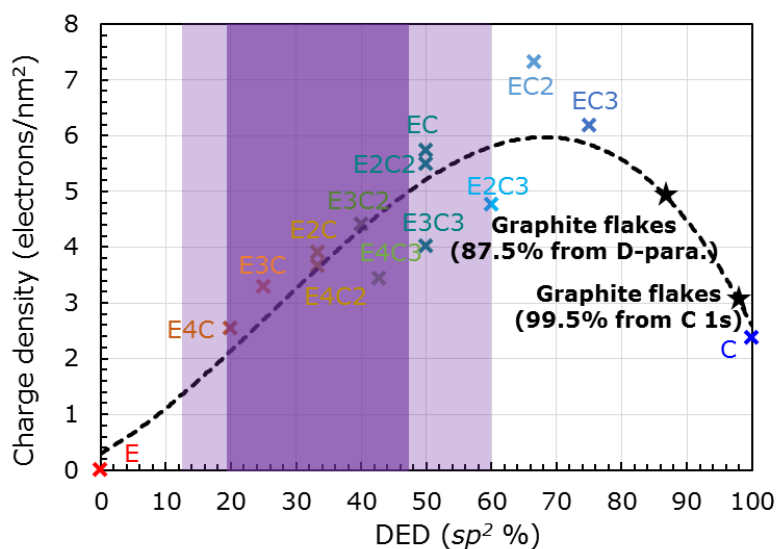


Figure 6-9. Correlation between the specific charge density integrated from the normalised DOS in between -1.0 and +1.0 eV of each GO models and the DED ($sp^2\%$). A Cubic of polynomial dash line was used to fit the overall tendency. The light and dark purple rectangular covered the range on the DED rulers that represents the DED estimated from the D-parameter and the C 1s deconvolution of XPS respectively according to data cited from Section 4.4, Chapter 4.

If the measured capacitance data obtained in Chapter 4 to 5 were collected and plotted versus the corresponding DED ($sp^2\%$) of each sample a very good consistency between experimental facts and theoretical prediction can be found. Figure 6-10 collected representative capacitive charge storage data from the untreated GO, POG samples and the PMG investigated in

Chapter 4 and 5. Both C 1s deconvolution and D-parameters methods were used to estimate the DED of these samples and highlighted in dark and light purple rectangular respectively. In spite of the difficulty of extracting the DED of PMG through the D-parameter method, the DED of PMG ca. 95% can still be estimated from the deconvolution of the high resolution C 1s as shown in Section 4.4, Chapter 4 considering the detectable OCGs in samples. Charge storage performance of all samples characterised by the specific capacitance (C_m) and the effective specific capacitance (SC_{Pi}) are extracted from the CVs and the EIS simulation respectively. For the POGs sample, the effective specific capacitance (SC_{Pi}) is the summation of the two charge transfer related contributions (SC_{P1} and SC_{P2}) based on the EIS simulation, referring to Section 4.6 in Chapter 4. For the PMG samples, the effective specific capacitance (SC_{Pi}) denotes the only faradaic capacitance term of CPE_F , seeing in Figure 5-7, Chapter 5.

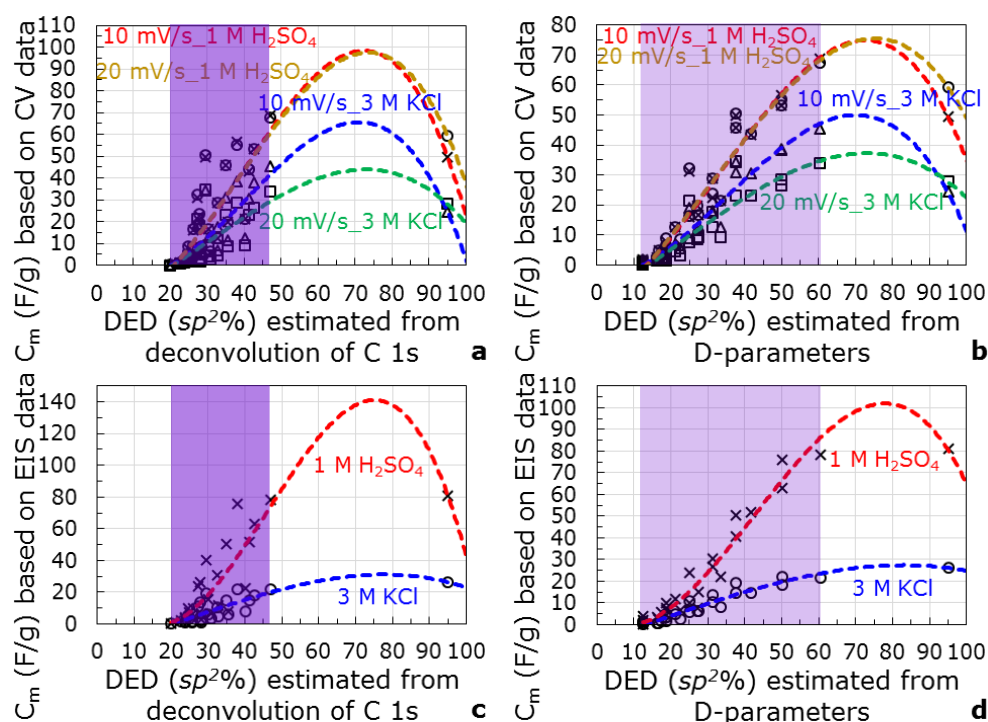


Figure 6-10. Representative capacitance performance extracted from the CV and EIS fitting data in Chapter 4 and 5 versus the corresponding DED ($sp^2\%$) estimated from the C 1s deconvolution and D-parameter of XPS respectively. Cubic polynomial trend lines were used in all figures to fit the overall tendency, and they were extrapolated to the 100% of DED. Note: the capacitance data points of monolayer graphene (to the left side with DED = 95%) were obtained in 3.0 M HCl rather than 1.0 M H_2SO_4 , cf. Section 4.5 and 4.6 in Chapter 4.

Considering the data vibration and deviation, cubic polynomial trend lines are used to fit the general tendency again. Although, exceptional deviations can still be seen, the cubic polynomial is still satisfactory on reflecting the correlation between the charge storage performance and the DED of samples particularly in the as-concerned DED region. It can be seen that there is a very good agreement between these experimental results and the theoretical prediction shown in Figure 6-9. Both two aspects of result indicated a maximum value of capacitance appears at ca. 65 to 75% of DED of POGs. This phenomenon was simultaneously proved through both theoretical and experimental routes.

In reality, partially reduced or oxidised GO were found to possess not only good EDL capacitance but also appreciable pseudocapacitance, thus have been proposed as a class of electrode materials with a great potential for supercapacitor applications [27,28,230]. Since the actual oxidation and reduction processes are highly non-uniform, a large number of partially reduced or oxidised GO species, or more precisely, GO fragments with a wide distribution of oxidation degree, are formed in the same batch of products under the identical or comparable experimental conditions [7,50,60]. Apparently, these species have different degrees of ED [230]. According to theoretical study in this chapter, discrete energy states near E_F with a narrow E_g of the order of a few hundred meV (0.0 to 0.666 eV) emerge in the electronic band structure of POGs with different degrees of ED. More significantly, as shown in Figure 6-6, these extra electronic states just reside in the region of the stable range of aqueous electrolyte and the scanning potential range of carbon-based supercapacitors. The distribution of width varies with different degrees of ED. For using POGs as electrode materials in a supercapacitor, these new discrete states near the E_F level can act as a series of charge storage states spreading over a sufficiently wide potential range to accept (or donate) electrons and therefore improve the faradaic reactivity of POGs, resulting in a boost of the pseudocapacitance in these species.

