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Electrocatalytic Oxidations and Reductions in Ionic Liquids

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Abstract

In this Thesis, surface electrocatalysis of several energy-conversion-relevant redox reactions in ionic liquid electrolytes is described. The first oxidation process investigated is the formation of surface oxide films on Pt electrodes by trace water oxidation in protic ionic liquids (PILs). This is followed by investigation of the oxidation of hydrazine (N_2H_4), formic acid (HCOOH), ethanol (EtOH) and dimethyl ether (DME) in PILs and a description of the role played by surface oxides during each oxidation process. Finally, the electrocatalytic reduction of CO_2 at a variety of electrode materials is explored in room temperature aprotic ionic liquids.

The data reveal that the surfaces of Pt electrodes become covered with oxide layers due to oxidation of trace water, which is omnipresent in PILs, at positive potentials ($E > 1.0 \text{ V vs. Pd-H}$). X-ray photoelectron spectroscopy (XPS) shows that the oxide layers grow to form thick films as the potential is made more positive and as the temperature and water concentration of the PILs are increased. The mechanism and kinetics of oxide film growth are also discussed.

Voltammetric analysis shows that the presence of residual surface oxides activates Pt electrodes towards electrooxidation of N_2H_4 . Furthermore, immersion of oxidized Pt electrodes in N_2H_4 -containing PILs deactivates the electrode indicating that N_2H_4 reacts with the residual surface oxides. Oxidation of HCOOH at Pt catalyst in PILs occurs mainly by dehydration plus CO_{ads} oxidation at a potential that coincides with the onset of the formation of Pt surface oxides. Compared to Pt electrocatalysts, the overpotential for electrooxidation of HCOOH is higher at Au catalyst but lower at Pd catalyst.

Oxidation of trace water in PILs at Pt also plays a pivotal role during the electrocatalytic oxidation of EtOH and DME in the PILs. Oxidation of both EtOH and DME coincides with coverage of the Pt surface by the adsorbed oxide species that helps to activate both processes by oxidizing the adsorbed poisoning CO and CO-like intermediate species via a 'bifunctional' reaction mechanism. Generally, higher overpotentials are observed for each oxidation, and higher activation energies are measured for EtOH oxidation in PILs than in aqueous electrolytes.

Finally, it is shown that CO₂ electroreduction takes place at lower overpotentials at Au and Ag electrocatalysts than at Cu, Pt and boron doped diamond (BDD) electrodes in the presence of ionic liquid electrolytes. Ag electrocatalysts reduce CO₂ at ~0.2 V lower potential when 1-ethyl-3-methylimidazolium ethylsulphate [emim][EtSO₄] is used as supporting electrolyte in acetonitrile compared to when the conventional supporting electrolyte tetrabutylammonium hexafluorophosphate [TBA][PF₆] is used. CO is a product of CO₂ reduction at Ag catalyst and the results highlight that Ag and imidazolium-based ILs could be a promising system for reduction of CO₂ to CO at low overpotentials.

Declaration

This Thesis is the result of my own investigations and is not being concurrently submitted in candidature for any degree.

Signed_____ (Candidate)

Date _____

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First of all, I would like to express my sincere gratitude to my supervisor, Dr. Darren. A. Walsh, for all his support, patience and constant guidance throughout the course of this research. He has provided me with great supervision and motivations for research. It has been a privilege to be his student. I would also like to express my heartiest appreciation to The University of Nottingham for the Vice Chancellor Scholarship, and Islamia College Peshawar, Pakistan for financial assistance for completion of this PhD study. Without the help of these institutions I would not have been able to complete my studies.

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Dedication

I would like to dedicate this Thesis to my creator Almighty Allah, the Most Gracious and the Most Merciful. Who provides us sustenance, made us grow, and made for us the faculties of hearing, seeing, feeling and understanding. The knowledge of the time is with Him alone. Without Allah's Mercy it would not be possible for me to accomplish this work.

List of Abbreviations

Abbreviation	Meaning
AES	Auger electron spectroscopy
APIs	Aprotic ionic liquids
BDD	Boron doped diamond
BE	Binding energy
[bmim][Ac]	1-butyl-3-methylimidazolium acetate
[bmim][BF ₄]	1-n-butyl-3-methylimidazolium tetrafluoroborate
[bmim][NO ₃]	1-n-butyl-3-methylimidazolium nitrate
[bmim][PF ₆]	1-n-butyl-3-methylimidazolium hexafluorophosphate
[bmmim][BF ₄]	1-n-butyl-2,3-dimethylimidazolium tetrafluoroborate
[bmmim][PF ₆]	1-n-butyl-2,3-dimethylimidazolium hexafluorophosphate
CPS	Counts per second
CV	Cyclic voltammogram
[dea][Ac]	Diethylammonium acetate
[dema][Tf ₂ N]	Diethylmethylammonium bis(trifluoromethanesulfonyl)imide
[dema][TfO]	Diethylmethylammonium trifluoromethanesulfonate
DME	Dimethyl ether
[dmea][HfB]	Dimethylethylammonium heptafluorobutanoate
[dmea][TfO]	Dimethylethylammonium trifluoromethanesulfonate
DMF	N, N'-dimethylformamide
DMSO	Dimethylsulfoxide
E _a	Activation energy
ECSA	Electrochemical surface area
[emim][BF ₄]	1-ethyl-3-methylimidazolium tetrafluoroborate
[emim][Br]	1-ethyl-3-methylimidazolium bromide
[emim][EtSO ₄]	1-ethyl-3-methylimidazolium ethylsulphate

[emim][Tf ₂ N]	1-ethyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide
[emim][Tf ₂ N]	1-ethyl-2,3-dimethylimidazolium bis (trifluoromethylsulfonyl) imide
[empyrr][EtSO ₄]	1-ethyl-1-methylpyrrolidinium ethylsulphate
E _{p,a}	Anodic peak potential
E _{p,c}	Cathodic peak potential
EQCN	Electrochemical quartz crystal nanobalance
EtOH	Ethanol
Fc	Ferrocene
Fc ⁺	Ferrocenium
¹ H NMR	Proton nuclear Magnetic resonance
HCOOH	Formic Acid
HER	Hydrogen evolution reaction
HOMO	Highest occupied molecular orbital
HOR	Hydrogen oxidation reaction
H _{UPD}	Under potential deposited hydrogen
Hz	Hertz
IC	Ion chromatography
IHP	Inner Helmholtz plane
ILs	Ionic liquids
i _{p,a}	Anodic peak current
i _{p,c}	Cathodic peak current
K.E	Kinetic energy
KF	Karl-Fischer
LSV	Linear sweep voltammogram
LUMO	Lowest unoccupied molecular orbital
MeCN	Acetonitrile
MLs	Monolayers

[n-bupy][BF ₄]	n-butylpyridinium tetrafluoroborate
NMR	Nuclear Magnetic resonance
OER	Oxygen evolution reaction
OHP	Outer Helmholtz plane
[omim][BF ₄]	1-n-octyl-3-methylimidazolium tetrafluoroborate
[omim][PF ₆]	1-n-octyl-3-methylimidazolium hexafluorophosphate
ORR	Oxygen reduction reaction
PEMFC	Polymer electrolyte membrane fuel cell
PILs	Protic ionic liquids
pK _a	Acid dissociation constant in logarithmic scale
Ppm	parts per million
QCM	Quartz crystal microbalance
RHE	Reversible hydrogen electrode
RTILs	Room temperature ionic liquids
SEM	Scanning electron microscopy
SOMs	Small organic molecules
[TBA][PF ₆]	Tetrabutylammonium hexafluorophosphate
[TEA][P]	tetraethylammonium perchlorate
TEM	Transmission electron microscopy
[Tf ₂ N] ⁻	bis(trifluoromethanesulfonyl)imide
[TfO] ⁻	Trifluoromethanesulfonate
XPS	X-ray photoelectron spectroscopy

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Chapter 1: General Introduction, Literature Review and Project Objectives

1.1. Introduction

The search for clean and renewable energy has increased in the past decades, and this has also increased interest in electrocatalysis of electrochemical reactions.^{1, 2} Redox processes such as the hydrogen evolution reaction (HER), hydrogen oxidation reaction (HOR), oxygen evolution (water splitting) reaction (OER), oxygen reduction reaction (ORR), reduction of CO₂, and oxidation of alcohols, HCOOH, DME and N₂H₄ are of technological and practical interest to energy storage and production. Therefore, understanding and controlling the processes occurring at electrode/electrolyte interface are very important in optimizing energy conversion devices such as fuel cells and electrolyzers.

Electrochemical reactions occur at the electrode/electrolyte interface^{2, 3} and Figure 1.1 shows a generalized electrode reaction which involves a heterogeneous electron transfer between an electrode and an electroactive species (Eqn. 1.1):



where O is the oxidized species, which is reduced to R. Initially, O is transported to the interfacial region where the charge transfer occurs. R is then transported away from electrode surface.

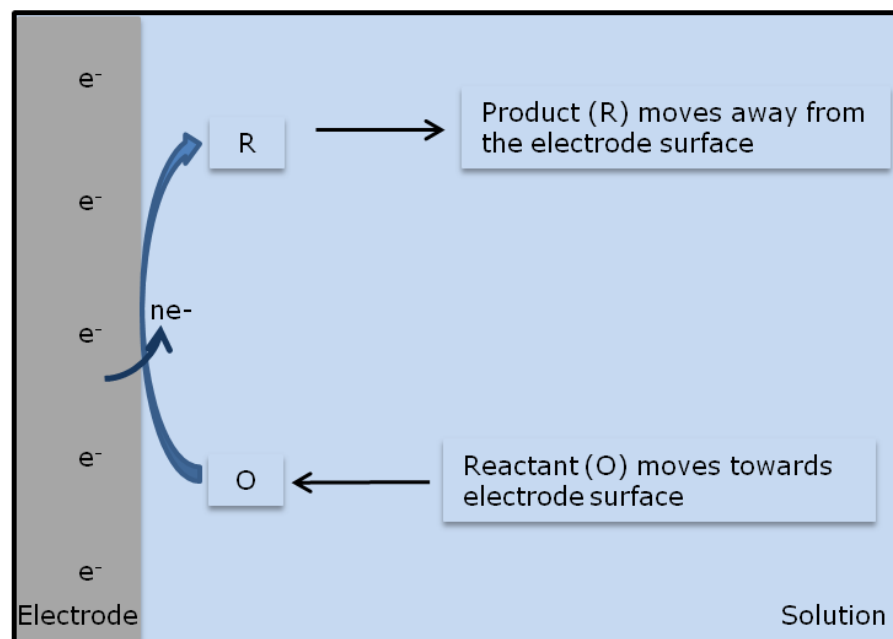


Figure 1.1 Schematic illustration of a heterogeneous electron transfer reaction.

Electrochemical reactions occurring at interfaces are governed by the interaction of the reactant both with the solvent and with the electrode. When a metal is partly immersed in an electrolyte, a potential is set up across the electrode/electrolyte interface i.e. an electrical double layer is set up at the interface. The electrical double layer consists of several layers as shown in Figure 1.2. The inner layer, closest to the electrode, contains solvent molecules and sometimes other species (ions or molecules) that are said to be 'specifically adsorbed' to the electrode surface.³ In the inner layer, which is also called the compact or Stern layer, the electrical center of the specifically adsorbed ion is called the inner Helmholtz plane (IHP). Another layer of non-specifically adsorbed solvated ions follows this layer; the center of the nearest solvated ions is called the outer Helmholtz plane (OHP). The interaction between the charged electrode and the solvated ions in the OHP is independent of the chemical nature of the ions due to long-range electrostatic forces. These non-specifically adsorbed solvated ions are scattered in three-dimensional regions due to thermal agitation in

the solution. The region between the OHP and bulk solution is known as the diffuse layer, the thickness of which depends on the total concentration of the ions in the solution.^{3, 4} The thickness of the entire double layer decrease with increase of concentration of the medium and for concentrations greater than 10^{-2} M, the thickness is less than $\sim 10^{-6}$ cm.³

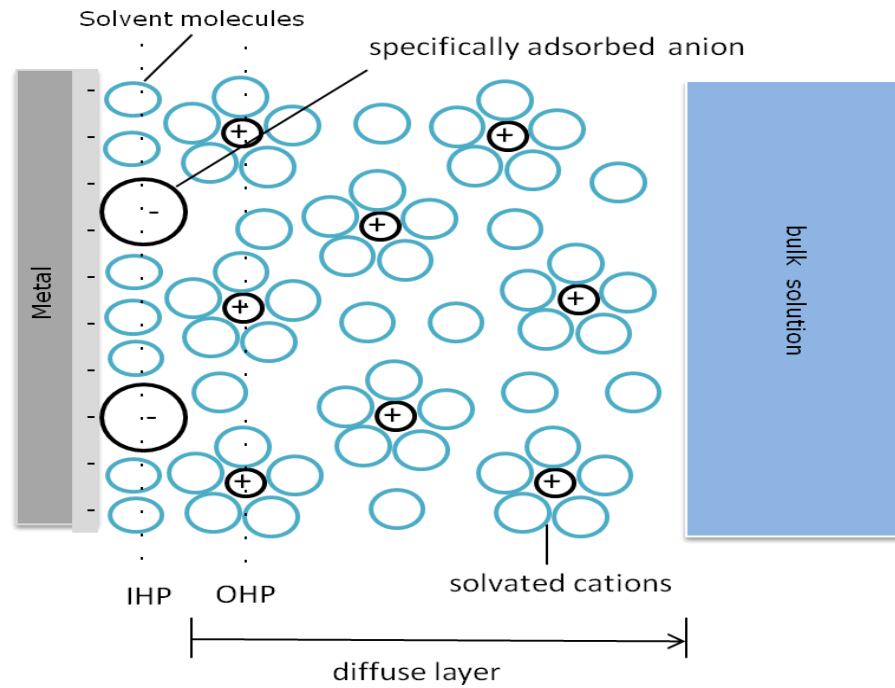


Figure 1.2 Distribution of ions in the double layer region under specifically anion adsorbed condition. IHP is the inner Helmholtz plane and OHP is the outer Helmholtz plane.

The total excess charge density ($\mu\text{C cm}^{-2}$) on the solution side of the double layer, σ^S , will be the sum of the total charge density from specifically adsorbed ions (σ^i) in the inner layer and the excess charge density in the diffuse layer (σ^d), which must counterbalance the charge density on the metal surface (σ^M), is given by Equation 1.2.³

$$\sigma^S = \sigma^i + \sigma^d = -\sigma^M \quad (1.2)$$

For interfacial electron transfer processes, the electron transfer either to or from a metal electrode depends on the difference in energies between the Fermi levels of the solid electrode and the molecular orbital energies of the reacting species. The difference in energy arises due to the potential applied to the electrode and we can vary the rate of electrochemical reactions by varying the applied potential.⁵ When a negative potential is applied, the energy of the electron in Fermi level rises and eventually reaches a point where its energy is equal to that of the lowest unoccupied molecular orbital (LUMO). Hence at this point the electrons jump to LUMO of the redox specie generating a cathodic current. By applying a positive potential to the electrode, the energy of the Fermi level decreases below the energy of electron in the highest occupied molecular orbital (HOMO) of the species in solution. Electrons then jump from the HOMO of the species in solution to the Fermi level of the electrode generating an anodic current.^{3, 6} The basic process is shown in Figure 1.3.

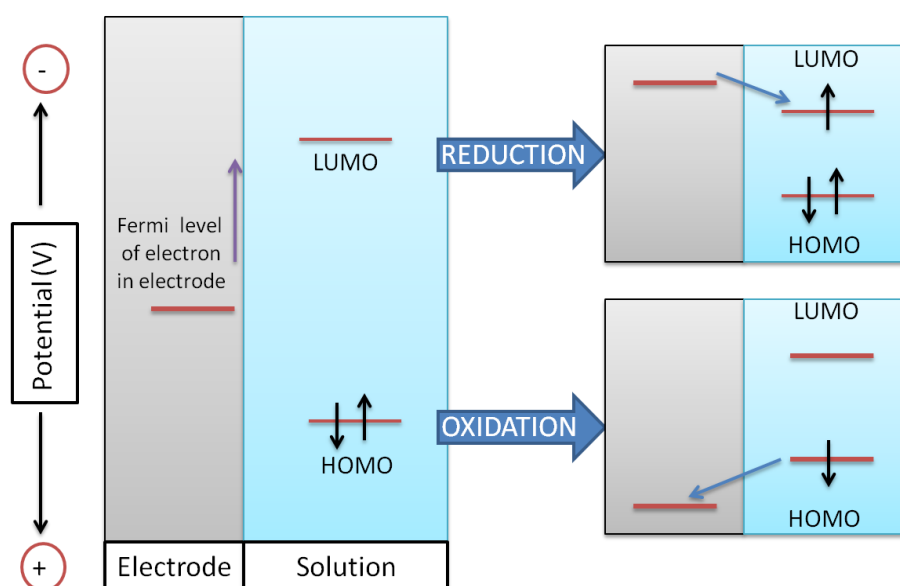


Figure 1.3 Illustration of the charge transfer energetic across the electrode/solution interface.

Electrochemical reactions can proceed through two general types of processes; outer-sphere and inner-sphere processes,^{3, 7-9} as illustrated in Figure 1.4. In an outer-sphere electrode reaction, the interaction of the reactive species with the electrode is weak as it is several angstroms away from the electrode preserving its solvation shell, and having no direct contact with the electrode surface.⁸ The electron transfer between electrode and reacting species takes place by tunneling across at least a monolayer of solvent as shown in Figure 1.4 (A).^{8, 10} In such electrochemical reactions, electron transfer involves the reorganization of the solvent in the vicinity of the reactant because reactant and product carry different charges. This reorientation of the solvent shell is the major factor that determines the rates of these reactions.⁸

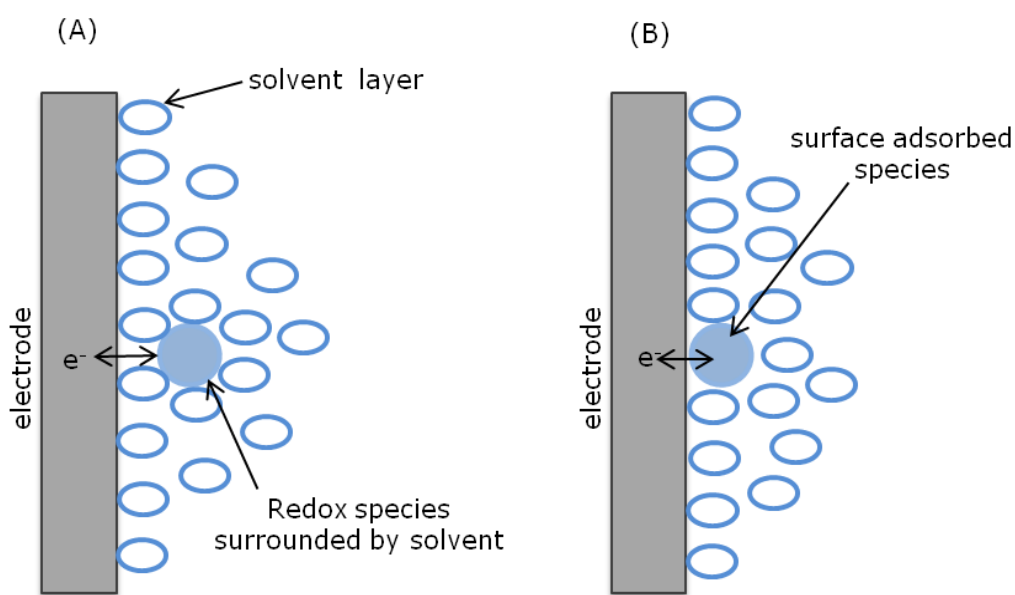


Figure 1.4 Schematic illustration of (A) outer-sphere and (B) inner-sphere electrode reaction mechanism.

Generally, the rate of outer-sphere electrode reactions is almost independent of the nature and composition of the electrode material (except for small double-layer or the presence of films that block

tunneling).^{3, 8, 10} For example, the oxidation of ferrocenemethanol ($\text{FcOH}/\text{FcOH}^+$), ferrocene to ferrocenium (Fc/Fc^+) and reduction of $[\text{Ru}(\text{NH}_3)_6]^{3+}$ to $[\text{Ru}(\text{NH}_3)_6]^{2+}$ are some of the examples of outer-sphere electrode reactions, which are insensitive to electrode materials, and show very similar electrochemical behaviour with Pt, Au, or C electrodes.^{3, 10} Figure 1.5 is a representative of outer-sphere reaction showing reversible oxidation of ferrocene to the ferrocenium ion at Au and Pt obtained in an ionic liquid, $[\text{emim}][\text{EtSO}_4]$. The figure clearly shows that ferrocene behave similarly at both Au and Pt electrodes.

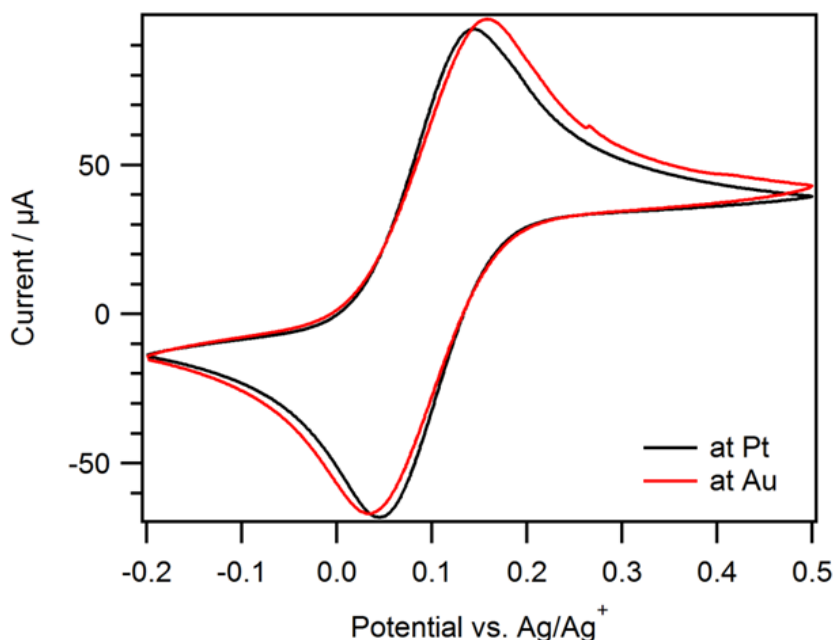


Figure 1.5 Cyclic voltammograms of reversible oxidation of ferrocene (5 mM) in $[\text{emim}][\text{EtSO}_4]$ at a 2 mm diameter Au and Pt electrodes at scan rate of 100 mV s^{-1} .

Alternatively, in inner-sphere electrode reactions the identity of the electrode material play a decisive role.⁸ In such reactions, the reactant, product and/or intermediate species are strongly bound (specifically adsorbed) to the surface of the electrode and electron transfer between the reactant and the electrode takes place through the surface bound species

as shown in Figure 1.4 (B).^{3, 10} The rate of these reactions may be enhanced by using different electrodes and/or electrolytes, or by even modifying the electrode surface. Many inner-sphere reactions have higher reaction rates at Pt electrode than at other electrode materials,¹¹ mainly due to dissociative adsorption of reactants which strongly interact with the metal atoms in such a way that causes breaking of old bonds and formation of new species. For example, H_2 dissociates to adsorbed hydrogen atoms, which are readily oxidized to protons and HCOOH dissociates to CO_2 and H atoms on Pt.^{10, 12}

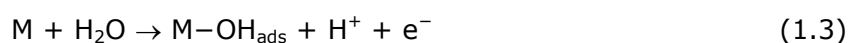
Inner-sphere reactions are also known as electrocatalytic reactions (those in which the reaction rate is sensitive to the nature of electrode material), and are most often studied using aqueous electrolytes. Such reactions, which include the ORR, HOR, HER, reduction of CO_2 , and oxidation of small organic molecules (SOMs), often play key roles in electrochemical energy conversion.¹³ The term electrocatalysis was coined by Kobosev and Monblanova at the beginning of the 20th century while investigating the effect of electrode materials on the rate of the HER.^{8, 11} Many advances in this research field have since been made in order to develop basic knowledge about various important electrocatalytic processes. Some of the inner-sphere electrocatalytic processes that are related to energy production and storage are discussed below.

1.2. Oxide Formation on Metal Surfaces

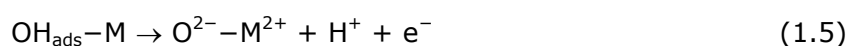
Noble metals can oxidize and become coated with thin oxide films under electrochemical conditions in aqueous solutions.¹⁴⁻²² The extent and mechanism of electrochemical surface oxidation of metals depend on the nature of the metal and its ability to form one or more oxide species, the

composition and pH of the electrolyte, and on the oxide growth polarization conditions such as polarization potential, polarization time and temperature.¹⁹ Due to their favorable electron transfer kinetics and wide anodic potential ranges, noble metals such as Pt, Au and Ag have been widely used as electrode substrates. However, the formation of surface oxide or adsorbed hydrogen layers on these noble metals in aqueous electrolytes may lead to high background currents, which strongly affect the kinetics of the electrode reaction.²³

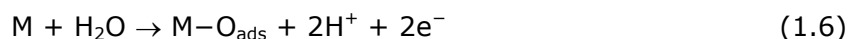
Noble metal atoms lose one or more electrons from their outermost surface layers during oxidation process, and form metallic cation. The O-containing species in solutions takes up the electron lost by metal atom to form surface oxide. In the case of aqueous acidic solutions, the surface oxide species on metals are formed by two pathways.¹⁷⁻²⁰ Pathway 1 involves three steps; in the first step, the electrochemical adsorption of OH_{ads} species at the metal due to splitting of H₂O takes place (Eqn. 1.3).



In the second step, exchange of metal surface atoms and electroadsorbed OH species occur (Eqn. 1.4) and results in a lattice formation. This process is called place-exchange mechanism which is then followed by transfer of another proton and electron from the lattice to form quasi three-dimensional metal oxide (Eqn. 1.5).



The second pathway is similar to the first one but the first step involves the direct discharge of water to electroadsorbed O_{ads} instead of OH_{ads} (Eqn. 1.6), and the release of two H^+ and two electrons, followed by place exchange and lattice formation (Eqn. 1.7).^{14, 18, 19}



Surface oxidation of noble metals can alter their electronic, magnetic and crystallographic properties compared to the bulk phase.²⁰ It is established that the oxide film present on Pt surface can have a significant effect on the mechanism, kinetics and thermodynamics of various redox reactions which occur at the electrode/solution interface.^{3, 18, 20, 24, 25} $Pt-OH_{ads}/Pt-O_{ads}$ can affect the energy changes of a redox reaction at the double layer, offer a barrier to charge transfer across the oxide films and influencing the adsorption behaviour of reaction intermediates and/or products at the catalytic surface by imposing active site-blocking.^{19, 20} The oxide species not only inhibit some reduction processes but also accelerate many oxidation processes taking place at the electrode/electrolyte interface.²⁶ Some of these important electrocatalytic redox reactions and the effect of surface metal oxides on their electrocatalysis are briefly discussed here.

1.2.1. Oxygen Reduction Reaction

The ORR (Eqn. 1.8) occurs at cathode of H_2-O_2 fuel cells. The ORR has a high theoretical reduction potential (1.23 V), showing that there is a

substantial thermodynamic driving force. However, this potential has never been achieved, as this cathodic half-cell reaction is very complex and kinetically slow.



Pt and Pt-based catalysts are most commonly used as electrocatalysts for ORR.²⁷ The cathodic ORR is six or more orders of magnitude slower at Pt-based catalysts than the anodic reaction in fuel cells, the HOR.^{28, 29} The high overpotential and sluggishness of ORR is mainly attributed to the blockage of the electrocatalyst's surface by oxide species, Pt–OH_{ads},³⁰⁻³³ formed due to water oxidation. The surface oxides block the approach of O₂ molecules to the electrocatalyst surface, which significantly reduces its rate of adsorption and reduction. This leads to efficiency loss in proton exchange membrane fuel cells.^{14, 34, 35}

1.2.2. Oxidation of Hydrazine

Electrooxidation of N₂H₄ in aqueous media is another example of an inner-sphere process that is significantly dependent for its voltammetry and kinetics on the surface composition of the electrode.^{24, 36-38} The electrochemical oxidation of N₂H₄ (Eqn. 1.9) has been the subject of study at Pt electrodes in both aqueous acidic and basic media.^{24, 36-39}



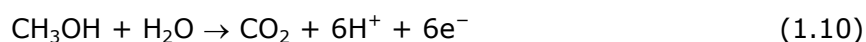
N₂H₄ oxidation at Pt in aqueous electrolytes is particularly sensitive to the composition of the electrode surface. Significant activation

overpotential is observed at Pt compared to the theoretically calculated thermodynamic standard potential, due to formation of various intermediates and adsorbed species, depending on the composition of the electrolyte and electrode facets.^{24, 37, 39} Burke and co-workers reported that catalysis of N₂H₄ oxidation by surface oxides that remain on Pt electrode occurs during potential sweeps.²⁶ Compton and co-workers have also shown recently that Pt-oxides remaining from preceding oxidative scans helps to accelerate N₂H₄ oxidation.²⁴

1.2.3. Oxidation of Small Organic Molecules

The direct electrocatalytic oxidation of SOMs is of major interest at the present time in connection with their great potential in technologies such as fuel cells.^{26, 40} The production, storage and distribution of H₂ are strong limitations for the development of H₂ fuel cells, so other hydrogen carrier fuels such as methanol, ethanol, formic acid, dimethyl ether etc., are being investigated.⁴¹ The direct oxidation of SOMs shows strong relationship between interfacial properties and reactivity.⁴²

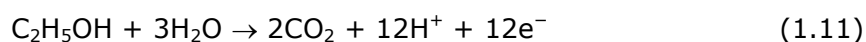
The most often studied fuel is methanol, which has several advantages with respect to H₂. It is a cheap liquid fuel, easily handled, transported and stored.^{41, 43, 44} Methanol oxidation on platinum electrodes in acidic electrolytes is a catalytic reaction producing CO₂ and six electrons per one CH₃OH molecule, (Eqn. 1.10).^{45, 46}



Although the standard equilibrium potential of methanol oxidation is 0.02 V vs. RHE,⁴⁶ a high activation overpotential is observed, even at Pt,

due to the difficulty in the oxidation of strongly adsorbed CO intermediate from the electrocatalysts.^{45, 46} Besides the well-studied methanol, other SOMs such as ethanol, formic acid, dimethyl ether etc. are gaining an increasing attention because they are often much less toxic than methanol.⁴⁰

The electrochemical oxidation of EtOH has drawn increasing interest in electrocatalysis and fuel cells in recent years,⁴⁷⁻⁵⁵ due to its low toxicity, renewability, high boiling point and a high theoretical energy density compared to methanol.⁴⁷ The oxidation of EtOH in aqueous media (see Eqn. 1.11) at Pt catalyst is a complex multiple-electron process that involves the transfer of twelve electrons and twelve protons:



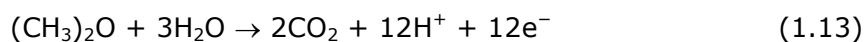
Pt is most commonly used anode catalyst for EtOH oxidation due to its excellent properties in the adsorption and dissociation of ethanol. The main challenge in EtOH oxidation is the cleavage of the C–C bond, that makes complete oxidation of the EtOH difficult and results in slow kinetics of the reaction.⁴¹ Also the formation of adsorbed intermediates, which results in poisoning of the Pt electrode, is another challenge during oxidation of EtOH in aqueous electrolytes.^{41, 44, 47, 54}

Studies of the electrooxidation of HCOOH at noble metal electrodes have increased in number substantially in recent years due to the relatively straightforward nature of the reaction (Eqn. 1.12). This reaction has a significant importance in fundamental research of the oxidation SOMs and practical application to fuel cells.⁵⁶



Generally, electrooxidation of HCOOH to CO₂ proceeds via two oxidation pathways, one involving dehydrogenation of the acid involving one or more weakly-adsorbed reactive intermediates, and the other involving dehydration plus CO_{ads} oxidation at a potential that coincides with the onset of the formation of OH_{ads}.^{47, 57-59} The electrocatalysts that promote the dehydrogenation pathway are preferred in direct formic acid fuel cells. Pt, Pd and Pd-Pt alloy are good electrocatalysts for the oxidation of formic acid. Pd enhances the rate of formic acid oxidation via the direct dehydrogenation path.^{41, 54}

DME is considered a promising alternative fuel in development of the direct DME fuel cells due to its ease of transport and storage, high energy density, minimal crossover, and lower environmental toxicity than methanol and formic acid.^{41, 60-63} DME shows facile electrooxidation activity due to its unique chemical structure (two C—O bonds but no C—C bonds) compared to EtOH and oxidizes completely in the presence of H₂O to CO₂ providing 12 electrons and 12 protons (Eqn. 1.13).^{60, 64, 65}



Pt and Pt-based electrocatalysts are mostly used for DME electrooxidation in aqueous electrolytes. DME oxidation has remarkable structure sensitivity. Various surface adsorbed intermediates such as (CH₃OCH₂—)_{ads}, (CH₃OC—)_{ads}, (HCO)_{ads} and CO_{ads} are observed along with traces of methanol and formic acid during DME electrooxidation at Pt.⁶⁶⁻⁶⁸ A fundamental understanding of the oxidation of DME is required at the electrode/electrolyte interface, not only for the development of a DME-

based fuel cell but also for basic understanding of the reaction mechanism and enhancing the reaction kinetics.

1.3. Electroreduction of CO₂

The industrial and domestic utilization of fossil resources results in the emission of the greenhouse gas CO₂ in to the atmosphere. The steady build-up of CO₂ in the atmosphere is of major environmental concern due to its potential impact on the Earth's climate and has become a topic of growing international interest.⁶⁹⁻⁸⁴ It is, therefore, important to reduce global CO₂ emissions in order to curb the undesirable effects of this major greenhouse gas on human society.⁸⁵ One approach is to reduce the CO₂ emission in every industrial sector. Another approach is to utilize atmospheric CO₂ either by capturing before it is emitted to the atmosphere or by recovering it from the atmosphere via photosynthesis in biomass or via some equivalent artificial process and then convert the gas into useful chemicals.⁸⁵ Although this will not 100 % mitigate CO₂ from the atmosphere as global CO₂ emissions are higher than its consumption in chemical and industrial processes,⁸⁵ it will help to utilize the gas for the production of other useful chemicals and fuel precursors. Various techniques including chemical,^{79, 86} biochemical,⁷⁹ photochemical,^{83, 87} and electrochemical^{75, 76, 79, 88-97} have been investigated for fixation of CO₂ into useful fuels and industrial chemicals. Electrochemical reduction is a promising way that involves the use of electricity to recycle CO₂ to useful chemicals under mild conditions.⁹⁸ Many valuable chemicals including CO, liquid fuels such as methanol, formic acid, and hydrocarbons such as methane, ethylene have been produced by electrochemical reduction of CO₂ in both aqueous and non-aqueous media. Metals such as Au, Ag, Zn, Pd, Ni, and Cd are classed as CO forming and metals such as Pb, Hg, Sn

and In as HCOOH forming metals. Hydrocarbons (CH₄ and C₂H₄), aldehydes and alcohols are formed by CO₂ reduction at metallic Cu catalyst.^{84, 97, 99, 100}

CO₂ is reduced at a high overpotential on most of the electrocatalysts. The high overpotential observed during CO₂ electrocatalysis is mainly due to the formation of a bent intermediate radical anion, CO₂^{•-} from a linear CO₂ molecule (see Eqn. 1.14) at a majority of metal catalysts in both aqueous, and other common non-aqueous media.



This high energy radical anion intermediate offers a huge barrier that must be overcome in order to convert CO₂ to more useful products at low overpotential. It is suggested that a suitable catalyst is required that could stabilize the intermediate radical anion and could help in decreasing the activation energy barrier (see Figure 1.6) and reduce CO₂ at low overpotentials.^{80, 81} The more stable and strongly adsorbed is the intermediate CO₂^{•-}, it is more likely that CO will be formed by CO₂ reduction and formic acid will be formed when CO₂^{•-} is free or weakly adsorbed to the electrode surface. Apart from an efficient catalyst, an electrolytic media is needed that can stabilize the formation of the intermediate CO₂^{•-} and can reduce activation energy for the reduction of CO₂.^{77, 80}

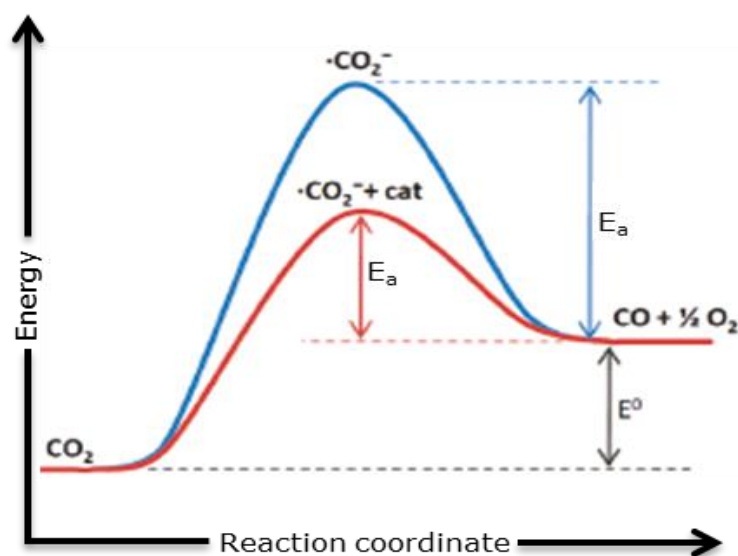


Figure 1.6 Energy profile diagram for CO_2 conversion reaction to product showing the importance of catalyst and co-catalyst (electrolyte) in lowering the activation energy (E_a) barrier for the intermediate anion radical, $\text{CO}_2^{\cdot-}$ formation, and thus improving the energetic efficiency of the conversion.

1.4. Ionic Liquids

Ionic liquids are salts that are liquids below $100\text{ }^\circ\text{C}$.¹⁰¹⁻¹⁰⁷ They are also known as room temperature ionic liquid (RTILs) or ambient temperature organic salts. ILs are easy to handle compared to inorganic molten salts, which are more viscous, highly corrosive, and melt at very high temperature (e.g. NaCl melts at 1074 K).^{108, 109} ILs typically contain one large and asymmetric organic cation and organic or inorganic anions. The radius of the IL's ions is substantially larger than that of an alkaline cation or halide ion composing molten inorganic salt.¹⁰⁴⁻¹⁰⁶ The electrostatic interactions between the molecular ions that comprise ILs are such that they are liquid at low temperature and in most cases, these coulombic forces are strong enough to make the vapor pressure of ILs negligible at room temperature.^{103, 108-110}

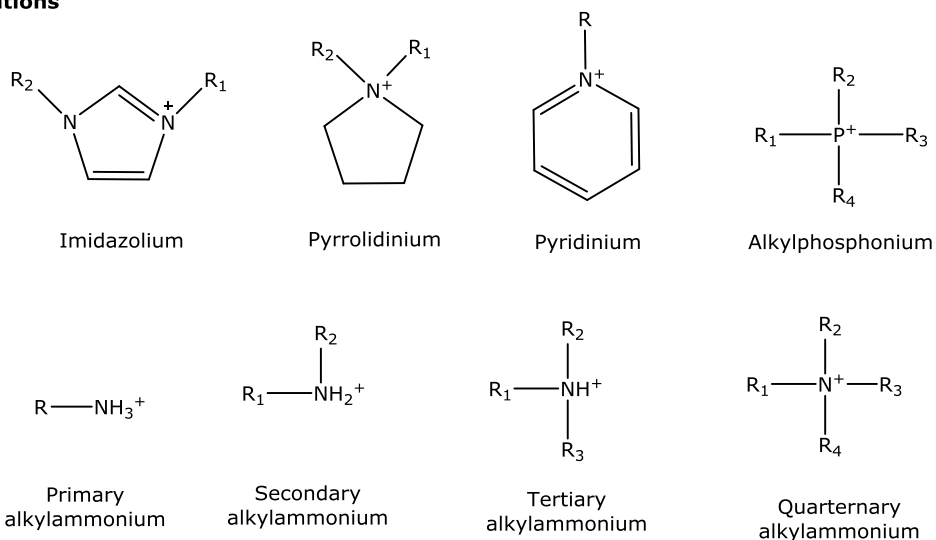
ILs are not new; the first report about them goes back to 1914, when the IL ethylammonium nitrate, $[\text{EtNH}_3][\text{NO}_3]$, was reported by Walden.^{105, 107} Since then a huge number of publications have appeared about the synthesis and bulk properties of these new solvent describing their unique physiochemical properties (common of which will be describe below), new solvents for synthesis and catalysis and multitude of potential applications.^{105, 107, 111} ILs are available in a large number due to the variety of different cations and anions used in their synthesis. The most common cations of ionic liquids are imidazolium, pyridinium, quaternary ammonium etc., and the anions can range from simple halides such as F^- , Cl^- , Br^- to bulk anions likes nitrate, NO_3^- sulphate, SO_4^- , acetate, CH_3COO^- tetrafluoroborate, BF_4^- , trifluoromethanesulfonate, CF_3SO_3^- or $[\text{TfO}]^-$, hexaflourophosphate, PF_6^- , bis(trifluoromethanesulfonyl) imide, $[\text{Tf}_2\text{N}]^-$. Some of the common cations and anions use to prepare RTILs are shown in the scheme 1.1.