It is also believed that, firstly, the distribution of these extra charge storage states decides the limits of the potential scanning window in which the behaviour of pseudocapacitance can be observed in the electrode material. As

can be found in Figure 6-6, all the charge storage states of POGs fall in an energy range wider than 2.0 eV, which compares well with the experimentally observed potential range of carbon materials in neutral aqueous electrolytes. Thus, charges can be injected into or extracted from these energy levels within the common range of the operating voltage of supercapacitors. Secondly, the population densities of these special states also decide the charge capacity in manners of pseudocapacitance of the electrode material. Here, it must be highlighted that this kind of charge storage is totally different from that in a traditional EDLC electrode as well as in a battery electrode that can be explained by the Nernst equation with one or several couples of faradaic peaks on the CVs. These extra energy states can distribute in a wide range of energy levels caused by different degrees of ED, hence obligate space to store charges in a quasi-continuous potential range. Also, these intensive energy states around the Fermi level can also improve the redox activity of POGs resulting in specific adsorption of ions, which has also been observed and proven in many studies on the catalytic activity of POGs.

Furthermore, through comparative study between the electronic structure of typical pseudocapacitive materials and that of POGs, it was proposed in this study for the first time that the extra charge storage states are delocalised valence states in essence. They may result to a variable Fermi level, or more precisely the equilibrium redox electrode potential (E_{eq}) of POGs during the charging/discharge of pseudocapacitance. Very recently, A linear dependence between the equilibrium potential and the oxidation state of the electrode material was observed in e.g. RuO_2 [274] and MnO_2 [275] and has been successfully used to explain and semi-quantitatively calculate the pseudocapacitance in these materials. According the further simulation on their CVs, characteristic rectangular CVs have also been obtained [64]. The oxidation state of the electrode materials denotes the local degree of oxidation. Such a linear variation is based on the fact that, in Nernst equation, the equilibrium potential (E_{eq}) is directly related to the oxidising and reducing species. In the case of solid state materials, the concentration of oxidising and reducing is usually set to 1, while this is an approximation and the activity coefficients of solid species are actually unknown. If it is considered that the activity coefficient

is dependent on the state of charge a variable E_{eq} versus the oxidation state is reasonable.

In detail, pseudocapacitive electrode materials have a movable E_{eq} following the variation of its oxidation state. Meantime the equilibrium potential is in nature correlated with the electronic structure of the electrode material. When charging electrons into or discharging holes from these electron states, the oxidation state of the electrode material (POGs in this study) decreases resulting to a negative movement of the E_{eq} . In contrast, the discharging electrons into or charging holes causes the increasing of the oxidation state, hence a positive movement of the E_{eq} . The linear variation behaviour of the equilibrium potential versus the charge state has also been confirmed by X-ray absorption spectroscopy in the literature [66-68] in the MnO_2 system. During the movement of the E_{eq} i.e. the charging/discharging process, charge transfer happens in the matrix of electrode materials rather than across the electrode | electrolyte interface. This is the main distinction between charge transfer of pseudocapacitance and that of the traditional redox process. In the former case, charges were stored in or extracted from the delocalised valence states of the electrode materials. However, in the latter case, charges were transferred between the electrode and external redox activities. This is the typical Nernst equation governed electrode process with charges being stored in or drew out from the localised valence states in either freely movable or surface restricted redox activities rather than in the electrode material itself.

Another important fact needs to be clarified is the difference between the delocalised states of pseudocapacitive materials e.g. POGs, RuO_2 [192,276] and MnO_2 [277], and that of in common metallic electrodes, such as Pt, Au, Cu, Ag and pure graphene. The former case is partially delocalised valence states residing around the Fermi level. These electronic states originated the delocalised valence states of p - and d -orbitals with a very high population of DOS because of high orbit angular quantum number, which directly determines the valence of active elements and the local oxidation state in the electrode materials. The latter case is fully delocalised state originated mainly from the outmost s -shell (Group IA and IIA in the periodic table), p -shell (Group IIIA and VIA in the periodic table), d -subshell (Group IB and VIIIB), as reviewed in

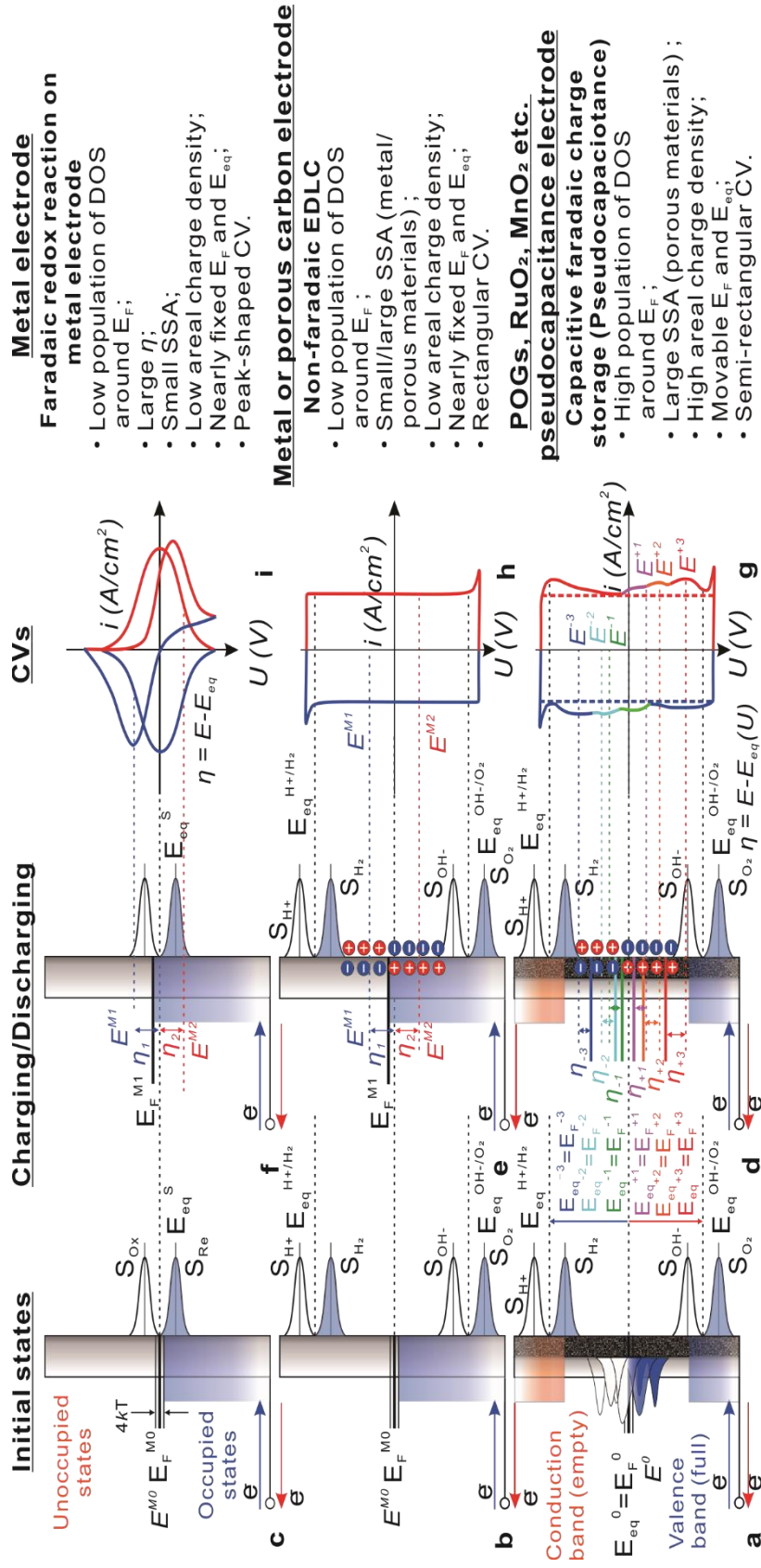
Section 1.1.3.2, huddling together in the condensed states of bulk metal. When redox reaction happens in pseudocapacitive materials both the conductivity and crystalline framework do not vary violently. What matters is as long as the redox reaction happened in the electrode matrix, no matter what kind of charges (counter ions) accumulation or insertion is happening, the energy band structure and DOS of the electrode materials do vary slightly. This can also lead to a slight variation of the electronic structure in the relevant region of electrode materials. The oxidation of electrode materials leads to a negative movement of the Fermi level or the equilibrium potential because more work has to be done to further extract more electrons from or inject more holes to the deeper valence levels which are closer to the active centres (-C=C- or POGs, Ru in RuO_2 and Mn atoms in MnO_2); vice versa. The reduction of the electronic structure leads to a positive movement of the Fermi level or the equilibrium potential because less work is needed to be done to inject holes into or extract electrons from the higher valence levels of the active centres (-C=C- or POGs, Ru in RuO_2 and Mn atoms in MnO_2), in other words, a more positive location of Fermi level or the equilibrium potential. More significantly, this movement of the Fermi level or the equilibrium potential accompanying with the redox reaction or variation of oxide states of electrode materials allows a relatively small over-potential maintaining on the electrode. This relatively small over-potential guarantees the interface of electrode material | electrolyte working in capacitive potential range rather than deviating too far into the faradaic decomposition of the electrode itself or the electrolyte. This results in a relatively wider effective capacitive potential range in pseudocapacitive materials. However, in the typical metal electrode, the gain/loss of electrons from the valence band may cause hydrogen evolution in aqueous electrolyte or ionisation or even oxidation of the metal surface. Charge transfer during these process is governed by the Nernst equation. Oxidation leads to the formation of insulating oxides layer on the surface of conductive bulk metal, which completely blocks the charging/discharging path of charge carriers. Even if it is in the effective capacitive potential range, the low DOS of the fully delocalised states in metal cannot allow an appearance charge storage in these states in comparison with the high DOS in POGs and RuO_2 . Additionally, extremely low SSA of the metal electrode again limits the accumulation of

counter ions from electrolyte. All these factors rule out the metallic electrode materials from the kingdom of pseudocapacitive materials.

It has to be mentioned that not all electrode materials with good electric conductance, for example Ag_2O , Cu_2O , TiO (see, Section 1.1.3.3), can show good pseudocapacitance. It has to consider not only the stability of the electrode materials in practical working electrolyte such as acidic medium or aqueous environment but also, more critically, whether the electrode material can happen multiple faradaic reactions during its redox without catastrophic decomposition of its crystal lattice, in the meantime preserving its good electric conductance within the working potential range. Besides, whether the electrode material can form large SSA to facilitate the accumulation of counter ions, of course, matters very much for a potential pseudocapacitance candidates.

Till now, a clearer picture of pseudocapacitance can be obtained based on the above discussions. Three major electrochemical charge storage mechanisms were sketched in the following Figure 6-11 in which clearer characteristics of pseudocapacitance can be summarised in comparison with the charge storage mechanism of traditional EDLC and Nernst redox process.

It can be concluded at this stage that faradaic capacitance is the essence of pseudocapacitance. Necessary conditions include multiple redox activities and high population of partial ED states around the Fermi level of the target electrode material. This allows a movable Fermi level or equilibrium potential of electrode materials (Note: it is NOT the equilibrium potential of electrolyte or redox couple in the electrolyte) as the oxidation state of electrode material is varied. Thus a relatively small over-potential ($\eta = E - E_{\text{eq}}$) can be preserved in a range potential window in which the electrode material and electrolyte are still stable. Charge transfer happened through injection and ejection electrons/holes into and from the partial delocalised states, which is the so-called 'transfer of Delocalised Electrons'. Relatively large SSA and good conductance are the sufficient conditions which benefit the EDL-type accumulation of counter ions from the electrolyte side. All these key points were summarised and sketched in Figure 6-11.



It is also believed that the mechanism of partial ED states enhanced pseudocapacitance should be applicable to other pseudocapacitive materials e.g. transition metal oxides (TMOs) and electrically conducting polymers (ECPs) which all have states of delocalised electrons. In the RuO_2 lattice, delocalised states originate from the overlapped d-orbitals of Ru atoms and the p-orbitals of O atoms [276]. In $\alpha\text{-MnO}_2$, insertion ions introduced charge-switching states within the band gap are responsible for the pseudocapacitance [65]. For ECPs, the conjugated bonds are responsible for electron delocalisation. Furthermore, to enable pseudocapacitance (or redox activity), electron delocalisation should be confined, at least partially, in suitable special dimensions such as the nano-structures in TMOs and the limited lengths of the conjugated bonds in ECPs.

6.6 Foundation and influential factors of pseudocapacitance

The statements in the following lines are extracts based on the above discussions to summarise the correlation between the electronic structure of graphene-based electrode materials and its interfacial charge storage performance:

- (1) Capacitive charge storage was only enhanced in partially oxidised graphene species because a bunch of extra energy states appear around the Fermi level within the effective capacitance potential range;
- (2) These extra energy states, intrinsically, originate from the partially delocalised electron states in partially oxidised graphene or graphene species with any type of defects;
- (3) These partial delocalised electron states can improve the interfacial capacitance of electrode materials through enhancing the surface charge density at the interface of electrode | electrolyte;
- (4) Electrode materials with an extremely high degree of ED, do not have the best capacitive charge storage performance neither in EDLC nor in faradaic reactions and pseudocapacitance;
- (5) Combining all the achievements obtained in this study, foundation and influential factors of pseudocapacitance can be summarised in the following hierarchy of Figure 6-12 in terms of the electronic structure of electrode

materials and the internal, logical relationship of properties of electrode materials.

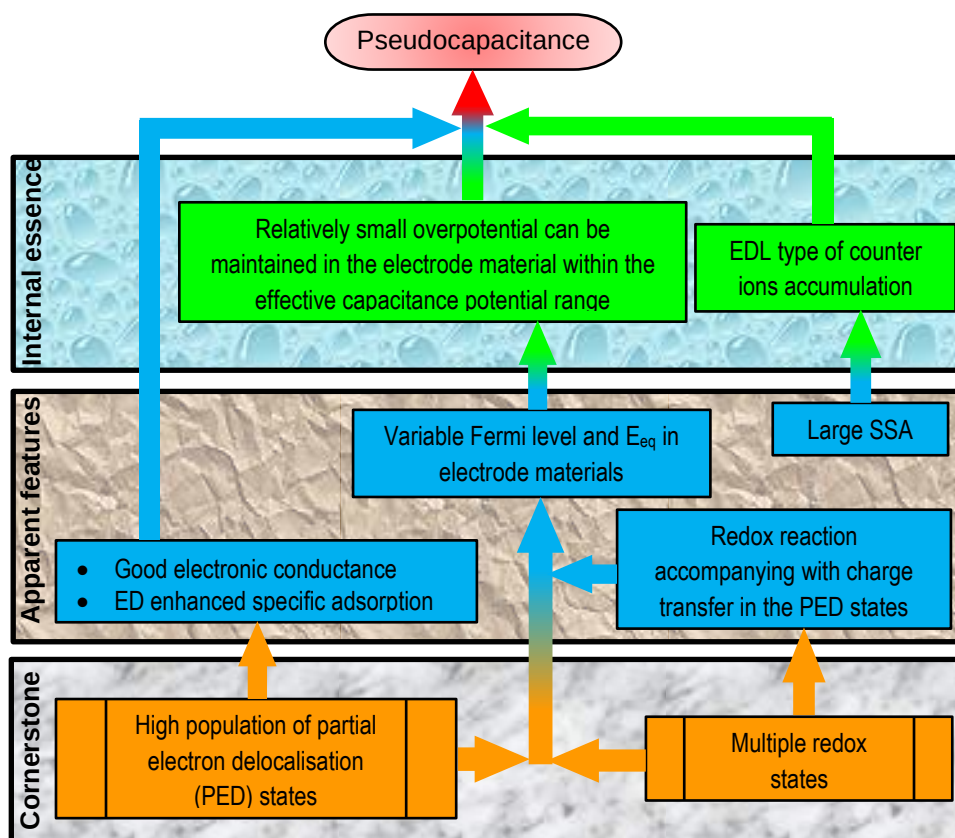


Figure 6-12. Foundation and influential factors of pseudocapacitance.