1.4.1. Classification of Ionic Liquids

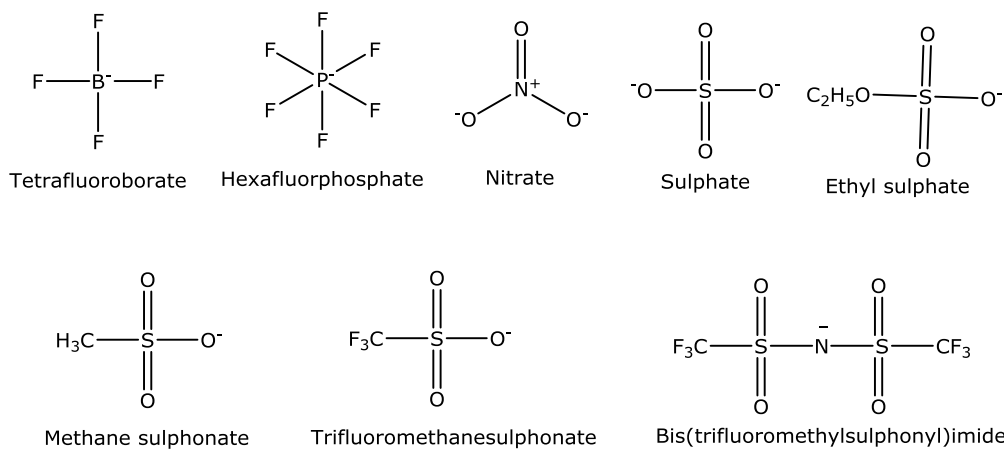
Based on the mechanism of cation formation and proton carrying capacity, ILs are generally divided into two main categories; protic ionic liquids (PILs) and aprotic ionic liquids (APILs).^{106, 112} In PILs, the cation is formed by accepting a proton from a Brønsted acid during neutralization reaction, while in APILs the cation is formed by accepting any group other than a proton to the basic site of the parent base molecule.^{106, 112-114} APILs generally have higher viscosities, higher melting points and lower ionic conductivities than protic ionic liquids.¹¹³ Aprotic ionic liquids have no electrochemically available mobile proton or proton acceptor/donor site in

their structure. In contrast, protic ionic liquids can conduct protons and therefore can be used as electrolyte for fuel cells.¹¹⁵⁻¹¹⁷

Cations



Anions



Scheme 1.1 Common cations and anions used for making ionic liquids.

PILs can be synthesized relatively easily on a large scale at low cost by simple acid-base neutralization reaction and without much necessity for further purification. Their physical and chemical properties are strongly dependent on the extent of proton transfer from the acid to the base.¹¹⁸ For the PIL to be a pure salt it is suggested that proton transfer should be

at least 99 %, and the difference between the pK_a of the acid and base, should be at least 10 to get the desired thermally stable and lowest vapor pressure PIL.¹¹³ Watanabe and co-workers reported that thermal stability of a PIL increases with the increasing acidity of the acid.^{116, 117} Transfer of the proton is energetic and a thermally stable PIL can be obtained by reacting super strong acid such as bis(trifluoromethanesulfonyl)imide, ($F_3CSO_2NHO_2SCF_3$) and triflic acid (F_3CSO_3H) with a strong base.^{106, 116} The concentration of protons of different PILs is different and is in the range of 5–10 M.¹¹⁸ While PILs have high H^+ concentration, their properties vary from strongly acidic to strongly basic in character.¹¹⁸

1.4.2. Electrochemically Important Properties of ILs

Ionic liquids have unique physiochemical characteristics, completely different from ordinary molecular liquids. Negligible volatility and low vapor pressure at ambient temperature, intrinsic ionic conductivity, high polarity as well as thermal, chemical and electrochemical stability are some of the unique properties of the ionic liquids. Their properties are dependent on the nature of cations and anions and can be tuned.^{104, 107, 119} Considering the broad range of available ILs and their applications, it is difficult to generalise their properties and to report general tendencies.¹²⁰ We describe below some the properties of ILs that are important for electrochemical studies of these solvents.

1.4.2.1. Electrochemical Window of Ionic Liquids

Electrochemical window is one of the important characteristic measured in electrochemical studies that give important information about the electrochemical stability of solvents.¹⁰⁶ The electrochemical window

represents the potential range between the cathodic potential limit (E_{CL}) and anodic potential limit (E_{AL}) of a solvent or electrolyte as shown in the figure 1.7.^{106, 121, 122} Linear sweep voltammetry or cyclic voltammetry are the most common electrochemical methods used to measure the electrochemical window of electroactive materials.

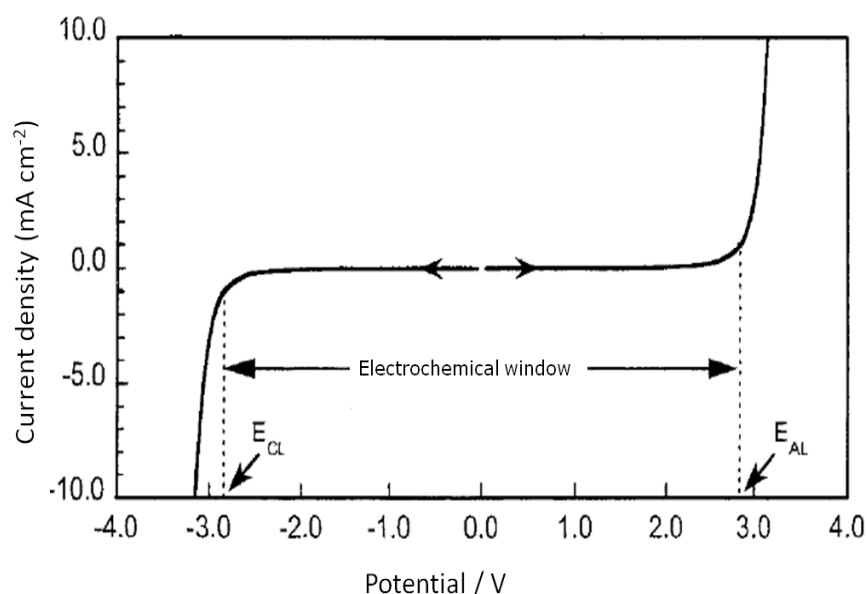


Figure 1.7 A typical CV showing the cathodic and anodic potential limits to evaluate electrochemical window.¹⁰⁶

ILs have wide electrochemical potential window, generally ranging from 3–6 V for most of PILs and APILs and even up to 7.0 V for ILs containing $[BMIm]^+$ cation and $[BF_4]^-$ anions.^{122, 123} The presence of any electroactive impurity narrows down the actual electrochemical window of the ILs at a particular electrode surface.^{106, 110, 122} Water is one of the common contaminants in ILs, even in hydrophobic ionic liquid; an increase of water concentration significantly reduces the electrochemical window of the ILs.^{124, 125} The electrochemical window of an IL also depends on the nature of the working electrode and is different at different electrode materials.¹²⁶

1.4.2.2. Conductivity of Ionic Liquids

Conductivity is the most important property of solvents in electrochemical analysis. IL conductivity is an interesting property to consider as ILs can play the role of both solvents and electrolytes in electrochemical reactions. ILs have intrinsic conductivity due to very high concentration of ions i.e. they have > 99 % ionicity.¹²⁰ Generally, ionic liquids have a broad range of conductivities, ranging from 0.1 to 20 mS cm⁻¹. Most of the ionic liquids have ionic conductivity of over 10 mS cm⁻¹ at ambient temperature larger than the ionic conductivity of 0.1 M KCl solution.^{103, 104} The conductivity of ILs depends on viscosity and the mobility of the ions.^{125, 127} Mobility of ions depends on the size and shape of the constituent ions in the ILs.¹²⁵ The ions mobilities in room temperature ionic liquids is high at room temperature, compared to conventional solvents and therefore, do not require any supporting electrolyte during electrochemical studies.^{103, 125} Many other factors such as viscosity, density, ion size, anionic charge delocalization and aggregations can also affect the conductivity of ILs.¹²⁸

1.4.2.3. Viscosity of Ionic Liquids

In electrochemistry, viscosity of the electrolyte material is of vital importance as it influences the ionic conductivity and transport properties such as diffusion.¹²⁰ The higher the viscosity of a solvent, the slower the rate of diffusion of the electroactive species towards the electrode surface as the diffusion coefficient (D) is inversely related to viscosity (η) by the Stoke-Einstein equation (Eqn. 1.15).^{3, 106, 120, 125}

$$D = kT / 6\pi\eta r \quad (1.15)$$

where k is Boltzmann constant ($1.3807 \times 10^{-23} \text{ J K}^{-1}$), T absolute temperature and ' r ' hydrodynamic constant or Stoke's constant.

Ionic liquids have relatively high viscosities, ranging from $20\text{--}30 \times 10^3 \text{ cP}$ at ambient temperature, which is one to three orders of magnitude higher than that of conventional solvents.^{103, 120, 125} The nature of cation and anion that constitute the IL have drastic effect on its viscosity and increase with increasing size, shape, chain length, and molecular mass of cation and anion.¹²⁵ The design of less viscous ILs is still a challenge for many applications.¹²⁰

1.4.3. Electrochemical Applications of Ionic liquids

Recently, the study of electrocatalytic reactions has extended to RTIL-based systems. Due to the diversity of cation-anion combinations and favorable properties, ILs are being used nowadays as alternatives to conventional aqueous and organic electrolytes in an increasing number of electrochemical investigations including both fundamental studies of mass and charge transport dynamics as well as the development of new electrochemical energy conversion and storage devices.^{13, 102, 106, 109, 120, 129} In many cases, these developments have been driven by a desire to fabricate new RTIL-based fuel cells and batteries that can operate at higher temperatures, or are safer, than conventional systems.¹³ They are also employed as electrolytes for enhancing the performance of dye-sensitized solar cells, supercapacitors, double layer capacitors and thermo-electrochemical cells, actuators (in which mechanical energy is produce from electrical energy) and electrolyzers.^{101-103, 129, 130} In addition, ILs are employed as gas sensors, for CO_2 capture agents and in electrochemical biosensing, electrodeposition, electrosynthesis and electrocatalysis.¹³¹

1.5. Objectives of the Project

Ionic liquids have generally been considered as an environmental friendly alternative to the conventional organic solvents in a variety of electrochemical reactions.^{132, 133} Most of the research on ILs have focused mainly on exploring relationships between bulk liquid properties, such as thermal stability, viscosity and conductivity, and electrochemical behaviour¹⁰² and a very little attention is paid to the surface electrocatalysis in the IL environment. Therefore, this project was designed to investigate a series of important oxidation and reduction electrocatalytic reactions that occur at electrode/ILs interface within the potential window of ionic liquids, using electrochemical tools in order to understand surface electrocatalysis in this newer electrolytic media.

The ultimate aim was to develop a complete understanding of the mechanism and kinetics of the growth of surface oxide films at Pt electrodes in PILs, and compare it with that in aqueous electrolyte systems. Therefore, a detailed investigation of the surface electrochemistry of polycrystalline Pt, especially the growth of oxide films from oxidation of trace water in PILs and the interfacial cyclic redox mechanism of electrocatalysis, was undertaken using different voltammetry techniques and discussed in detail in Chapter 3.

The catalytic role of the surface Pt-oxides during electrocatalytic oxidation of N_2H_4 , HCOOH , EtOH , and DME in PILs have also been investigated and discussed in detail in the following chapters.

Keeping in view the electrocatalytic importance of ionic liquids, the electrocatalytic reduction of CO_2 in aprotic ionic liquids was also investigated at various planar electrocatalyst surfaces, and the results have been discussed in Chapter 7.

Chapter 2: Experimental and Review of Techniques

2.1. Electrochemical Techniques

A variety of electrochemical techniques including linear sweep voltammetry, cyclic voltammetry and chronoamperometry have been used for the electrochemical analysis of electron transfer reactions taking place at the electrode/electrolyte interface.^{3, 4, 119} The electroanalytical techniques that were used in this work are described below.

2.1.1. Linear Sweep Voltammetry

Voltammetry is an electrochemical technique used for measurement of current (i) as a function of potential (E).¹³⁴ Linear sweep voltammetry is a potential sweep voltammetric technique in which the potential of the working electrode is ramped from an initial value (E_i) to a final limit (E_f), as shown in the figure 2.1 A, at a constant sweep rate.⁴ The "sweep rate" or "scan rate" is the rate of potential change denoted by ' ν ' and has the units of volts per second ($V\ s^{-1}$). The current flowing through the working electrode for the reaction of interest (either oxidation or reduction) is measured during the potential sweep. The flow of current recorded during linear sweep voltammetry is plotted on the vertical axis in units of current, typically ranging from A to μA . Alternatively the current may be expressed as current density, (current/electrode area) $A\ cm^{-2}$. The potential in units of volts is plotted on the horizontal axis. The resulting output having a peak shape, as shown in Figure 2.1 B, is known as a linear sweep voltammogram (LSV).³

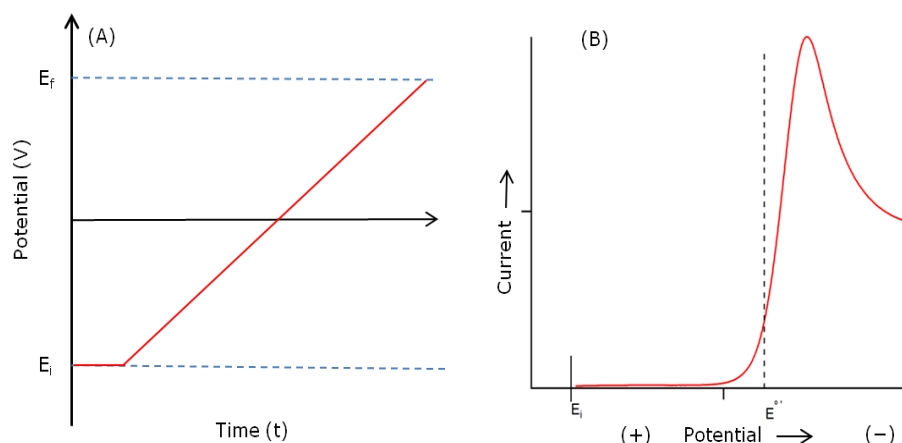


Figure 2.1 (A) Linear potential sweep from lower potential, E_i to upper potential, E_f (B) The corresponding current-potential response.

Let us assume the following general redox reaction is taking place at the working electrode.



Let us also assume that only the oxidized form (O) of the redox couple is initially present in the solution. The potential of the working electrode is scanned from a positive value to the negative potential limit. Initially, at a potential well positive of formal potential ($E^{0'}$) of the redox couple, the current flowing is non-faradaic until the potential approaches $E^{0'}$. The non-faradaic current is current that flows to charge the double layer. It is evident from the current rise in Figure 2.1 B that at certain potential, slightly positive of $E^{0'}$, the reduction of O begins to form the reduced species R ($O + ne^- \rightarrow R$). This cathodic current, which is due to charge transfer across the electrified interface, is known as faradaic current because it obeys Faraday's law (i.e. a charge of $n \times 96,485$ coulombs is associated with the electrolysis of 1 mole of a substance). In this potential

range, i.e. in the vicinity of the formal potential of the species, $[O] > [R]$, but still some R is formed to satisfy the Nernst equation (2.2).^{3, 135}

$$E = E^{\circ'} + \frac{RT}{nF} \ln \frac{[O]}{[R]} \quad (2.2)$$

where R is the universal gas constant, $8.3143 \text{ J K}^{-1} \text{ mol}^{-1}$, T is absolute temperature, F is the Faraday constant ($96,485 \text{ C mol}^{-1}$), and n is the number of electrons involved in the redox reaction. $[O]$ and $[R]$ are the concentrations of the oxidized and reduced forms of the electroactive species.³ $E^{\circ'}$ is related to the standard redox potential, E° by Equation 2.3.

$$E^{\circ'} = E^{\circ} + \frac{RT}{nF} \ln \frac{\gamma_O}{\gamma_R} \quad (2.3)$$

where γ_O and γ_R are the activity coefficients of species O and R, respectively. As the potential continues to move beyond $E^{\circ'}$ (i.e. growing more negative), the surface concentration of O decreases and the concentration of R increases in order to satisfy the Nernst equation; hence the current rises. This creates a concentration gradient, called the *diffusion layer*. The thickness or width of the diffusion layer, δ_D varies with time, t is given by Equation 2.4.

$$\delta_D = (\pi Dt)^{1/2} \quad (2.4)$$

Reactant O moves from the bulk solution to the electrode surface (mass transfer) down the concentration gradient and is consumed at the

surface of the electrode. The current becomes limited by mass transport causing the cathodic peak current ($i_{p,c}$) and the potential at this point is known as the cathodic peak potential ($E_{p,c}$). Beyond this point the current decreases with the passage of time showing chronoamperometric behaviour (i.e. obeying Cottrell Equation, described in Section 2.1.3) and is independent of potential. The mode of mass transfer down a concentration gradient is called diffusion. Two other modes, migration (movement of a charged body under the influence of an electric field) or convection (hydrodynamic transport by stirring) can also be employed for the movement of material from bulk solution to the surface of electrode in the solution. However, it is not desirable to use all the three modes of mass transfer because it makes the electrochemical system complicated. Therefore, electrochemical systems are designed to avoid the contribution of one or two of the mass-transfer modes. The migration of charged reactants and products in the voltammetry experiments is suppressed by adding an inert electrolyte, called a supporting electrolyte, at a concentration much higher than that of the electroactive species. Mass transport from convection is prevented by avoiding vibrations or stirring, so that the solution remain quiescent in the electrochemical cell.^{3, 4}

The characteristics of the linear sweep voltammogram depend on the potential sweep rate, nature of electrolyte and rate of electron transfer between the electrode and electrolyte. The potential scan rate is calculated from the slope of the line shown in the Figure 2.1 A. The shape of the LSV varies with scan rate; the magnitude of the peak current increases with increasing scan rate.⁴ Depending on the potential scan rate, the diffusion layer near to the electrode has different characteristics. For example at high scan rates, the thickness of the diffusion layer is low and the flux of electroactive species is high towards the electrode surface.

2.1.2. Cyclic Voltammetry

Cyclic voltammetry, like linear sweep voltammetry, is a type of potential sweep voltammetry in which the potential of an electrode is ramped at a constant rate between preselected limits, and the current flowing through the electrode is measured. When the potential of the working electrode is swept from the initial limit to another value, and then the direction of potential scan is reversed, (Figure 2.2. A), it completes a cycle; therefore the term 'cyclic' is used for this voltammetric technique. The product formed on the forward sweep can be detected in the reverse sweep if the product is both stable and electrochemically active. The resulting i - E plot (Figure 2.2 B), is known as a *cyclic voltammogram (CV)* ^{3, 4, 119}

Considering the above example general Equation 2.1, when the scan is reversed at E_r , then product R, formed during forward sweep, will start to be oxidized back to O ($R \rightarrow O + ne^-$) and anodic current flows. The anodic current rapidly causing the current to peak and is called the anodic peak current ($i_{p,a}$) and the peak potential at this stage is called anodic peak potential ($E_{p,a}$). Beyond this point the current decays and the vicinity of the electrode is depleted of R until the starting potential is reached. One CV cycle has now been completed. The number of cycles recorded depends on the information required.

Cyclic voltammetry is one of the most popular and widely used electrochemical techniques available for initial investigations of new electroactive substances and can provide a significant amount of information within a low experimental time.^{3, 4} It is the most commonly encountered method applied to study the kinetics, thermodynamics, and mechanism of simple as well as complicated electrode reactions including biosynthetic and enzymatic catalysis.^{3, 4, 122, 134} This technique can be utilized and applied in the analysis of media with and without adding

supporting electrolyte, solutions, suspensions, polymers, solids, and biological systems such as enzymes.¹²²

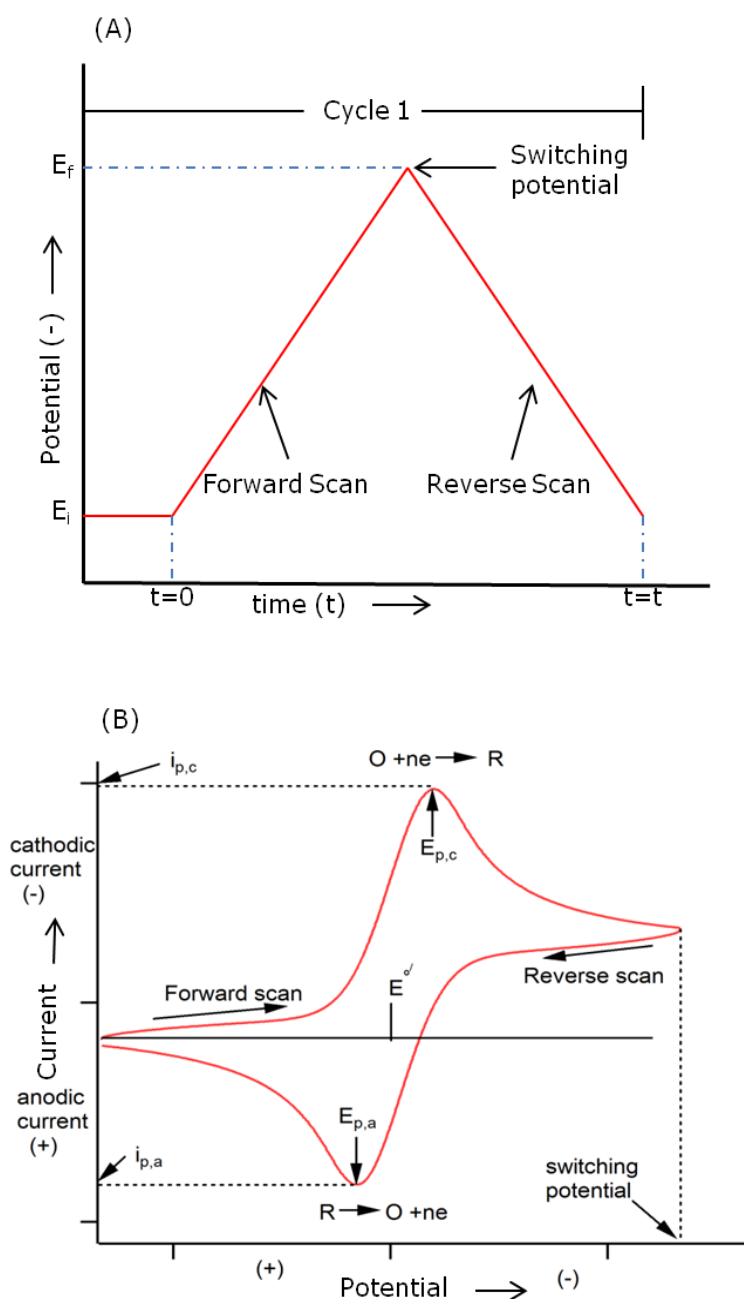


Figure 2.2 (A) The triangular potential waveform and (B) corresponding i - E response-cyclic voltammogram.

2.1.2.1. Electrochemical Reversibility and Data Interpretation

A redox reaction that obeys the Nernst Equation (2.2) is an electrochemically reversible or Nernstian reaction. For example, hydrogen

oxidation at a Pt electrode in aqueous acid system shows Nernstian behaviour. Some other criteria for diagnosing reversibility of an electrochemical process during cyclic voltammetry are:^{3, 4, 134}

- The magnitude of i_p is directly proportional to the bulk concentration of analyte, C (in mol dm^{-3}) and the square root of the scan rate, $v^{1/2}$ at 25 °C and is given by Randles-Sevcik equation (2.5).^{3, 134}

$$i_p = (2.69 \times 10^5) n^{3/2} A C D^{1/2} v^{1/2} \quad (2.5)$$

where D is the diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$).^{3, 4, 134} Peak current is measured by comparing the maximum recorded current with the baseline current that has been extrapolated from the flat current observed before the onset of the redox process of interest. This means that a plot of i_p versus $v^{1/2}$ will give a straight line, with the slope equal to $(2.69 \times 10^5) n^{3/2} A C D^{1/2}$.

- The cathodic peak current must be equal to the anodic peak current ($i_{p,a} = i_{p,c}$)
- The formal potential for a reversible redox mediator is related to the peak potentials and is the average of $E_{p,c}$ and $E_{p,a}$ (Equation 2.6)⁴

$$E^0 = (E_{p,a} + E_{p,c})/2 \quad (2.6)$$

- Both $E_{p,a}$ and $E_{p,c}$ are independent of the scan rate
- The separation between $E_{p,a}$ and $E_{p,c}$ i.e. ΔE_p is related by Equation 2.7 for an n -electron redox couple, at 25 °C.

$$\Delta E_p = E_{p,a} - E_{p,c} = 59/n \text{ mV} \quad (2.7)$$

By contrast, if an electrochemical process in cyclic voltammetry does not obey the Nernst equation and/or the above criteria then the electrochemical process is *irreversible* or *quasi-reversible*.^{3, 4, 134}

2.1.3. Chronoamperometry

Chronoamperometry ('Chrono-' meaning time and 'amp' meaning current) is a potential step electrochemical technique in which the working electrode potential is usually stepped from an initial value, at which no electrochemical reaction occurs, to a second potential, at which the reaction occurs at the diffusion-controlled rate. The resulting current is recorded as a function of time.¹³⁴ Again, consider the general reaction (2.1) in which O reduces to R. Let E_1 be the potential where faradaic processes or electrochemical reduction do not occur. At certain sufficiently negative potential the kinetics for reduction of O become so rapid that the surface concentration of O goes nearly to zero and become "mass-transfer-limited"; let it be E_2 (Figure 2.3 A). This current that flows at short times is very high. This creates a concentration gradient that in turn produces a flux of O to the electrode surface. Since this arriving material cannot coexist with the electrode at E_2 , it must be eliminated by reduction. Hence the flux of O as well as the current is proportional to the concentration gradient at the electrode surface. However, the continued O flux causes the zone of O depletion to thicken; thus the slope of the concentration profile at the surface decreases with time as shown in the Figure 2.3 B. The faradaic current also declines with time (Figure 2.3 C) as described by the Cottrell Equation (2.8).

$$i = nFACD^{1/2}\pi^{-1/2}t^{-1/2} \quad (2.8)$$

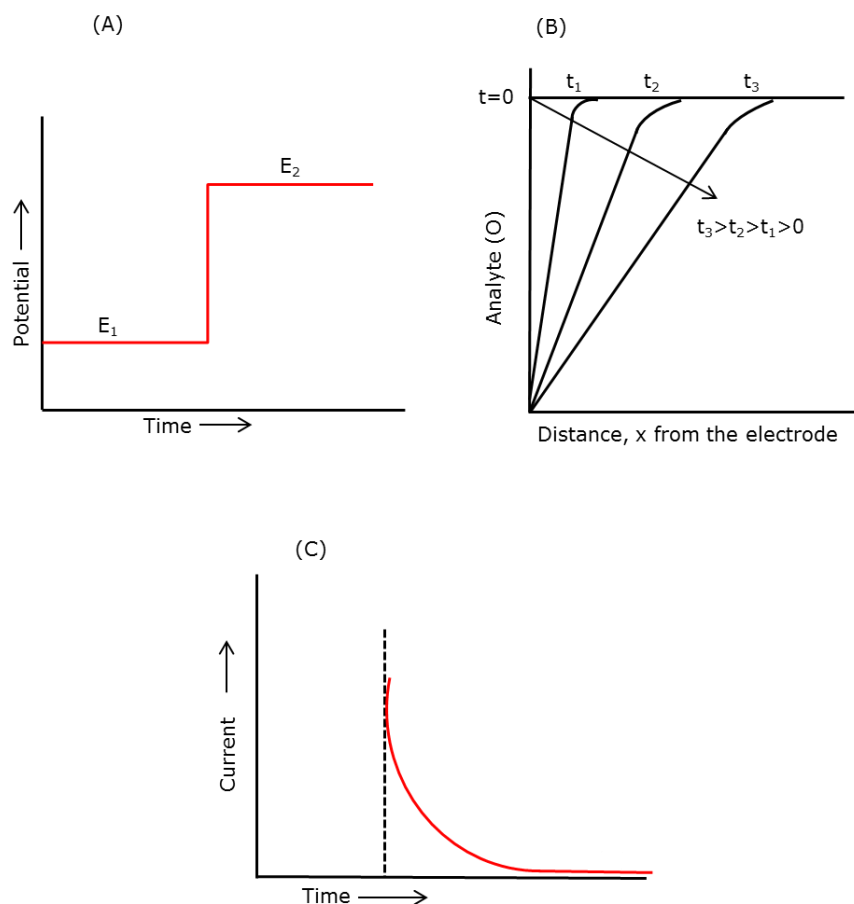


Figure 2.3 (A) Waveform for a potential step experiment in which species O is electrochemically inactive at initial applied potential E_1 , but is reduced at a diffusion-limited rate at a potential E_2 (B) Concentration gradient for the analyte O showing the growth of diffusion layer thickness with time. (C) Current flow vs. time.

The Cottrell Equation predicts that current decreases inversely with the square root of time, $t^{1/2}$. When i is plotted against $t^{-1/2}$, a straight line passing through the origin will be obtained, and this is often used as a test for diffusion control. The gradient of the plot can be used to find the diffusion coefficient of the species O if C is known. During chronoamperometry experiments, t should not exceed 10 s due to natural convection caused by the density gradients,³ and the experiment will cease to remain diffusion controlled. In addition, data recorded at time less than 1 ms is affected by charging of the electrode and therefore, data

between 1ms and 10 s is usually analyzed. Also the solution needs to be stirred between successive experiments to re-establish the initial condition where the concentration of oxidized species O at the electrode surface is restored, and is the same as the bulk concentration of O.³

2.2. X-Ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) provides information on the chemical and electronic environments of elements and their relative concentrations near the surface region of solid materials. This technique, which was developed by Kai Siegbahn in 1981, is probably the most widely used surface sensitive spectroscopic technique. XPS can be employed for surface analysis of both insulators and conductors in surface areas from a few microns to a few millimeters across. This surface analytical technique has applications in many research fields including polymer science, metallurgy, microelectronics and heterogeneous catalysis.^{111, 136, 137}

XPS measures the binding energies of electrons when samples become ionized upon X-ray irradiation (experiments are usually undertaken in vacuum with pressures between 10^{-8} and 10^{-6} mbar) obtained from a metal source with characteristic energy, (e.g. Al K α = 1486.6 eV). X-rays are passed through a monochromator containing a diffracting quartz crystal, which results in an intense photon flux that can be focused onto a sample surface and penetrates several micrometers into a sample to eject photoelectrons from the surface region of the sample are ejected and detected. It is for this reason this technique is a surface sensitive analytical technique.¹¹¹

When a core electron is ejected by the incident X-rays, the hole created by the escaping electron is filled by an outer electron which is

shown at the right side of Figure 2.4. The energy of this transition is balanced by the emission of a characteristic X-ray or by an Auger electron. That is why in XPS Auger electrons analysis are also detected.^{111, 138} The emitted photoelectron and Auger electrons then pass through a lens that reduces their speed and focuses them onto an electron energy analyzer called a concentric hemispherical analyzer (CHA). Here in the analyzer, the photoelectrons pass between two concentric plates set at different voltages. Then a detector called a channel electron multiplier detector multiplies the electron signals and measures their energy as a function of velocity. By counting the emitted electrons (photoelectrons and auger electrons), as counts per second (CPS) versus binding energy, BE (the energy difference between the initial state and final state of atom after emission of the photoelectrons), a spectrum representing the surface composition is obtained (Figure 2.4).^{111, 136, 137}

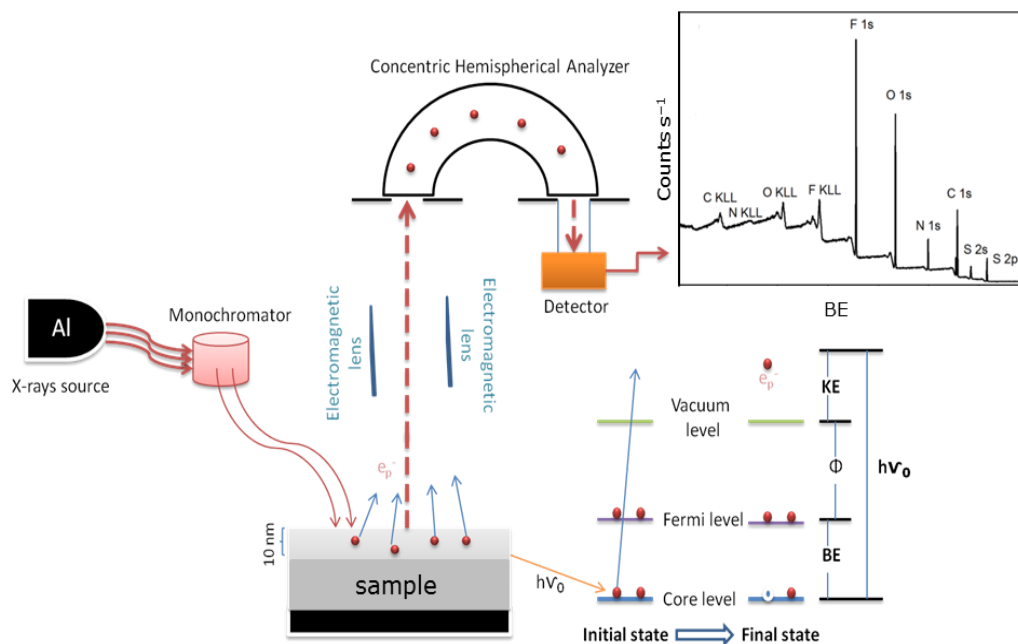


Figure 2.4 Schematic of the XPS experimental set-up and the ionization pattern in the sample after passing X-rays.

In the XP spectrum, the energy of each peak is characteristic of an element, the area under the peak gives quantitative information, and the

peak shape and position is related to the oxidation states and chemical environment of atoms present in the sample volume.^{111, 139} The kinetic energy (K.E) of the ejected photoelectrons is recorded and the BEs calculated according to the Einstein Equation 2.9.

$$KE = h\nu_0 - BE - \Phi \quad (2.9)$$

where $h\nu_0$ is the incident energy of X-rays and Φ is the energy required to move an electron to vacuum from its Fermi level and is called the work function.

The use of UHV conditions is important as it limits the adsorption of gas molecules onto the sample surface, and also allows a collision-free environment so that the emitted photoelectrons are not scattered by inelastic collisions with gas molecules when travelling from the sample to the detector.^{111, 136, 137} For this purpose turbomolecular and sputter ion sublimation pumps are typically used in order to achieve the required pressures in the main analysis chamber.¹³⁸ The monochromator has quartz crystals which is important as it eliminates residual intensities of other wavelength radiations (i.e. satellite and Bremsstrahlung radiation), intensifies the flux of photons passing through a small spot (10 μm) on the sample surface and also increases the distance between the sample and X-ray source, hence, reducing the risk of back scattering of electrons and overheating.¹¹¹

Two types of XP spectra can be recorded, either as a high-resolution scan, or a wide (or survey) scan. Wide scan spectra are recorded across the whole energy range of emitted photoelectrons (for example in the case of Al K α approximately around 1486.6 eV). Figure 2.5 shows a wide scan

spectrum obtained for the ionic liquid diethylmethyammonium trifluoromethanesulfonate, [dema][TfO].

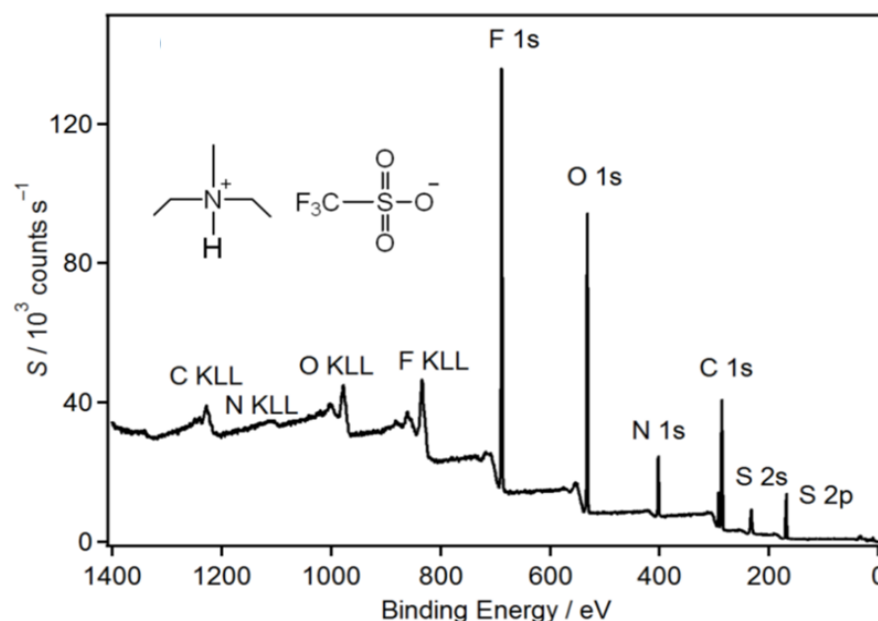


Figure 2.5 A typical wide scan spectrum of the ionic liquid [dema][TfO] (structure shown in the inset).¹⁴⁰

It consists of sharp, core peaks (0 to < 800 eV) that correspond to the photoelectrons emitted from the sample without any collisions or energy losses, which are characteristic of each element to be identified, except for H and He. Each element also yields, along with core lines, some characteristic lines between 1400–800 eV, which are called Auger marks that are useful to get information about the composition of the elements. For example in the Auger line range, in the line denoting KLL, the photoelectron belonged to the K shell and the relaxing and emitted electrons are from the L shell.^{111, 139} Sometimes, low intensity lines are obtained at BE <30 eV that correspond to the emission from the valence bands of the sample. The survey scan can also have a background signal of the electrons that suffer energy losses due to inelastic collisions before escaping from the surface.¹⁴⁰ The relative atomic concentration of all elements present in the sample can be calculated from the wide scan XP

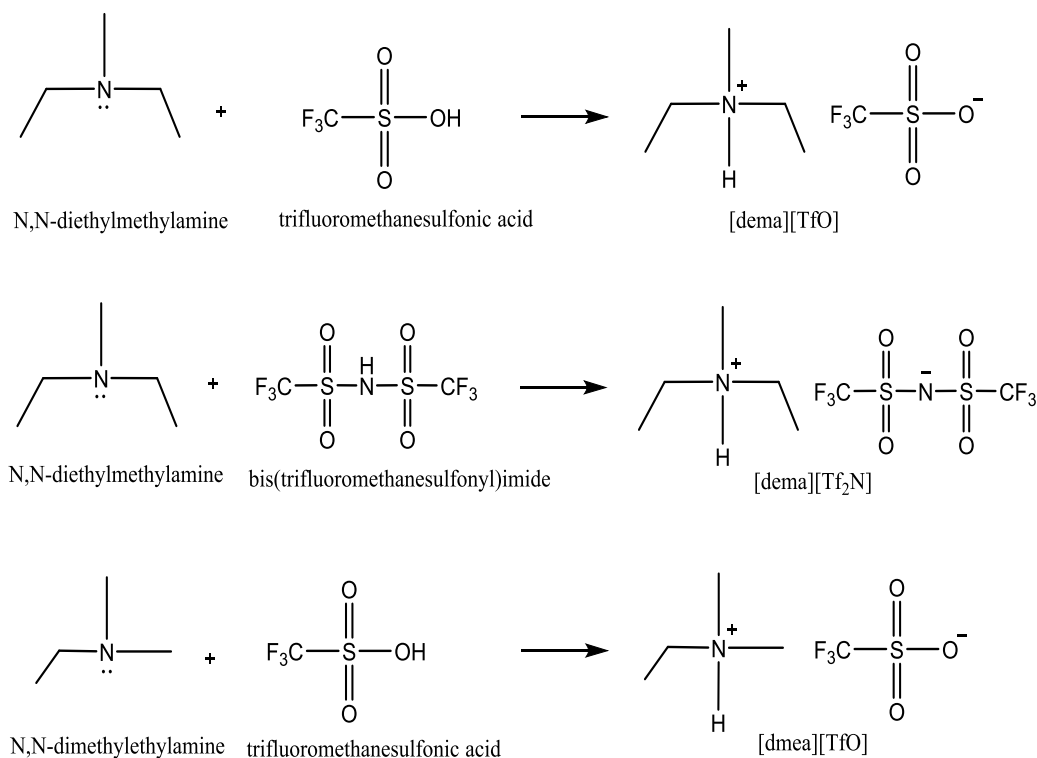
spectra by employing the relative sensitivity factor (RSF) obtained from the Kratos Library. Typically, a fitting procedure is developed with consideration of the stoichiometry and chemical structure of the sample.¹¹¹ High-resolution scans focus on a particular energy region (usually 10–40 eV) to evaluate the oxidation state or bonding nature particularly of elements. A specific element may show many core peaks in the wide scan, however, in high resolution spectrum the most intense photoemission peaks are analysed. Time for analysis, at each energy value, is longer, and pass energy of 20 eV or less is generally used.

2.3. Synthesis of Ionic Liquids

The ionic liquids used in the study were the protic ionic liquids diethylmethylammonium trifluoromethanesulfonate, [dema][TfO], diethylmethylammonium bis(trifluoromethanesulfonyl)imide, [dema][Tf₂N] and dimethylethylammonium trifluoromethanesulfonate, [dmea][TfO]. They were synthesized in our laboratory by simple neutralization of the precursor acids and bases (Scheme 2.1), using standard procedures.^{113, 116, 141, 142} The synthesis of PILs is relatively simple, and provided that the parent acid and base are pure, little post-synthesis purification is necessary.¹⁴³

To describe the process briefly, equimolar amounts of the acid and base in each case were reacted together in a dry three-necked flask. Since the acid-base reactions were highly exothermic, addition of acid to the base (or base to the acid H[Tf₂N], which is solid) was carried out drop wise, and the temperature was controlled and kept around 0 °C using an ice bath. A slight excess of base was used in each case to ensure complete neutralization of the acid. The mixtures were stirred continuously in an

argon atmosphere during the reaction, and once the reactants were all added, stirring continued for another 2-3 hours at room temperature. The synthesized PILs were then dried under vacuum (6×10^{-2} mbar) at 70 °C for 48 hours to remove excess base along with trace water, and then stored in a desiccator over silica gel.



Scheme 2.1 Chemical reactions showing the synthesis of [dema][TfO], [dema][Tf₂N], and [dmea][TfO].

2.4. Characterization of Ionic Liquids

For electrochemical measurements, the electrolyte under investigation must be highly pure, as impurities can affect the electrochemistry of the substance. Water is omnipresent as an impurity in PILs.^{106, 107, 124} Therefore, the residual water content of each PIL, after drying, was determined by Karl-Fischer (KF) titration, described in Section 2.4.1. The PILs were further characterized for purity using nuclear magnetic

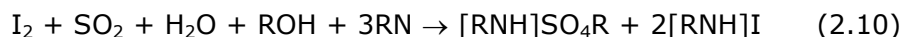
resonance spectroscopy (NMR) and ion chromatography (IC), discussed in Sections 2.4.2 and 2.4.3, respectively.

2.4.1. Karl-Fischer Analysis

Water is one of the common impurities and is always present in the PILs in trace amounts, even after drying under vacuum for a long time.^{121, 124-126, 141} The presence of water in the PILs can significantly affect their electrochemical behaviour and therefore, it is important to know the water content of the PIL of interest prior to an electrochemical investigation. The residual trace water in the ionic liquids was quantified using coulometric Karl-Fischer titrations. A KF titration is a coulometric titration method used in analytical chemistry for the detection of trace amounts of water in dry solvents. The KF titrator was the Mitsubishi CA-100 coulometric Moisturemeter.

A small portion (around 0.5 mL) of the ionic liquid was loaded into a syringe which has a long needle. After weighing, the sample was injected into the titrator containing anolyte for titration. The anolyte contained in the anodic compartment of the instrument is a solvent (alcohol), a base (pyridine) and SO_2 along with iodine in the form of iodide. Iodine is generated from the electrochemical oxidation of iodide present in the mixture at a Pt working electrode. Water present in the sample is titrated versus iodine and sulphur dioxide in the presence of the base and the solvent shown by the chemical reaction 2.10, and the concentration of water was noted from the Moisture Meter when a predefined end point is reached (as a minute excess of iodine is formed). In the reaction, H_2O and I_2 are consumed in a 1:1 ratio, that is, one mole of I_2 is consumed for each

mole of H₂O present. The amount of water in a sample is determined by the instrument from the charge necessary to form the required iodine.



2.4.2. Nuclear Magnetic Resonance Spectroscopy

The structure and purity of the PILs were examined by NMR spectroscopy. The transfer of proton from the acid to the base was confirmed by collecting ¹H NMR spectra of each PIL using a DPX300 NMR instruments using DMSO-d₆ as the solvent. About 20-40 mg of the PIL sample was dissolved in DMSO-d₆ and NMR spectra were recorded. Chemical shifts (δ) are reported in parts per million (ppm) and coupling constant (J) are given in Hertz (Hz).

2.4.3. Ion Chromatography

Ion chromatography is a separation and quantification technique that is used for analysis of both organic and inorganic cations and anions in an ionic solution using the principles of liquid chromatography.¹⁴⁴ It involves an eluent or mobile phase that carries the ions in the sample solution which are separated by a stationary phase, usually an ion exchange resin. The detector works on the basis of conductivity, which then measures the quantity of the eluent ions as a function of retention time and gives a plot of ion abundance versus retention time. This plot is called a chromatogram. The ions with a greater affinity for the stationary phase are retained in the column for a longer time and vice versa. The position of the peak in the chromatogram corresponds to specific ion, and the size of the peak to the concentration of that ionic species.¹⁴⁴

IC measurements of the ionic liquids were performed with an ICS-3000 DC ion chromatography system, Dionex UK, equipped with a Dionex AS20 (2 × 250 mm) analytical column, a Dionex CG 20 guard column (2 × 50 mm), and a conductivity detector. The eluent or mobile phase was comprised of 60 % water, 25 % acetonitrile and 15 % 0.1 M NaOH and the flow rate used was 0.25 mL min⁻¹. 5 mg of the ionic liquid sample was dissolved in 10 mL of ultrapure H₂O. A small amount of the sample (2 mL) was injected to the column for anion peak measurement. Prior to sample injection, the column was heated to 40 °C.

2.5. Electrochemical Measurements

Electrochemical measurements were performed in a conventional three-electrode cell (Figure 2.6) containing an electrolyte, counter (or auxiliary) electrode, a reference electrode and a working (or indicator) electrode. In the 3-electrode set up, the current flows through the analyte between the working and a counter electrode and the reaction of interest occurs at the working electrode. The potential of the working electrode is measured against that of the stable reference electrode.

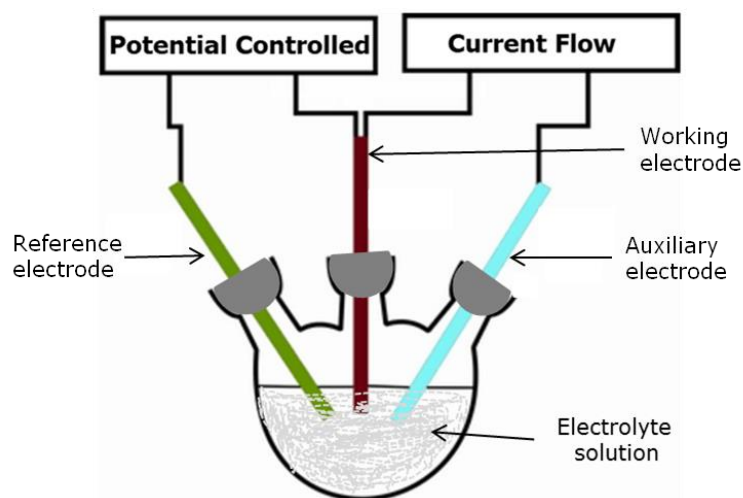


Figure 2.6 The 3-electrode cell arrangement that was used in the electrochemical measurements.

Chapter 3: The Electrolytic Growth of Surface Oxides at Pt and their Kinetics in Protic Ionic Liquids

3.1. Introduction

The Pt/Pt oxide system is one of the most widely investigated noble metal-oxide systems. A great number of studies on the nature of the oxide, the extent of surface coverage, the oxide growth mechanism and the reaction kinetics have been undertaken using a variety of electrochemical and surface science techniques.^{14, 16, 18, 20, 21, 145-152} The interest is due to the fact that Pt is a noble metal that is widely used as a very effective catalyst for a variety of electrocatalytic processes such as HOR, HER, ORR, and oxidation of methanol and hydrazine, etc. which have direct relevance to energy devices such as fuel cells.¹⁵³

It has been established that a surface oxidation occurs at platinum electrodes when polarized at oxidizing potentials, forming Pt surface hydroxide/oxide (Pt–OH_{ads}/PtO_{ads}) films in aqueous acid electrolytes.^{145, 154} Pt surface oxide formation in acidic solutions proceeds in the potential range (0.85 V to 1.4 V vs. RHE).^{14, 15, 18} According to current theories, surface oxidation of Pt in aqueous solutions involves several steps,^{14, 18, 20, 146, 147, 149} including; (i) Physisorption of H₂O (in aqueous acids) or OH[–] in potential region 0.40 V < E < 0.85 V. At potentials positive of H_{upd} desorption (E > 0.40 V), Pt electrode surfaces possess a slightly positive charge which attracts dipolar water molecules, which adsorb onto Pt (Eqn. 3.1 and Figure 3.1A).¹⁴

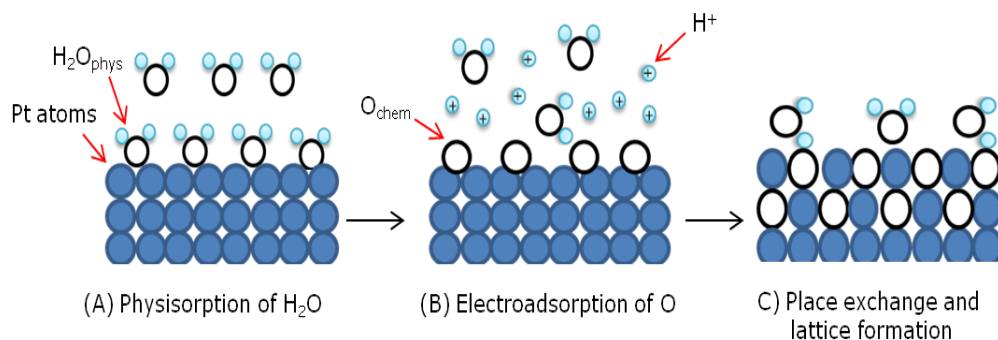
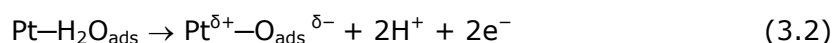


Figure 3.1 Schematic representation of the mechanism of oxide films growth at Pt surface in aqueous acidic media.

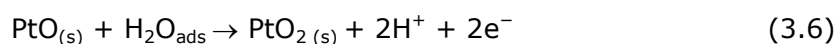
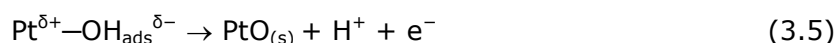
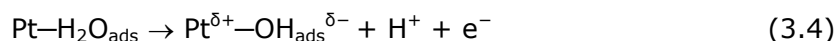
(ii) The electrochemical discharge of H_2O to form electroadsorbed oxygen O_{ads} or hydroxyl group OH_{ads} in the potential range of 0.85 V to 1.10 V^{14, 17-20, 145, 146} simultaneously leads to the electroadsorption of oxygen, O_{ads} , on Pt surface with the departure of two H^+ and two electrons (Eqn. 3.2) forming a sub-monolayer of chemisorbed O_{ads} on Pt surface (Figure 3.1 B).

(iii) Further splitting of another half of a monolayer of O from $\text{H}_2\text{O}_{\text{ads}}$ occurs in the potential range (1.10 V to 1.40 V). To reduce the strength of the repulsion, the initial chemisorbed O atoms start moving from surface sites and enter the Pt subsurface (place exchange),¹⁸ as shown in Figure 3.1 C. The phenomenon of place exchange between Pt atoms on the surface, and O_{ads} species in the adlayer results in the electrochemically irreversible formation of PtO comprised of Pt^{2+} and O^{2-} (Eqn. 3.3).^{17, 18, 20, 145, 146, 155} Due to the place exchange process, more Pt atoms are exposed at the surface for further oxidation forming a quasi-three dimensional (3-D) Pt-oxide lattice containing Pt^{2+} and O^{2-} under strong polarization conditions that can facilitate Pt dissolution.^{14, 34, 156, 157}





In another pathway,¹⁷⁻²⁰ the initial electrochemical discharge of $\text{H}_2\text{O}_{\text{ads}}$ in the low potential region results in the direct electroadsorption of hydroxyl group (OH_{ads}) (Eqn. 3.4), which is followed by redistribution between Pt and OH_{ads} and further oxidation to form PtO (Eqn. 3.5). At higher potentials (>1.4 V), PtO_2 can form on the top of the initial PtO layer (Eqn. 3.6), after which bulk oxygen evolution takes place at more positive potentials that depends on oxide film thickness.¹⁵⁸



According to the literature, PtO and PtO_2 are stable surface species and $\text{Pt}-\text{OH}_{\text{ads}}$ is a short-lived intermediate..^{14, 18, 145, 147, 149, 150} Birss *et. al*,¹⁴⁷ confirmed through cyclic voltammetry and quartz crystal microbalance (QCM) that the initial oxide growth on Pt surfaces involve the direct formation of PtO and PtO_2 and the development of OH_{ads} layers was not observed. Jerkiewicz and co-workers,^{14, 17, 18, 150} have proved, using cyclic voltammetry, electrochemical quartz crystal nanobalance (EQCN) and Auger electron spectroscopy (AES), that the initial oxide growth leads directly to PtO formation. The extent and mechanism of anodic surface oxidation of Pt depends on the electrochemical experimental conditions such as polarization potential (E_p), polarization time (t_p) and temperature (T) of the medium.^{19, 20, 145, 149} The amount of oxide formed at the Pt anode surface is expressed either as the oxide charge, Q_{ox} (measured in coulombs, C), measured from the charge under the oxide stripping peak

through electrochemical techniques such as linear sweep voltammetry and cyclic voltammetry or as the oxide charge density, q_{ox} (oxide charge per unit area of the electrode surface = Q_{ox}/A , measured in $C\ cm^{-2}$).¹⁹

Charge transfer across the Pt/electrolyte interface follows either direct logarithmic oxide growth kinetics or inverse logarithmic growth kinetics. In direct logarithmic kinetics, the quantity of charge or the charge density is directly proportional to the logarithm of the oxide growth polarization time and in the case of inverse logarithmic growth kinetics, the reciprocal of the oxide charge density is directly proportional the logarithm of the oxide growth polarization time.^{17-20, 145, 159} The kinetics of oxide film growth on Pt surfaces depends on the thickness of the oxide, as thick oxide films have different electronic properties to thin oxide films. The growth of thick oxide films is often restricted by the transfer of electrons across the surface oxide or by exchange of ions (Pt^{2+} and O^{2-}). After the place exchange process, an oxide layer to certain thickness is reached across which a strong electric field develops causing the inverse logarithmic growth kinetics.^{14, 20}

PILs, as described in detail in Chapter 1, have gained popularity as electrolytes in electrochemistry and are being proposed for an increasing number of electrochemical applications. Many PILs have also been proposed as potential electrolytes for capacitors¹⁶⁰ and Li-ion batteries¹⁶¹ due to their thermal stability and non-flammable nature. Regardless of their application, when using PILs as electrolytes, oxides can develop on metal electrodes surfaces in PILs as a result of water oxidation, which is always present in trace amount as a common impurity in the liquids.¹²⁴⁻¹²⁶ These oxides can affect electrocatalytic processes.^{121, 124, 162} Considering the unique environment within ionic liquids, and the fact that water is often at trace levels, it may be useful to understand in detail the surface

oxidation of metals (especially Pt due to its use as a catalyst in fuel cells and other catalytic processes) in PILs, the mechanism by which surface oxidation takes place, and the effects of the oxide species on the electrocatalysis of various redox processes. It is important to establish under which conditions surface oxides are present on Pt surfaces in PILs and how stable they are in these new electrochemical environments.

In this chapter, we describe the surface electrochemistry of polycrystalline Pt in the PILs [dmea][TfO], [dema][TfO] and [dema][Tf₂N] using voltammetry. The PILs chosen in this study have high proton conductivity, negligible vapor pressure, and high thermal and electrochemical stability.^{102, 116, 121} The formation of surface oxides on Pt at various potentials and polarization times was confirmed using XPS and information about the chemical state of Pt oxides was obtained from XPS data. For the first time, the influence of polarization potential, time, and temperature on the growth of Pt-oxides in ionic liquids is described. By fitting electrochemical data to oxide growth kinetic theories, we have obtained new insights into the growth of these oxide films. In addition, the behavior of these films in PILs is compared to that observed using aqueous electrolytes.

3.2. Experimental Section

3.2.1. Reagents and Apparatus

All chemicals were analytical grade and were used as received without further purification. Anhydrous trifluoromethanesulfonic acid (triflic acid, TfOH, 99 %) and diethylmethylamine (DEMA, 98 %) were from Sigma-Aldrich, bis(trifluoromethylsulfonyl)imide (HTf₂N, ≥ 95 %) from Fluka

analytical, and dimethyl ethylamine (DMEA, $\geq 99\%$) was purchased from Merck. All PILs were prepared according to the procedure described in Section 2.3. PILs were dried under vacuum (6×10^{-2} mbar) at 70 °C for 48 hours. Trace water contents of the PILs were determined using a coulometric Karl-Fischer apparatus (Mitsubishi Moisturemeter CA 100) and are described in the Results and Discussion section. Electrochemical measurements were performed using a computer-controlled model CHI700C potentiostat (CH Instruments, Austin, TX) and unless otherwise mentioned, the same potentiostat was used throughout this thesis. XPS was recorded using a Kratos Axis Ultra spectrometer with a monochromatic Al K α X-ray source ($E = 1486.6$ eV).

3.2.2. Electrochemical Measurements

Electrochemical measurements were performed in a conventional three-electrode cell (Figure 2.6) containing a Pt flag (0.5 cm $\times$ 0.4 cm $\times$ 0.1 cm) as the counter electrode and a 2 mm diameter Pt disk as the working electrode. The same working and counter electrodes were used throughout this thesis unless otherwise mentioned. The reference electrode was a Pd-H reference electrode (unless otherwise described), which was prepared by first annealing Pd wire and then inserting into a stream of H₂ for 25–30 minutes.¹¹³ The Pd-H reference electrode was introduced by Angell and co-workers and provides a stable potential defined by the hydrogen redox equilibrium at the Pd/PIL interface. In this work, the potential of the reference electrodes were compared by measuring the onset potential for H₂ oxidation/H⁺ reduction in the PILs and this was approximately 35 mV negative of the RHE reported previously by Watanabe and co-workers in PILs.^{115, 163}

Prior to use, Pt disk electrodes were polished using an aqueous suspension of 0.05 μm alumina (Buehler, Lake Bluff, Illinois) on soft polishing pads (Buehler consumable, USA). After polishing, the electrode was rinsed thoroughly with deionised water, sonicated in an ultrasonic bath in a small amount of deionized water for 2 min rinsed again thoroughly with deionised water and dried in a stream of N_2 . The real surface area of the Pt working electrode was estimated to be 0.046 cm^2 by integrating charge passed during stripping of an adsorbed layer of under potential deposited hydrogen (H_{UPD}) from the electrode during cyclic voltammetry in 0.1 M HClO_4 at 25 $^\circ\text{C}$ assuming a stripping charge density of $210 \mu\text{C cm}^{-2}$ required to oxidize a monolayer of hydrogen from Pt surface.³ All the current data were normalized to this area.

For electrochemical measurements, the electrochemical cell was charged with approximately 5 mL of the appropriate PIL. Prior to each measurement, PILs were deaerated with high-purity N_2 for 20–30 minutes and a blanket of N_2 was maintained above the electrolyte during the measurements. The same procedure was adopted for cleaning the working electrode and for removing dissolved O_2 from the electrolyte solution in all of the measurements in this thesis. Temperature-controlled measurements were performed by immersing the entire cell in an oil bath on a hot plate equipped with a thermocouple.

3.2.3. XPS Analysis of the oxidised Pt Surface

The surface oxide species formed after electrochemical polarization of the Pt electrode in the PILs were analyzed by XPS analysis of the Pt surface. A 2 mm diameter Pt disk was used as the XPS substrate. Prior to use, the substrate was polished, rinsed and dried in the same way as described

above in Section 3.2.2. The dried substrate was inserted into the sealed 3-necked electrochemical cell, described above, containing 5 mL of [dema][Tf₂N] and then polarized at the desired potential and temperature for the appropriate time. The oxidized Pt substrate was removed from the cell, rinsed with acetonitrile and stored in 10 mL of acetonitrile for 20 min to remove residual [dema][Tf₂N] from the surface. The substrate was then dried at 75 °C for 30 min in an oven and, after cooling, transferred to the XPS chamber for analysis. The sample was introduced into the instrument immediately after preparation to avoid the absorption of moisture or solid dust.¹⁶⁴ XPS was performed using a Kratos Axis Ultra spectrometer with hybrid (magnetic/electrostatic) optics, a hemispherical analyser and a multichannel plate and delay line detector (DLD). The X-ray source used was a monochromatic Al K α (E =1486.6 eV) source and an X-ray angle of incidence of 30° relative to the surface normal with X-ray gun power of 150 W. An entrance aperture of 300 × 700 μ m was used to record high-resolution spectra with pass energy of 20 eV and 80 eV was used for wide scans. The sensitivity of the instrument was 7.5×10^5 counts s⁻¹ and the pressure in the main chamber remained $<1 \times 10^{-9}$ mbar during experimental measurements. The XP spectra are discussed in the Results and Discussion section.

3.3. Results and Discussion

3.3.1. Characterization and Structure Identification of PILs

At room temperature [dmea][TfO] is solid, while [dema][TfO] and [dema][Tf₂N] are liquids with melting points of 41.6 °C, -13.1 °C and 24

°C, respectively.¹¹⁶ The densities of the PILs were determined by accurately weighing 1 mL of the sample PIL. The density of [dmea][TfO] at 50 °C was 1.34 g cm⁻³, and of [dema][TfO] = 1.36 g cm⁻³ and [dema][Tf₂N] = 1.60 g cm⁻³ at room temperature.

3.3.1.1. Structure Identification of the PILs Through NMR

NMR spectra of [dema][TfO], [dmea][TfO] and [dema][Tf₂N] were recorded and Figure 3.3.1 shows ¹H NMR spectra carried out in a neat sample of [dema][TfO] at ambient temperature. A peak was observed at a chemical shift of about 8.95 ppm, which corresponds to the proton attached to the N of the amine after transferring from the Brønsted acid. The two methylene protons (shown as 2 in the figure) appear at chemical shift between 2.94 to 3.22 showing complex multiplicity due to coupling with the protons of the neighbouring methyl groups. The behaviour is reminiscent of that observed by Mori *et. al*,¹⁶⁵ which they attribute to the restricted rotation of the N—C bond due to steric hindrance in [dema][TfO] at ambient temperature. Also this complex behaviour of methylene group protons could be the result of coupling with the N—H proton.¹⁶⁵ The methyl group protons appeared in the spectrum from 1.0 to 2.75 ppm. The peak associated with the protons of the methyl group attached directly to N (shown as 3 in the figure) were observed at 2.71 ppm as a duplet with a coupling constant 5.1 Hz and that of methyl groups (shown as 4 in the figure) attached to methylene as a triplet at 1.18 ppm with a coupling constant 7.3 Hz. A similar NMR spectrum was obtained for the ammonium cation in [dema][Tf₂N] as shown in Figure S 1 (A) in Appendix 1. For the ammonium cation in [dmea][TfO], however, the spectrum was slightly different to the other two PILs (see Figure S 2 (B) in Appendix 1).

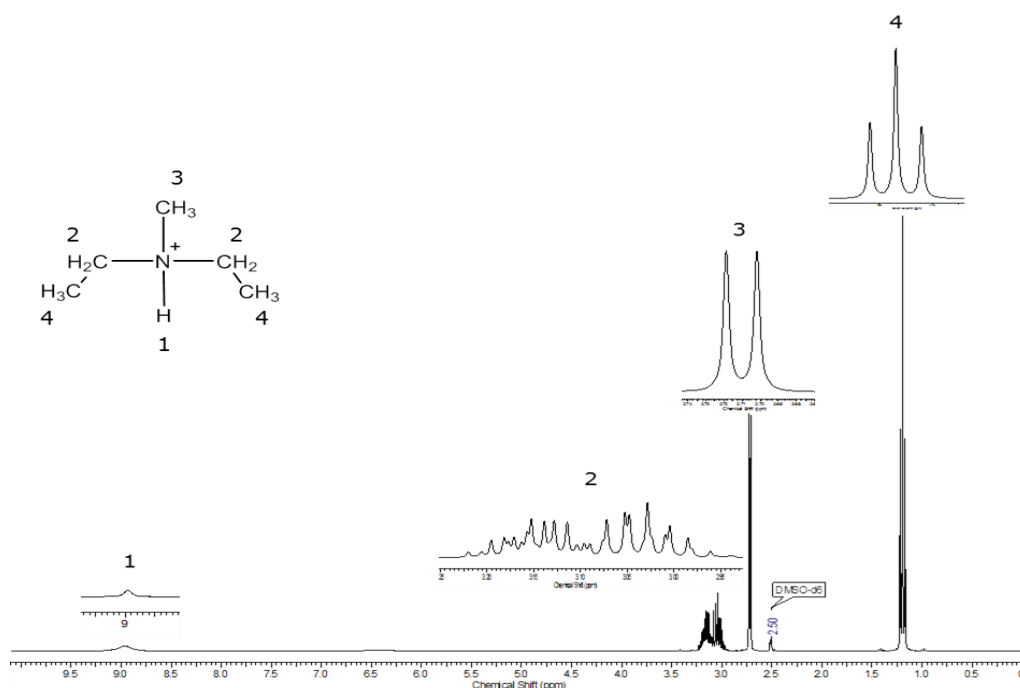


Figure 3.3.1 ^1H NMR of $[\text{dema}][\text{TfO}]$ in $\text{DMSO}-d_6$.

The peaks corresponding to the protons of the methyl groups neighbouring methylene group were at 1.18 ppm with a coupling constant, $J = 7.3$ and those of the other two methyl group (6 protons), after coupling with in N–H proton, were a high intensity duplet at an average chemical shift of 2.75 ppm in the spectrum of dimethylethylammonium cation. The overall peak positions along with their multiplicity and coupling constants are summarized below:

$[\text{dema}][\text{TfO}]$

^1H NMR (300.13 MHz, $\text{DMSO}-d_6$) $\delta\text{H} = 1.18$ (t, $J = 7.3$ Hz, 6H), 2.71 (d, $J = 5.1$ Hz, 3H), 2.94–3.22 (complex multiplet, 4H), 8.95 (s, 1H)

$[\text{dema}][\text{Tf}_2\text{N}]$

^1H NMR (300.13 MHz, $\text{DMSO}-d_6$) $\delta\text{H} = 1.19$ (t, $J = 7.3$ Hz, 6H), 2.71 (d, $J = 5.1$ Hz, 3H), 2.93–3.22 (complex multiplet, 4H), 8.96 (s, 1H)

[dmea][TfO]

^1H NMR (300.13 MHz, $\text{DMSO}-d_6$) δH = 1.18 (t, J = 7.3 Hz, 3H), 2.75 (d, J = 5.1 Hz, 6H), 3.03–3.12 (dd, J =7.1 and 5.1, 2H), 9.15 (s, 1H)

3.3.1.2. Purity of the PILs by Ion Chromatography

IC analysis for the $[\text{TfO}]^-$ anions in [dema][TfO] and [dmea][TfO] and $[\text{Tf}_2\text{N}]^-$ in [dema][Tf_2N] was performed. The chromatogram show a sharp peak at retention time 6.71 minutes in the case of [dema][TfO], 6.41 minutes in case of [dmea][TfO] and at 21.42 minutes in [dema][Tf_2N] (Figure 3.3.2). Peak retention times were compared to the anion chromatograms of silver triflate and lithium bis-(trifluoromethylsulfonyl) imide which confirmed the $[\text{TfO}]^-$ and $[\text{Tf}_2\text{N}]^-$ ions in the PILs. The $[\text{Tf}_2\text{N}]^-$ ion was retained for a longer time in the column, showing greater affinity with the stationery phase compared to the $[\text{TfO}]^-$ anion. A small peak above 5 min in the IC of [dmea][TfO] and 8 min in that of [dema][Tf_2N] were observed showing trace impurity that is also confirmed from the ^1H NMR in these liquids (Figure S 1 (A) and (B) in Appendix 1), presumably coming from the precursor chemicals.

3.3.1.3. Water Contents of the PILs

As mentioned in Chapter 2, water is commonly found as a trace impurity in ILs. The potential sources of water in the ILs could be the precursor reagents used for their synthesis and absorption of moisture from air during the course of an experiment or during storage.¹²⁴ Therefore, it is difficult to completely remove water from the PILs even by drying under vacuum at high temperature and for long time. Water content of the PILs

was determined using a coulometric Karl-Fischer titration discussed in Section 2.4.1.

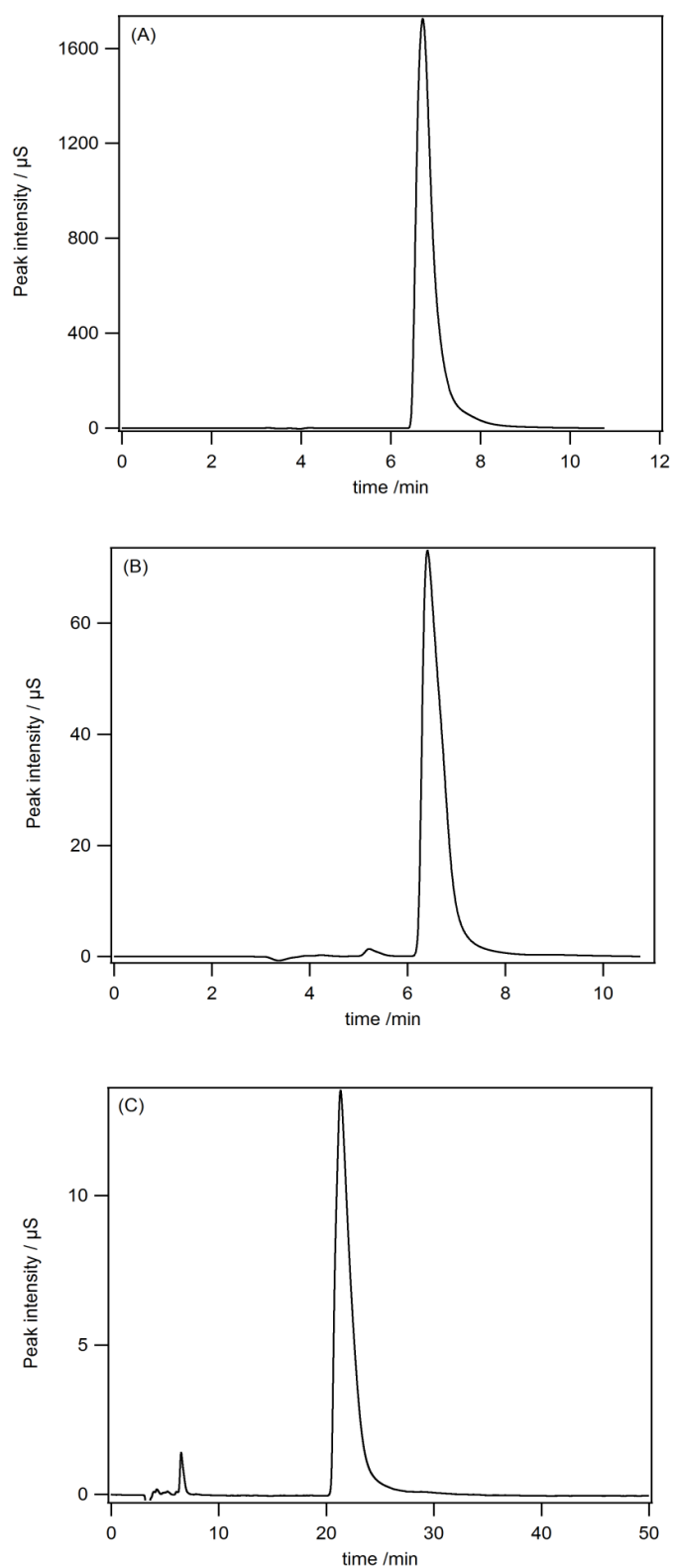


Figure 3.3.2 Ion chromatograms for the anions of (A) $[\text{dema}][\text{TfO}]$, (B) $[\text{dmea}][\text{TfO}]$ and (C) $[\text{dema}][\text{Tf2N}]$.

The average concentration of water (in ppm) was 186 ppm, 240 ppm and 450 ppm in [dmea][TfO], [dema][TfO] and [dema][Tf₂N], respectively. The amount of water in an ionic liquid and the extent to which ionic liquids can be dried depend mainly on the anion of the IL. Water has a strong H-bonding interaction with the anion of the ILs forming an anion---HOH---anion bridge.¹⁶⁶ Cammarata *et. al*, has found that when ILs absorb water from atmosphere, they form 'liquid-like associated aggregates' with relatively strong anions which can affect the reactivity of the metal catalysts and other solutes in the ILs.¹⁶⁶ In addition, they suggested that water may act as a co-solvent in the ILs that can dissolve substances that would otherwise not be soluble in the ILs. The presence of water in ILs can significantly affect their vapor pressure, viscosity, density, solubilization, diffusivity, electrical conductivity, electrochemical window etc. of ILs.^{124, 125, 166} It is always advisable to measure the concentration of the residual water in ILs prior to electrochemical investigation.

3.3.2. Electrochemical Characterization of PILs

The PILs were electrochemically characterized by measuring their potential windows and various adsorptions and desorption reactions taking place in this media at Pt electrodes. As mentioned in Chapter 1, the potential window is an important indicator of electrochemical stability of ionic liquids. Therefore, the electrochemical potential windows of [dmea][TfO], [dema][TfO] and [dema][Tf₂N] were examined at a Pt electrode using cyclic voltammetry. Figure 3.3.3 shows CVs recorded in blank (A) [dmea][TfO], (B) [dema][TfO] and (C) [dema][Tf₂N] at a 2 mm diameter Pt disk working electrode vs. Pd-H at 50 mV s⁻¹ and at 50 °C.

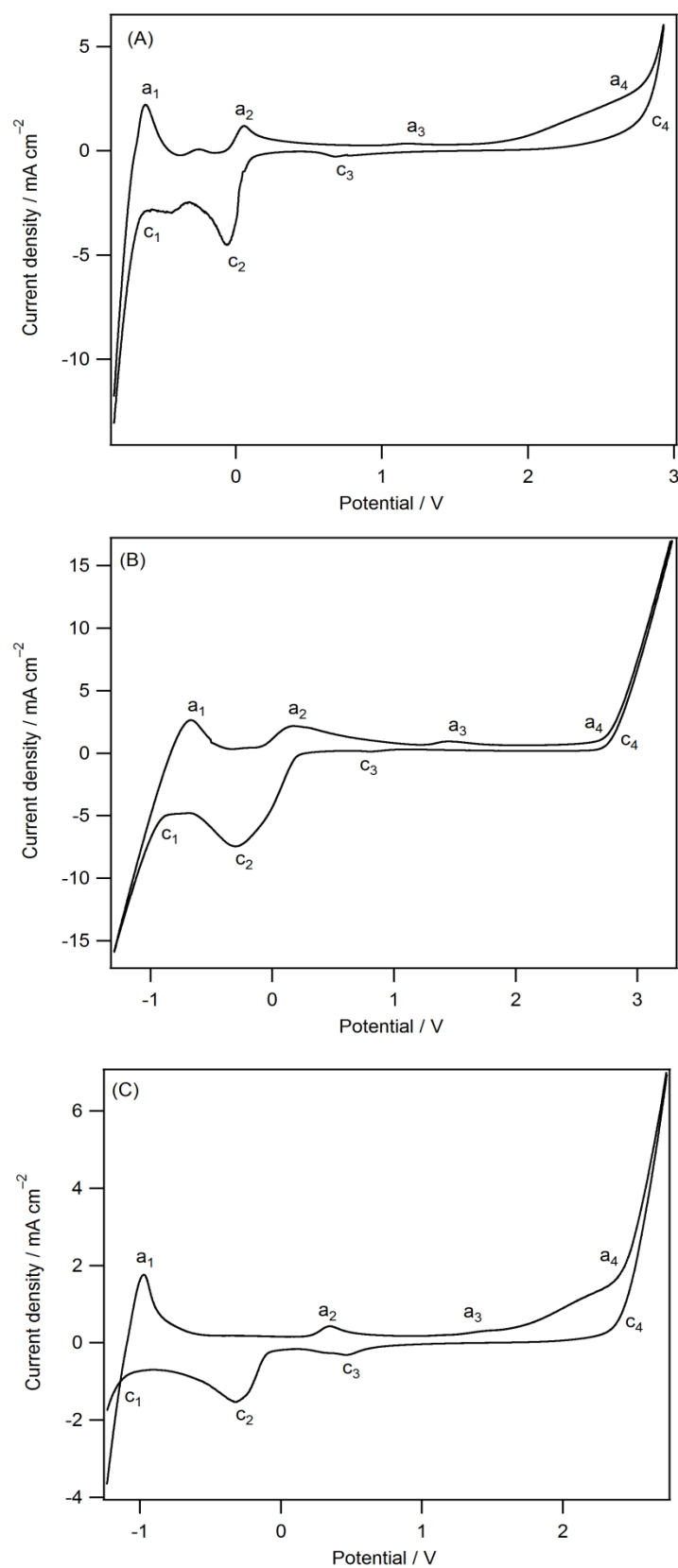
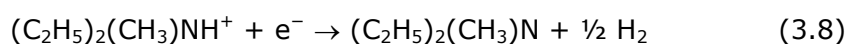
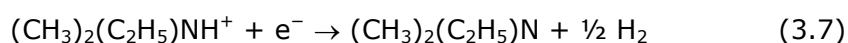
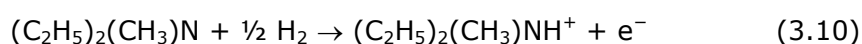
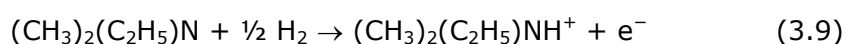


Figure 3.3.3 Cyclic voltammograms obtained at a 2 mm diameter Pt disk electrode in N_2 purged, (A) $[dmea][TfO]$ (B) $[dema][TfO]$ and (C) $[dema][Tf_2N]$ at 50°C at a sweep rate of 50 mV s^{-1} in the case of (A) and 100 mV s^{-1} in both (B) and (C).