As can be seen in Figure 6-12:

- Above all, as one of the cornerstones of pseudocapacitance, partial electron delocalisation states must have a high population of DOS around the Fermi level of electrode materials. Additionally, they must reside in the effective capacitance potential range, no matter what the origin. Examples of this are the extra energy states of POGs observed in this study, the intrinsic valence level states in RuO_2 or the insertion ions-introduced 'charge-switching states' in $\alpha\text{-MnO}_2$. These special electronic states endow electrode materials with not only better electronic conductance but also the electron delocalisation enhanced

interfacial capacitance;

- Multiple redox states as the second cornerstone, within the effective capacitance potential range, enable redox reactions of the electrode material to occur sequentially accompanying the transfer of delocalised valence electrons in partial electron delocalisation states;
- Combining the above two aspects, the electrode material can be endowed with variable or more precisely movable Fermi level or equilibrium potential (E_{eq}) during its redox process;
- A relatively small over-potential (η) can be maintained because of the variable Fermi level or equilibrium potential (E_{eq}) when the electrode material is oxidised or reduced;
- Large SSA benefits the accumulation of counter ions in the matrix of electrode materials in order to balance the excessive charges due to the redox of the electrode materials, namely the partial electron delocalisation enhanced capacitance. In essence, this partial electron delocalisation enhanced capacitance is a double layer-type capacitive charge storage.

6.7 Summary

An ab initio study was carried out in this chapter in order to learn the detailed electronic structures of a series of simple whereas new models of GO with various coverage areas of epoxy groups and ED zones with the aid of the DFT method. Modelling and geometric optimisation were done on the established GO models firstly to acquire the relatively stable and rational crystal lattices on an atomic level. Thereafter, the information of energy band and DOS were further obtained through calculation based on optimised models. A tuneable E_g value ranging from 0 eV to 0.666 eV was observed, depending on model structures. A bunch of extra energy states near the E_F level were identified only in all the studied POGs but not in PG and FOG. This finding may not be surprising or unexpected, but it is not yet reported in the literature. Projected DOS analysis was performed and indicated a stronger correlation of the DOS maximum with the sizes of the ED zones, instead of that covered by the epoxy groups. These findings predict transfer of partially delocalised

electrons over a wide range of potentials. Such behaviour is in line with the experimentally observed pseudocapacitance but contradicts that governed by the feature potential of the Nernst's Law for the transfer of localised valence electrons. Through the integration did over the normalised PDOS of GO models, the specific charge density that can be stored in GO was successfully correlated with their DED. This result was also in line with the variation tendency of the interfacial charge storage against the DED observed in POGs and PMG in Chapter 4 and 5. Hence, both theoretical prediction and experimental facts support the mechanism of partial ED states enhanced pseudocapacitance in GO. The conclusion is that extra energy states originated from the partial ED in POGs around the Fermi level contribute the charge storage of pseudocapacitance. Further discussion and comparative study between the electronic structure of POGs and that of typical pseudocapacitive materials established a clearer picture of pseudocapacitance in pseudocapacitive electrode materials. At the end, the foundation and influential factors of pseudocapacitance was illustrated as one of the main achievements in this research.

Chapter 7 Conclusions and Future Work

7.1 Conclusions

In this work, the pseudocapacitance and degree of electron delocalisation (DED) have been investigated through both experimental and theoretical aspects in three graphene species, including graphene oxide (GO), partially oxidised graphene (POG) and polycrystalline monolayer graphene (PMG). Electrochemical reduction (ECR) was carried out to partially reduce the GO into POG. Raman and XPS spectroscopies were used to qualitatively characterise the DED%. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were applied to monitor the charge storage and help analysis of the pseudocapacitive contribution. The variation of pseudocapacitance versus the DED% has been established based on the above characterisation results.

Theoretical calculation on the electronic structures of representative GO models was carried out, aided by the first-principles density functional theory (DFT). It has offered unprecedented theoretical evidence to confirm the correlation between the charge storage capacity and the DED% of these GO models. Further, the correlation between the partial electron delocalisation and pseudocapacitive charge storage was also established based on the theoretical and experimental findings. The key conclusions that can be drawn from this work are reiterated in the following sections.

7.1.1 Determination of DED% in graphene species

It was found in this work that Raman spectroscopy can qualitatively characterise the variation of DED% in GO and POG. The results showed that as the ECR cycles increased from 10 to 1000, the I_D/I_G ratio of GO samples gradually decreased from 1.55 to 1.10 which indicates a recovery of the sp^2 covered region in partially reduced GO, i.e. an increase of DED%.

The deconvolution of the C 1s peak and D-parameter interpolation based on the XPS data can semi-quantitatively characterise the variation of DED% in these graphene based materials. A DED% equation was established

to calculate the sp^2/sp^3 ratio based on the deconvolution of the main peak C 1s into the sp^2 and sp^3 components.

The results showed that the DED% of the original GO (without the ECR treatment) and the PMG was about 14.8% and 95.0%, respectively. When the ECR of GO progressed gradually via potential cycling from 0 to 1000 cycles, the DED% of the resulting POG increased from 19.9% to 47.1% as estimated from the deconvolution of C 1s peak, or from 12.5% to 60.4% as estimated from the D-parameter interpolation.

7.1.2 Effect of the DED on the pseudocapacitance of POGs

It was found in this work that the EIS analysis may help differentiate the pseudocapacitive component from the EDL component in the total charge storage of GO species.

Based on CV characterisations, the specific capacitance of the POG electrode improved from 0.1 to 38.0 F/g in 3.0 M KCl and from 0.2 to 62.0 F/g in 1.0 M H_2SO_4 respectively as the DED% increased from 19.9% to 47.1%, or 12.5% to 60.4%. The pseudocapacitive contribution improved from 0.1 to 22.0 F/g in 3.0 M KCl and from 0.1 to 78.0 F/g in 1.0 M H_2SO_4 respectively based on EIS analyses.

7.1.3 DED% and pseudocapacitance of PMG

Raman characterisation indicated that various defects, such as oxygen-containing groups (< 20%) and boundaries, existed in the PMG. These defects were the major reason for the decrease of the DED of the PMG to about 95.0%.

The CV results showed that the specific capacitance of PMG was ~27.6 F/g in 3.0 M KCl and ~63.6 F/g in 3.0 M HCl, and the areal capacitance was ~4.1 $\mu F/cm^2$ in 3.0 M KCl and ~9.6 $\mu F/cm^2$ in 3.0 M HCl. The EIS analyses showed that the areal capacitance of PMG was ~4.0 $\mu F/cm^2$ in 3.0 M KCl and ~13.8 $\mu F/cm^2$ in 3.0 M HCl.

The equivalent circuit simulation showed that ca. 95% of the total apparent capacitance resulted from the pseudocapacitive component. These capacitance values are just comparable with those observed on the POG electrodes, although the PMG held was about 95% of DED. This means that

there is a non-linear relationship between the DED and pseudocapacitance in these oxygen containing graphene materials

7.1.4 Theoretical predictions of the correlation between DED and pseudocapacitance in GO

Extra delocalised states with a width of about 2 to 3 eV around the Fermi level were observed only in the band energy and DOS of GO with partial ED, i.e. POGs, but in neither fully oxidised nor pure graphene.