Generally, each of these CVs (Figure 3.3.3) shows four oxidation peaks, a_1 , a_2 , a_3 and a_4 during the positive going sweep, and their corresponding reduction peaks, c_1 , c_2 , c_3 and c_4 on the reverse sweep. The steep current increase at c_1 and a_4 in each CV corresponds to the reduction of the cations and oxidation of the anions of the PILs, respectively, at the cathodic and anodic potential limits.^{113, 122, 167, 168} Cathodic current c_1 corresponds to the reduction of the PIL cations; dimethylethylammonium (Eqn. 3.7) in the case of [dmea][TfO] and diethylmethylammonium (Eqn. 3.8), in the case of both [dema][TfO] and [dema][Tf₂N]. This reduction results in the formation of respective amines. This represents the cathodic potential limit of the PILs.



The bases formed by the reduction of the cations, as described above, remain in the vicinity of the electrode, and oxidize back to their respective cations during forward scan depicted by the steep oxidation current (a_1) in each CV, represented by Equations 3.9 and 3.10.



The sharp increase in current at more positive potentials (a_4) in each PIL is ascribed to the oxidation of the anion, [TfO]⁻ (Eqn.3.11) in the case

of [dmea][TfO] and [dema][TfO] and [Tf₂N]⁻ (Eqn.3.12) of [dema][Tf₂N]. On reversing the scan direction after reaching anodic potential limit, the current observed is due to the corresponding reduction of the species formed during the forward sweep, and is shown by the backward arrow sign in the Equations 3.11 and 3.12.

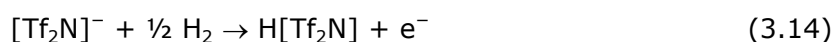
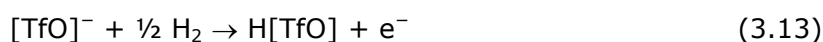


The potential windows of the PILs were calculated from the difference between the anodic potential limit and the cathodic potential limit. The potential windows of [dema][TfO], [dema][Tf₂N] and [dmea][TfO] were approximately 3.57 V, 3.55 V and 3.44 V, respectively at Pt and at 50 °C.

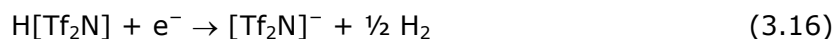
Water molecules are electrochemically active and their presence in an ionic liquid significantly affects the electrochemistry of the IL. The effect of water on the potential window of [dmea][TfO] was examined by cyclic voltammetry and is shown by Figure S2 in Appendix 1. The electrochemical window of RTILs decreased with an increase in the concentration of water,^{119, 122, 125} because water in an ionic liquid decreases its viscosity, which in turn increases the conductivity and diffusivity of the constituent cation and anions.¹¹⁹ Similarly, the influence of temperature on the electrochemical windows of the protic ionic liquids was explored (Figure S 3 in Appendix 1). It is observed that with increasing temperature, the electrochemical window of [dmea][TfO] decreases. The reason for this is presumably that by increasing the temperature of the PIL, the strength of bonding between [dema]⁺ and [TfO]⁻ decreases, which decreases the viscosity of the ionic liquid and increases the diffusivity of the ions towards

the electrode surface which leads to an enhanced conductivity of the bulk ionic liquids.^{125, 169}

In each PIL (Figure 3.3.3), when the potential of the electrode was scanned in positive direction an anodic current (labeled a_2) was observed, peaking at 0.101 V in (A), 0.157 V in (B) and 0.347 V in (C). By scanning the potential of the electrode in the negative direction, its corresponding reduction wave, depicted by c_2 was observed at peak potentials, -0.016 V, -0.207 V and -0.315 V in [dmea][TfO], [dema][TfO] and [dema][Tf₂N], respectively. The appearance of this oxidation and reduction peaks has also been observed by Lee *et al.*¹⁶³ in [dema][TfO] and [dema][Tf₂N] and by Bautista-Martinez *et al.*¹¹³ in [dmea][TfO], [dema][TfO] and [dema][Tf₂N]. The oxidation peak, a_2 in each PIL is attributed to the oxidation of H₂ released, formed by the reduction of free acid at c_2 , to form protons that combine with conjugate base (anion in each case) and produce corresponding acid, as given by Equations 3.13 in the case of [TfO]⁻ based PILs and 3.14 in the case of [dema][Tf₂N].



The Brønsted acid generated above in each case, remains local to the electrode and reduces back to conjugate base, as given by Equations 3.15 and 3.16 below to form hydrogen again shown by the reduction wave at c_2 in each Figure 3.3.3. H₂ at c_2 can also form from the free acid during negative going sweep. The formation of H₂ at the electrode below 0.0 V in [dema][TfO] was confirmed in our group by using in-situ gas chromatography.¹⁴⁰



In order to further confirm that peak a_2 is due to oxidation of H_2 and peak c_2 due to corresponding reduction of the H^+ , a cyclic voltammogram was recorded at 2 mm diameter Pt at 50 mV s^{-1} and room temperature in blank $[\text{dema}][\text{TfO}]$ and after adding 10 mM triflic acid, as shown in the Figure 3.3.4. The figure shows that by addition of triflic acid (i.e. H^+) to $[\text{dema}][\text{TfO}]$ both peaks increased relative to the peaks obtained in blank $[\text{dema}][\text{TfO}]$. This shows that by adding H^+ to $[\text{dema}][\text{TfO}]$ the peak current due to proton reduction increased and as a result corresponding the oxidation peak current also increased due to additional hydrogen formation.

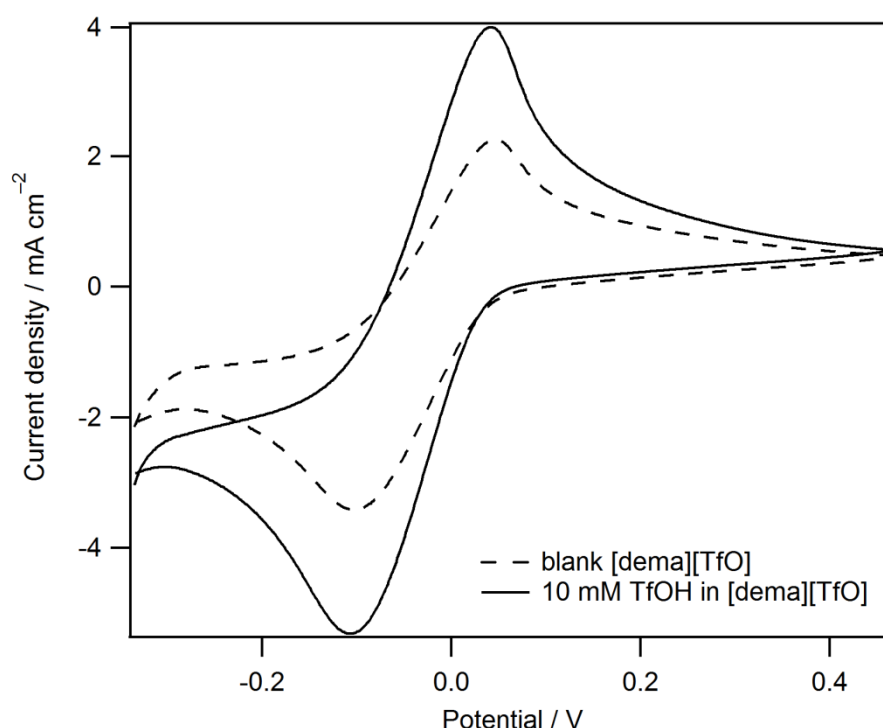


Figure 3.3.4 CVs obtained at 2 mm diameter Pt disk electrode at 50 mV s^{-1} and at 25°C obtained in N_2 saturated (A) $[\text{dema}][\text{TfO}]$ and (B) 10 mM TfOH solution in $[\text{dema}][\text{TfO}]$.

From Figure 3.3.3, it is clear that the peak-to-peak separation for H₂ oxidation peak and proton reduction peak is small in [dema][TfO] and [dmea][TfO], showing reversible electrochemistry and so fast electron transfer kinetics for the two processes. In contrast to the two TfO-based PILs, the peak to peak separation for both processes are slow in [dema][Tf₂N], showing that this PIL has quite poor activity for H₂ oxidation to H⁺ and its corresponding reduction. This is in agreement with other studies that have shown poor activity of [dema][Tf₂N] for hydrogen oxidation reaction.^{113, 163}

3.3.2.1. Surface Oxidation of Pt in PILs

As shown in Figure 3.3.3 above, an oxidation peak at a potential slightly positive of 1.0 V and a corresponding reduction peak negative of 1.0 V in each of the PILs was also observed, which looks very small in the wide window voltammogram shown in Figure 3.3.3. However, in the narrower potential window, shown in Figure 3.3.5 clear cathodic and anodic waves are seen. The figure shows cyclic voltammograms obtained in N₂ saturated (A) [dema][TfO], (B) [dema][Tf₂N] and (C) [dmea][TfO] at a 2 mm diameter Pt disc working electrode, with the potential swept at 50 mV s⁻¹ at 25 °C except in the case of (C) in which the CV was recorded 50 °C. Gross similarities between CVs recorded in the PILs and that in the aqueous acidic solution can be seen from the figures. The shape of the CVs in the positive potential regions in the PILs (see Figure 3.3.5 A, B and C) is similar to the voltammogram recorded at Pt in the acidic solution (see Figure 3.3.5 D). The significant difference between the two systems is that in both TfO-based ionic liquids, an oxidative current starts flowing at a potential slightly above 1.0 V and 1.2 V in [dema][Tf₂N] as opposed to at 0.8 V in the acid solution. The anodic current increased gradually until 1.8

V in both TfO-based PILs and 2.0 V in [dema][Tf₂N], at which point a drastic increase in the oxidation current was observed in each case (not shown in the Figure 3.3.5 but can be seen from current rise in Figure 3.3.3 prior to the anion oxidation currents) which is also observed in aqueous acid electrolytes.³ During the return sweeps, the oxide species formed at the Pt surface in the forward going scan were reduced well below 0.8 V.

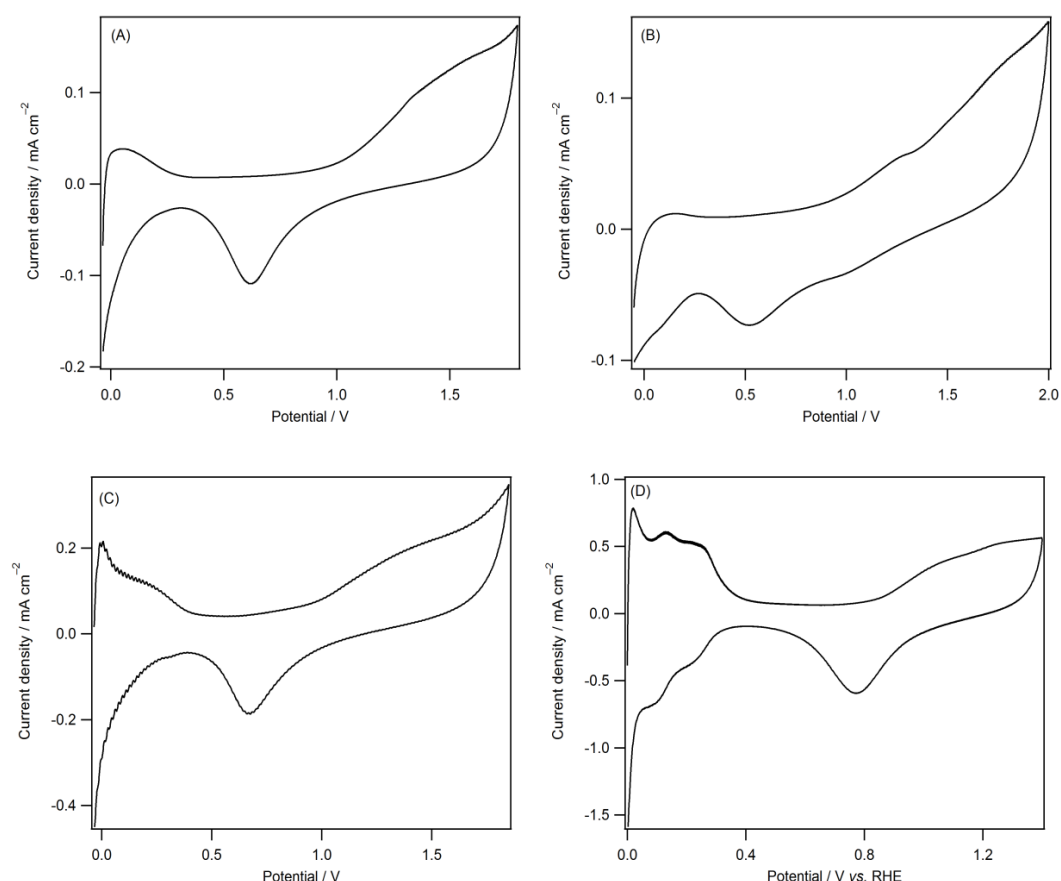


Figure 3.3.5 CVs obtained in N₂-saturated blank (A) [dema][TfO], (B) [dema][Tf₂N], (C) [dmea][TfO] and (D) 0.5 M H₂SO₄(aq.) at a 2 mm diameter Pt disk at 50 mV s⁻¹ at 25 °C except in the case of (C) in which the temperature was 50 °C. The potential of the electrode was cycled from an initial value, -0.035 V to (A) 1.8 V, (B) 2.0 V and (C) 1.85 V vs. Pd-H and from 0.0 V to 1.4 V vs. RHE in H₂SO₄ (aq.).

Assuming that the formation of oxides at Pt in the PILs was from trace water oxidation, an increase in the water content of the PILs should result in an increase of the extent of Pt surface oxidation, and shift the onset potential of the process to less positive values. Therefore, to

investigate the origin of these peaks and the formation of adlayer of Pt-oxides, two experiments were designed. The first experiment was to obtain CVs at Pt by adding additional H₂O to the PILs and examine the CVs as described in the next section, 3.3.3. Another experiment was designed to analyze the surface composition of the Pt electrode using XPS before and after an electrochemical treatment in the PILs (see Section 3.3.4).

3.3.3. Influence of Water Concentration on Pt Surface

Oxidation in PILs

To confirm that the surface oxidation of Pt was due to trace water in the PILs, cyclic voltammograms were recorded at a Pt electrode in vacuum dried samples of (A) [dmea][TfO] and (B) [dema][TfO] at scan rates of 50 mV s⁻¹ and temperatures of 50 °C, shown by the dotted lines in the Figure 3.3.6. The initial water concentration, determined by Karl-Fischer titration, was ~14 mM in [dmea][TfO] and ~18 mM in [dema][TfO]. Then de-ionized water was added deliberately to the cell containing PILs in 100 µL steps, and each time a new CV was recorded within the same potential window as was scanned for the dried PIL. After each addition, the new concentration of water in the PILs was found from the known concentrations. It is clear from the figure that with the addition of water to the dry PILs, the total charge of the anodic and cathodic processes increased significantly. This confirms that these oxidative and reductive waves are due to the oxidation of water in the ionic liquids to form Pt oxides. Also, with the addition of water more oxygen atoms became available for adsorption at Pt surfaces; therefore, oxide formation at Pt began at less positive potentials. As a result, rearrangement between Pt atoms and adsorbed O atoms results in place-exchange mechanism and causes formation of thick oxide layers on

the Pt surface.^{18, 20} On the reverse scan the removal of the surface oxides becomes difficult and the reduction process is slow. Hence, the oxide reduction peak shifts towards less positive potentials and a decrease in peak potential is observed with rising water content.

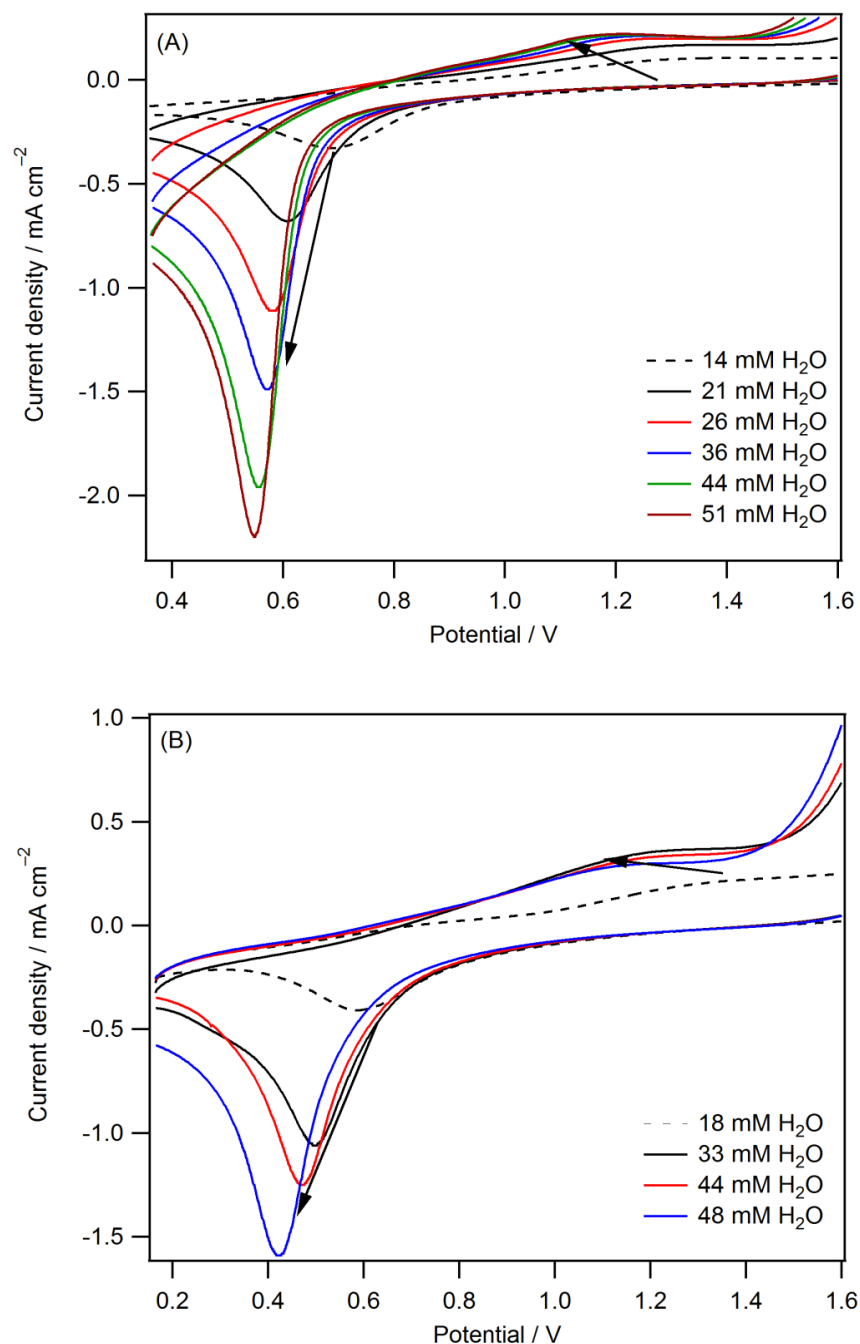


Figure 3.3.6 A series of CVs obtained at a 2 mm Pt disk working electrode at a scan rate 50 mV s⁻¹ in blank (A) [dmea][TfO] and (B) [dema][TfO], containing various concentrations of H₂O at 50 °C. The upper potential limit was 1.95 V (data up to 1.6 V shown here), and lower limit 0.35 V in (A) and 0.15 V in (B).

It is further observed that the peak current corresponding to the reduction of the oxides from Pt surface in the PILs increased and the peak potentials shifted to less positive potential value with increasing the concentration of H₂O. The peak current in the case of [dmea][TfO] increased from approximately 10.3 μ A to around 85 μ A, while the peak potential decreased from 754 mV to 551 mV when the water concentration of the PIL was increased from 14 mM to 51 mM. Similarly, a decrease of 155 mV of the peak potential in case of [dema][TfO] and an increase of approximately about 39 μ A in the reduction peak current was observed when the concentration of water was raised from 18 mM to 48 mM. Similar oxide behaviour was observed by Bond *et al*¹²⁶ using the protic ionic liquid diethylammonium acetate, [DEA][Ac] at a Au working electrode.

Figure 3.3.7 shows the integrated charge density, q_{ox} (charge, Q normalized to the real surface area of Pt calculated from acid CV) under the oxide reduction peak observed by cathodic stripping voltammetry as a function of H₂O concentration of (A) [dmea][TfO] and (B) [dema][TfO]. The numbers of monolayers (MLs), θ of oxides formed on Pt, are also shown on the right side vertical axis in each figure. The number of MLs of oxides on Pt surface were determined by dividing the charge density under the oxide reduction peaks on the theoretical charge density, 440 μ C cm⁻² assuming 1:1 of Pt and O atoms. The figure shows a linear correlation between the magnitudes of charge densities under the Pt oxide reduction peak, and the concentration of H₂O. q_{ox} under the oxide reduction peak obtained at 50 °C in [dmea][TfO] containing 14 mM water is 1110 μ C cm⁻² that corresponds to 2.5 ML of oxide by assuming 1:1 of Pt and O atoms (theoretical charge, 440 μ C cm⁻²). The q_{ox} value reaches 3450 μ C cm⁻² when the concentration of H₂O in the PIL was raised to 51 mM and which corresponds to 8 ML of Pt surface oxides. In the same way, in [dema][TfO], q_{ox} was 1350 μ C cm⁻²

(equivalent to 3 ML) which increased to $5430 \mu\text{C cm}^{-2}$ (equivalent to 12.4 ML) when the H_2O content of the PIL was increased from 18 mM to 48 mM. The plot shows that the number of oxide layers in both of the ionic liquids increased with the increase of H_2O concentration showing that the oxide formation is due to water oxidation in the ionic liquid environment.

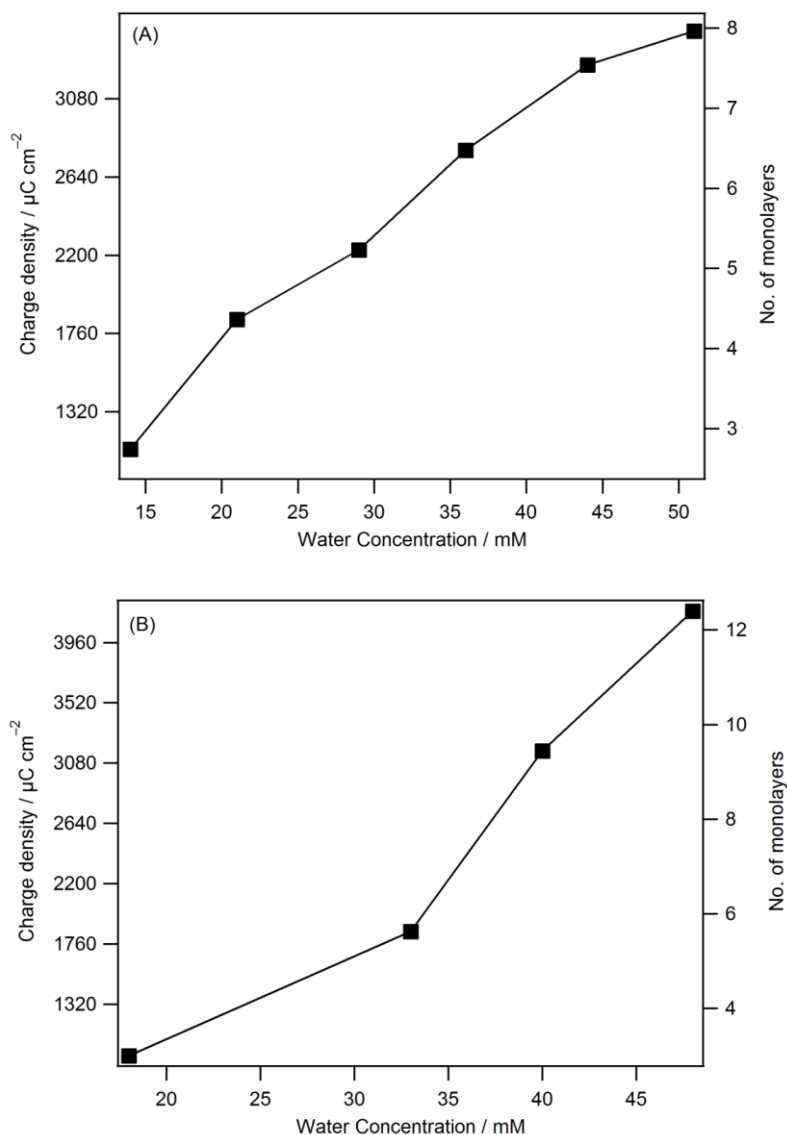


Figure 3.3.7 Shows the integrated charge density, q_{ox} as a function of water concentration in (A) [dmea][TfO] and (B) [dema][TfO], respectively.

3.3.4. Analysis of Pt Surface by XPS

The formation of oxide species at the surface of Pt by water oxidation in aqueous acid electrolytes has been confirmed by using XPS and other

surface sensitive techniques.¹⁸ To confirm that adlayers of oxides were formed at Pt surface by trace water oxidation in the PILs, high resolution XP spectra were recorded of an electrochemically polarized Pt surface in [dema][Tf₂N] shown in Figure 3.3.8 (A) by solid line. Also shown in Figure 3.3.8 (A) spectra recorded after etching the oxidized Pt surface (dotted line) to a 10 nm depth by bombardment with Ar⁺ ions (4 kV). A polarization potential of 2.3 V was applied for 300s at 100 °C in order to oxidise the Pt surface in [dema][Tf₂N]. After polarization, an increase in the intensities at binding energies of Pt in the spectrum of the electrochemically oxidized Pt surface can be observed compared to the one recorded at the etched Pt surface. The appearance of shoulder peaks at approximately 73 and 77 eV are indicative of the formation of surface bound species, probably due to formation of a PtO adlayer, after polarization.

Figure 3.3.8 (B) shows a theoretical fitting for Pt 4f and (C) for O1s of the high resolution XP spectra data obtained at a Pt substrate in [dema][Tf₂N] under aforementioned polarization conditions. It is evident from the fitted data that an intense doublet appeared at approximately 71 eV and 75 eV corresponding to metallic Pt. The second doublet at 72.3 and 75.6 eV was the signal due to oxidized Pt present in Pt²⁺ (PtO) and the third doublet at 73.6 and around 77 eV was due to the presence of Pt⁴⁺ oxide (PtO₂).¹⁴⁹ It is clear from the XP spectrum fitted for the O 1s (C) that an increase in the peak intensity was observed in the energy range 530–531 eV. The source of the O 1s peak at about 532 eV (greenish blue line) are the O of [Tf₂N]⁻, and from the air at about 533 eV. This observation shows that an increase in the O 1s peak intensity at 530–531 eV range was a clear evidence for the formation of oxide species^{162, 170} on Pt when immersed in [dema][Tf₂N] at a high polarization potential.

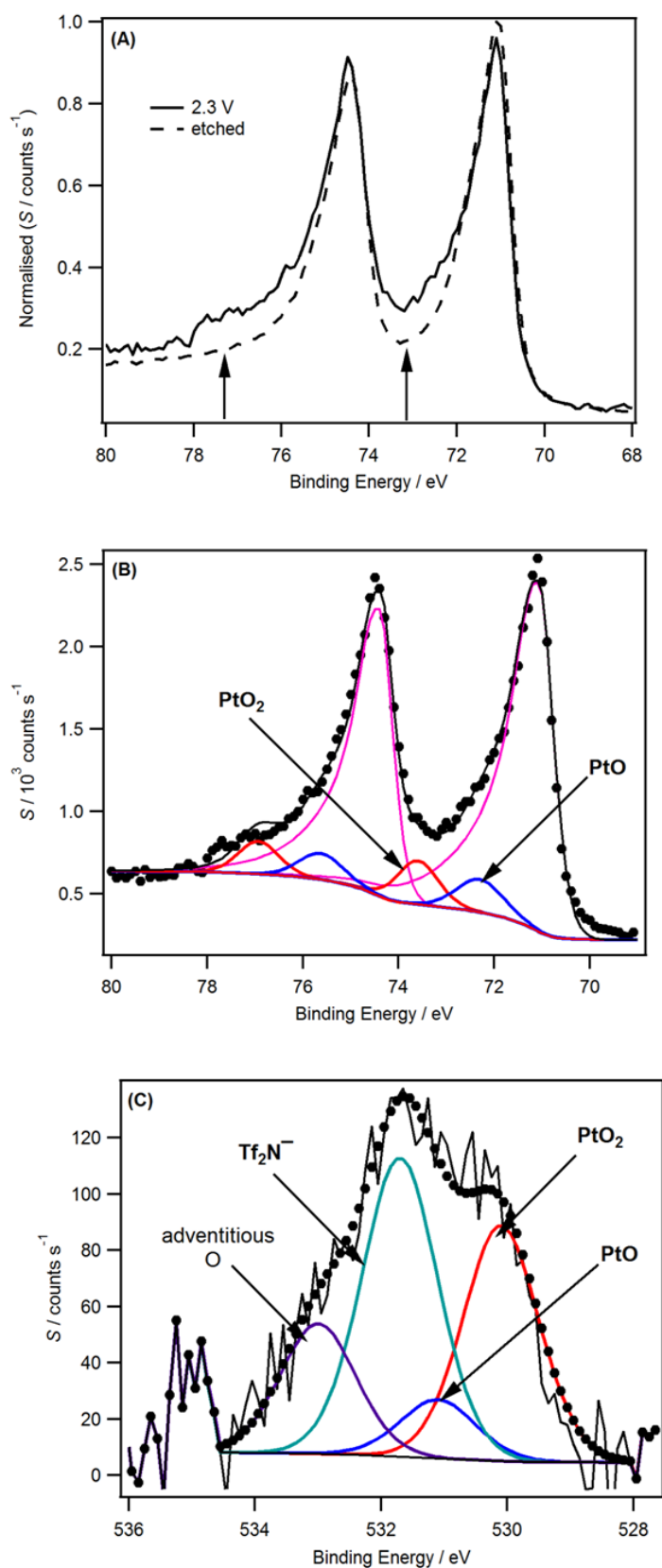


Figure 3.3.8 (A) High-resolution XP spectra obtained at Pt surfaces after polarisation at 2.3 V in [dema][Tf₂N] at 100 °C for 5 min (solid line) and the Pt 4f doublet normalized to the intensity of the Pt 4f_{7/2} peak (dotted line) and theoretical fit of high resolution spectra for Pt 4f (B) and O1s (C).

A similar XPS analysis has been reported by Jonson *et. al.*¹⁶² for the formation of surface oxide on Pt in the ionic liquid [dema][TfO]. The XPS analysis of Pt oxidized surface in [dema][Tf₂N] at 100 °C and a polarization potential of 2.3 V confirm that surface oxides were formed at Pt in the ionic liquid, and initial layer formed on Pt was that of PtO, which followed by another layer of PtO₂ forming on the top of initial layer.¹⁴⁹

3.3.5. Effect of Anodic Potential Limit on Pt Surface

Oxidation

Figure 3.3.9 shows CV profiles for a 2 mm Pt disk working electrode with the potential swept at 50 mV s⁻¹ and $T = 100$ °C in N₂ saturated (A) [dmea][TfO], (B) [dema][TfO] and (C) [dema][Tf₂N], respectively, by increasing the anodic potential limit systematically. Inset of Figure 3.3.9 (A), (B) and (C) are plots of the integrated charge density, q_{ox} obtained from the oxide reduction peaks and the number of monolayers of oxides formed on Pt in [dmea][TfO], [dema][TfO] and [dema][Tf₂N] as a function of positive potential limit. It is clear from the figure that as the positive potential limits were increased in each PIL, the magnitudes of both oxidation and reduction waves increased. The thickness of oxides on Pt surface above 1.0 V in [dmea][TfO] and [dema][TfO] and above 1.2 V in [dema][Tf₂N] increased with the rise in anodic potential limits, which is evident from the increase of the charge densities (see inset of the figure 3.3.9) under the oxide reduction peaks. Also with an increase of positive potential limits the onset of the oxide reduction and its peak potentials shifted towards more cathodic side showing that more irreversible oxide can form on Pt surface at high positive potentials, while keeping temperature constant.

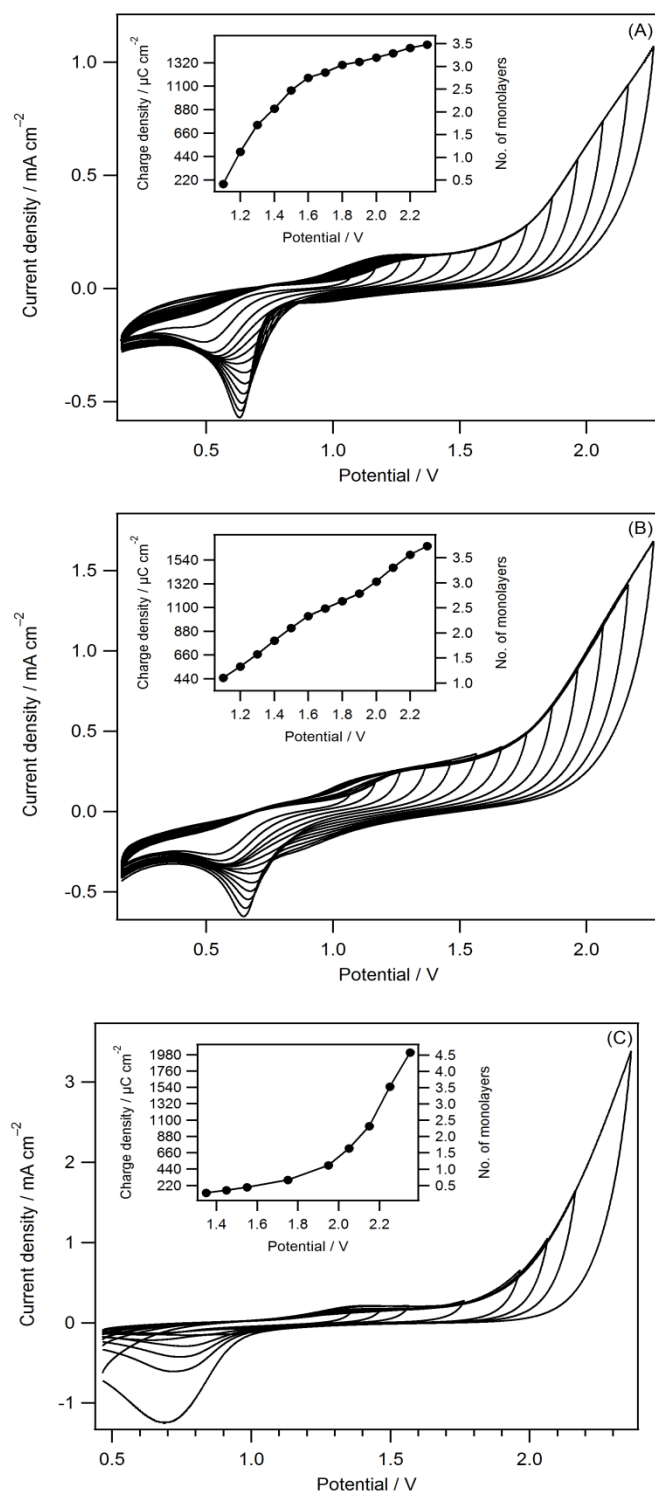


Figure 3.3.9 CVs obtained on a 2 mm diameter Pt disk electrode at 50 mV s⁻¹ and at 100 °C in (A) [dmea][TfO], (B) [dema][TfO] and (C) [dema][Tf₂N] keeping the initial potential 0.15 V and changing anodic potential systematically to 1.1 V, 1.2 V, 1.3 V, 1.4 V, 1.5 V, 1.6 V, 1.7 V, 1.8 V, 1.9 V, 2.0 V, 2.1 V, 2.2 V and 2.3 V in the case of (A) and (B), and in the case of (C) initial potential was 0.45 V and anodic potential limits were increased to 1.4 V, 1.5 V, 1.6 V, 1.8 V, 2.0 V, 2.1 V, 2.2, 2.3 V and 2.4 V. Inset of each figure show plot of integrated charge density under the oxide reduction peak as a function of anodic potential limit.