A non-linear relationship has been established between the 'specific charge density' and the DED with a peak between 65.0 and 75.0% of the DED by carrying out a definite integration on normalised DOS within ± 1 eV around the Fermi level of GO and different POG models. A similar non-linear relationship was found between the experimentally measured pseudocapacitance of GO, POG and PMG samples and also the experimentally achieved DED%. Thus, based on both theoretical and experimental studies, the peak shaped non-linear correlation between the pseudocapacitance and partial electron delocalisation has been confirmed in this work.

7.2 Future work

Despite that the innovative efforts made in this study has correlated the partial electron delocalisation with the pseudocapacitance in graphene-based electrode materials for the first time, it has to stress that this is just a beginning of the story to consider the pseudocapacitance from the viewpoint of electronic structure of electrode materials. As a matter of fact, there are still many issues which need further study. In order to address these issues, many efforts, particularly experimental investigations need to be carried out in the future. Some of these are outlined below.

In-situ spectroscopic characterisations can be carried out to detect the detailed variation of the electronic structures on the pseudocapacitive electrode material during its charging/discharging. The techniques may include, but not limited to, ultraviolet photoelectrons spectroscopy (UPS) and X-ray absorption spectroscopy (XAS).

Although a peak-shaped non-linear relationship has been found between the pseudocapacitance and the DED in oxygen containing graphene electrode materials, there still is a gap in between the 65.0 and 75.0% of the DED. More POG samples with their DED% located in this gap should be investigated to complete the whole picture of this relationship.

A more accurate adjustment and characterisation on the DED% of GO and POGs can be carried out in experiments at an atomic level. Thus the charge storage can also be observed at such a level.

More direct evidence of the pseudocapacitive contribution and its percentage in the total charge storage can be studied by means of other spectroscopic and electrochemical techniques.

Quantitative analysis and calculation of pseudocapacitance in electrode materials can be carried out based on those well-known porous electrode material models, including the transmission line models, specifically focusing on the explanation and simulation of the origin of the rectangular cyclic voltammograms from pseudocapacitive electrode materials.

Last, but not the least, more research and development can be focused on the design and preparation of new pseudocapacitive electrode materials based on the correlation between the partial electron delocalisation and pseudocapacitance.

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Appendix

A. SEM characterisation of graphite flakes

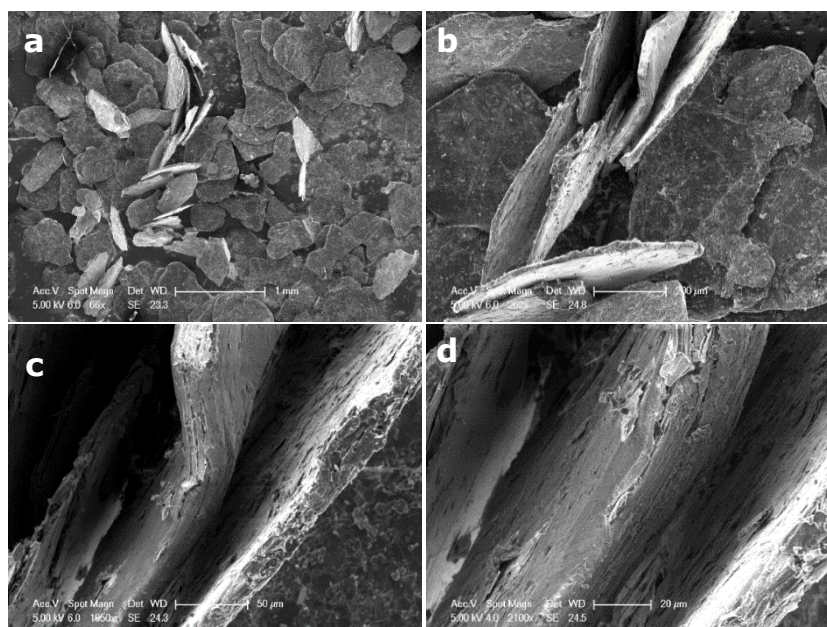


Figure A-1. SEM images of graphite flakes

SEM characterisation was carried out on the raw material, i.e. graphite flakes, before the practical synthesis of GO. This is important because the quality and characteristic of products, here the GO, are dependent on the characteristics of the raw material to some extent. Commercial graphite flakes were used directly without any pre-treatment. Figure A-1 showed the SEM images of this raw material under different magnifications. On the one hand, the image (a) under low magnification showed many flaky graphite discs with particle size about 0.5 mm. In the images under higher magnification, the thickness of each graphite flake can be identified about 10 to 20 μm . Layer-like structures can even be detected on the edge side of individual flake as shown in Figure A-1 c. As has been confirmed, the average thickness of a single layer graphite and the interlayer distance of the graphite crystal is about 0.335 nm (0.000335 μm) [216], that is to say, there are at least $3 \sim 6 \times 10^4$ layers of single layer graphene stacking in one piece of such graphite flake.

B. Raman characterisation of graphite flakes

Raman scattering behaviour is one of the most important spectroscopic characteristics of carbonaceous materials, including graphite and graphene species. It is not only a non-destructive characterisation tool, but also can detect informative structural features, such as defects, atomic configuration of materials, especially some specific scattering peaks and bands. Raman studies carried out on graphite flakes showed three specific bands around 1250 cm^{-1} to 1400 cm^{-1} , 1587 cm^{-1} and 2550 cm^{-1} to 2800 cm^{-1} , corresponding to the D, G and 2D bands respectively. The inspecting points were chose mainly on the basal plane of flakes under the optical microscope through a 50X objective lens. The corresponding Raman spectroscopy was collected and shown on the right panel of Figure A-2.

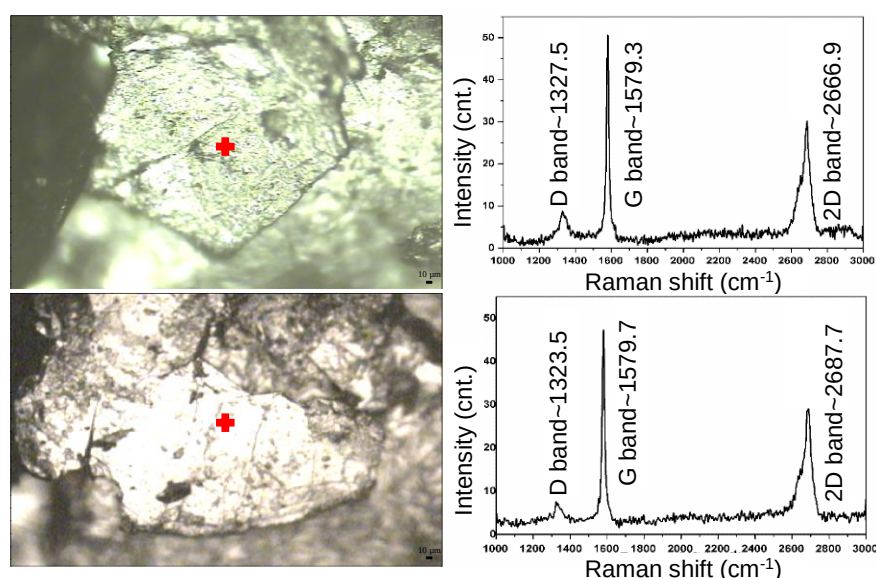


Figure A-2. Selected spots for laser Raman scattering of graphite flakes.

Normally in graphite, the G band always stands the highest intensity and the smallest FWHM indicating a multilayer graphitic feature because it is in-plane vibrational mode of sp^2 carbons. A relatively weak D band indicates the low defects concentration. The 2D band which corresponds to the overtone of defect-induced D mode always has only a half intensity of the G band. The specific peak ratio I_D/I_G is about 0.15 to 0.2, and I_{2D}/I_G is about 0.35 to 0.4, all indicating a very high degree of sp^2 -hybridisation.