Inset of each figure shows that the charge density values increased linearly with an increase of positive potential limit, indicating that after scanning to more positive potentials, a greater amount of Pt oxide was present. The q_{ox} values under the oxide stripping wave at 1.1 V was $183 \mu\text{C cm}^{-2}$ in [dmea][TfO] and $448 \mu\text{C cm}^{-2}$ in [dema][TfO], that increased to $1490 \mu\text{C cm}^{-2}$ and $1670 \mu\text{C cm}^{-2}$ respectively, when the positive potential limit was increased to 2.3 V. Similarly, the q_{ox} value under the oxide reduction wave when a switching potential of 1.4 V was used was $120 \mu\text{C cm}^{-2}$ in [dema][Tf₂N], and reached a maximum of $2010 \mu\text{C cm}^{-2}$ at 2.4 V. Inset of the figure 3.3.9 also shows a correlation between the positive potential limits and number of monolayers formed on Pt at each potential in each of the ionic liquid. Initially at lower potential limit c.a. 1.1 V in [dmea][HfB], the q_{ox} value corresponds to nearly half of a monolayer of Pt-oxide and to a monolayer in [dema][TfO], which increased to 3.4 monolayers and 3.8 monolayers, respectively when the positive potential limit was increased to 2.3 V. Similarly, in [dema][Tf₂N], the q_{ox} value at 1.4 V corresponds to even less than half of a monolayer and which then reached to 4.5 monolayers when anodic potential limit was raised to 2.4 V. This behaviour also suggests that thick and thermodynamically more stable oxides films are formed, during the forward sweep, at Pt surfaces with an increase of positive potential limit constant temperature (100 °C) and scan rate (50 mV s^{-1}) which makes their removal more difficult, during the reverse sweep, and as a result, the irreversibility of the surface reaction is increased.^{20, 146, 148, 149, 171}

3.3.6. Influence of Temperature on Oxide Growth in PILs

The growth of oxide layers on electrode surfaces is highly dependent on temperature in aqueous media.^{14, 17, 18, 145, 159, 162} The influence of

temperature variation on the growth of surface oxide species on Pt during positive going scans and their consequent reduction from the surface during reverse scans was studied in PILs. Figure 3.3.10 shows a series of CVs recorded at a 2 mm diameter Pt electrode, recorded at a potential sweep rate of 50 mV s^{-1} in N_2 saturated (A) [dmea][TfO], (B) [dema][TfO] and (C) [dema][Tf₂N] at a range of temperatures (50 °C, 60 °C, 80 °C, 100 °C and 120 °C). It is clear from the figure that the surface oxidation of Pt begins at a less positive potential during positive going sweep as the temperature was increased in each of the PILs. Also, the surface oxide was reduced at lower potentials in the negative going sweep at high temperatures as the reduction peaks shifted towards less negative potentials. It is also evident from the figures that the distance between the oxide formation and reduction waves (peak to peak separation) decreased with increasing temperature and resulted in an increase of the rate of formation of surface oxides on Pt in the PILs and the corresponding reduction of the Pt-surface oxides. It is obvious that with increasing temperature, the rate of reactions are enhanced. For example, in [dmea][TfO], the peak potential for the oxides formation shifted by 0.091 V towards cathodic side when temperature was increased from 50 °C to 120 °C. Also the surface oxides formed on Pt in the liquid was reduced at lower potential at 120 °C than the surface oxides reduced at 50 °C as the the reduction peak potential shifted by 0.083 V towards less negative potential. The peak-to-peak separation between the oxidation and reduction peaks decreased from 0.685 V to 0.511 V when temperature was increased from 50 °C to 120 °C. In addition, with increase of temperature the oxidation peak currents for the formation of Pt-surface oxides in [dmea][TfO] and the reduction peak currents for the corresponding reduction of the Pt-surface oxides, have increased. Similar shifts in the anodic peak potentials, cathodic peak

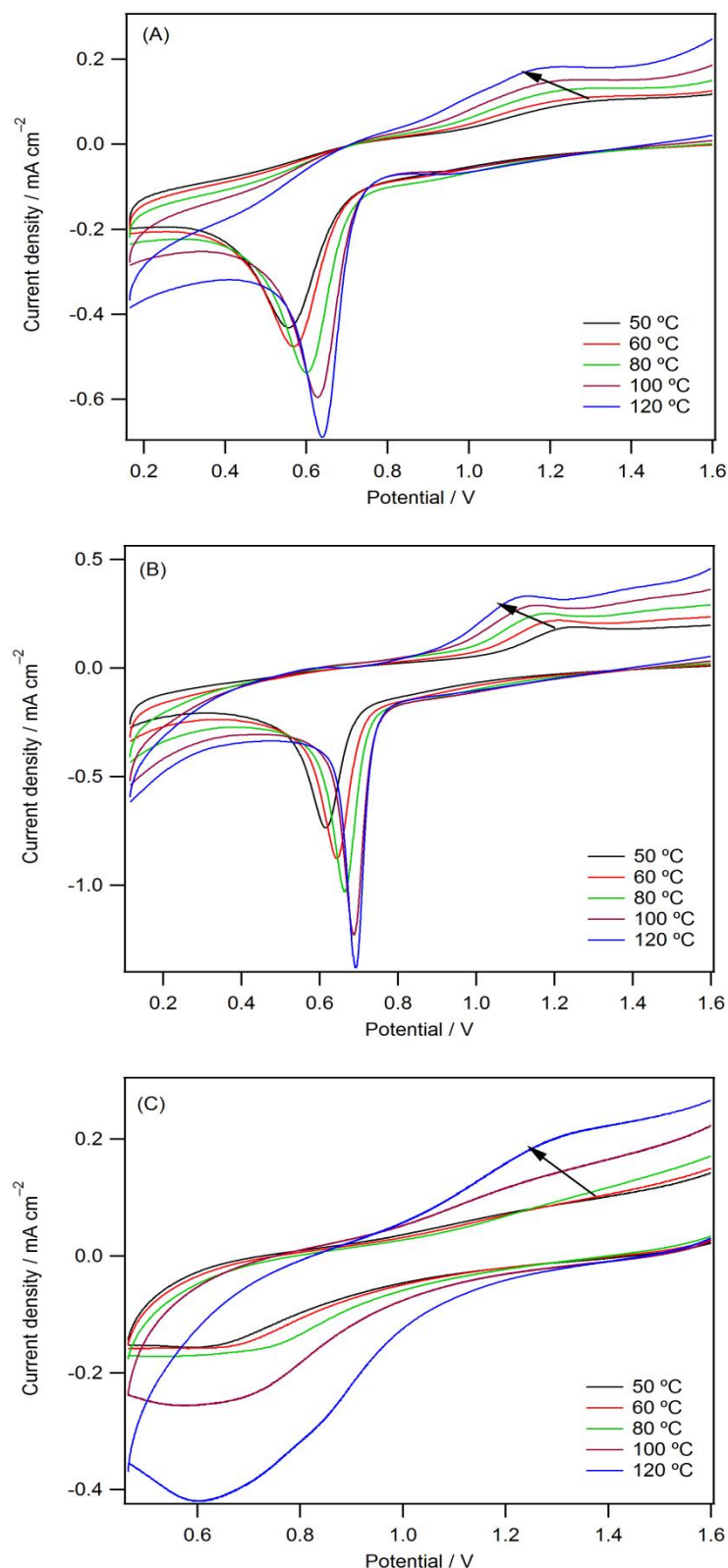


Figure 3.3.10 CVs profiles, recorded at 2 mm diameter Pt disk electrode, at 50 mV s^{-1} and different temperatures (50 °C, 60 °C, 80 °C, 100 °C and 120 °C) in blank, (A) [dmea][TfO], (B) [dema][TfO] and (C) [dema][Tf₂N]. The potential cycled from 0.15 to 2.35 V in (A), 0.10 to 2.4 V in (B), and from 0.45 to 1.75 V in case of (C). Data up to 1.6 V is shown in each figure to show only the oxides formation and reduction potential region.

potentials and anodic and cathodic peak currents for the Pt surface oxidation-reduction were noticed in the other two PILs. In both TfO-based ionic liquids, the peak to peak separation decreased drastically when the temperature was raised compared to [dema][Tf₂N], indicating that the kinetics of the oxide formation and reduction process in TfO based ionic liquids are faster than Tf₂N-based PIL as T is raised. The shifting of the oxidation peak towards more negative potentials and the reduction peaks towards more positive potentials upon temperature rise has been reported in aqueous acid system by Conway *et al.*¹⁴⁵ on Pt and Jerkiewicz *et al.* for Pt,¹⁴ Au¹⁷ and Pd¹⁵⁹. Walsh *et al.*¹⁶² also reported a decrease in peak to peak separation with temperature increase in a PIL and Bond *et al.*¹²⁴ reported similar results for the effect of temperature on oxide formation and reduction on gold surfaces in aprotic ionic liquids.

Analysis of the charge density under the oxides reduction peaks at various temperatures in the PILs shows that the charge density values increased with increase of temperature of the PILs. For instance, the charge density under the oxide reduction peaks increased from 1050 $\mu\text{C cm}^{-2}$ at 50 °C to 1230 $\mu\text{C cm}^{-2}$ after raising the temperature for [dmea][TfO] to 120 °C. The analysis of extent of oxidation of Pt and corresponding reduction from trace water in the PILs indicating that at high temperatures and constant potential and scan rate, the surface of Pt was covered with thick oxide films. In [dmea][TfO], the number of monolayers of oxides formed on Pt from trace water oxidation from 50 °C to 120 °C ranging from 2.3 to 2.8 layers. The q_{ox} values under the oxide reduction waves in [dema][Tf₂N] were smaller at all temperatures keeping potential constant in comparison with that in the two TfO-based PILs. Less than a monolayer of oxide was formed at 50 °C (0.198 ML), 60 °C (0.224 ML), 80

°C (0.314 ML) and 100 °C (0.456 ML) that reach to a complete monolayer (1.12 ML) at 120 °C.

3.3.7. Mechanism of Oxide Growth on Pt in PILs

The formation of oxide layers (sub monolayer, monolayer and multilayers) on the surface of noble metals such as Pt, Au, Pd etc in aqueous media follows either logarithmic or inverse logarithmic kinetics.^{14, 17, 18, 20, 145, 146} It is suggested that for sub-monolayer coverage of metal with oxide the integrated charge density, q_{ox} is directly related to the logarithm of the oxide deposition time, $\log t$ and the inverse of q_{ox} is proportional directly to $\log t$ for multilayers of surface oxides. To explore such behavior at Pt in protic ionic liquids, linear sweep voltammograms during cathodic sweeps at Pt at a fixed scan rate were recorded in [dmea][TfO], [dema][TfO] and [dema][Tf₂N] at different potentials and temperatures for a range of time periods. The oxides formed on the surface of Pt were stripped from the Pt surfaces voltammetrically during the cathodic potential sweep, and integrated charge values for the entire set of experiments were measured in each PIL and then normalised to the real surface area of the electrode (0.046 cm²) to get charge densities (C cm⁻²). The data obtained was fitted to the two kinetic models and the best fit comparison for these PILs discussed.

Figures 3.3.11, 3.3.12 and 3.3.13 show plots of q_{ox} and $1/q_{ox}$ versus $\log t$ at various deposition potentials and deposition times in [dmea][TfO] and [dema][TfO] and [dema][Tf₂N], respectively, at a constant temperature (100 °C). The potentials at which surface oxides were formed on Pt were 1.0 V, 1.1 V, 1.2 V, 1.4 V and 1.7 V in both TfO-based PILs and 1.6 V, 1.7 V and 1.8 V in [dema][Tf₂N] by holding the electrode for 1 s, 3

s, 5 s, 10 s, 20 s, 40 s, 60 s, 80 s, 100 s, 120 s, 180 s and 220 s at each potential in each of the PILs. Then charge was measured under the oxide wave during cathodic sweeps at each deposition potential and time. Generally the charge versus $\log t$ figures show that thick oxides layers (more than monolayers) were formed at Pt in each of these PILs at high polarization times and/or high potentials. At low polarization potentials and low deposition times submonolayer and monolayer growth of oxide films occurred.

The q_{ox} values under the oxide stripping wave at 1.0 V in [dmea][TfO] (Figure 3.3.11 A) shows that less than a monolayer of oxide formed at Pt at low deposition times ($t < 40$ s) which then reached 1 ML when t was 40 s and above. At 1.0 V in [dmeaTfO], the shortest polarization time $t = 1$ s results in ~ 0.3 ML and at $t = 220$ s in ~ 1.4 ML of oxides at Pt. Similarly, for $E = 1.1$ V, the q_{ox} values shows that before 5 s, the Pt surface is not completely covered and less than 1 ML of oxides were grown which then grows to 1 ML at a deposition time of 10 s. The transition from 1 ML to multilayers occurred at 1.1 V at higher t values and almost reached to 2 ML at 220 s. However, at high deposition potentials ($E = 1.2$ V, 1.4 V and 1.7 V), more than 1 ML of oxides were formed at Pt in [dmea][TfO], ranging from 1-3 ML, at all deposition times. The growth of less than 1 ML at low deposition time (2 s) and 100 °C at 1.1 V and multilayers at high anodic potentials are supported from the study of the effect of anodic potential limit on the oxide growth in [dmea][TfO], described in Section 3.3.4.

Observation of linear q_{ox} versus $\log t$ and $1/q_{ox}$ versus $\log t$ plots points to the applicability of the kinetic laws. The q_{ox} vs. $\log t$ plots are linear for $q_{ox} < 440 \mu\text{C cm}^{-2}$ for the growth of oxides at Pt and when q_{ox} exceeds the value of $440 \mu\text{C cm}^{-2}$, the q_{ox} vs. $\log t$ plots shows a non-

linear behavior and $1/q_{\text{ox}}$ vs. $\log t$ then show a linear behaviour showing that the oxide formation at Pt follows inverse logarithmic growth kinetics.¹⁴

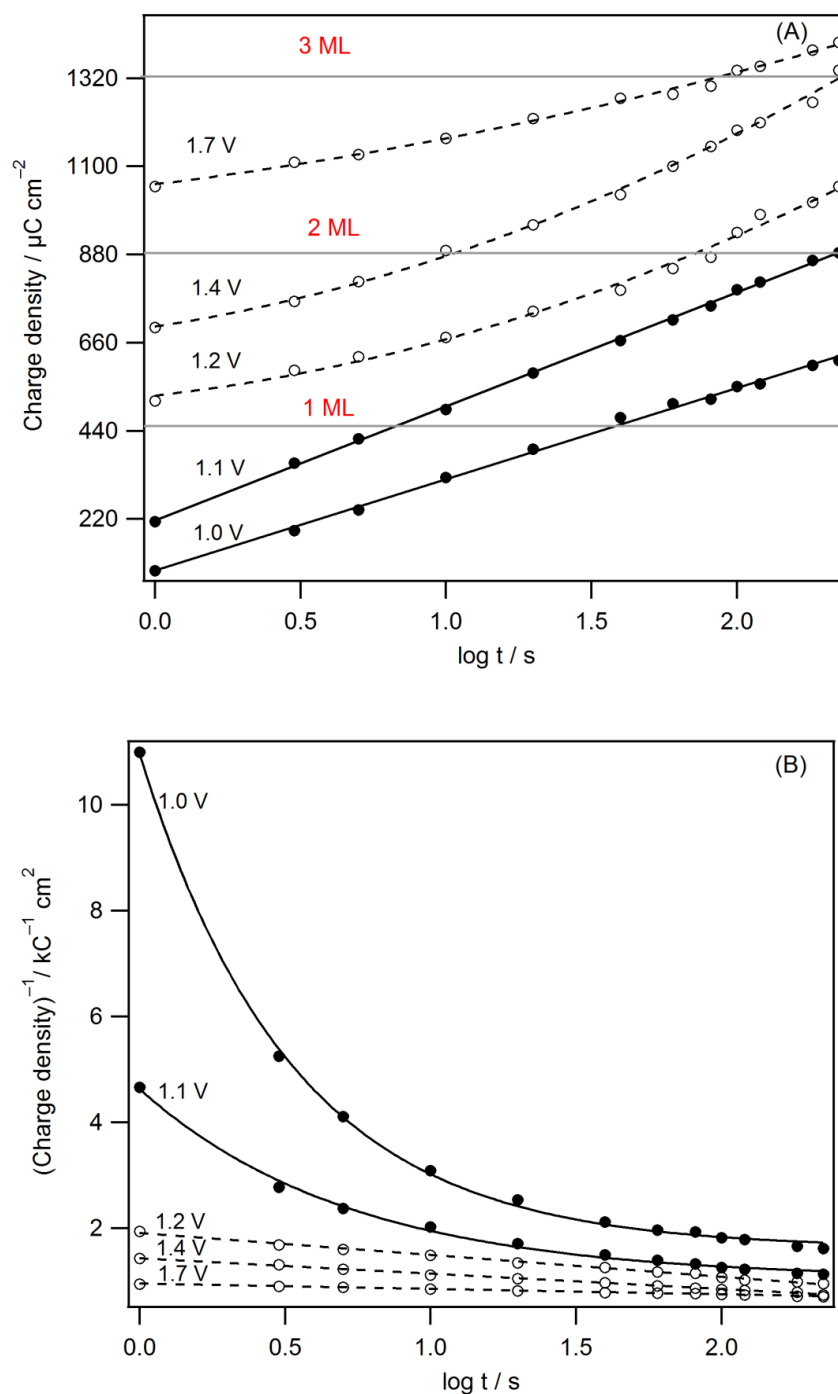


Figure 3.3.11 (A) Plots of the charge density under the oxide reduction peak vs. $\log$ of deposition time ($\log t$) and (B) inverse of charge density vs. $\log t$ for a set of deposition potentials (1.0 V, 1.1 V, 1.2 V, 1.4 V and 1.7 V) at 100 °C and at a scan rate of 50 mV s^{-1} in $[\text{dmea}][\text{TfO}]$.

Figure 3.3.11 shows that the charges under the oxide stripping wave at 1.0 V and 1.1 V increases linearly with the logarithm of the deposition time at each potential for [dmea][TfO] (see solid lines with solid dots in Figure 3.3.11 A) and the plot of $1/q_{ox}$ vs. $\log t$ shows non-linear behavior (see dotted lines with open dots in Figure 3.3.11 B). This linear increasing behavior of the q_{ox} with $\log t$ shows that the initial growth of surface oxide at Pt in [dmea][TfO] at 1.0 V and 1.1 V follows direct or linear logarithmic kinetics and not the inverse oxide growth kinetics. At $E \geq 1.2$ V (i.e. 1.2 V, 1.4 V and 1.7 V), the growth of more than 1 ML of Pt oxide occurred and deviation from linearity from the plot of q_{ox} vs. $\log t$ was observed (see dotted line with open dots in Figure 3.3.11 A). At these potentials the surface oxide growth at Pt in PILs follows inverse logarithmic kinetics for the oxide growth at all deposition times as the plot between $1/q_{ox}$ vs. $\log t$ was linear (see dotted lines with open dots in Figure 3.3.11 B) and the plot between q_{ox} vs. $\log t$ was non-linear (see solid lines with solid dots in Figure 3.3.11 A).

Kinetic behaviour similar to that observed for the oxides growth on Pt in [dmea][TfO] was observed by kinetic study of the Pt surface oxidation in [dema][TfO]. However, the transition from submonolayer to monolayer of oxide formation at Pt occurred in [dema][TfO] at 1.1 V, and multilayer formation started between 1.2 V and 1.8 V even at short polarization times, shown by Figure 3.3.12 A, B and C. In [dema][TfO], the growth of oxides on Pt is <1 ML at 1.0 V at $t=1$ s, 3 s, 5 s and 10 s, which then form 1 ML at high deposition times at 100 °C. At 1.0 V the growth of oxide films at Pt in [dema][TfO] follows direct logarithmic oxide growth kinetics as the plot of q_{ox} vs. $\log t$ was linear (see solid line with solid dots in Figure 3.3.12 A) and that of $1/q_{ox}$ vs. $\log t$ was non-linear (see solid line with solid dots in Figure 3.3.12 B).

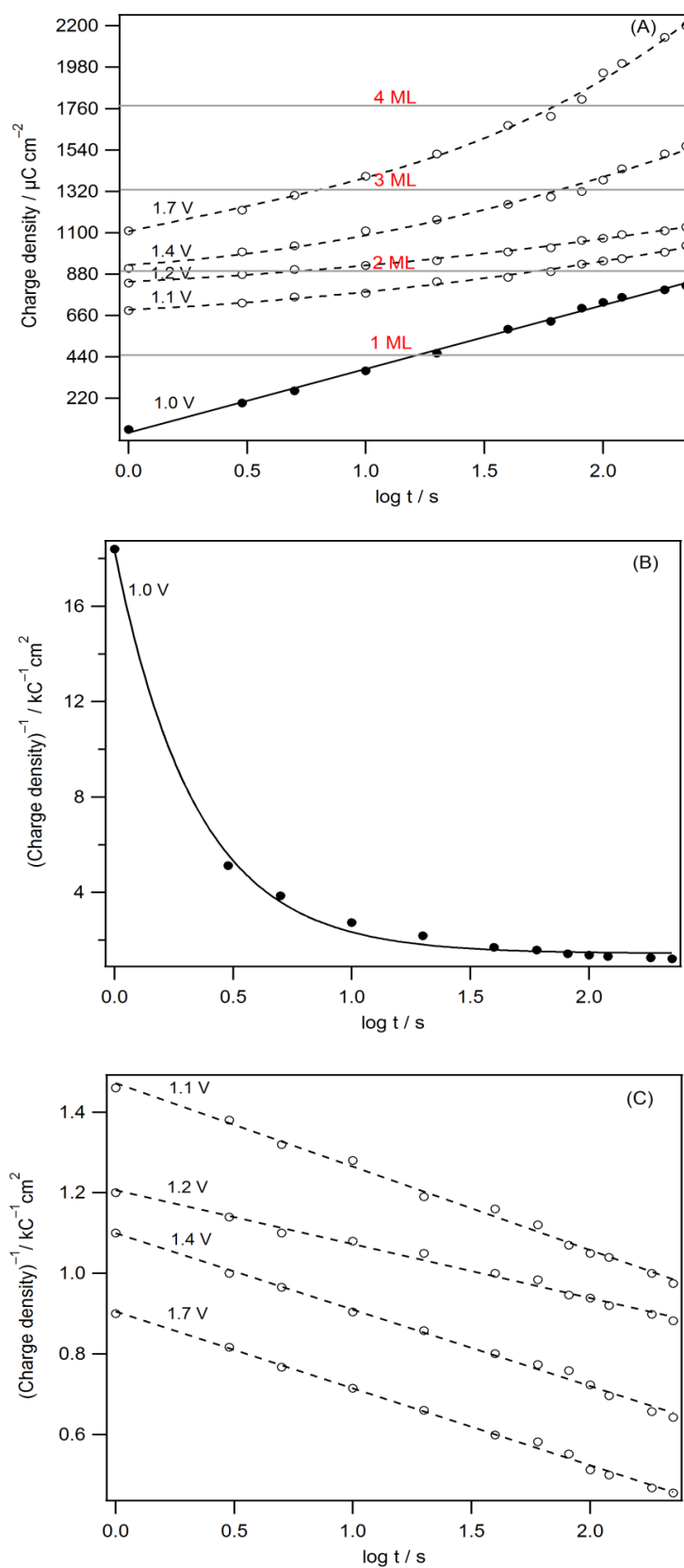


Figure 3.3.12 (A) Plots of the charge density vs. $\log t$ (of deposition time) and (B) and (C) represents plots of the inverse of charge density vs. $\log t$ for a set of deposition potentials (1.0 V, 1.1 V, 1.2 V, 1.4 V and 1.7 V) at 100 °C and at a scan rate of 50 mV s^{-1} in [dema][TfO].

At potentials higher than 1.0 V ($E=1.1$ V, 1.2 V, 1.4 V and 1.7 V) the q_{ox} values are $> 440 \mu\text{C cm}^{-2}$ forming 1–3.5 ML of oxides at all deposition times and follows inverse logarithmic oxide growth kinetics in [dema][TfO] at 100 °C and not the direct oxide growth kinetics (see dash lines with open dots in Figure 3.3.12 C compared to the dash lines in Figure 3.3.12 A), due to formation of multilayers of oxides at Pt.

In the case of [dema][Tf₂N] (Figure 3.3.13), the oxide growth was slow compared to the both TfO-based ionic liquids in which the oxide formation starts above 1.2 V, which is also described in Section 3.3.4. Even at the potentials 1.6 V and 1.7 V less than a ML of oxide formed at Pt at lower deposition times. At $E=1.6$ V at 100 °C, less than 1 ML of oxide formed at Pt in [dema][Tf₂N] at t until 80 s as the q_{ox} values were $< 440 \mu\text{C cm}^{-2}$ which then increased at $t>80$ s and resulted in the formation of a complete monolayer at 220 s. At both of these potentials (1.6 V and 1.7 V), the kinetics for oxide growth were logarithmic, as is evident from the linear plot of q_{ox} and $\log t$ (see solid lines with solid dots from Figure 3.3.13 A), and non-linear between $1/q_{ox}$ vs. $\log t$ (see solid lines with solid dots from Figure 3.3.13 B). At the high potential of 1.8 V, deviation from linearity of q_{ox} vs. $\log t$ occurred in [dema][Tf₂N] and followed inverse logarithmic kinetics due to the growth of more than a ML of oxide at Pt as the q_{ox} values are $> 440 \mu\text{C cm}^{-2}$ at all of the deposition times ($1 \text{ s} \leq t \leq 220 \text{ s}$) and reaches 2 ML at 60 s and above.

Generally in each of these PILs, at constant temperature an increase in the thickness of oxide layers is observed with an increase of deposition potentials and deposition times. The charge density vs. $\log t$ plots follow direct logarithmic kinetics at lower potentials and when less than 1 ML of oxide are formed. The plots start deviating from linearity as soon as the charge under the oxide reduction peaks attained values corresponding to 1

ML. When q_{ox} values increased such that they correspond to multilayer formation (2–3 ML), then at that potential condition, plots of q_{ox} vs. $\log t$ became non-linear and plots of $1/q_{\text{ox}}$ vs. $\log t$ became linear. The growth of thick oxide films follow then inverse logarithmic kinetics similar to that observed at aqueous acid solutions.^{14, 17}

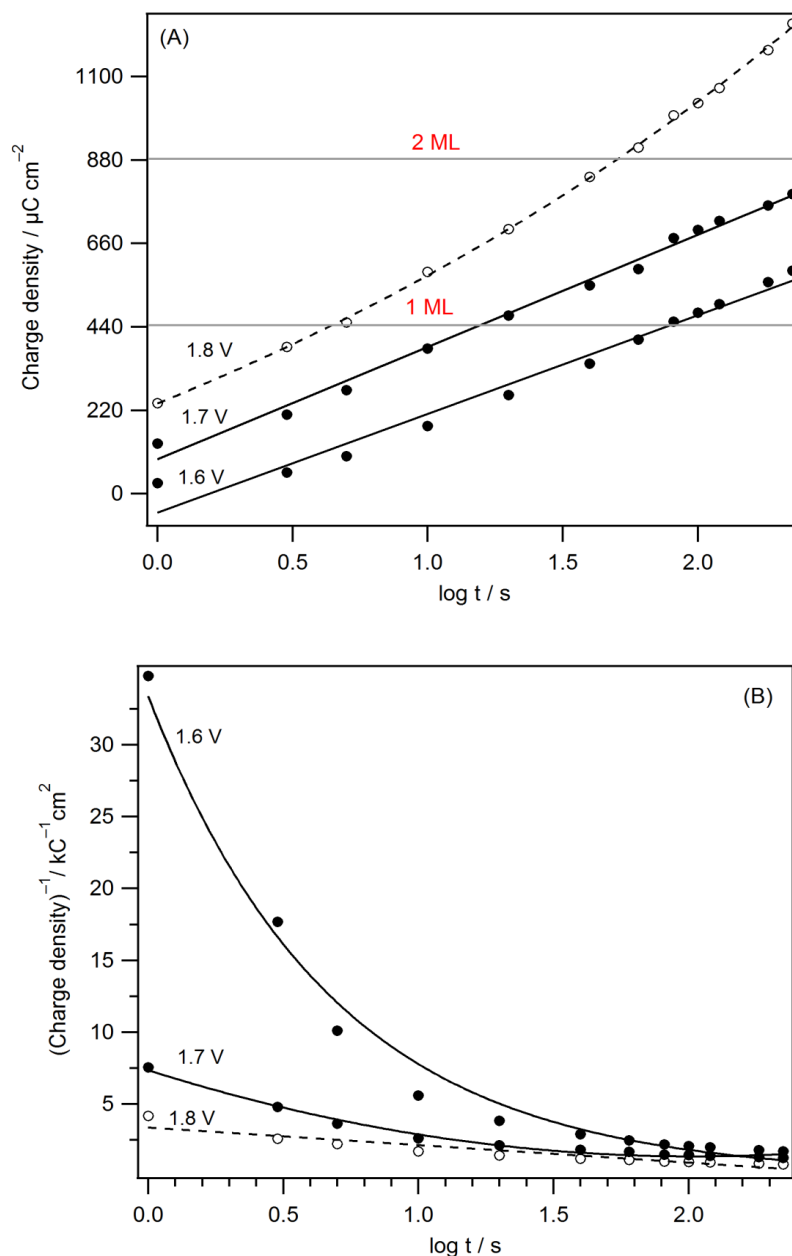


Figure 3.3.13 Graphs of the charge density under the oxide reduction peak vs. $\log$ of deposition time ($\log t$) (A) and inverse of charge density vs. $\log t$ (B) for a set of deposition potentials (1.6 V, 1.7 V and 1.8 V) at 100 °C and at a scan rate of 50 mV s^{-1} in $[\text{dema}][\text{Tf}_2\text{N}]$.

Figure 3.3.14 present q_{ox} vs. $\log t$ and $1/q_{ox}$ vs. $\log t$ plots for various temperature, $T = 50\text{ }^{\circ}\text{C}$, $60\text{ }^{\circ}\text{C}$, $80\text{ }^{\circ}\text{C}$ and $100\text{ }^{\circ}\text{C}$ in $[\text{dmea}][\text{TfO}]$ and $60\text{ }^{\circ}\text{C}$, $80\text{ }^{\circ}\text{C}$ and $100\text{ }^{\circ}\text{C}$ in $[\text{dema}][\text{Tf}_2\text{N}]$, showing the effect of temperature on the oxide growth kinetics. The q_{ox} values were obtained from the oxide stripping peaks during a potential sweep at constant polarization potentials, 2.0 V in $[\text{dmea}][\text{TfO}]$ and 2.4 V in $[\text{dema}][\text{Tf}_2\text{N}]$ recorded during linear sweep voltammetry at various time intervals, 1, 3, 5, 10, 20, 40, 60, 80, 100, 120, 180 and 220 seconds. Figures (A) and (C) shows q_{ox} vs. $\log t$ plots for $[\text{dmea}][\text{TfO}]$ and $[\text{dema}][\text{Tf}_2\text{N}]$ and (B) and (D) are their respective $1/q_{ox}$ vs. $\log t$ plots.

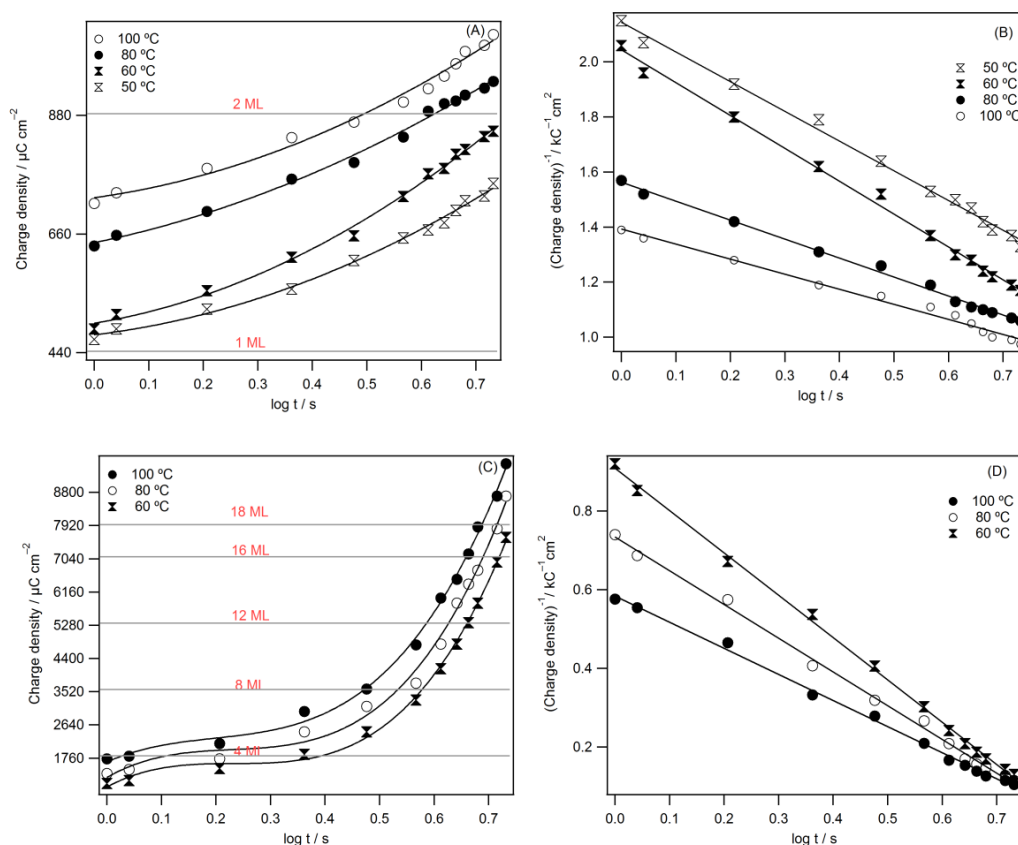


Figure 3.3.14 Plots of the integrated charge density vs. $\log t$ obtained (A) in $[\text{dmea}][\text{TfO}]$ and (C) in $[\text{dema}][\text{Tf}_2\text{N}]$ or inverse charge density vs. $\log t$ in (B) in $[\text{dmea}][\text{TfO}]$, and (D) in $[\text{dema}][\text{Tf}_2\text{N}]$.

The results show that these plots are non-linear as q_{ox} was $> 440\text{ }\mu\text{C cm}^{-2}$ for all the temperatures and at each deposition time at the specific

potential in each of the PIL. A growth of 2 ML to 3 ML at 100 °C and 2 V was observed in the case of [dmea][TfO] at all deposition times. In the case of [dema][Tf₂N], an increase of temperature from 60 °C to 100 °C at 2.4 V polarization potential and minimum deposition time results in an increase of oxide layer thickness by approximately 1.5 ML.

In each of the PILs, at each temperature, the oxide formation on a Pt surface follows inverse logarithmic growth kinetics (i.e. $1/q_{ox}$ vs. $\log t$) and not linear kinetics (q_{ox} was not linearly proportional to $\log t$). The data demonstrates that temperature has a drastic effect on the thickness of the oxide layers formed on Pt from electrooxidation of water in the PILs. The data also agrees with that described in Figure 3.3.10 that multilayers of oxide are formed at Pt in the PILs at high temperatures.

3.4. Conclusions

A detailed study of the electrochemical behaviour of Pt has been carried out in [dmea][TfO], [dema][TfO] and [dema][Tf₂N] using cyclic voltammetry, linear sweep voltammetry and XPS. It was found that the surface of Pt became covered with stable oxide films while in contact with the PILs, as confirmed by analysis of Pt surface using electrochemical and XPS techniques. The oxide films formed on Pt due to trace water oxidation in the PILs. The extent of oxidation and surface charge density values under the Pt-oxides reduction peaks increased upon an increase of water contents in the PILs. Analysis of the electrochemical data revealed a significant increase in the oxide film thickness and oxide stripping charges, when the oxide films were grown at higher deposition potentials, deposition times and elevated temperatures. At low oxidizing potentials, PtO was formed but when the potential was increased, a thicker film of PtO₂ was

grown on the top of PtO at 100 °C, as evident from the XPS analysis of the polarized surface of Pt in [dema][Tf₂N].

The growth of these oxide layers increases from sub-monolayer to a ML and then to several MLs at higher temperatures and deposition times. The growth of the Pt oxide species to sub-monolayer and a ML follows direct logarithmic growth kinetics, and after which the oxide formation follows inverse logarithmic kinetics in the PILs. The Pt oxide growth in each of the PILs follows inverse logarithmic growth kinetics at high temperatures ($50\text{ }^{\circ}\text{C} \leq T \leq 100\text{ }^{\circ}\text{C}$) at all deposition times studied at a high deposition potential.

To conclude further from this chapter, it is suggested that the trace water, omnipresent in PILs, cannot be ignored when studying electrocatalytic reactions in these electrolytes. The oxidation of water in PILs to cover Pt surfaces with oxides can hinder or facilitate various electrocatalytic processes. Therefore, we have investigated electrocatalytic oxidation of hydrazine, formic acid, ethanol, and dimethyl ether in PILs, in order to explore the role of the surface Pt-oxides in these electrocatalytic processes, which will be discussed in detail in the following chapters.

Chapter 4: Electrocatalytic Oxidation of Hydrazine at Pt in Protic Ionic Liquids: The Role of Residual Surface Oxides

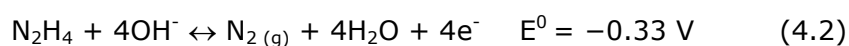
4.1. Introduction

The presence of adsorbed oxide species on noble metal electrodes such as Pt can play an important role in both the inhibition and promotion of various electrochemical processes.²⁴ The potential region in which anodic oxidation of some adsorbed inorganic or organic species occurs may overlap with that of surface oxide formation, and the overall oxidative current may correspond to both of the processes taking place simultaneously.¹⁷² For example, electrochemical reactions such as the OER at Pt electrodes are electrocatalyzed in the presence of surface oxide species on the electrode. OER occurs on the top of surface oxide films on Pt, and the rate of this process is influenced significantly by the thickness of oxide layers.¹⁵⁸ Electrooxidation of hydrazine in aqueous media is another reaction that is significantly dependent for its voltammetry and kinetics on the surface composition of the electrode.^{24, 36-38}

Hydrazine is an important inorganic material with the chemical formula of N_2H_4 . Hydrazine is used widely as a strong reducing agent, an anticorrosive material,^{24, 37} in the propulsion and explosives industries,²⁴ as an insecticide and plant-growth regulator,¹⁷³ as a foaming agent in preparing polymer foams, and as a fuel in rockets.⁵² The relatively high heat of combustion value (-622 kJ mol^{-1}),³⁸ high open circuit voltage ($\sim 1.61 \text{ V}$) and 100% theoretical efficiency ($\Delta G/\Delta H$) of hydrazine fuel cells

have prompted interest in this material for the development of the direct hydrazine fuel cells (DHFCs).¹⁷⁴

Hydrazine exists in solution either in a protonated form as hydrazinium ion (N_2H_5^+), mainly in acidic media, or in an unprotonated form (N_2H_4), mainly in basic media. The oxidation reactions of hydrazine at a Pt electrode in acidic (Eqn. 4.1) as well as alkaline media (Eqn. 4.2) vs. RHE are given below;³⁹



The electrochemical oxidation of hydrazine has been the subject of study at Pt electrodes in both aqueous acidic and basic media.^{24, 36-39} The oxidation of hydrazine is a very facile process and the best electrocatalyst used is Pt. Oxidation proceeds via initial adsorption of hydrazine at Pt. The intermediates are relatively weakly adsorbed, and typically no electrode poisoning is observed.³⁶ However, an overpotential ($> 0.3 \text{ V}$) is observed compared to the theoretically calculated thermodynamic standard potential.^{24, 37}

The mechanism of the electrooxidation of hydrazine depends on the composition of the electrolyte, pH of the medium and electrode facets.^{24, 37, 39} Rosca et al.,³⁷ studied the mechanism of the electrocatalytic oxidation of hydrazine in aqueous NaOH at Pt using cyclic voltammetry and reported that oxidation of hydrazine at Pt occurs at high overpotential. The voltammetry of hydrazine oxidation is significantly influenced by the prior history of the Pt surface and the residual oxides on the electrode are mainly responsible.³⁶ Compton et. al.,²⁴ investigated the role of residual oxides at Pt ultra-microelectrodes during hydrazine oxidation in aqueous

acidic and basic media. They found that the rate of hydrazine oxidation depends on the pre-history of the electrode, and occurs at more negative potentials during second and subsequent scans due to the presence of residual oxides at the electrode that activate the electrode for further oxidation processes. Bard highlighted that extended immersion of a pre-oxidized electrode in hydrazine results in its deactivation, as a result of the reaction of hydrazine with residual oxides, the potential for hydrazine oxidation then shifts more positive, coinciding with Pt oxide formation.

Most research on the electrochemical oxidation of hydrazine has been performed in aqueous acid or alkaline systems and no literature is available on the reactivity of surface oxides in ionic liquid media. As mentioned in the previous chapter, the anodization of Pt in PILs can lead to the formation of surface oxide films by oxidation of trace water in the liquids. Therefore, it would be interesting to know about the role that these surface oxides play during hydrazine oxidation in PILs.

In this chapter, we describe the electrocatalytic oxidation of hydrazine in PIL environments, and explore the reactivity of surface oxides formed at polycrystalline Pt in the PILs [dmea][TfO], [dema][TfO] and [dema][Tf₂N]. To the best of my knowledge this is the first such investigation where the role of surface Pt oxides in the electrocatalysis of hydrazine in ionic liquids has been investigated. A significant activation of the Pt electrode towards hydrazine oxidation was observed during potential cycling in the TfO- based PILs and this is due to the participation of residual oxides, which remain on the electrode surfaces during potential cycling. Our investigation also revealed gradual deactivation of the pre-oxidized Pt electrode in [dmea][TfO], which can be attributed to a reaction of hydrazine dissolved in the PIL with the residual surface Pt-oxides. However, the electrochemical behaviour of hydrazine oxidation was

different in [dema][Tf₂N] compared to the two TfO-based PILs, the possible reasons for which will be discussed in the Results and Discussion section.

4.2. Experimental Section

4.2.1. Chemical Reagents

Hydrazine monohydrate (N₂H₄·H₂O) was purchased from Sigma-Aldrich (> 99 %) and used as received. Hydrazine solutions in the PILs were prepared in a fume hood.

4.2.2. Electrochemical Measurements

Electrochemical measurements were performed in a conventional three-electrode cell containing a 5 mm diameter Pt disk as the working electrode. The current in the measurements was normalized to the geometric surface area (0.1964 cm⁻²) of the electrodes. The reference electrode and counter electrodes were those described in Section 3.2.2. The electrode was polished and deaerated per previous procedure described in Section 3.2.2.

4.3. Results and Discussion

4.3.1. Electrochemistry of Hydrazine at Pt in PILs

Figure 4.3.1 displays fifteen consecutive cyclic voltammograms recorded at a clean 5 mm diameter Pt disk electrode in 50 mM hydrazine solution in [dmea][TfO] at 45 °C and 50 mV s⁻¹. It shows that during the 1st scan (red line) no oxidation peak was observed until 1.0 V when a broad oxidative

wave appeared, coinciding with the onset of Pt oxide formation. The oxidation current was high during the reverse sweep until it decreased drastically at the onset of Pt-oxides reduction. Comparing the 2nd scan (blue line) and consequent scans (black lines) to the 1st scan, an oxidative shoulder for hydrazine oxidation appeared at about 0.6 V (about 0.4 V negative of the 1st scan) at an average peak potential of 0.8 V. This shows that the activation of the electrode surface occurred due to the formation of Pt oxides during the first sweep that persisted on the surface for the next scans to facilitate electrooxidation of hydrazine.²⁴ The height of the oxidation peak increased during successive cycles until it stabilized beyond the 10th cycle. The peak potential of the anodic shoulder shifted to less positive potentials by as much as 0.5 V, which agreed with Bard's observation for an aqueous solution of hydrazine.¹⁷⁵ A behaviour similar to this was observed by Jiang *et. al.*,² for an aqueous methanol system during potential cycling of Pt electrodes.

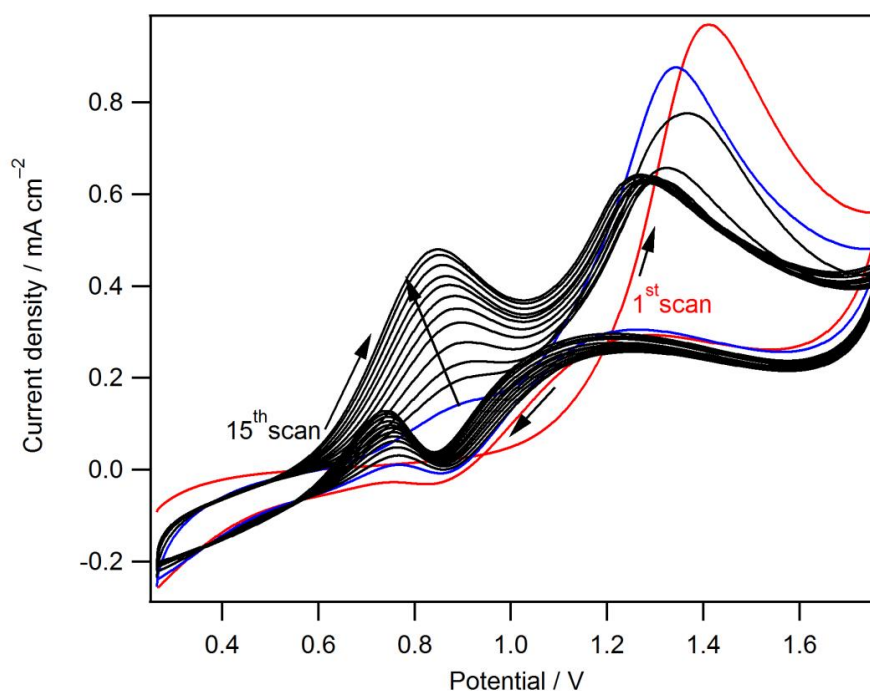


Figure 4.3.1 CV profiles in 50 mM N_2H_4 in $[dmea][TfO]$ at a 5 mm diameter Pt disk electrode at 50 mV s^{-1} and $45\text{ }^\circ\text{C}$, cycled from an initial potential of 0.25 V up to 1.75 V.

In each of these cycles (except the 1st scan), on the positive going scan, the magnitude of the current of the first oxidative wave increased and then decreased slightly followed by a second current increase. The decrease observed after the first hydrazine oxidation wave at a potential slightly above 1.0 V was due to the onset of formation of surface oxide on Pt. Once surface oxide species were formed at Pt at about 1.1 V in [dmea][TfO], the oxidative current began to rise again, corresponding to the bulk oxidation of hydrazine. On the reverse scan, hydrazine oxidation continued from 1.4 V to 1.1 V and then began decreasing until approximately 0.9 V, coinciding to the reduction of surface oxides (which happens in [dmea][TfO] from 0.8 V to 0.6 V), freeing up catalytic sites and allowing the oxidation reaction to occur again between $0.8\text{ V} \geq E \geq 0.6\text{ V}$.

The voltammetric behaviour of hydrazine in [dema][TfO] was also studied and Figure 4.3.2 shows five successive CV profiles obtained at a freshly polished 5 mm diameter polycrystalline Pt electrode at a sweep rate of 100 mV s^{-1} and $25\text{ }^{\circ}\text{C}$ in 50 mM solution of hydrazine in [dema][TfO]. The electrochemical response in this PIL was similar to that observed in [dmea][TfO]. During the first sweep, an oxidation peak appeared at about 1.0 V due to the formation of surface oxides on Pt. On the second and subsequent scans a shoulder peak (centered at 0.80 V) corresponding to hydrazine oxidation appeared. The increase in the height of this shoulder peak and the shifting of its oxidation potential value towards less positive values with increasing cycles was also visible, and closely resembles the pattern observed in [dmea][TfO]. This observation also supports the conclusion drawn above, that surface oxides which persist on the Pt surface during potential cycling and catalyse hydrazine oxidation in the PILs at polycrystalline Pt electrodes. However, compared to [dmea][TfO], the peak currents in [dema][TfO] due to hydrazine oxidation both at activated

electrode sites at 0.6 V and the bulk oxidation peak near 1.4 V, were smaller. This difference can be attributed in part to the instability of hydrazine in [dema][TfO] because it was found that as the experimental time progressed, the hydrazine/[dema][TfO] solution became cloudy and this was reflected in a loss of the voltammetric signals at extended times.

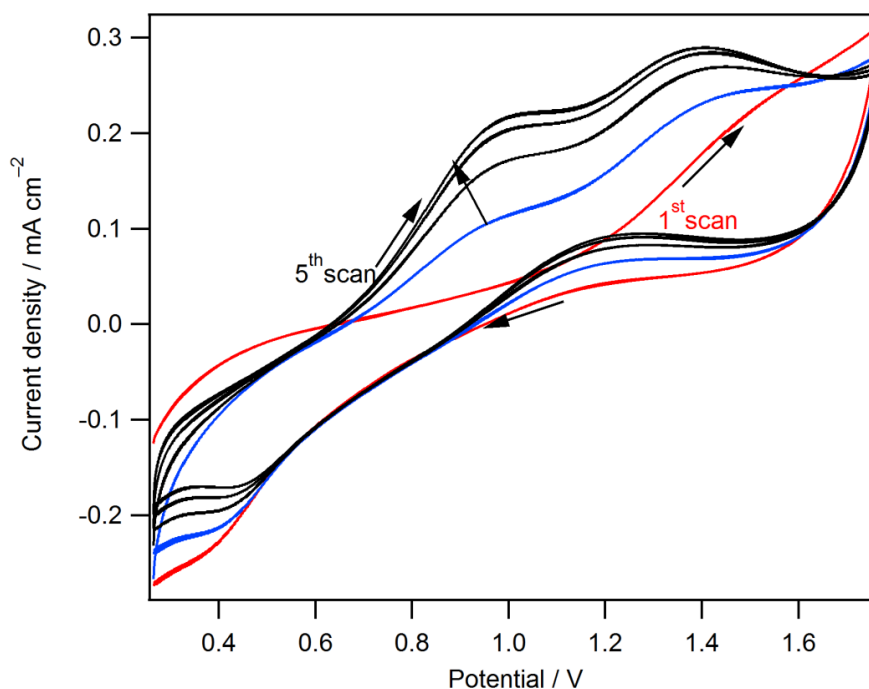


Figure 4.3.2 CV profiles obtained in 50 mM N_2H_4 in [dema][TfO] at a 5 mm diameter Pt disk electrode at 100 mV s^{-1} and $25\text{ }^\circ\text{C}$, between 0.25 V and 1.75 V.

In contrast to both [dmea][TfO] and [dema][TfO], [dema][Tf₂N] has a different anion to the former two PILs studied, and the voltammetric response of hydrazine in this PIL was also different. Figure 4.3.3 shows a series of CVs recorded at a clean 5 mm diameter Pt disk electrode in a 50 mM hydrazine solution in [dema][Tf₂N] under the same experimental conditions as in [dmea][TfO]. Oxidation of hydrazine was observed with an onset potential of 0.6 V right from the first scan, as opposed to [dmea][TfO] and [dema][TfO] where the same happened but only in the second and consequent scans. This shows activation had occurred of the

electrode surface prior to the first scan in this ionic liquid compared to the others. A slight decrease in the oxidation current was also observed at potential above 1.0 V, which corresponds to the surface Pt oxide formation, similar to that observed during hydrazine oxidation in TfO-based PILs.

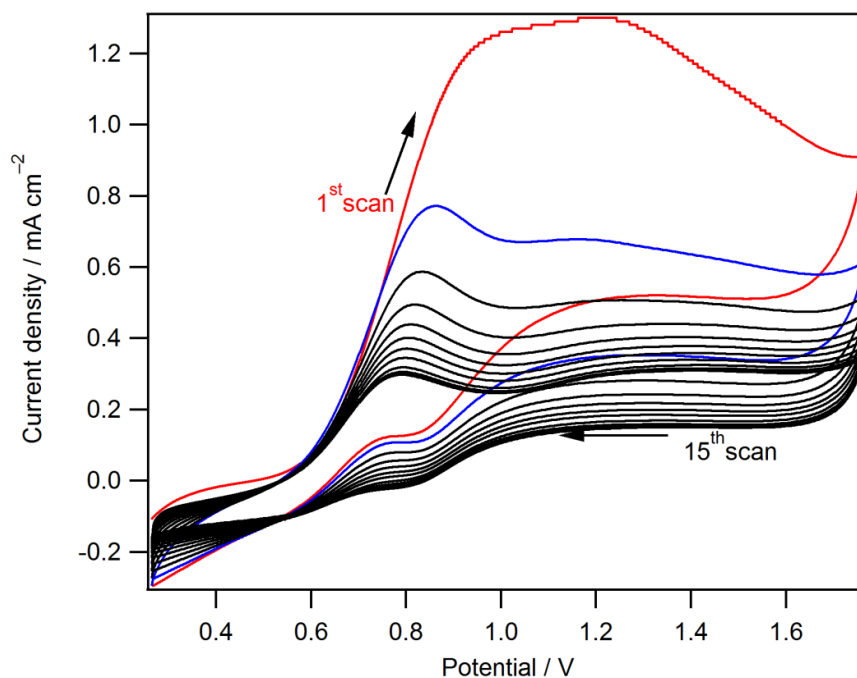


Figure 4.3.3 CV profiles (15 cycles) obtained in [dema][Tf₂N] containing 50 mM N₂H₄ at a 5 mm diameter Pt disk electrode at 50 mV s⁻¹ and 45 °C, cycled from an initial potential of 0.25 V up to a potential of 1.75 V.

However, instead of an increase in the hydrazine oxidation peak current, the peak current for the oxidation reaction decreased drastically during successive sweeps, which may be due to poisoning of the electrode surface in the PIL. In addition, no shift in the peak towards less positive potential for the onset of hydrazine oxidation was observed, even until the 15th cycle. This different electrochemical behaviour of hydrazine oxidation in the PIL could be due to unusual activation, presumably due to oxygen of the [Tf₂N]⁻ adsorbing strongly to the electrode surface compared to TfO⁻ which caused hydrazine oxidation on the oxide-free electrode surface in this ionic liquid.¹⁷⁰

4.3.2. Effect of Positive Potential Limits on Hydrazine

Oxidation

The effect of varying the positive potential limit on the electrochemical oxidation of hydrazine in PILs was also studied, in order to explore further the role of residual surface oxides. Figure 4.3.4 shows a series of LSV profiles obtained in 50 mM hydrazine in [dmea][TfO] at a clean, polished 5 mm diameter Pt disk electrode at 100 mV s^{-1} and 45°C . In each case after recording 5 complete activation cycles, the 6th forward sweep has been shown.

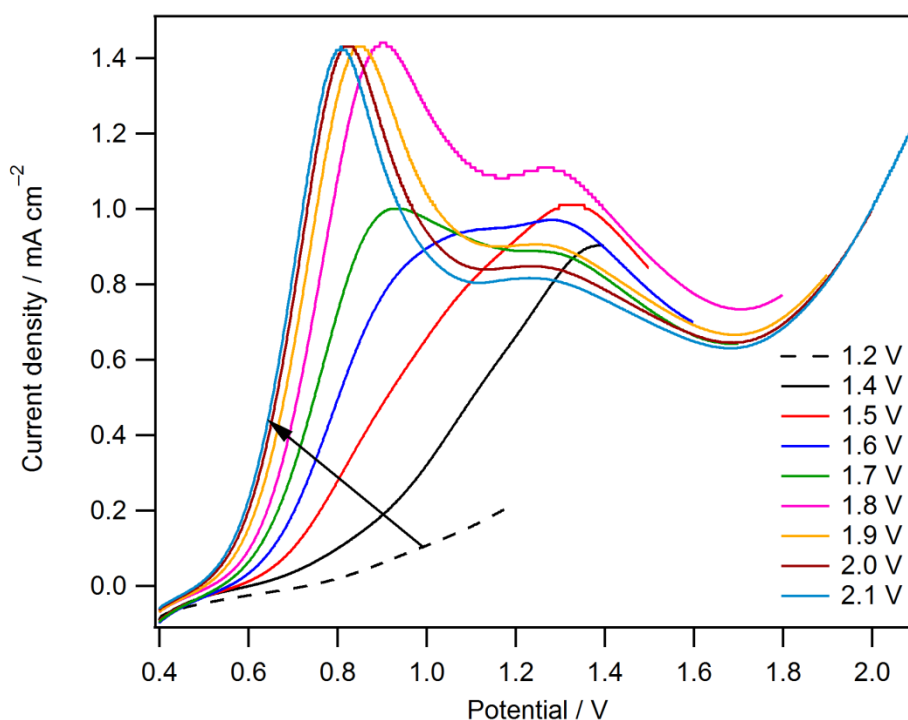


Figure 4.3.4 Linear sweep voltammograms recorded at a 5-mm diameter Pt disk electrode at 100 mV s^{-1} in 50 mM N_2H_4 in [dmea][TfO] at 45°C when the initial potential was 0.4 V and the positive potential limits were (in ascending order) 1.2 V, 1.4 V, 1.5 V, 1.6 V, 1.7 V, 1.8 V, 1.9 V, 2.0 V and 2.1 V. Each response was obtained after completing five full potential cycles between 0.4 V and the appropriate upper limit and the arrow shows the responses obtained after scanning to successively higher potentials.

It is evident from the figure that as the positive potential limit was increased, the current due to hydrazine oxidation in [dmea][TfO] also increased and the onset potential for the oxidation progressively shifted to more negative potentials. This behaviour became more pronounced until the positive limit was 1.8 V or greater in the activation cycles, after which stable oxidative response was observed. As described in Chapter 3 (Figure 3.3.9 A), by increasing positive potential limits, thicker oxide films can form at a Pt surface in [dmea][TfO]. As a result, at more positive potentials, the amount of the residual surface oxide species at the electrode surface increased; hence more platinum oxide was available to catalyse hydrazine oxidation in subsequent sweeps.

4.3.3. Influence of the Time of Immersion of the Activated Pt Electrode during Hydrazine Oxidation

To study the effect of the time of immersion of pre-oxidized Pt electrode on the electrocatalysis of hydrazine oxidation, an experiment was performed in which a freshly polished polycrystalline Pt was pre-activated in 50 mM hydrazine solution of [dmea][TfO] by cycling from an initial potential (0.4 V) to a potential positive enough to form surface oxides (1.8 V) for ten cycles. The electrode, after activation, was then allowed to stand in the hydrazine solution for extended periods of time (10 min, 20 min, 40 min and 80 min) and cyclic voltammograms were recorded at 45 °C and 100 mV s⁻¹, (Figure 4.3.5). With no standing time, the hydrazine oxidation wave expected at an activated Pt electrode was observed with an onset potential of about 0.6 V. However, as time progressed the oxidation wave decreased drastically until at t = 80 min only a very small oxidation shoulder was observed.

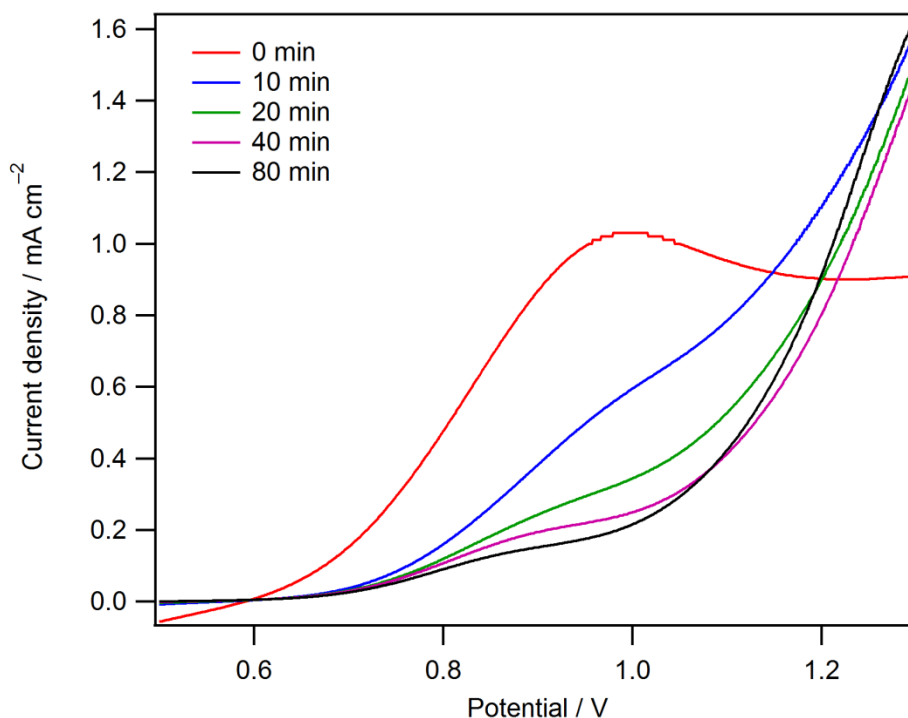


Figure 4.3.5 LSV profiles at a 5-mm diameter Pt disk electrode at 100 mV s^{-1} in 50 mM hydrazine in [dmea][TfO], after pre-activating the electrode by cycling from 0.4 V to 1.8 V (data only until 1.3 V shown) ten times and then waiting for 10, 20, 40 and 80 min before starting the CV.

In addition, the onset of the hydrazine oxidation shifted to more positive potentials, showing a deactivation of the pre-oxidized electrode after extended immersion in ionic liquid containing hydrazine and affecting the catalysis of the hydrazine oxidation reaction.^{24, 175} This either shows a decrease of the electrode surface oxide layer within the ionic liquid at the open circuit potential as a result of reaction of hydrazine with residual oxides, or that the oxides were soluble in the PIL environment. To confirm that the oxides layers were not reduced within the ionic liquid at the open circuit potential or that they were soluble in the PIL, an additional control experiment was carried out in which a Pt electrode was activated by potential cycling between 0.4 and 1.8 V and then stored at open circuit potential (OCP) for 20 min in blank [dmea][TfO]. When the electrode was transferred into 50 mM hydrazine in [dmea][TfO] and the potential sweep

experiment repeated, the response expected for an activated Pt surface was obtained (note that after a similar period of time immersed in 50 mM hydrazine/[dmea][TfO] the Pt showed significant loss of activity). This confirms that the oxides were not soluble in the PILs but were susceptible to deactivation by dissolved hydrazine.

4.4. Conclusions

The reactivity analysis revealed that the surface oxides formed at Pt in PILs helped in accelerating the electrooxidation of hydrazine in the PILs. It was observed that in the presence of residual surface oxides from activation of the electrode at high positive potentials, hydrazine oxidation occurred more readily with the onset potential shifting to less positive values in both TfO-based PILs. However, during investigation of hydrazine electrochemistry in [dema][Tf₂N], the electrode appeared to be activated prior to performing any potential sweeps. In addition, it appears that the reaction between adsorbed oxides and hydrazine depends on the amount of the residual oxides on the surface during potential cycles. Finally, this study is a basic investigation that would be helpful in the understanding of the surface electrochemistry of hydrazine in ionic liquid electrolytes.

Chapter 5: Electrochemistry of Formic Acid at Noble Metals in Protic Ionic Liquids

5.1. Introduction

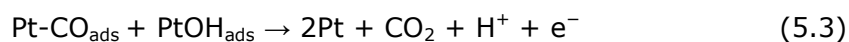
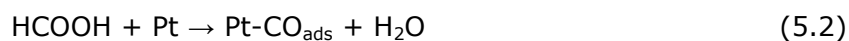
Studies of the electrooxidation of formic acid at noble metal electrodes have increased in number substantially in recent years. In part, this growth is due to the relatively straightforward nature of the reaction, which means that it is often considered a model for the electrooxidation of small organic molecules.¹⁷⁶⁻¹⁷⁹ Another reason is the relevance of formic acid electrooxidation in fuel cell technology; HCOOH is an intermediate in direct methanol fuel cells, while there is growing interest in direct formic acid fuel cells, which benefit from the relatively low toxicity of HCOOH, have relatively high theoretical open circuit potentials of 1.45 V, and low fuel crossover through the electrolyte.¹⁸⁰⁻¹⁸²

It is generally accepted that the electrooxidation of HCOOH (Equation 5.1) proceeds via dual mechanism: a direct route that involve dehydrogenation and proceeds via one or more weakly-adsorbed reactive intermediates, such as HCOO_{ads} ,^{183, 184} COH_{ads} , COOH_{ads} and $\text{HCOOH}_{\text{ads}}$,^{56, 185} to yield CO_2 :



The other oxidation pathway is indirect oxidation involving dehydration reaction plus the formation of adsorbed carbon monoxide, CO_{ads} (Eqn. 5.2). CO_{ads} can then be oxidized to form CO_2 at a potential that coincides with

the onset of the formation of surface oxides (often called OH_{ads}), by Langmuir-Hinshelwood mechanism (see Eqns. 5.3).

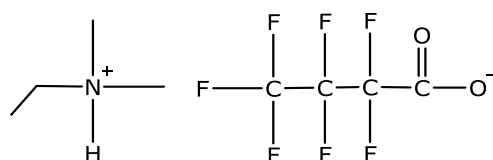


As the direct oxidation pathway does not involve oxidation of strongly-adsorbed poisoning intermediates, the direct pathway occurs at more negative potentials than those required for CO oxidation and electrocatalysts that promote this route are preferred in direct formic acid fuel cells.^{36, 185-187} For electrocatalytic oxidation of HCOOH, Pt-based and Pd-based catalysts are commonly used.⁵⁹ The use of Pd is becoming more common as it is generally accepted that Pd shows better catalytic activity for HCOOH oxidation than Pt, when the oxidation process is complicated due to formation of various adsorbed carbonaceous intermediates and by-products.¹⁸⁸⁻¹⁹⁴ The introduction of a second metal catalyst (third body) such as Pd and Ru on to Pt can also enhance the catalytic activity of Pt by reducing the number of adsorption sites for the chemisorption of the intermediates (e.g. surface poisoning CO_{ads}) during the reaction due to geometric hindrance^{194, 195}

In recent years, a number of groups have begun to study the effects of adsorbed species, such as surface oxides,¹⁷⁰ underpotential-deposited hydrogen, H_{upd} , and PIL ions¹⁰² on electrocatalytic reaction rates in PILs. To the best of our knowledge, no work has focused on the electrooxidation of HCOOH in PILs. The unique environment within PILs could reveal interesting phenomena. We do note that Feng and co-workers used different percentage of a PIL, n-butylamine nitrate in water as a solvent for

the electrochemical oxidation of HCOOH at Pd catalyst and reported that Pd has shown much higher catalytic activity for the oxidation of HCOOH in the PIL than in aqueous solutions of H₂SO₄, HClO₄ and phosphate buffer.¹⁴²

We investigated the electrocatalytic oxidation of HCOOH at Pt catalyst in PILs, [dema][TfO] and [dmea][HfB] (structure of the [dmea][HfB] is shown in Scheme 5.1). The influence of experimental parameters such as anodic potential limits, sweep rates and water concentration of the PILs on electrooxidation of HCOOH at Pt was investigated and it is shown that the catalytic activity of Pt toward oxidation of HCOOH increase with increasing positive potential limits, sweep rates and concentration of H₂O in the PILs. In addition to Pt, we investigated the electrocatalysis of HCOOH oxidation in the PILs at Au and Pd catalysts. We found that Pd shows excellent catalytic activity for anodic oxidation of HCOOH at room temperature compared to Pt and Au catalysts. The Pd catalyst promotes the direct pathway (Eqn. 5.1) occurring at a more negative potentials suggesting that HCOOH oxidation can be more easily carried out at Pd electrocatalysts in PILs than at Pt and Au catalysts.



Scheme 5.1 Structure of [dmea][HfB].

5.2. Experimental Section

5.2.1. Reagents and Apparatus

All chemicals, HCOOH (90 %, Fischer-Scientific), H₂PtCl₆·6H₂O (Pt 38 %, Sigma-Aldrich), PdCl₂ (Pd 59 %, Across Organics), H₂SO₄ (98 %, Merck),

HCl (36.5–38 %, BDH), were analytical grade and were used as received without further purification. The viscosity of [dema][TfO] and [dmea][HfB] of the PILs was determined at 25 °C and 50 °C using an Anton Paar AMVn Automated Micro Viscometer and are described in the Results and Discussion section.

5.2.2. Electrochemical Measurements

The working electrodes were a 2 mm diameter Pt disk, a 2 mm diameter Au disk, and Pd/GC and Pt/GC electrodes. For preparation of Pt/GC electrode a CV was recorded at a clean 3 mm diameter GC electrode (geometric area, 0.07 cm^2) in 0.1 M HCl containing 5 mM $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ by sweeping potential of the working electrode from 1.1 V to -0.2 V vs. Ag/AgCl/KCl (sat.) at a scan rate of 100 mV s^{-1} (see Figure S 4 (A) in Appendix 1), in order to determine the potential at which the deposition of Pt takes place. Then PtNPs were electrochemically deposited via potential step electrolysis (Figure S 4 (B) in Appendix 1) by stepping the potential of the working electrode from 0.5 V to -0.2 V for 600 s vs. Ag/AgCl/KCl (sat.). For electrodeposition of PdNPs, a CV was obtained at the GC electrode in 1.0 mM PdCl_2 in 0.1 M H_2SO_4 by sweeping the potential from 1.2 V to -0.2 V vs. Ag/AgCl/KCl (sat.), (see Figure S 5 (A) in Appendix 1). PdNPs were then electrodeposited using potential step electrolysis by stepping potential of the electrode from 0.5 V to -0.2 V for 600 s vs. Ag/AgCl/KCl (sat.) (Figure S 5 (B) in Appendix 1).

After deposition, electrodes were rinsed with de-ionized water and dried in a stream of N_2 and were further cleaned electrochemically by cycling in 0.1 M HClO_4 (aq.) from -0.2 V until 1.0 V at 500 mV s^{-1} . After electrochemical cleaning, a CV was obtained in the same solution between -0.2 V and 1.3 V at each electrode at 50 mV s^{-1} and shown in Figure S 6 in

Appendix 1). The active electrochemical surface area (ECSA) of Pt/GC electrode was estimated from the value of the integrated charge of the hydrogen adsorption/desorption regions obtained by the integration of $i-E$ curve in the CV dividing by the charge required to oxidize a monolayer of hydrogen from Pt surface, $210 \mu\text{C cm}^{-2}$.^{166, 194} For Pd/GC electrodes, the ECSA was determined by integrating the charge under the palladium oxide stripping using a normalizing factor of $424 \mu\text{C cm}^{-2}$ as the theoretical charge for a monolayer of palladium oxide stripping.¹⁹⁶⁻¹⁹⁸ The calibration of catalytic activity was done directly through dividing the oxidation current by ECSA for both Pt/GC and Pd/GC electrodes and on geometric surface area for the 2 mm diameter Pt and Au electrodes.

5.3. Results and Discussion

5.3.1. Electrochemistry of HCOOH in PILs at Pt

Figure 5.3.1 shows the cyclic voltammograms of the Pt catalyst in N_2 saturated (B) [dema][TfO] and (C) [dmea][HfB] with 0.5 M HCOOH. The black dash lines in each of these figures (B) and (C) shows the CVs recorded in N_2 saturated [dema][TfO] and [dmea][HfB] without HCOOH, respectively. The electrochemical behaviour of Pt during HCOOH oxidation in H_2SO_4 electrolyte is also shown in the figure 5.3.1 (A) for comparison. Before discussing the electrooxidation of HCOOH in the PILs, we describe here briefly the electrochemical responses obtained in aqueous acid. In Figure 5.3.1 (A), the cyclic voltammograms recorded using a Pt electrode in blank aqueous H_2SO_4 is compared with that recorded in H_2SO_4 containing 0.5 M HCOOH. In blank aqueous solution of H_2SO_4 , typical H_{upd} adsorption/desorption and oxide adsorption/desorption features are visible

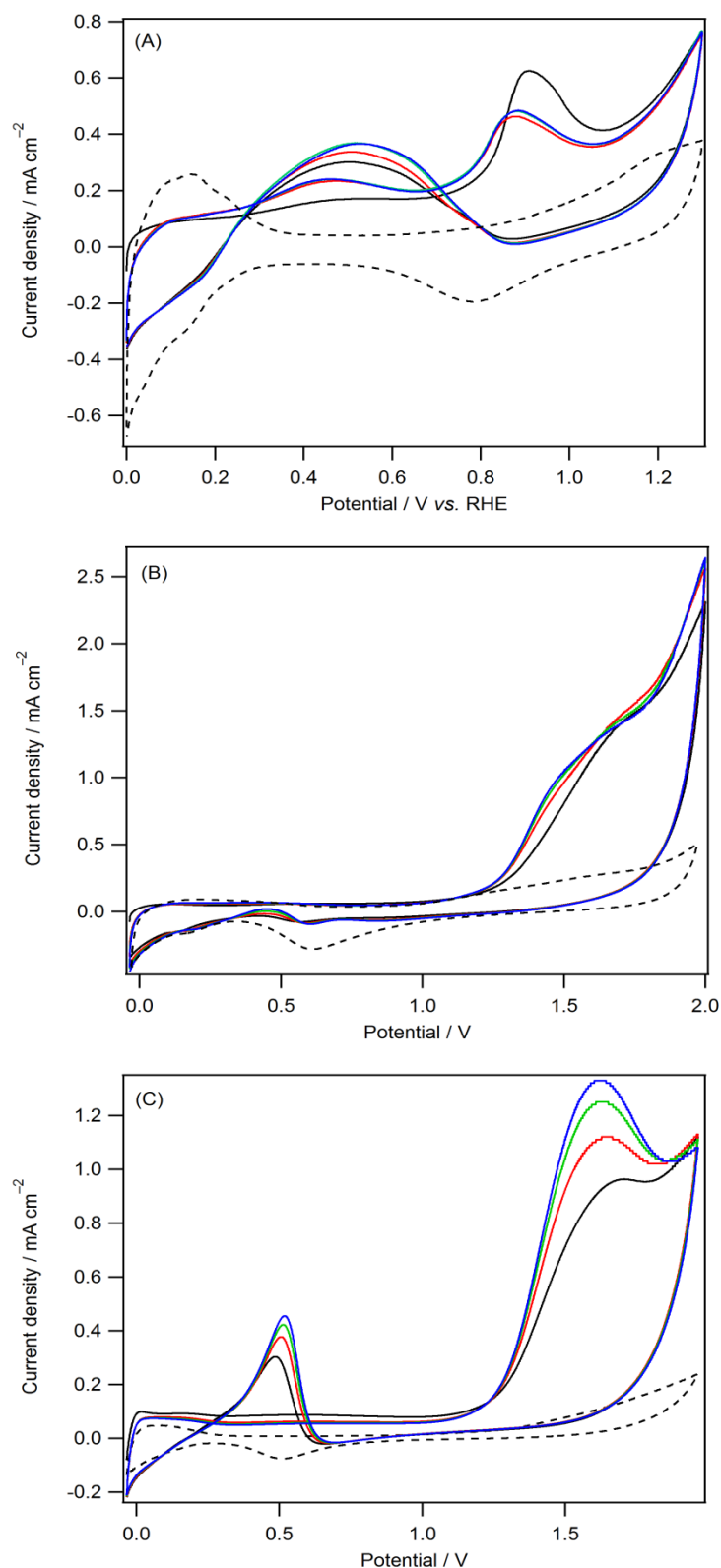


Figure 5.3.1 CV showing the four consecutive recorded cycles (black–1st, red–2nd, green–3rd and blue line–4th cycle) for the oxidation of 0.5 M HCOOH in (A) 0.5 M H₂SO₄ (aq.), (B) [dema][TfO] and (C) [dmea][HfB] at a 2 mm diameter Pt disk electrode at a sweep rate of 50 mV s⁻¹ and room temperature. The dashed line shows CVs measured in each liquid saturated with N₂, before adding HCOOH.

between 0.0–0.4 V and 0.6–1.3 V, respectively. During the forward sweep in the HCOOH-containing H₂SO₄, the H_{upd} adsorption/desorption features are suppressed and a plateau in the HCOOH current is observed between 0.0 V and 0.5 V. The current then increases significantly, yielding a peak at 0.9 V. During the reverse sweep, a peak is observed at 0.5 V. These features are typical of those expected for HCOOH oxidation at Pt in aqueous media.^{57, 199-201} During the positive sweep, direct reaction commences in the H_{upd} region and leads to the plateau in current, until oxidation of CO_{ads} co-deposited at low potentials by the parallel dehydration path commences as OH_{ads} is formed on the Pt surface near 0.8 V. During the reverse sweep, the current remain positive until 0.7 V and below which the current decreases showing a small cathodic peak that corresponds to the reduction of the surface PtOH_{ads}. The liberation of active Pt sites allows HCOOH to recommence by the direct route.^{176, 202} It is observed that compared to the first sweep, the electrode become activated in the subsequent sweeps for HCOOH oxidation, due to presence of the residual oxides on the electrode surface.

During the positive sweep in [dema][TfO] (blank), an anodic wave with an onset potential, 1.1 V is visible (Figure 5.3.1 B) and can be attributed to the formation of PtOH_{ads} by oxidation of the residual trace water (0.044 %) present in the PIL. Bulk electrolyte oxidation occurs as the potential sweep is extended positive of 1.7 V. During the negative sweep, a cathodic wave with a peak potential, $E_p = 0.6$ V is visible due to the reduction of PtOH_{ads}¹⁷⁰ and cathodic evolution of H₂ occurs negative of 0.0 V. In the presence of 0.5 M HCOOH, an HCOOH oxidation wave that coincides with the onset of surface oxidation appeared with an $E_p \sim 1.6$ V. During the negative sweep, a second HCOOH oxidation wave is observed ($E_p = 0.45$ V), which coincides with reduction of PtOH_{ads}. Similar to that in

aqueous system, HCOOH oxidation in the ionic liquid is activated in the second and subsequent cycles compared to the first cycle due to residual oxides on the electrode.

In general, the responses obtained in [dmea][HfB] (Figure 5.3.1 C) are similar to those observed in [dema][TfO] (Figure 5.3.1 B), with bulk oxidation of HCOOH coinciding with the formation of PtOH_{ads} in the PIL. However, a couple of notable differences can be observed. First, the peak currents, i_p , for HCOOH oxidation (observed at $E_p = 1.6$ V in the forward sweep and 0.45 V in the reverse sweep) are higher than those observed in [dema][TfO]. This difference is not attributable to differences in the viscosities, η of the PILs as $\eta_{[\text{dmea}][\text{HfB}]}$ (50 mPa s at 25 °C) is only slightly higher than $\eta_{[\text{dema}][\text{TfO}]}$ (44 mPa s). Instead, this difference is attributed to the higher concentration of trace water in [dmea][HfB] (0.08 %).⁴⁵ The higher water content of [dmea][HfB] may also be at least partly the reason that PtOH_{ads} reduction occurs at more negative potentials in [dmea][HfB] than in [dema][TfO]; it has been shown previously that increasing the water content of RTILs makes PtOH_{ads} adsorption/desorption less reversible (Section 3.3.2.2). A notable and significant difference between the CVs recorded in [dema][TfO] and [dmea][HfB] is also observed in the low-potential region. Between 0.0 V and 1.1 V in [dema][TfO], the CVs recorded in the blank PIL and the HCOOH-containing PIL overlap in the positive sweeps. In contrast, the current recorded during the positive sweep in HCOOH-containing [dmea][HfB] is higher at all potentials than in the blank PIL, and a small peak with $E_p \sim 0.8$ V is almost distinguishable, suggesting that oxidation of HCOOH may occur at low potentials in this medium. This effect is clarified further in Figure 5.3.2, which shows CVs recorded in [dmea][HfB] at a series of voltammetric scan rates, u . As u increases, the oxidation peak currents (i_p) for oxidation waves 1 and 2 in

the positive scan direction and the oxides reduction peak 3 as well as reverse oxidation peak 4 during negative going scan and E_p for the peak shifted in a negative direction. For example, $E_p = 0.80$ V at 100 mV s^{-1} and this decreases to 0.68 V at 500 mV s^{-1} . The appearance of an additional oxidation wave (labelled 1 in Figure 5.3.2) and its increase in height shows that at higher scan rate HCOOH oxidation in [dmea][HfB] started at low potential due to faster mass transport. The observation of an early HCOOH oxidation current in the PIL is reminiscent to that observed in aqueous media (Figure 5.3.1 A). However, the current corresponding to this oxidation wave is lower than in the aqueous system. In the aqueous system a well-defined oxidation wave which increased significantly with increasing scan rate, is observed in the low potential.^{57, 203, 204}

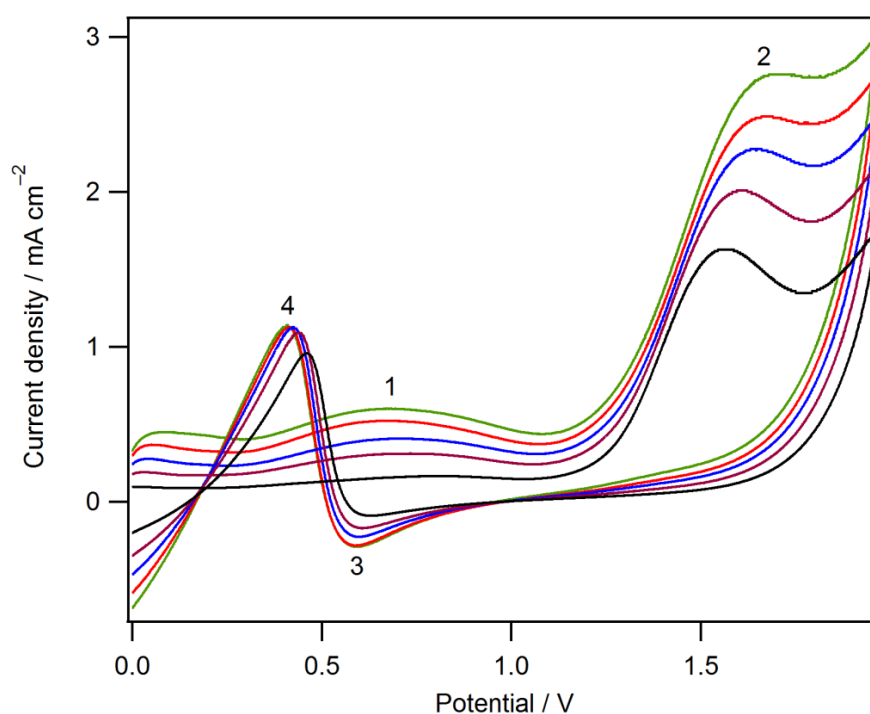


Figure 5.3.2 Cyclic voltammograms showing the effect of scan rate (from top to bottom 500, 400, 300, 200 and 100 mV s^{-1}) on the electrooxidation of 0.5 M HCOOH in [dmea][HfB] at a 2 mm diameter Pt disk electrode.

For the second strong oxidation wave 2, the oxidation peak current (i_{p2}) increased and onset shifted towards negative potentials with

increasing sweep rates. This is due to the fact that at high scan rates more surface oxides/hydroxides can form at lower potentials that can help to oxidize the adsorbed intermediates (CO_{ads}) during HCOOH oxidation. However, due to surface processes (surface oxidation of Pt and removal of CO_{ads} , Eqns. 5.3 and 5.4) involved in this potential region, the peak potentials (E_{p2}) for the main oxidation wave 2 shifted more positive with increasing scan rates. Figure 5.3.2 also shows that the peak current of the reverse oxidation peak 4 increased with higher scan rates. However, the peak position for both oxide reduction and reverse oxidation peak shifted to lower value with increasing scan rates which is attributed to the more stable surface oxides formed at positive going scan in potentials >1.1 V at higher scan rates that was difficult to reduce from the surface. A similar kind of behaviour was observed during investigation of kinetic characteristics and influence of scan rates on the electrocatalytic oxidation of HCOOH at Pt in $[\text{dema}][\text{TfO}]$ electrolyte (Figure S 7 in Appendix 1).