C. Optimisation of the loading mass of GO on Ti plate

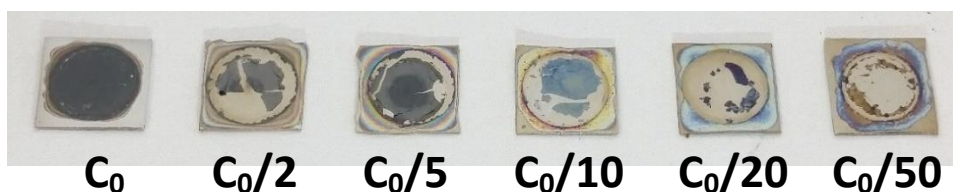


Figure A-3. Different loading masses of GO on $1 \times 1 \text{ cm}^2$ Ti plates after the ECR treatment. The variation of loading mass was achieved by coating $25 \mu\text{L}$ GO suspension with different concentration. C_0 is the initial concentration of the original GO suspension about $4 \pm 0.4 \text{ g/L}$

Six home-made titanium plates were covered by $25 \mu\text{L}$ GO suspension with gradient decrease of concentrations from C_0 to $C_0/50$. Here C_0 is the initial concentration of the original GO suspension about ca. $4 \pm 0.4 \text{ g/L}$. After drying, the GO coated working electrode was prepared. All above samples were treated with the same procedures of ECR to examine their stability and duration. Due to the binder-free property of the GO coating layer and long-term electrochemical treatment in aqueous electrolyte, the GO coating layer on substrate may suffer from some bad effects during the treatment. Therefore, it is important to obtain a stable electrode with a proper loading mass of activated materials. It was found that as the concentration of the GO suspension decreased GO coating layer became thinner and thinner. The optimised loading mass of GO was determined by observation the variation and stability of the GO coating layer during and after a long-term electrochemical treatment. As shown in Figure A-3, too less loading mass of GO cannot cover the working area on the Ti plates. Therefore, apparent stripping off and fracture can be observed during and after the ECR treatment. Finally, GO of $25 \mu\text{L}$, ca. $4 \pm 0.4 \text{ g/L}$, i.e. ca. $100 \pm 10 \mu\text{g}$, was confirmed to be an optimal loading mass on the homemade Ti plates without apparent adverse variation and failure of coating layer occurs during the ECR treatment.

Electrochemical characterisation before ECR treatments: (initial $i = 1$, $j = 1$)
where, $i = 1$ to 3, corresponding to the three ECR potential ranges:

j=1 to 8, corresponding to 10, 20, 40, 80, 100, 300, 500 and 1000 cycles of CV scan of ECR treatment

Si_1_1: CV characterisation in 3.0 M KCl before ECR, 0.5mV of potential step, potential range 0.0 to +0.8V vs. Ag/AgCl:

5 mV/s (5cycles), 10 mV/s (10cycles), 20 mV/s (5cycles), 50 mV/s (5cycles), 100 mV/s (5cycles);

Si_1_2: EIS characterisation in 3.0 M KCl before ECR, at +0.4 V of stand-by potential:

[illegible]

ECR treatment:

Si 2 p: (i) cycles of CVs in the (i) range at 200mV/s;

[illegible]

Electrochemical characterisation after (j) cycles of ECR treatments:

Si₃j: CV characterisation in 3.0 M KCl after (j) cycles of ECR, 0.5mV potential step, within 0.0 to +0.8V:

10 mV/s (10 cycles);

Si_4_j: EIS characterisation in 3.0 M KCl after (j) cycles of ECR, at +0.4 V of stand-by potential;

$j = j+1$, then go to procedure Si 2 j till $j = 8$;

[illegible]

$i = i+1$, then go to procedure S_{i-1} till $i = 3$ and $j = 8$.

\$ Procedure ends-----

E. Circuit elements used to simulate the EIS based on the equivalent circuit shown in Figure 4-18:

Table A.1 EIS data recorded on samples listed in Table 4-4

Experimental condition*	ESR (Ohm)	Q_{EDLC} ($\mu S \cdot s^n$)	n_{EDLC}	SC_{EDLC} (F/g)*	R_{ct1} (Ohm)	Q_{p1} ($mS \cdot s^n$)	n_{p1}	SC_{p1} (F/g)*	R_{ct2} (Ohm)	Q_{p2} ($mS \cdot s^n$)	n_{p2}	SC_{p2} (F/g)*	χ^2 (10^{-4})
Untreated_00	18	7.9	0.9247	0.040	347	0.02	0.9420	0.152	6788	0.02	0.8291	0.137	2.48
PW1_10	18	6.4	0.9437	0.038	392	0.06	0.9101	0.427	1473	0.09	0.9489	0.832	1.61
PW1_20	18	6.1	0.9442	0.037	371	0.06	0.9292	0.463	661	0.2	0.9379	1.803	1.47
PW1_40	18	6.1	0.9418	0.036	401	0.07	0.9328	0.558	427	0.3	0.9344	2.677	1.67
PW1_80	18	6.2	0.9396	0.036	527	0.06	0.9324	0.482	319	0.4	0.9332	3.559	1.76
PW1_100	18	6.3	0.9380	0.036	713	0.04	0.9318	0.318	281	0.5	0.9304	4.451	1.55
PW1_300	19	6.5	0.9379	0.037	915	0.06	0.8836	0.422	352	0.9	0.9382	8.602	1.20
PW1_500	19	6.0	0.9405	0.035	597	0.2	0.7664	1.079	449	1.0	0.9764	10.112	2.26
PW1_1000	18	6.0	0.9423	0.035	501	0.3	0.7752	1.785	877	1.1	0.9993	11.340	2.93
PW2_10	17	5.9	0.9490	0.036	650	0.08	0.8765	0.533	1150	0.1	0.9737	0.953	2.17
PW2_20	18	5.7	0.9495	0.035	592	0.08	0.9132	0.605	395	0.2	0.9383	1.710	1.98
PW2_40	18	5.4	0.9513	0.034	621	0.09	0.8464	0.539	300	0.4	0.9580	3.682	1.24
PW2_80	18	5.7	0.9427	0.033	619	0.1	0.8219	0.553	294	0.5	0.9614	4.676	2.26
PW2_100	18	5.9	0.9395	0.033	575	0.1	0.8287	0.560	318	0.6	0.9556	5.612	2.29
PW2_300	18	5.6	0.9439	0.033	397	0.4	0.8069	2.601	870	0.9	1.0000	9.091	2.39
PW2_500	18	5.6	0.9463	0.034	580	0.4	0.7521	2.496	899	1.2	0.9913	12.129	2.46
PW2_1000	18	6.1	0.9443	0.036	482	0.5	0.7423	3.082	745	1.6	0.9956	16.174	3.25
PW3_10	17	6.2	0.9439	0.037	339	0.07	0.8960	0.467	554	0.2	0.9543	1.856	2.33
PW3_20	17	5.9	0.9475	0.037	406	0.07	0.8730	0.430	233	0.3	0.9499	2.688	1.97
PW3_40	18	5.8	0.9465	0.036	435	0.1	0.8291	0.540	212	0.5	0.9615	4.712	1.71
PW3_80	18	5.8	0.9449	0.035	496	0.2	0.8001	1.158	246	0.7	0.9714	6.852	1.74
PW3_100	18	6.0	0.9426	0.035	565	0.2	0.7871	1.143	295	0.8	0.9659	7.838	1.93
PW3_300	17	5.8	0.9442	0.035	447	0.4	0.7553	2.361	917	1.2	1.0000	12.371	3.00
PW3_500	18	5.9	0.9464	0.036	435	0.4	0.7597	2.372	681	1.5	0.9895	15.467	2.56
PW3_1000	18	6.7	0.9300	0.035	506	0.5	0.7641	3.372	729	1.3	1.0000	13.402	3.12

* PWi refers to the ECR potential range. PW1: -1.0 to 0.0 V, PW2: -1.1 to -0.5V and PW3: -1.15 to -0.5V; numbers after underline denote the numbers of CV cycles from 10 to 1000. The effective capacitance (SC) of each CPE is calculated from the equation of $C_{EFF} = (R_{ct} \times Q)^{1/n} / R_{ct}$, for a series connection of the CPE- R_{ct} branch.