We assume that the behavior in the ionic liquid in potential region below 1.0 V is due to poisoning of the electrode from adsorbed intermediates produced by the “non-faradaic” dissociation of HCOOH . These adsorbed intermediates are oxidised above 1.1 V through Langmuir-Hinshelwood mechanism (Eqn. 5.3) along with the bulk oxidation of HCOOH . In order to prove that adsorbed species could form at Pt surface in lower potential region ($E < 1.0$ V), from the non-faradaic dissociation of HCOOH , a chronoamperometry experiment was performed in which a freshly polished Pt disk electrode was first held at 0.7 V vs. Pd-H in $[\text{dema}][\text{TfO}]$ containing 0.5 M HCOOH for 600 s. The electrode was then rinsed with de-ionized water, dried under a stream of N_2 and immersed in 0.2 M aqueous H_2SO_4 . Two consecutive cycles were then recorded at the electrode at a sweep rate of 50 mV s^{-1} vs. Ag/AgCl for the oxidative

stripping of intermediate adsorbates accumulated from HCOOH saturated solution of [dema][TfO] as shown in the figure 5.3.3. The voltammetry response, 1st cycle (red line) and 2nd cycle (black line), was compared with that obtained at clean Pt electrode of the same diameter in N₂ saturated 0.2 M aqueous H₂SO₄ (black dash line in the figure 5.3.3). It is clear from the figure that during the first cycle (red line) current due H_{upd} adsorption/desorption in the potential region below 0.0 V to -0.20 V is suppressed compared to that in the blank CV. For example, the peak current for the H-desorption wave is 3.674 μ A compared to 8.693 μ A in the blank CV. Similarly, the integrated charge under the H-desorption wave decreased by is 16.2 μ C in comparison to the blank.

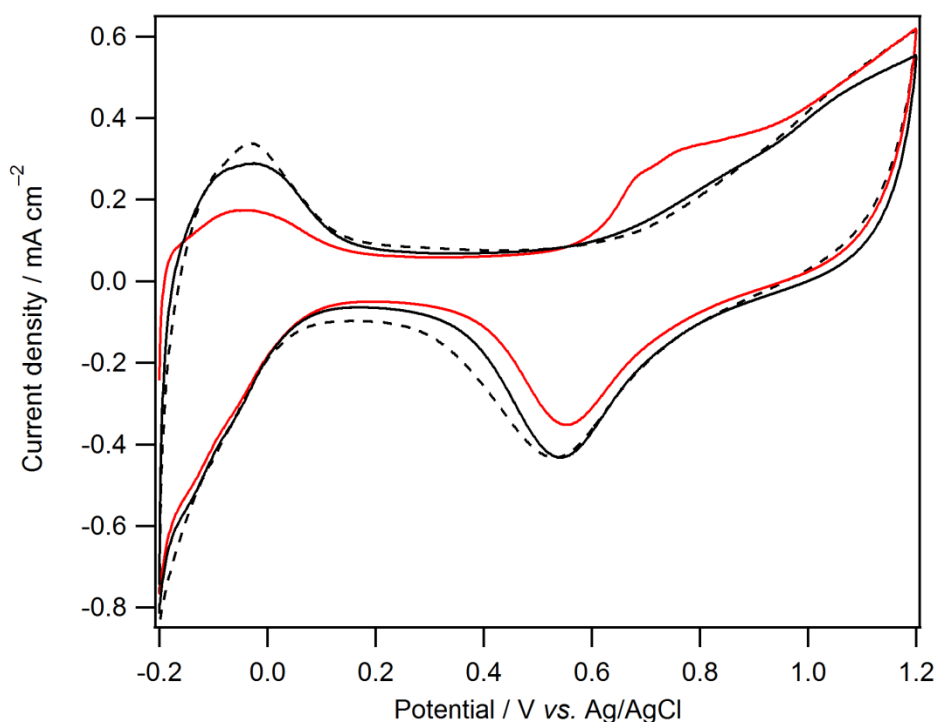


Figure 5.3.3 CVs of a 2 mm diameter Pt disk electrode at a scan rate of 50 mV s⁻¹ in 0.2 M H₂SO₄ showing the oxidative stripping of intermediate adsorbates (1st cycle-red lines and 2nd cycle-black line) accumulated from HCOOH saturated solution of [dema][TfO] at 0.7 V vs. Pd-H. The dashed black line is the blank CV obtained in N₂ saturated 0.2 M H₂SO₄ at Pt disk electrode vs. Ag/AgCl.

These observations suggest that some intermediate species were pre-adsorbed at Pt electrode during chronoamperometry experiment which was oxidized as a broad oxidation wave appeared at onset of about 0.60 V vs. Ag/AgCl in 0.2 M H₂SO₄ (red line in Figure 5.3.3). The onset potential of this peak corresponds to the onset of surface Pt-oxides formation at Pt in the blank solution. This shows that the adsorbed species were electrochemically oxidized by the Pt-oxide species, PtOH_{ads}. The pre-adsorbed species were stripped off the surface after scanning the potential up to 1.2 V in the first scan, as no significant increase in current was observed during the second scan (solid black line) in this potential region (0.60 V to 1.2 V). Also during the second sweep current due to the oxidation of hydrogen from -0.20 V to 0.0 V increased and was almost similar to that in the blank CV, showing the regeneration of the electrode surface, free of the poisonous adsorbates. However, the charge under the oxidation wave between 0.60 V and 1.0 V was low suggesting that a very small amount of HCOOH are decomposed and a very low coverage of the surface species were obtained at this potential (0.7 V).

To confirm that the Pt-adsorbed intermediates were from the decomposition of HCOOH within the ionic liquid and not from the ionic liquid, similar chronoamperometric experiment was performed in blank [dema][TfO] in which a freshly polished Pt disk electrode was held at 0.7 V vs. Pd-H for 600 s, in [dema][TfO] without any HCOOH. The current response in the i-t curve was near to zero for all times and when CV was recorded at the electrode in 0.2 M H₂SO₄, the response was similar to that obtained at clean Pt in the solution, showing that no adsorbed species can form in blank ionic liquid and were from HCOOH dissociation.

To further confirm that the adsorbed species were due to non-faradaic dissociation of HCOOH at low potentials, an additional experiment

was carried out in which a Pt electrode was stored at OCP for 600 s in [dema][TfO] containing 0.5 M HCOOH. Then the electrode, after rinsing and drying, was transferred into 0.2 M H₂SO₄ and two consecutive CVs were recorded at a sweep rate of 50 mV s⁻¹ vs. Ag/AgCl as shown in the figure 5.3.4.

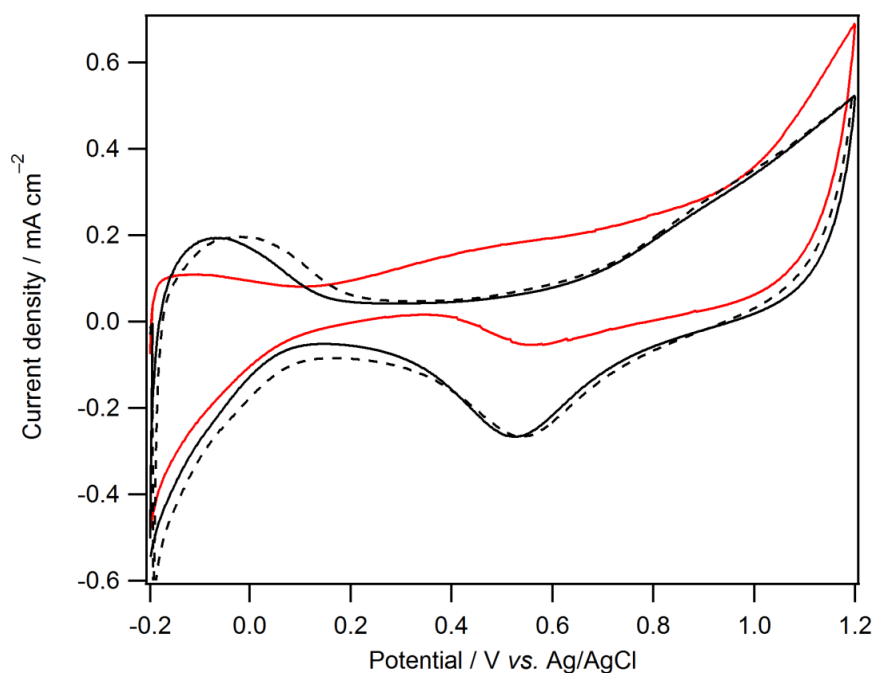


Figure 5.3.4 CVs of a 2 mm diameter Pt disk electrode at a scan rate of 50 mV s⁻¹ in 0.2 M H₂SO₄ showing the oxidative stripping of intermediate adsorbates (1st cycle-red lines and 2nd cycle-black line) accumulated from HCOOH saturated solution of [dema][TfO] at open-circuit potential vs. Pd-H. The dashed black line is the blank CV obtained in N₂ saturated 0.2 M H₂SO₄ at Pt disk electrode vs. Ag/AgCl.

The voltammetry response similar to that shown in Figure 5.3.3 is obtained that shows an oxidation wave in the first sweep, corresponding to the stripping of the intermediates pre-adsorbed at OCP in the HCOOH solution in [dema][TfO]. This confirms that the adsorbed intermediates can form at low potentials from the non-faradaic dissociation of HCOOH in [dema][TfO]. However, compared to the oxidation of the intermediates pre-adsorbed at 0.7 V (Figure 5.3.3), the oxidation of the intermediates

accumulated from HCOOH in [dema][TfO] open-circuit potential were oxidized at earlier potentials. This shows that at OCP the intermediate formed from the dissociation of HCOOH are more weakly adsorbed than that formed at high potential (0.7 V vs. Pd-H).

5.3.1.1. Effect of Upper Potential Limit on HCOOH Oxidation in PILs

In order to correlate the surface Pt oxide species formed at various positive potential limits with the electrocatalytic oxidation of HCOOH, CVs were recorded in [dmea][HfB] containing 0.5 M HCOOH by systematically changing the positive potential limit. Figure 5.3.5 shows a series of cyclic voltammograms of HCOOH oxidation in [dmea][HfB] recorded on Pt wire (exposed surface area 0.0707 cm²) at 50 mV s⁻¹ and 25 °C, showing the effect of positive potential limit on the oxidation process under study. It is clear from the figure that the current for oxidation of HCOOH is strongly dependent on the positive potential limit. By increasing the potential limit the current corresponding to electrooxidation of HCOOH in [dmea][HfB] increased both below 1.0 V and above 1.0 V. The peak position for the oxides reduction wave in the negative going scan, between 0.8 V and 0.5 V, shifted to a more negative value as more stable oxide layers are forming on Pt at high positive potentials. Consequently the regeneration of the electrode is delayed and hence the peak potential for oxidation of the HCOOH below 0.6 V also shifted negatively. The peak current for this oxidation wave increased as positive potential limit was increased, which could be due to the residual oxide left over on the electrode. A similar correlation between the electrooxidation of HCOOH and Pt surface oxide species was observed during a series of CVs measured at various positive potential limits in 0.5 M HCOOH in [dema][TfO] (Figure S 8 in Appendix 1).

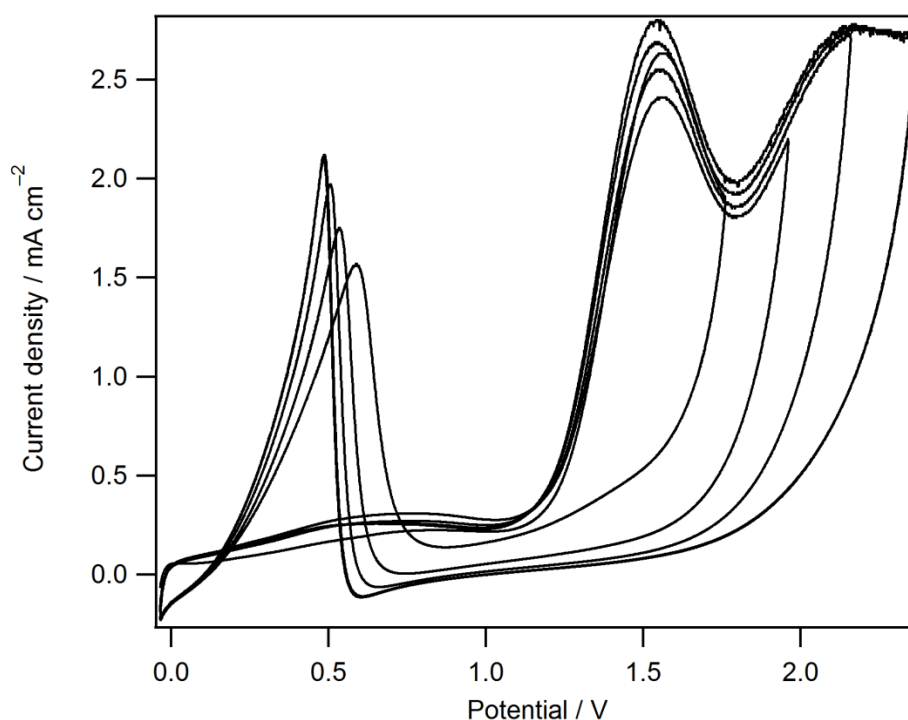


Figure 5.3.5 CVs recorded at Pt wire (exposed area 0.0707 cm^2) at 50 mV s^{-1} and 25°C showing the effect of anodic reversal potential on the electrooxidation of 0.5 M HCOOH in $[\text{dmea}][\text{HfB}]$. The potential was scanned from -0.035 V and switched back at upper potential limits 1.75 V , 1.95 V , 2.15 V and 2.35 V .

5.3.1.2. Electrocatalytic Oxidation of Formic Acid as a Function of Water Concentration in PILs

The surface oxide growth on metal electrode depends strongly on the water concentration in ionic liquids.^{45, 124, 170} We have also investigated the effect of adding water in various PILs on the development of surface oxides at Pt and have found that the oxide formation at Pt takes place more readily when increasing water concentration of the PILs (Section 3.3.2.2). Therefore, increasing the concentration of water should help to accelerate oxidation processes that require surface oxides OH_{ads} for oxidation. Figure 5.3.6 displays LSVs in the positive going sweep recorded at Pt electrode at 50 mV s^{-1} in (A) $[\text{dema}][\text{TfO}]$ and (B) $[\text{dmea}][\text{HfB}]$ containing 0.5 M HCOOH in each electrolyte containing varying amounts of H_2O . In each

case, the black line represent LSV of HCOOH oxidation in [dema][TfO] and [dmea][HfB] containing the residual water 0.044 % in [dema][TfO] and 0.08 % in [dmea][HfB]. However, by adding successively higher concentrations of H₂O to the PIL, the HCOOH oxidation current increases in both solutions.

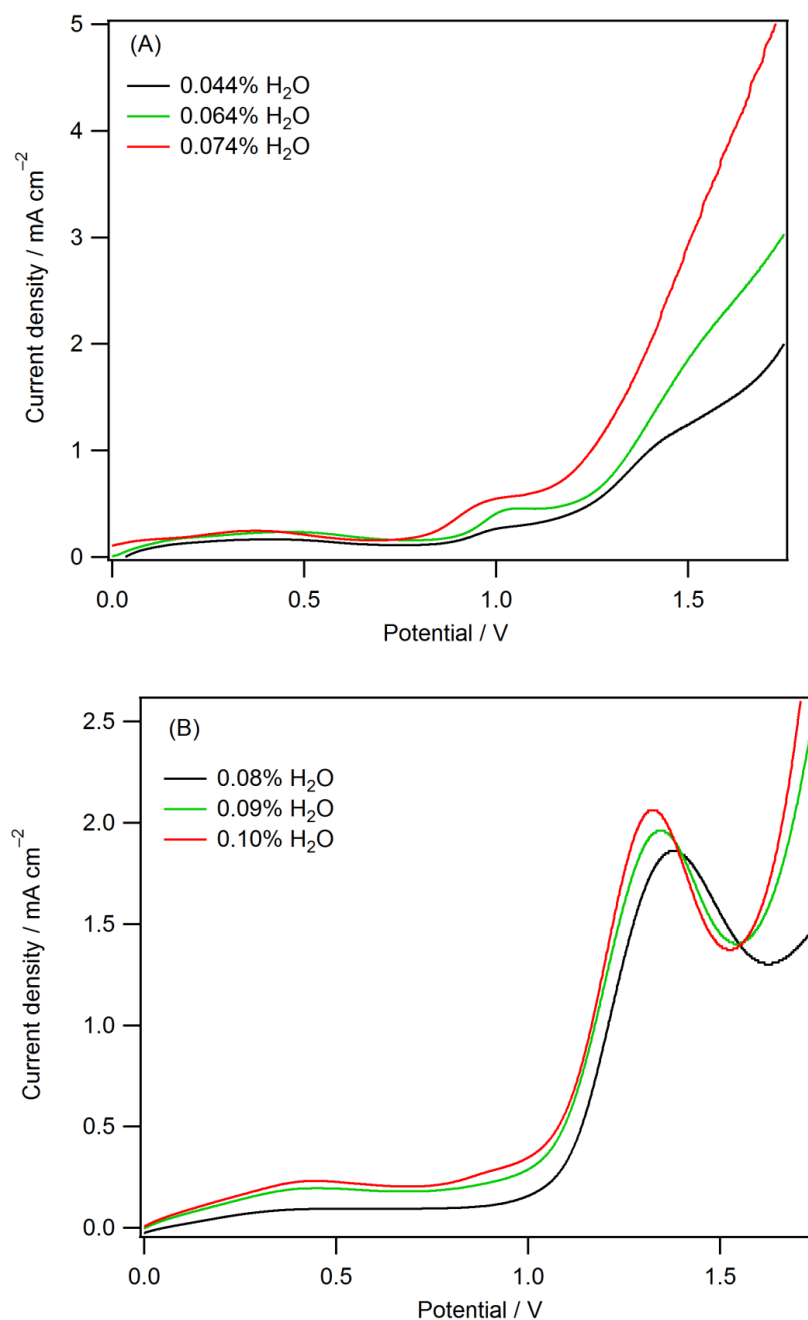


Figure 5.3.6 LSVs obtained in 0.5 M solution of HCOOH in (A) [dema][TfO] and (B) [dmea][HfB] containing various concentration of water at a 2 mm diameter Pt disk electrode vs. Pd-H at 50 mV s⁻¹ and 25 °C, in potential range from 0.0 V to 1.75 V.

Also, increasing the water concentration in the PILs containing HCOOH resulted in a progressive shift of the oxidation wave to less positive potentials depicting more facile oxidation of HCOOH as the H₂O content of the PIL was increased. This shift of the oxidation process to less positive potentials, with the increase of H₂O concentration in the PILs, is due to the increased coverage of the Pt surface with oxide species (OH_{ads}) at lower potentials (Section 3.3.2.2) that facilitate the oxidation process. It is evident from the figure that the oxidation current increases and the peak position shifts more negative in the low potential region (0.3 V to 0.7 V). It is presumably due to decrease in viscosity of the PILs with adding water that help in the diffusion of HCOOH to the electrode surface.

5.3.2. Electrooxidation of HCOOH in PILs at Au

Au is the most inert and noble of metals and has very poor electrocatalytic activity towards many reactions. In general, Au has not been investigated for the direct electrooxidation of small organic molecules such as HCOOH in aqueous electrolytes as much as Pt. Despite the fact that Pt has better electrocatalytic activity than Au, yet a considerable oxidation of HCOOH has been observed at Au catalyst in acidic solutions, particularly in the potential region where Au oxide formation occurs.^{205, 206} It is known that oxide species can form at Au due to the oxidation of residual water present in ionic liquid electrolytes.¹²⁴ We investigated the electrochemical behaviour of a polycrystalline Au electrode in PILs and its electrocatalytic activity towards HCOOH oxidation in the PILs and compared the results with that using Pt catalyst. Figure 5.3.7 displays typical cyclic voltammograms obtained in (A) [dema][TfO] and (B) [dmea][HfB] each containing 0.5 M HCOOH at a 2 mm diameter Au disk electrode. The dashed line in each Figures (A) and (B) shows blank CVs measured in N₂ saturated

[dema][TfO] and [dmea][HfB] before adding HCOOH. The voltammetric response of Au electrode in each of the PILs (blank), exhibits analogous behaviour to that reported in aqueous media as the characteristic formation and reduction of gold oxides are similar to that observed in aqueous acid solutions.^{205, 206}

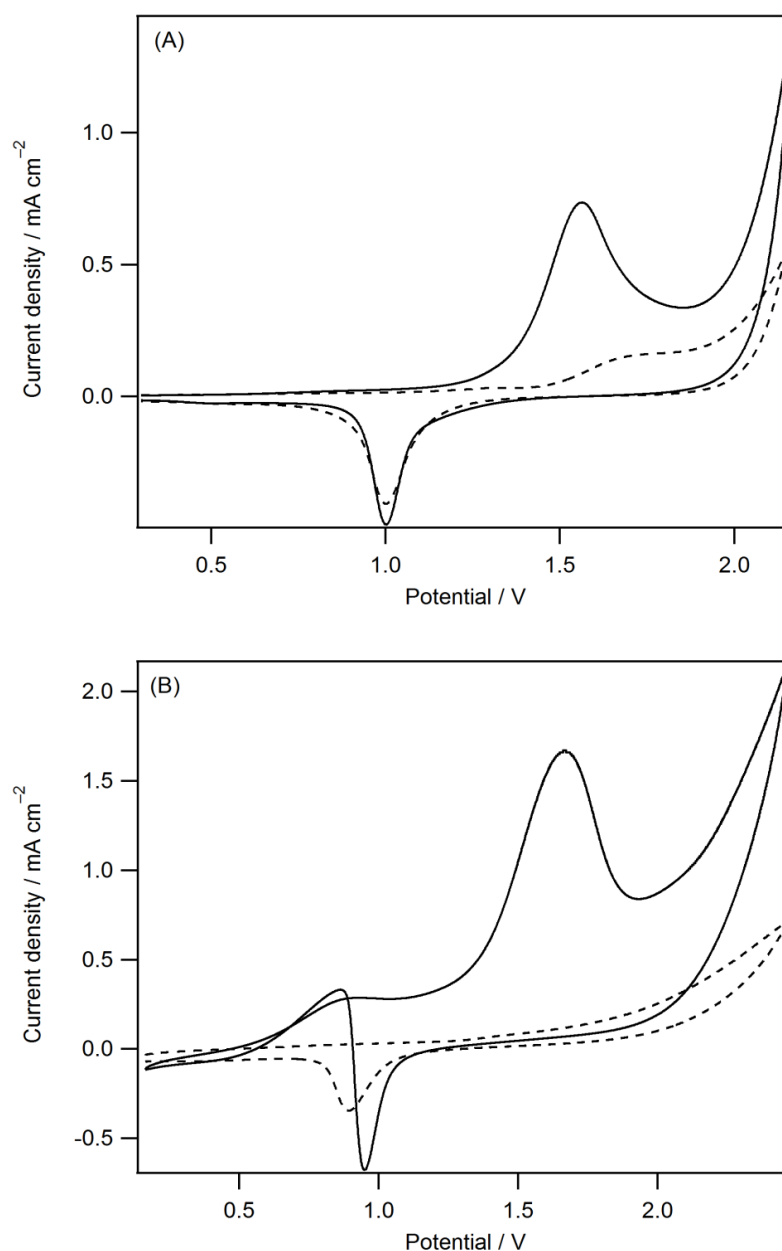


Figure 5.3.7 CV obtained on a 2 mm diameter Au disk vs. Pd-H at 50 mV s⁻¹ and 25 °C in 0.5 M solution of HCOOH in (A) [dema][TfO] and (B) [dmea][HfB] in a potential range from 0.3 V to 2.15 V and 0.15 V to 2.5 V, respectively. The dashed line in both figures, (A) and (B) shows CVs measured in the N₂ saturated [dema][TfO] and [dmea][HfB] before adding HCOOH.

The increase in anodic current above 1.5 V in [dema][TfO] and above 1.4 V in [dmea][HfB] is attributed to the formation of oxide layers on the surface of Au.¹²⁴ The earlier onset for the oxide formation at Au in [dmea][HfB] compared to that in [dema][TfO] is due to more residual water in the former than the latter. The reduction of surface Au oxides occurs at ~ 1.05 V when the potential is scanned back to the initial limit in each of the PILs. In Figure 5.3.7 (A) and (B), the solid line shows current response obtained at Au electrode in 0.5 M HCOOH in [dema][TfO] and [dmea][HfB], respectively. In both cases, the presence of HCOOH causes the current to differ from the current response obtained during the blank CVs, both in the potential region prior to oxide formation.

In [dema][TfO], Au electrode shows very low catalytic activity for the oxidation of HCOOH in the potential region prior to oxide formation, with an onset of oxidation at approximately above 0.80 V. In [dmea][HfB], the oxidation of HCOOH begins at potential above 0.6 V. In both of these solutions, current corresponding to oxidation of HCOOH increased rapidly and maximum activity accompanied surface oxides formation. Subsequently the faradaic current decayed rapidly after which the oxidation of the ionic liquid begins. Thus a slow oxidation of HCOOH occurred in a potential region prior to oxide formation and a fast oxidation in the region of oxide formation, a phenomenon also observed in aqueous acid media.²⁰⁵ The peak current for the oxidation wave in the more positive potential region in [dmea][HfB] was 40 μA compared to that 22.9 μA in [dema][TfO]. When the oxides were reduced from Au in [dmea][HfB] below 1.0 V and the electrode was regenerated, another oxidation wave (centered at 0.85 V) was observed which was not visible in the case of the [dema][TfO] solution. This second oxidation wave corresponds to the direct oxidation of HCOOH in [dmea][HfB] in the presence of more residual water

than in [dema][TfO] as high water concentration in the PILs favor the oxidation of HCOOH which has been proved by adding water to the HCOOH solution of [dema][TfO] and [dmea][HfB] and as discussed earlier.

If we compare the catalytic activity of Au for the electrooxidation of HCOOH in both of the PILs with that at Pt, it is observed that Pt shows better electrocatalytic activity for the oxidation than Au, although the self-poisoning of Pt with intermediate adsorbed species is not observed at Au surface as proved by the in situ IR measurements.^{206, 207} At Au catalysts the oxidation of trace water starts at more positive potentials compared to that at Pt catalysts in both electrolytes, resulting in a higher overpotential for HCOOH oxidation.

5.3.3. Catalytic Activity of Pd for Oxidation of HCOOH in PILs

The electrooxidation of HCOOH in [dema][TfO] and [dmea][HfB] was also examined at a carbon-supported Pd catalyst by cyclic voltammetry and the results were compared with that at Pt catalyst supported on carbon. Figure 5.3.8 shows cyclic voltammograms obtained on Pt/GC (dashed line) and Pd/GC (solid line) catalysts at 50 mV s^{-1} in (A) [dema][TfO] and (B) [dmea][HfB], each containing 0.5 M HCOOH. The inset of each figure shows only the positive going sweep. As mentioned earlier, in the presence of 0.5 M HCOOH, a strong oxidation wave corresponding to HCOOH oxidation that coincides with the onset of surface oxidation (above 1.1 V) appears at Pt/GC catalyst during the positive going sweep in both [dema][TfO] (Figure 5.3.8 A) and [dmea][HfB] (Figure 5.3.8 B). In the case of the Pd catalysts in [dema][TfO] containing 0.5 M HCOOH (solid line in Figure 5.3.7 A), the strong anodic wave which should be associated with

the oxidation of HCOOH emerged at an onset of 0.9 V in the positive going scan. Current due to the oxidation of HCOOH increased until 1.4 V after which a slight decrease in current was seen after which a further increase oxidation current was observed.

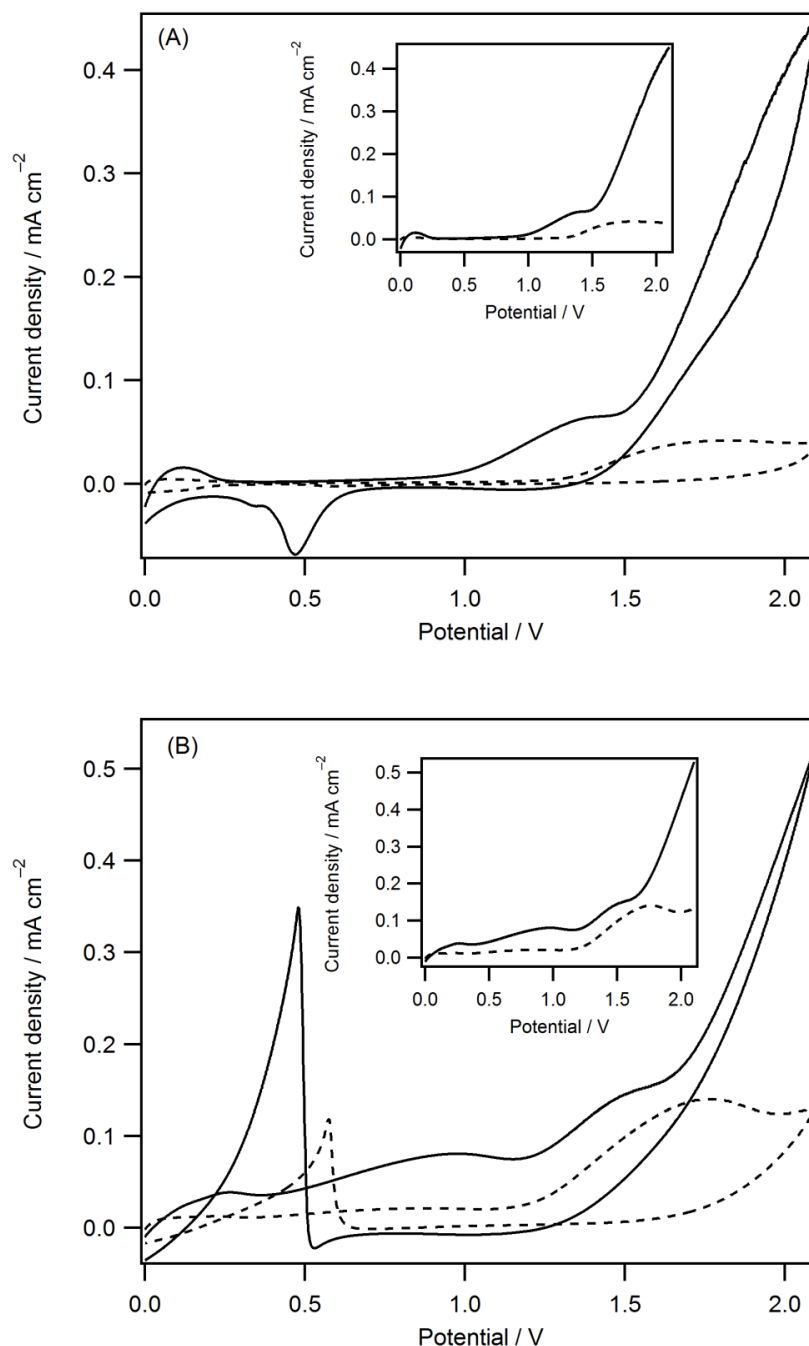


Figure 5.3.8 Cyclic voltammograms obtained in (A) [dema][TfO] and (B) [dmea][HfB] each containing 0.5 M HCOOH on Pt/GC (black dashed line) and Pd/GC (black solid line) catalysts at 50 mV s⁻¹ vs. Pd-H in a potential range between 0.0 V to 2.1 V. The Inset of each figure shows only the forward sweeps.

During the reverse sweep, a decrease in the current was observed below 0.6 V due to reduction of oxides from the surface of Pd/GC catalyst. It can be seen that oxidation of HCOOH in [dema][TfO] at Pd/GC catalyst started at about 300 mV more negative than at Pt/GC catalyst, suggesting that HCOOH is more prone to oxidation on Pd.

In the case of [dmea][HfB] containing 0.5 M HCOOH (Figure 5.3.8 B), the electrochemical responses obtained at Pd/GC catalyst were similar to those observed in [dema][TfO] at higher potentials c.a. above 1.1 V, with the bulk oxidation of HCOOH coinciding with the formation of oxides at catalyst surface in the PIL. However, a notable difference can be observed in the low potential region (between 0.0 V and 1.1 V) for HCOOH oxidation at Pd/GC catalyst in [dmea][HfB] compared to [dema][TfO]. A small oxidation wave between 0.4 V and 1.1 V with $E_p \sim 0.8$ V emerged in the positive going sweep suggesting that oxidation of HCOOH may occur at low potentials in HCOOH-containing [dmea][HfB].

In contrast to HCOOH-containing [dema][TfO], an oxidation peak with $E_p \sim 0.48$ V can also be observed in HCOOH-containing [dmea][HfB] at Pd/GC during negative going sweep, which can be attributed to the direct oxidation of HCOOH. The two oxidation peaks (observed at $E_p = 0.89$ V in the forward sweep and 0.48 V in the reverse sweep) at Pd/GC catalyst in [dmea][HfB] (Figure 5.3.8 B) were not observed in [dema][TfO] containing HCOOH (Figure 5.3.8 A). Also the peak currents for HCOOH oxidation at Pd/GC catalysts were higher than those observed at Pt/GC catalyst in both of the PILs. These observations show that Pd has better catalytic activity for HCOOH oxidation in PILs than Pt in both [dema][TfO] and [dmea][HfB].

5.4. Conclusions

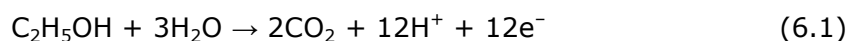
The electrochemical oxidation HCOOH has been investigated at Pt, Au and Pd catalysts in [dema][TfO] and [dmea][HfB]. Our results signify that in contrast to the behavior in aqueous media, the electrooxidation of HCOOH at Pt catalyst in the liquids proceeds mainly through indirect dehydration or CO_{ads} intermediate step in contrast to aqueous system. The complete oxidation of HCOOH and adsorbed CO occurred due to the adsorbed oxygen species, OH_{ads} that formed by the oxidation of trace H₂O present in the PILs. Electrochemical investigation of the adsorbed intermediates during HCOOH oxidation in the PILs shows that some weakly-adsorbed intermediate species sticks to the catalyst surface at low potentials, passivating the catalyst with respect to HCOOH oxidation in the PILs. The identity of the poisoning intermediates is not clearly established during electrochemical investigation but we suggest that these adsorbed species could be mainly CO-like intermediates in the ionic liquids similar to that observed in aqueous systems.¹⁸⁵ The rate of HCOOH oxidation in the PILs increased and overpotential decreased by increasing anodic potential limits and also water content of the liquids. Comparing the catalytic activity of Pt, Au and Pd for the electrooxidation of HCOOH in the PILs, shows that the electrooxidation activity in the PILs decreases in the order Pd>Pt>Au.

The inclusion of readily oxidised metals such as Pd, Ru to the Pt catalyst to form bimetallic catalysts may also aid in reducing the overpotential for HCOOH oxidation. These metals can provide synergetic effect to Pt, which can orient the catalysts in favor of the oxidation of HCOOH through the direct dehydrogenation path at lower potentials.^{54, 192} Therefore future work should focus on exploring this possibility.

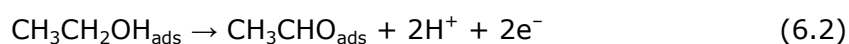
Chapter 6: Electrocatalytic Oxidation of Ethanol and Dimethyl Ether in Protic Ionic Liquids

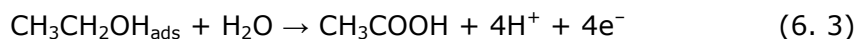
6.1. Introduction

The electrochemical oxidation of ethanol has drawn increasing interest in electrocatalysis and fuel cells in recent years due to its large scale production from the biomass, low toxicity, renewability, high boiling point and a high theoretical energy density compared to methanol.⁴⁷⁻⁵⁵ The oxidation of EtOH in aqueous media at Pt catalyst is a complex multiple-electron process that involves the transfer of twelve electrons and twelve protons (Eqn. 6.1).



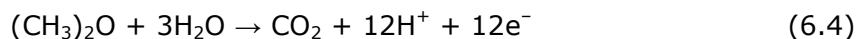
Just like formic acid oxidation, EtOH oxidation proceeds via a so-called dual-pathway mechanism.^{47, 50, 54, 208} The first mechanistic pathway proceeds via CO_{ads} intermediate to form CO_2 in acid solution (or carbonate in alkaline solutions) by delivering 12 electrons. The second pathway mainly leads to the formation of acetic acid (or acetate in alkaline solutions) by delivering four electrons (Eqn. 6.3) and/or acetaldehyde by delivering two electrons (Eqn. 6.2).⁴⁷





The electrocatalytic oxidation of EtOH is complicated and the main challenge is the cleavage of the C–C bond, which makes complete oxidation of the EtOH difficult, resulting in slow kinetics of the reaction in aqueous electrolytes. Pt is the most commonly used anode catalyst for EtOH oxidation due to its excellent properties in the adsorption and dissociation of ethanol. The Pt-catalyst poisoning by strongly adsorbed intermediates, e.g. CO_{ads} that results from the dissociation of EtOH at low temperatures is another electrocatalytic problem that arises due to the relative complexity of the reaction mechanisms.^{47, 48, 51, 54} Therefore, designing of an electrocatalysts that can efficiently break C–C bond in EtOH is an essential challenge for the desired complete oxidation to CO_2 . One approach to solving the problem of Pt poisoning is the utilization of Pt based bimetallic catalysts. Metals such as Sn and Ru can readily form surface oxide that can oxidize the surface bound intermediates and facilitate the complete oxidation of EtOH to CO_2 . The alternative approach will be to perform the reaction at high temperatures, which can reduce poisoning of the catalyst by destabilising the adsorbed intermediate.

Dimethyl ether shows facile electrooxidation activity due to its unique chemical structure (two C–O bonds but no C–C bonds) compared to EtOH and oxidizes completely in the presence of H_2O to CO_2 providing 12 electrons and 12 protons (Eqn. 6.4).^{60, 64, 65} Pt and Pt based electrocatalysts are commonly used for DME electrooxidation in aqueous electrolytes. However, the reaction mechanism has not been well understood compared to the oxidation of other organic fuels such as methanol and formic acid,^{60–62} hence; different mechanisms have been proposed for the reaction.



Various surface adsorbed intermediates such as $(\text{CH}_3\text{OCH}_2-)_\text{ads}$, $(\text{CH}_3\text{OC}-)_\text{ads}$, $(\text{HCO})_\text{ads}$ and CO_ads along with traces of methanol and formic acid have been detected during DME electrooxidation at Pt in acid electrolytes by Muller *et. al.*,⁶⁸ using cyclic voltammetry and gas chromatography studies, and Shao *et. al.*,⁶⁶ using surface enhanced infrared absorption spectroscopy and cyclic voltammetry. Similar to ethanol oxidation,⁴⁵ DME oxidation also requires surface oxidants ($\text{O}/\text{OH}_\text{ads}$) for the removal of surface poisoning species.⁶⁰

We investigated electrocatalytic oxidation of EtOH and DME on at Pt catalyst in [dema][TfO] by cyclic voltammetry and describe here the catalytic effect of the surface Pt-oxides on the electrocatalysis of EtOH and DME oxidation in the liquid. To the best of our knowledge, no such studies are undertaken for electrooxidation of EtOH and DME in PILs. The experimental results presented, will give an insight into understanding the mechanism of anodic oxidation of EtOH and DME at Pt in a PIL environment.

6.2. Experimental Section

6.2.1. Reagents and Apparatus

Ethanol (absolute, 99.99 %) and dimethyl ether (DME, 99.99 %) were obtained from Fisher Chemicals and BOC gases (Nottingham, UK), respectively and were used as received.

6.2.2. Electrochemical Measurements

The reference electrode was Ag/AgCl/KCl (sat.) for measurements involving aqueous solutions and Pd-H for measurements involving ILs. The working electrode was a Pt/GC electrode for EtOH oxidation measurements in the PIL and a 2 mm diameter Pt disk, in DME oxidation measurements. PtNPs were electrochemically deposited on a clean GC electrode from 0.1 M HCl containing 5 mM $\text{H}_2[\text{PtCl}_6] \cdot 6\text{H}_2\text{O}$ via potential step electrolysis by stepping the potential of the working electrode from 0.5 V to -0.2 V for 1000 s vs. Ag/AgCl/KCl (sat.). The ECSA of Pt-GC catalyst was estimated to be 1.23 cm^2 . The currents in each measurement were normalized to the ECSA for calibration of catalytic activity of the electrodes for oxidation of EtOH.