Electrochemical characterisation before ECR treatments: (initial $i = 1$, $j = 1$)

10 mV/s (10cycles), 5 mV/s (5cycles), 20 mV/s (5cycles), 50 mV/s (5cycles), 100 mV/s (5cycles):

FCR treatment:

Sij 2 1: (j) cycles of CVs in the (i) range at 200mV/s;

Electrochemical characterisation after ECR treatments:

Sij_2_2: CV characterisation in 3.0 M KCl after (j) cycles of ECR, 0.5mV potential step, within 0.0 to +0.8V:

10 mV/s (5cycles), 2 mV/s (3cycles), 5 mV/s (3cycles), 20 mV/s (5cycles), 50 mV/s (5cycles), 100 mV/s (5cycles);

Sij_2_3: EIS characterisation in 3.0 M KCl after (j) cycles of ECR, 0.0 to +0.8V vs. RE, 0.05V potential intervals, 10mV amplitude of AC potential perturbation, under 8 specific frequency points: 100 kHz、10 kHz、1kHz、100 Hz、10 Hz、1 Hz、0.1 Hz、10 mHz;

Sij_2_4: EIS characterisation in 3.0 M KCl after (j) cycles of ECR at specific potential points within 0.0 to +0.8V vs. RE, 10mV, frequency range: 100kHz to 10mHz;

Sij_3_1: CV characterisation in 1.0 M H₂SO₄ after (j) cycles of ECR, 0.5mV potential step, within 0.0 to +0.8V:

10 mV/s (5cycles), 2 mV/s (2cycles), 5 mV/s (3cycles), 20 mV/s (5cycles), 50 mV/s (5cycles), 100 mV/s (5cycles)

Sij_3_2: EIS characterisation in 1.0 M H₂SO₄ after (j) cycles of ECR, 0.0 to +0.8V vs. RE, 0.05V potential intervals, 10mV amplitude of AC potential perturbation, under 8 specific frequency points: 100 kHz、10 kHz、1kHz、100 Hz、10 Hz、1 Hz、0.1 Hz、10 mHz;

Sij_3_3: EIS characterisation in 1.0 M H₂SO₄ after (j) cycles of ECR at specific potential points within 0.0 to +0.8V vs. RE, 10mV, frequency range: 100kHz to 10mHz;

\$ Procedure ends-----

G. Circuit elements used to simulate the EIS based on the equivalent circuit shown in Figure 4-18:

Table A.2 EIS data was recorded on samples listed in Table 4-1 in 3.0 M KCl electrolyte

Sample number*	ESR (Ohm)	Q_{EDLC} ($\mu S \cdot s^n$)	n_{EDLC}	SC_{EDLC} (F/g)*	R_{ct1} (Ohm)	Q_{P1} ($mS \cdot s^n$)	n_{P1}	SC_{P1} (F/g)*	R_{ct2} (Ohm)	Q_{P2} ($mS \cdot s^n$)	n_{P2}	SC_{P2} (F/g)*	χ^2 (10^{-4})
S00	20	6.53	0.9214	0.03	752	0.005	0.9194	0.032	/	/	/	/	1.87
S11	20	9.17	0.8897	0.14	424	0.007	0.9425	0.051	23	0.2	0.9405	1.467	3.18
S12	20	7.30	0.9073	0.13	377	0.003	0.9424	0.020	23	0.2	0.9488	1.542	1.78
S13	28	6.40	0.9163	0.05	230	0.2	0.9368	1.675	58	0.2	0.9501	1.632	1.98
S14	24	7.00	0.9067	0.03	29	0.3	0.9484	2.389	110	0.3	0.9329	2.420	1.82
S15	19	7.20	0.9112	0.03	96	0.2	0.9453	1.640	114	0.5	0.9449	4.362	2.14
S16	21	6.90	0.9206	0.01	200	0.3	0.8961	2.232	293	0.9	0.9571	8.740	2.12
S17	23	11.00	0.8544	0.02	78	0.3	0.8177	1.339	176	1.3	0.9400	12.198	4.88
S18	25	7.60	0.9256	0.01	404	0.3	0.8243	1.972	403	1.7	0.9642	17.281	1.63
S21	22	6.30	0.9165	0.03	42	0.008	0.9549	0.057	108	0.1	0.9413	0.777	3.35
S22	27	6.90	0.9164	0.02	76	0.006	0.9508	0.042	145	0.1	0.9343	0.765	3.80
S23	26	6.00	0.9184	0.07	194	0.009	0.9269	0.056	37	0.2	0.9428	1.531	2.83
S24	21	5.20	0.9401	0.03	162	0.006	0.9399	0.040	98	0.3	0.9269	2.342	2.35
S25	21	4.50	0.9468	0.02	264	0.2	0.7983	0.981	170	0.5	0.9985	5.136	4.10
S26	24	5.00	0.9365	0.01	111	0.3	0.8803	1.947	206	0.9	0.9645	8.720	2.08
S27	30	4.60	0.9446	0.01	226	0.4	0.8090	2.338	469	1.2	0.9851	12.264	2.40
S28	31	4.50	0.9470	0.01	333	0.4	0.7917	2.426	461	1.9	0.9813	19.538	1.73
S31	37	5.50	0.9266	0.01	67	0.1	0.9580	0.828	387	0.009	0.9462	0.067	2.68
S32	51	5.00	0.9325	0.01	86	0.2	0.9569	1.717	220	0.2	0.9452	1.720	2.13
S33	28	5.40	0.9337	0.03	69	0.2	0.9488	1.636	94	0.4	0.9335	3.264	2.41
S34	20	5.20	0.9356	0.01	121	0.2	0.9138	1.451	394	0.5	0.9572	4.793	2.50
S35	32	4.80	0.9348	0.01	165	0.2	0.9182	1.522	201	0.7	0.9502	6.512	1.67
S36	43	4.80	0.9359	0.01	208	0.4	0.8122	2.321	477	1.2	0.9931	12.323	2.68
S37	36	5.20	0.9352	0.01	183	0.5	0.8221	3.072	348	1.5	0.9756	15.215	3.75
S38	32	4.80	0.9360	0.01	159	0.6	0.8063	3.517	304	1.8	0.9711	18.227	0.88

* Refer to Table 5-1 for the corresponding sample numbers and experimental parameters. The effective capacitance of each constant phase element was calculated from the equation of $C_{EFF} = (R_{ct} \times Q)^{1/n} / R_{ct}$, for a series connection of the CPE- R_{ct} branch.

Table A.3 EIS data was recorded on samples listed in Table 4-1 in 1.0 M H₂SO₄ electrolyte

Sample number*	ESR (Ohm)	Q _{EDLC} (μS·s ⁿ)	n _{EDLC}	SC _{EDLC} (F/g)*	R _{ct1} (Ohm)	Q _{P1} (mS·s ⁿ)	n _{P1}	SC _{P1} (F/g)*	R _{ct2} (Ohm)	Q _{P2} (mS·s ⁿ)	n _{P2}	SC _{P2} (F/g)*	X ² (10 ⁻⁴)
S00	13	2.20	0.5934	0.00	3	0.008	0.9398	0.042	/	/	/	/	2.39
S11	17	14.10	0.8690	0.17	14	0.3	0.9167	1.881	438	0.04	0.9584	0.346	2.01
S12	21	9.40	0.9178	0.19	65	0.5	0.9136	3.728	180	0.05	0.9820	0.473	1.42
S13	25	7.30	0.9323	0.07	180	0.3	0.8692	1.993	397	0.6	0.9353	5.601	1.67
S14	17	8.10	0.9195	0.03	84	0.4	0.8622	2.398	280	0.8	0.9380	7.471	1.51
S15	19	8.30	0.9272	0.04	243	0.4	0.7406	1.823	1541	0.8	0.9894	8.266	4.44
S16	18	7.80	0.9368	0.01	334	0.5	0.7576	2.907	687	2	0.9729	20.802	1.46
S17	15	14.00	0.8663	0.02	115	0.8	0.7699	4.042	312	2.2	0.9751	22.464	6.95
S18	26	10.00	0.9181	0.01	249	0.8	0.7794	5.224	343	3.4	0.9709	35.213	1.11
S21	22	9.70	0.9158	0.04	77	0.2	0.9119	1.378	182	0.3	0.9225	2.422	1.93
S22	38	9.70	0.9197	0.03	157	0.3	0.9133	2.314	74	0.2	0.9071	1.339	1.60
S23	21	8.30	0.9336	0.12	255	0.2	0.8422	1.181	651	0.5	0.9152	4.646	6.17
S24	27	7.30	0.9414	0.04	225	0.4	0.7310	1.700	4161	0.5	0.9988	5.159	6.61
S25	25	6.60	0.9422	0.02	189	0.6	0.7412	2.893	1371	1.2	0.9938	12.410	5.93
S26	21	12.10	0.9102	0.03	160	1	0.7548	5.684	666	2.4	0.9853	24.916	3.52
S27	28	7.90	0.9293	0.01	125	1.4	0.7942	9.188	291	4	0.9778	41.380	1.72
S28	23	6.30	0.9360	0.01	273	1.4	0.7828	11.052	253	6.2	0.9694	64.832	1.22
S31	38	6.10	0.9531	0.01	377	0.2	0.6904	0.647	12600	0.2	0.9671	2.128	8.69
S32	50	6.40	0.9477	0.02	457	0.3	0.7370	1.522	3306	0.5	0.9703	5.235	7.17
S33	24	6.40	0.9465	0.04	229	0.5	0.7439	2.444	1663	0.9	0.9826	9.345	6.57
S34	20	5.20	0.9363	0.01	130	0.4	0.9068	3.043	446	0.5	0.9467	4.737	2.31
S35	30	8.70	0.9243	0.02	188	0.8	0.7643	4.598	852	1.7	0.9860	17.618	3.55
S36	38	10.30	0.8928	0.01	134	1.3	0.7938	8.512	226	4.2	0.9747	43.240	2.44
S37	21	8.60	0.9223	0.01	103	1.8	0.8062	12.376	222	4.9	0.9792	50.606	1.27
S38	33	11.70	0.8885	0.01	311	0.3	0.7088	1.167	91	7.7	0.9287	77.243	1.53

* Refer Table 5-1 for the corresponding sample numbers and experimental parameters. The effective capacitance of each constant phase element was calculated from the equation of $C_{EFF} = (R_{ct} \times Q)^{1/n} / R_{ct}$ for a series connection of the CPE- R_{ct} branch.

H: Table A.4. Detailed structure parameters of each GO models and pure graphene after geometry optimisation

Models	Molecular Formula ^a	DED ($sp^{2\%}$)	Unit Cell Parameters	Abbreviated forms ^b	Number of k-points used in calculation ^c
FOG	C ₂ O (C:O = 2)	0	SpaceGroup: P1 $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$ A = 4.27 Å, B = 4.93 Å, C = 20 Å C-C bond length: 1.43-1.46 Å C=C bond length: N/A C-O bond length: 1.45 Å	E	3×3×1
Partially reduced GO (POG)	C ₄ O (C:O = 4)	20	SpaceGroup: P1 $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$ A = 4.93 Å, B = 4.27 Å, C = 20 Å C-C bond length: 1.45-1.46 Å C=C bond length: 1.37-1.42 Å C-O bond length: 1.465 Å	EC	5×7×1
	C ₆ O (C:O = 6)	25	SpaceGroup: P1 $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$ A = 4.93 Å, B = 12.81 Å, C = 20 Å C-C bond length: 1.45-1.46 Å C=C bond length: 1.40-1.42 Å C-O bond length: 1.47 Å	EC2	5×5×1
	C ₈ O (C:O = 8)	33.33	SpaceGroup: P1 $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$ A = 4.93 Å, B = 8.54 Å, C = 20 Å C-C bond length: 1.45-1.47 Å C=C bond length: 1.40-1.42 Å C-O bond length: 1.46 Å	EC3	5×3×1
	C ₃ O (C:O = 3)	33.33	SpaceGroup: P1 $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$	E2C	5×2×1

			A = 4.93 Å, B = 12.81 Å, C = 20 Å C-C bond length: 1.44-1.46 Å C=C bond length: 1.37-1.42 Å C-O bond length: 1.44-1.48 Å		
	C ₄ O (C:O = 4)	40	SpaceGroup: P1 $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$ A = 4.93 Å, B = 8.54 Å, C = 20 Å C-C bond length: 1.45-1.47 Å C=C bond length: 1.40-1.42 Å C-O bond length: 1.44-1.48 Å	E2C2	5×3×1
	C ₅ O (C:O = 5)	42.86	SpaceGroup: P1 $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$ A = 4.93 Å, B = 21.35 Å, C = 20 Å C-C bond length: 1.45-1.47 Å C=C bond length: 1.40-1.42 Å C-O bond length: 1.44-1.48 Å	E2C3	5×1×1
	C ₈ O ₃ (C:O = 2.7)	50	SpaceGroup: P1 $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$ A = 4.93 Å, B = 8.54 Å, C = 20 Å C-C bond length: 1.45-1.47 Å C=C bond length: 1.36-1.42 Å C-O bond length: 1.44-1.46 Å	E3C	5×3×1
	C ₁₀ O ₃ (C:O = 3.3)	50	SpaceGroup: P1 $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$ A = 4.93 Å, B = 21.35 Å, C = 20 Å C-C bond length: 1.44-1.47 Å C=C bond length: 1.40-1.42 Å C-O bond length: 1.44-1.48 Å	E3C2	5×3×1
	C ₄ O (C:O = 4)	50	SpaceGroup: P1 $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$	E3C3	5×3×1

			A = 4.93 Å, B = 12.81 Å, C = 20 Å C-C bond length: 1.44-1.47 Å C=C bond length: 1.40-1.42 Å C-O bond length: 1.44-1.48 Å		
	C_5O_2 (C:O = 2.5)	60	SpaceGroup: P1 $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$ A = 4.93 Å, B = 21.35 Å, C = 20 Å C-C bond length: 1.43-1.46 Å C=C bond length: 1.36-1.42 Å C-O bond length: 1.44-1.47 Å	E4C	5×1×1
	C_3O (C:O = 3)	66.67	SpaceGroup: P1 $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$ A = 4.93 Å, B = 12.81 Å, C = 20 Å C-C bond length: 1.44-1.46 Å C=C bond length: 1.40-1.42 Å C-O bond length: 1.44-1.48 Å	E4C2	5×3×1
	C_7O_2 (C:O = 3.5)	75	SpaceGroup: P1 $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$ A = 4.93 Å, B = 29.90 Å, C = 20 Å C-C bond length: 1.44-1.47 Å C=C bond length: 1.40-1.42 Å C-O bond length: 1.44-1.48 Å	E4C3	5×1×1
PG	C (C:O = ∞)	100	SpaceGroup: 6/mmm $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 120^\circ$ A = 2.47 Å, B = 2.47 Å, C = 20 Å C-C bond length: N/A C=C bond length: 1.42 Å C-O bond length: N/A	C	20×20×1

^a This is the nominal molecular formula also indicates the ratio of carbon to oxygen atoms ;

^b E represents the column number of epoxy groups, C the π -conjugation column number;

^c The corresponding direction in the reciprocal space is $a \times b \times c$, and c is perpendicular to the basal plane of graphene species.