For EtOH oxidation measurements, the electrochemical cell was charged with approximately 5 mL of the [dema][TfO] containing 0.5 M of EtOH. For comparison, CVs were also recorded for EtOH oxidation using 0.5 M H_2SO_4 as supporting electrolyte. Experiments for the oxidation of DME were performed in [dema][TfO] saturated with the gas for 45 minutes.

6.3. Results and Discussion

6.3.1. Electrochemistry of Ethanol in Protic Ionic Liquids

6.3.1.1. Electrochemistry of Ethanol at Pt/GC in [dema]TfO]

The electrochemical behaviour of Pt/GC catalyst during EtOH oxidation in H_2SO_4 (aq.) and in the PIL, [dema][TfO] electrolytes are shown in the Figure 6.3.1. Figure 6.3.1 (A) shows the cyclic voltammograms of the Pt/GC catalyst in N_2 saturated 0.5 M EtOH in 0.5 M H_2SO_4 (aq.) and (B) 0.5 M EtOH in [dema][TfO]. The black dash lines in each of these figures (A)

and (B) shows the CVs recorded in N₂ saturated 0.5 M H₂SO₄ (aq.) and [dema][TfO] without EtOH, respectively. The electrochemical responses obtained for EtOH oxidation in aqueous acid is briefly described here, before discussing the electrooxidation of EtOH in [dema][TfO].

During the positive going (forward) sweep in the EtOH-containing H₂SO₄, the H_{upd} adsorption/desorption features (< 0.4 V) were inhibited compared to blank CV. The current rise for EtOH oxidation started at ~ 0.5 V and yielded two oxidation peaks, at ~0.95 V (peak I) and ~1.3 V (peak II). During the negative going (reverse) potential sweep, a small cathodic peak appeared (peak III) at 0.7 V, which corresponds to the reduction of the surface PtOH_{ads} as can be seen from the blank CV. The reduction peak is followed by an oxidation peak at a peak potential 0.6 V (peak IV). The liberation of active Pt sites allows EtOH oxidation to recommence. These features are typical of those expected and explained for EtOH oxidation at Pt in aqueous media.^{49, 50, 52, 55, 209, 210}

During the forward sweep, in the EtOH-containing [dema][TfO], an EtOH oxidation wave appeared at ~1.0 V that coincides with the onset of surface oxidation in blank [dema][TfO] (Figure 6.3.1 B, dashed line). This broad oxidation wave with E_p ~1.4 V (wave II) has a shoulder wave (I) that increases in magnitude in second and higher scans showing that EtOH oxidation is activated in the second and consequent scans compared to the 1st scan due to residual oxides on the electrode. The oxidation wave II also increased in magnitude and shifted to less positive potential during second and consequent scans. On the negative sweep, similar to that in aqueous system, the current gradually decayed and a small cathodic peak appeared (peak III) at 0.7 V that corresponds to the reduction of the PtOH_{ads} on Pt/GC catalysts in the liquid. After regeneration of electrode, current due to the oxidation of EtOH again started increasing below 0.7 V and resulted a

third oxidation wave at $E_p \sim 0.547$ V (peak IV). This anodic peak appeared at the potential where PtOH_{ads} removal from the Pt surface occurred (Figure 6.3.1 B dotted line), suggesting that, during the negative sweep, EtOH oxidation restarted as some OH_{ads} was removed from the surface.^{45, 50, 52, 55}

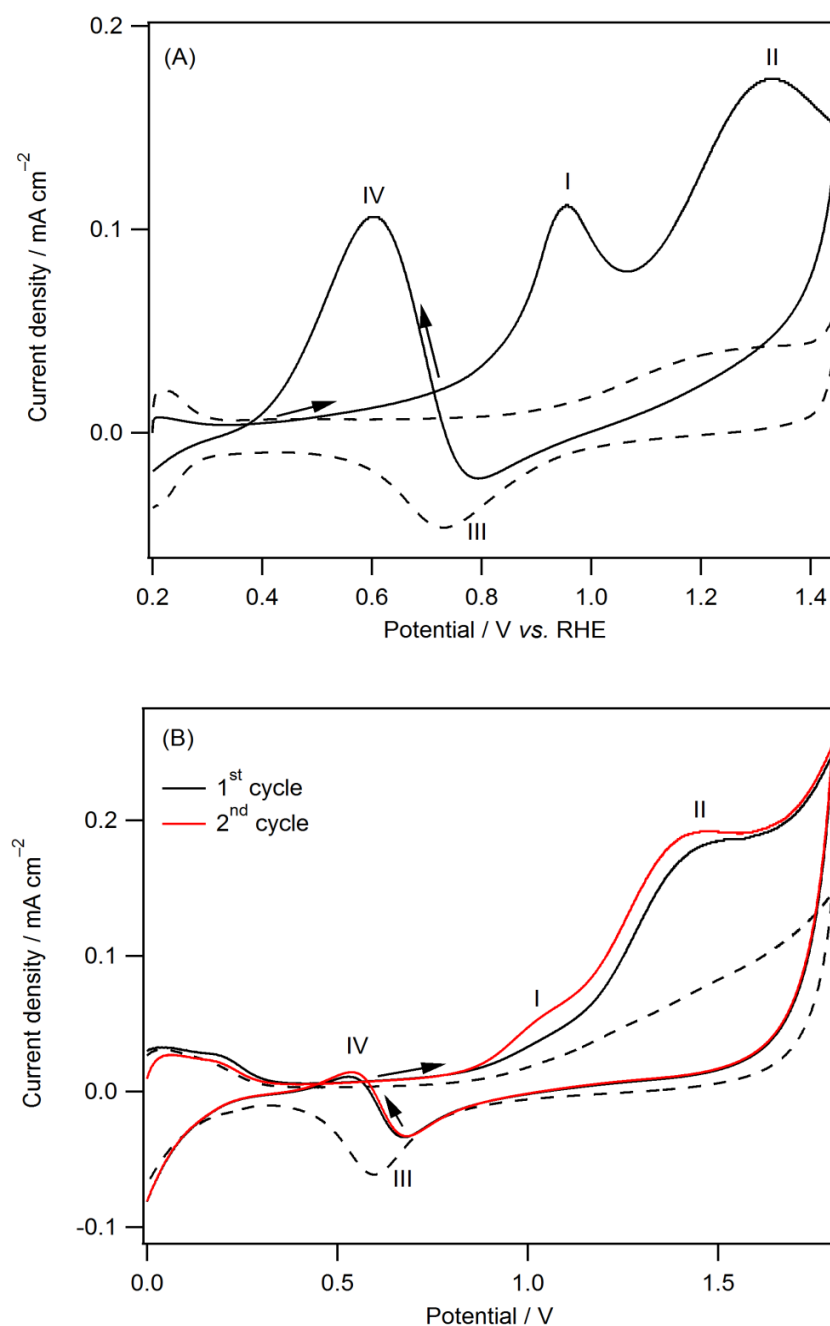


Figure 6.3.1 Cyclic voltammograms showing the oxidation of 0.5 M EtOH in (A) 0.5 M H₂SO₄ and (B) [dema][TfO] at a Pt/GC electrode at 50 mV s⁻¹. The potential of the working electrode was cycled from 0.0 V to 1.25 V vs. Ag/AgCl (data reported vs. RHE) in (A) and 0.0 V to 1.8 V vs. Pd-H in (B). The dashed line in each figure shows CVs measured in each liquid saturated with N₂, before adding EtOH.

As described in Section 3.3.4 Pt surface oxidation in [dema][TfO] starts just above 1.0 V forming PtOH_{ads} that then undergoes a place exchange phenomenon at higher potentials to form PtO or PtO_2 . The two oxidation peaks, I and II obtained for EtOH electrooxidation in the ionic liquid during positive going potential sweep can be attributed to the oxidation of EtOH by the two kinds of chemisorbed oxygen species, PtOH_{ads} and PtO, respectively. The onset of EtOH oxidation for peak I (~ 1.0 V) intersects with that of the onset of PtOH_{ads} formation on Pt (Figure 6.3.1 B dotted line). At higher potential (>1 V), surface of the catalyst is further covered with monolayers of oxide, leading to a decrease in the EtOH oxidation current. The surface oxide formed at higher potentials, mainly PtO, further facilitates EtOH oxidation by providing O species to form oxidation products. The reduction of the oxide species during the reverse sweep allows fresh adsorption and oxidation of EtOH giving peak IV. However, in the 2nd and consequent scans, some surface oxides, formed during the 1st scan, are left over on the catalyst surface that enhances EtOH oxidation leading to increase in oxidation currents both for peak I and peak II on subsequent scans.

For the electrochemical oxidation of EtOH on smooth Pt electrode in H_2SO_4 , Gupta and Datta suggested a similar reaction mechanism where they associated the lower potential peak to the oxidation of ethanol and/or ethanoic residues through oxygen transfer from a PtOH_{ads} species while the second, higher potential peak from Pt–O oxygen transfer.²¹⁰ Shao and Adzic has shown, using surface enhanced infrared absorption spectroscopy with the attenuated total reflection technique that formation of adsorbed acetate occurred at Pt from the direct oxidation of EtOH at lower potential.⁶⁷ Also, Hitmi et al.,²¹¹ reported that at a lower potential (<0.6 V)

ethanol oxidizes in acid media to acetaldehyde and at a higher potential (>0.8 V) to acetic acid.

In the ionic liquid, the electrochemical response for EtOH oxidation is similar to that in acid solution. The current response for EtOH oxidation in [dema][TfO] for peaks I and II are lower than for both the peaks in H_2SO_4 . The low current response may be due to high viscosity of [dema][TfO] and low mass transport of EtOH in the PIL compared to 0.5 M aqueous H_2SO_4 . However, similar to aqueous acid solution, we also suggest that the lower oxidation peak may be due to partial oxidation of EtOH to acetaldehyde at lower potential and acetic acid at higher potential due to provision of the O species from PtOH_{ads} and PtO formed at Pt surface from trace water in the ionic liquid at lower and higher potentials, respectively.^{48, 49}

6.3.1.2. Effect of Temperature on Ethanol Oxidation in the PIL

The influence of temperature on the electrocatalytic oxidation of EtOH was investigated on Pt/GC electrocatalyst in [dema][TfO]. Figure 6.3.2 shows a series of CV profiles at various temperatures ranging from 30 °C to 120 °C obtained at Pt/GC electrode in 1.0 M EtOH in [dema][TfO]. It is noted that a significant activation of the electrode for the electrooxidation of EtOH was observed at elevated temperatures. With the increase of temperature of the liquid, an increase of the oxidation current with a negative shift in the onset potential during the positive going sweep and a positive shift in the re-oxidation peak during the negative going sweep was observed, as indicated by arrows in the figure 6.3.2. A shift of ~ 150 mV in the onset potential for EtOH oxidation in [dema][TfO] was observed by increasing temperature from 30 °C to 120 °C. Also increases in the currents for peaks I, II, and IV were observed by elevating temperature from 30 °C to 120

°C. This negative shift of peak potential for EtOH oxidation is due to increased rate of water oxidation in the PIL as explained in Section 3.3.5 that leads to more surface adsorbed OH_{ads} species.^{121, 162, 170} Also with increasing temperature, the onset potential of PtOH_{ads} reduction shifts positively,¹⁶² hence; a distinct positive shift of the re-oxidation peaks is observed with increase in temperature. The increased catalytic activity of Pt/GC electrode for EtOH oxidation at elevated temperature may also be associated to the decrease in the coverage of the electrode poisoning adsorbed intermediates such as CO_{ads} and also to the enhancement of the electrode reaction kinetics.²¹⁰

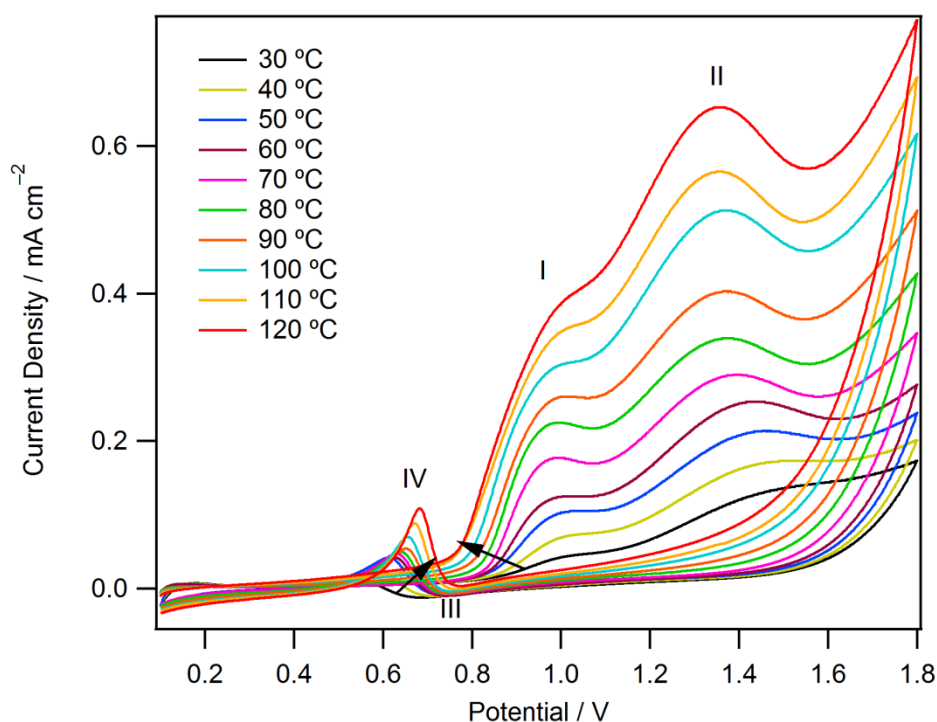


Figure 6.3.2 Cyclic voltammograms on Pt/GC electrode at a series of temperatures in N_2 saturated, 1.0 M EtOH in $[\text{dema}][\text{TfO}]$, by sweeping potential of the electrode from 0.1 V to 1.8 V at 50 mV s^{-1} .

Figure 6.3.3 shows Arrhenius plot of the $\ln$ (current density) versus $1/T$ at 1.0 V (red line) and 1.3 V (black line) for the oxidation of EtOH in

[dema][TfO]. The data obtained at both of the oxidation potentials, 1.0 V and 1.3 V shows a good fit to the Arrhenius Equation 6.5.

$$\ln(\text{current density}) = \ln A - E_a/RT \quad (6.5)$$

where A is the pre-exponential factor or Arrhenius constant, E_a is the activation energy, R is the universal gas constant ($8.3143 \text{ J K}^{-1} \text{ mol}^{-1}$) and T is absolute temperature.

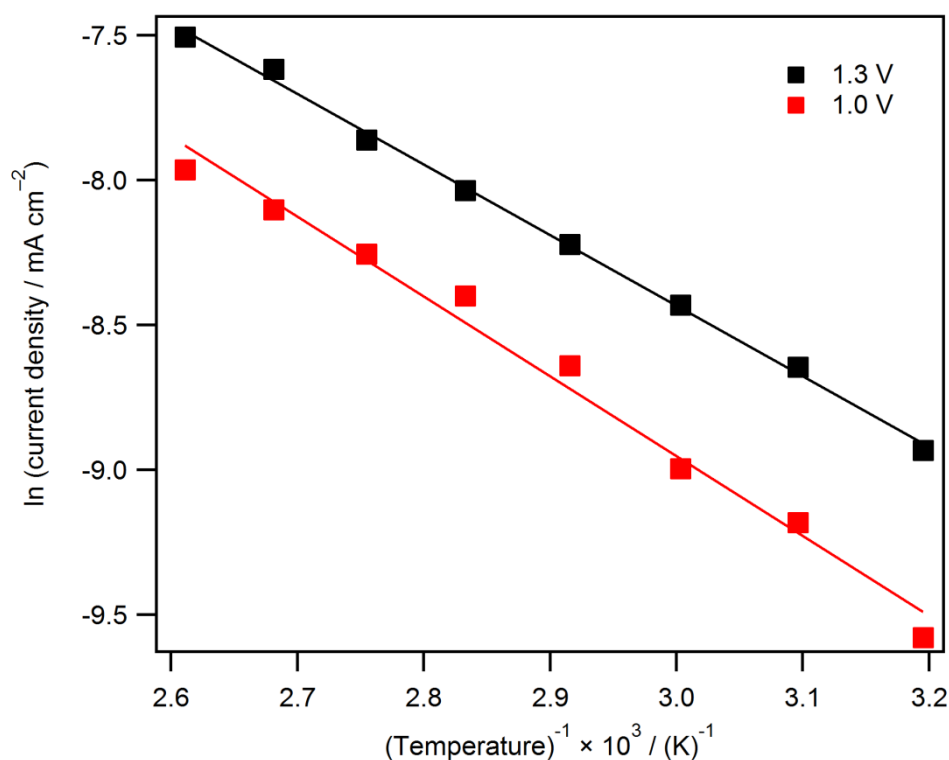


Figure 6.3.3 Arrhenius plots at 1.0 V and 1.3 V for the oxidation of EtOH in [dema][TfO]. The slope of the plots gave activation energy, $E_a = 24 \text{ kJ mol}^{-1}$ at 1.0 V and 19 kJ mol^{-1} at 1.3 V.

From the plot, the activation energy calculated for EtOH oxidation in [dema][TfO] at Pt/GC electrode for the anodic peak I was 24 kJ mol^{-1} at 1.0 V and 19 kJ mol^{-1} at 1.3 V for the anodic peak II. The E_a value for the 1st anodic peak was higher than the 2nd anodic peak, which is supported from literature as Lee et al.,⁵⁵ also observed a higher E_a for the anodic peak

I (22.1 kJ mol^{-1}) compared to the anodic peak II (13.9 kJ mol^{-1}) for ethanol oxidation on Pt in acidic media. However, E_a is generally slightly higher in the PIL compared to aqueous systems, showing that the oxidation process is slow in the PIL. This can be seen from the low current and high onset potential for the oxidation of EtOH in [dema][TfO] compared to 0.5 M H_2SO_4 as described in Figure 6.3.1. Similarly, the high activation energy obtained at lower potential, 1.0 V vs. Pd-H in [dema][TfO] and by Lee et al., at 0.933 V vs. RHE in acid media shows that the rate of EtOH oxidation reaction is slow at lower potentials compared to that at higher potentials, at which low activation energy was obtained. It may be due less surface OH_{ads} species formed at lower potential that are not sufficient to carry out complete oxidation of EtOH than at high potential 1.3 V in [dema][TfO] where the electrode surface is covered with more oxide species. The oxide acts as catalyst for EtOH oxidation, therefore, low activation energy is obtained at 1.3 V than at 1.0 V.

6.3.1.3. Influence of Scan Rate on Ethanol Oxidation

Figure 6.3.4 shows linear sweep voltammograms for EtOH oxidation in [dema][TfO] at 100 °C on Pt/GC electrode recorded at a series of voltammetric scan rates, ν . Generally, the oxidation peak currents (i_p) for both oxidation waves I and II in the positive scan direction increase with the scan rate. It is also found that the peak potentials of peaks, I and II show a slight dependence on scan rate as the peak potentials for both peaks shifted positive with the scan rate, showing some irreversibility in the charge-transfer process. The onset for the oxidation shifts towards negative potentials with increasing sweep rates. It is due to the fact that at high scan rates the rate of mass transport increase and EtOH oxidation rate increase with increasing scan rate at 100 °C.

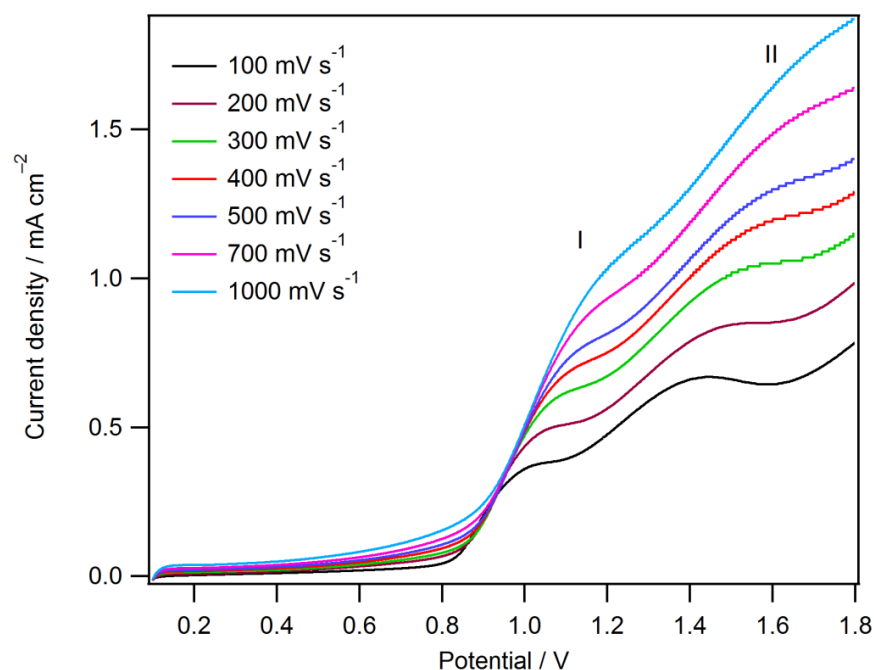


Figure 6.3.4 Linear sweep profiles at different scan rates at a Pt/GC electrode in 0.5 M EtOH in [dema][TfO] at 100 °C.

6.3.2. Electrochemistry of Dimethyl Ether in PILs

6.3.2.1. Electrooxidation of DME in [dema][TfO]

To examine the electrochemical behaviour of DME oxidation in ionic liquids, a polished 2 mm diameter Pt disk electrode was immersed in [dema][TfO] saturated with DME and CVs were recorded at 100 mV s⁻¹ in a potential range between -0.05 V and 1.65 V. DME was bubbled into [dema][TfO] for 45 minutes. Figure 6.3.5 shows the voltammetry response obtained for electrooxidation of DME during the first 10 cycles at Pt in DME saturated [dema][TfO]. The dashed line in the figure shows blank CV measured in [dema][TfO] in N₂ atmosphere. Compared to the blank CV, no significant oxidation current is seen up to 0.6 V during the first positive going potential sweep (red solid line). At c.a. ~6.0 V, an increase in current is observed and the current due to this oxidation process continued

increasing until the switching potential, 1.65 V. This continues increase in the oxidation current between 0.6 V and 1.65 V is attributed solely to DME oxidation in the liquid,²¹²⁻²¹⁴ catalysed by surface adsorbed Pt-oxides.⁶⁰ This result is quite similar to the results obtained by Ejigu and co-workers, during hydrodynamic voltammetry study for methanol oxidation at Pt in the same ionic liquid.⁴⁵

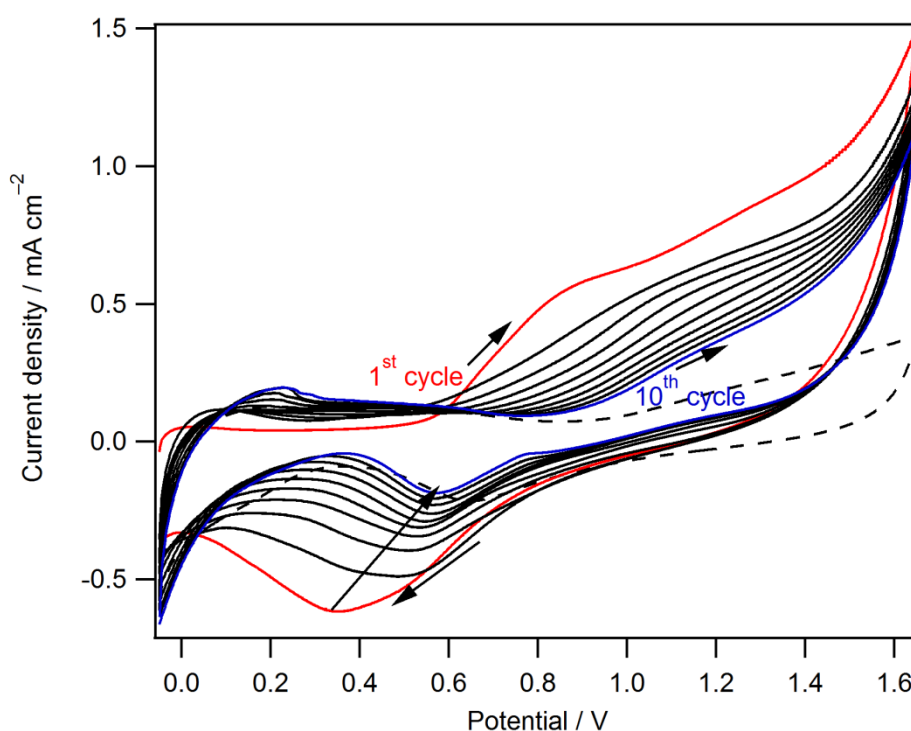


Figure 6.3.5 A series of CVs obtained for electrooxidation of DME on a 2 mm diameter Pt disk electrode at 100 mV s^{-1} in [dema][TfO] saturated with DME (solid lines) or without DME (dashed line) under N_2 atmosphere at room temperature in a potential range between -0.05 V and 1.65 V .

However, in the second and subsequent sweeps (black solid lines) the current response due to oxidation of DME decreased until reaching a stable value in the 10th cycle (blue solid line). The onset potential for the oxidation process also shifted to the positive side in the subsequent sweeps and reaching to $\sim 0.8 \text{ V}$ in the 10th sweep compared to 0.6 V in the first sweep. In the potential range between 0.6 V and 1.65 V , the 10th CV curve with DME saturated solution is not completely superimposed on the blank

CV, showing that DME oxidation still happen in the 10th cycle but the current response is has decreased compared to that in the first cycle. This decrease in current during subsequent sweeps shows that some adsorbed intermediates could be formed on the clean Pt surface during the first sweep that poison the electrode for further oxidation in the subsequent scans leading to a decrease in the current response.^{64, 65, 212}

The surface oxide reduction peaks during the negative-going sweep also shifted more cathodic c.a. to 0.4 V compared to 0.7 V in the blank, due to the presence of the adsorbed intermediates formed on Pt during the positive-going sweep. However, it should be noted that peak position for the oxides reduction wave shifted toward positive potential as the number of scan increased and was comparable to the blank in the 10th sweep where the oxide reduction was observed at 0.6 V, indicated by an arrow in the figure. It could also be noted that the current in the H_{UPD} region (between -0.05 V and 0.4 V) is subdued significantly in the presence of DME during the first cycle compared to the current corresponding to the H-adsorption/desorption region in blank [dema][TfO]. Compared to the first cycle, the current in the H_{UPD} region increased and another oxidation wave formed in the subsequent cycles,. The height of this oxidation wave at ~0.2 V increased and the onset potential shifted negatively during subsequent scans. This oxidation wave also corresponds to the direct oxidation of DME which is catalysed by the residual surface Pt-oxides remaining on the electrode in the subsequent scans. During the first scan the electrode surface was clean and there were no oxides present, therefore, no DME oxidation current was observed in the low potential region between -0.05 V and 0.4 V.

As described above that some adsorbed intermediate species could be formed on Pt surface during first scan (red line) at potentials > 0.6 V in

positive-going sweep that caused shifting of the Pt-oxides reduction wave more cathodic during the negative-going sweep (indicated by arrow in Figure 6.3.5). Zhang *et. al.*⁶⁴ has proved through an electrochemical and *in situ* IR measurements that a reaction intermediate ($-\text{CH}_2\text{OCH}_3$) can be formed in low potential region from oxidation of DME at Pt in aqueous acid electrolyte which is then oxidized to CO_{ads} and finally to CO_2 at high potentials. In addition, Muller *et al.*, described that DME oxidation proceeds in many steps involving formation of reaction intermediates in lower potential region that are finally oxidized to CO_2 at higher potentials.⁶⁸ In order to electrochemically investigate the various potential-dependent intermediates forming during DME oxidation in $[\text{dema}][\text{TfO}]$, we recorded CVs at freshly polished cleaned Pt by scanning the potential to 2.15 V as shown in Figure 6.3.6.

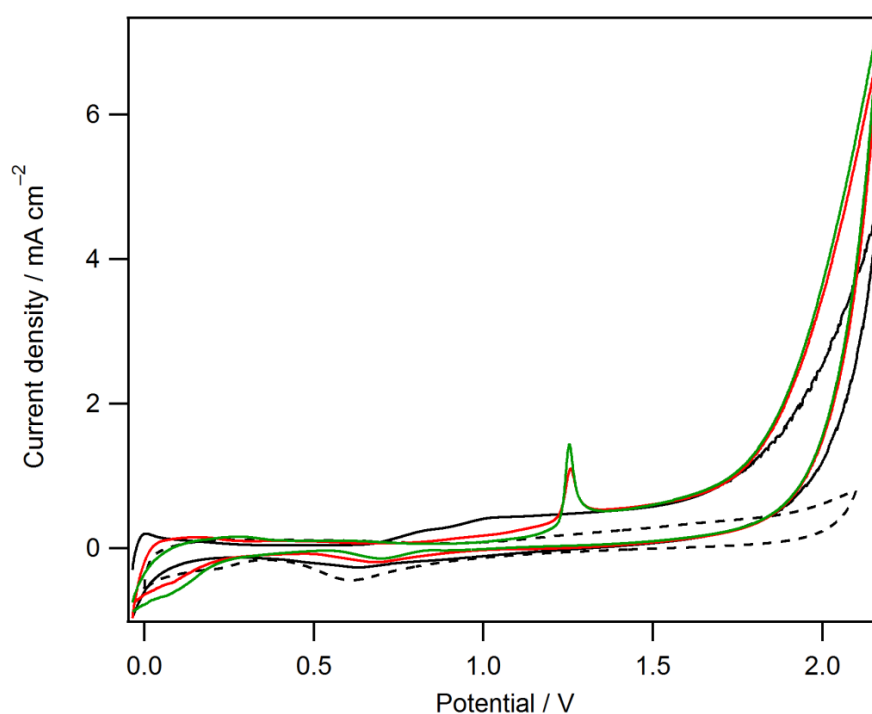


Figure 6.3.6 Three consecutive cycles (black–1st cycle, red–2nd cycle and green–3rd cycle) obtained at a 2 mm diameter Pt disk electrode at 100 mV s^{-1} and 25 °C in $[\text{dema}][\text{TfO}]$ saturated with DME in a potential range between initial potential, -0.05 V and upper potential limit, 2.15 V. The dashed black line in the figure represents CV obtained in N_2 saturated blank $[\text{dema}][\text{TfO}]$ without DME.

A voltammetry response, similar to that in Figure 6.3.5, was obtained for the first cycle (solid black line) during positive-going sweep in which the oxidation of DME started at about 0.6 V and the current increased at high potentials and then become stable until 1.8 V after which a sharp increase in the oxidation current was observed that kept on increasing until the switching potential 2.15 V. It is worth noting that this sharp increase in oxidation current beyond 1.8 V cannot be observed in the blank CV (dashed line in the figure 6.3.6) obtained at the same electrode. This indicates that the sharp oxidation current was not due to oxidation of the anion of the ionic liquid, $[\text{TfO}]^-$ but is due to bulk oxidation of DME and/or could be due to the oxidation of the strongly adsorbed CO-like intermediates formed in the potential range between 0.6 V and 1.8 V as suggested by Zhang *et. al.*⁶⁴ The electrode seemed to be further deactivated during the second sweep (red line) and oxidation of DME above 0.6 V was suppressed compared to the first CV (black line) until 1.2 V. At around 1.2 V a sharp increase in the oxidation current was observed, which then stabilized until 1.8 V and again increased sharply in the same pattern after this potential as in the first CV (black line) but the magnitude of current was high in the second cycle. Similar voltammetry behaviour was observed in the 3rd (green line) and subsequent cycles (not shown on the figure). The sharp oxidation peak at around 1.2 V observed during 2nd and 3rd positive-going scan could be due to the oxidation CO_{ads} by Pt-OH_{ads}/PtO_{ads} via Langmuir-Hinshelwood mechanism. The strongly adsorbed CO_{ads} could be formed by the oxidation of methanol which is one of the intermediate product during DME oxidation proposed by Muller *et al.*⁶⁸

To further investigate the surface adsorbed intermediate species forming at Pt during DME oxidation in ionic liquids, DME stripping experiment was carried out. Initially, a freshly polished clean 2 mm

diameter Pt was inserted in DME saturated [dema][TfO] solution and cycled at 500 mV s^{-1} for fifty cycles between 0.7 V and 2.3 V (see Figure S 9 in Appendix 1). The electrode was then removed from solution, rinsed with de-ionized water, dried in a stream of N_2 and CVs were obtained at 50 mV s^{-1} in $0.2 \text{ M H}_2\text{SO}_4$ as shown in Figure 6.3.7.

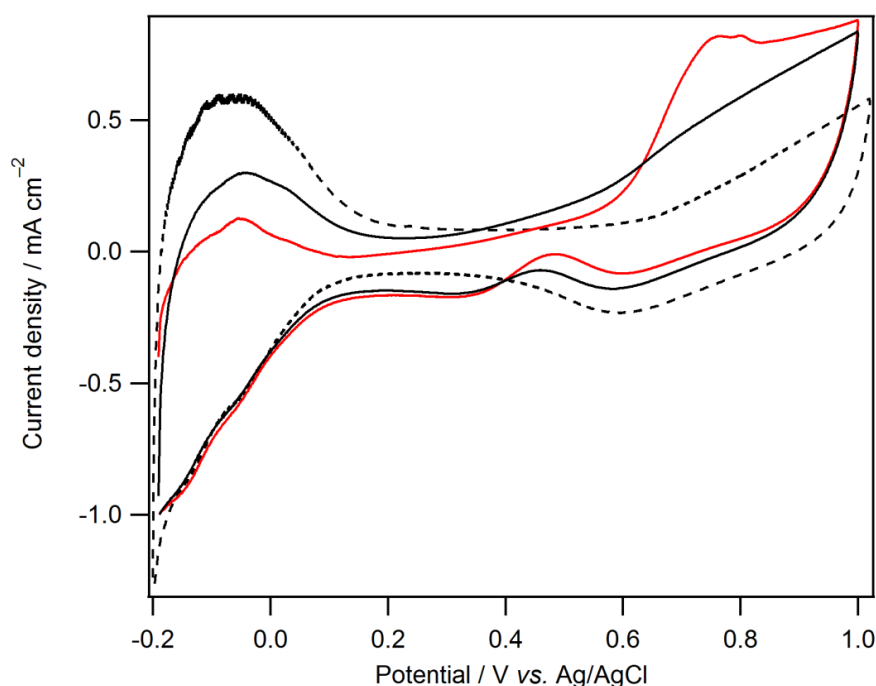


Figure 6.3.7 CVs of a 2 mm diameter Pt electrode in $0.2 \text{ M H}_2\text{SO}_4$ (solid red line-1st cycle and black solid line-2nd cycle) showing the oxidative stripping of DME adsorbates, accumulated from DME saturated solution of [dema][TfO] after cycling the electrode at 500 mV s^{-1} in a potential range between 0.7 V and 2.3 V for fifty cycles. The dashed black line is the blank CV obtained in N_2 saturated $0.2 \text{ M H}_2\text{SO}_4$.

The figure shows the oxidative stripping of DME adsorbates, accumulated from DME saturated solution of [dema][TfO]. The black dash line is the blank CV obtained at a clean Pt (the same diameter) in N_2 saturated $0.2 \text{ M H}_2\text{SO}_4$ vs. Ag/AgCl. Compared to the blank CV, there are two main features to mention. During the first cycle (red solid line), current in the H_{upd} adsorption/desorption features ($< 0.2 \text{ V}$) are suppressed compared to blank CV. These observations suggest that some

intermediates were pre-adsorbed at Pt electrode during DME oxidation in [dema][TfO]. These adsorbates were oxidized in the broad oxidation peak that appeared at about 0.60 V, on top of the formation of surface OH_{ads} species, at Pt in the acid solution (red solid line—1st cycle). This shows that the adsorbed species, probably $(\text{CH}_3\text{OC}-)_{\text{ads}}$, $(\text{HCO})_{\text{ads}}$ and CO_{ads} ,^{60, 68} were electrochemically oxidized by the Pt-oxide species, OH_{ads} by Langmuir-Hinshelwood mechanism. The pre-adsorbed species were not completely stripped-off the surface in the first cycle as current in hydrogen region is still suppressed compared to blank CV and also high oxidation current is observed above 0.6 V during the second cycle (solid black line in Figure 6.3.7). In subsequent cycles oxidation current matched with that of the blank CV and the electrode was regenerated and freed of the poisonous adsorbates. Our observations are similar to the electrooxidation of DME at Pt studied by Li and co-workers²¹² in H_2SO_4 and Zhang *et. al.*,²¹³ in HClO_4 . From the oxidation of DME in [dema][TfO] at Pt catalyst, we assume that at lower potentials, intermediates such as $(\text{CH}_3\text{OCH}_2-)_{\text{ads}}$ or $(\text{CH}_3\text{OC}-)_{\text{ads}}$ were formed at Pt surface in the IL environment similar to aqueous systems,^{63, 68} which then transform at high potentials to $(\text{HCO})_{\text{ads}}$ and/or CO_{ads} and that oxidized finally to CO_2 at more positive potentials. We confirmed that the Pt-adsorbed intermediates were from the decomposition of DME within the ionic liquid and not from the ionic liquid, through a similar chronoamperometric experiment performed in blank [dema][TfO].

6.4. Conclusion

We demonstrated that the ionic liquid [dema][TfO] could be employed as the electrolyte for electrocatalysis of ethanol and dimethyl ether at Pt electrocatalyst. It is found that the adsorbed surface oxide, OH_{ads} formed at Pt by oxidation of trace water plays an important activating role during

both the oxidation processes, and helps in complete oxidation of EtOH and DME. From the cyclic voltammetric study of the electrooxidation of EtOH in [dema][TfO] at Pt/GC catalyst, we conclude that similar to EtOH oxidation in aqueous media, two oxidation peaks during positive going potential sweep and a re-oxidation peak during reverse sweep can be obtained. However, the oxidation current density is lower for all of the three peaks compared to that in aqueous media. EtOH exhibits increase in the oxidation current densities as temperature increases. It is also found that the peak potentials change with respect to changing scan rate, showing some irreversibility in the charge-transfer process. From the electrochemical measurement of adsorbed intermediates during DME electrocatalysis at Pt in the ionic liquid, we found that a potential-dependent chemisorption of the various intermediate occurred on Pt followed by surface processes.

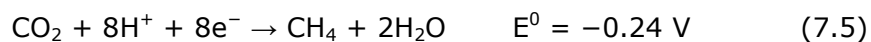
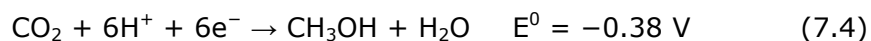
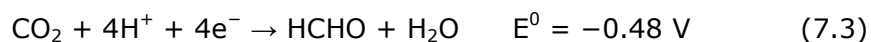
For facile electrocatalytic oxidation of ethanol, an active electrocatalyst is required that helps in C-C bond breaking, can promote direct dehydration of EtOH, and form earlier surface adsorbed oxygen species, OH_{ads} that can help in the removal of catalyst's poisoning species such as CO_{ads} . The catalyst poisoning can be overcome by modifying the Pt surface with another metal such that to increase its coverage in adsorbed OH species coming from water that are necessary for the oxidation of CO-like adsorbed species that comes from EtOH dissociation. Lin *et al.*²¹⁵ has recently shown that adding Sn to Pt surface to form a bimetallic catalyst undergo EtOH oxidation at much lower potentials due to facile formation of OH_{ads} at lower potentials on Sn compared to bare Pt. Therefore, future work should be to make Pt-Sn bimetallic catalyst for further exploring the electrocatalysis of EtOH and DME oxidation using PILs as supporting electrolytes.

Chapter 7: Electrocatalytic Reduction of Carbon Dioxide in Room Temperature Ionic Liquids

7.1. Introduction

Electrochemical reduction of CO₂ is one of the promising approach that involves the use of electricity to convert CO₂ to other useful chemicals under mild conditions.⁹⁸ The conversion of CO₂ to useful fuels using electricity from renewable sources (sunlight, wind, and geothermal) is of interest, especially in light of the environmental cost and finite availability of fossil fuels.^{10, 74, 78, 91, 216} This will help to chemically store the excess of renewable energy from intermittent sources, thus reducing our dependence on fossil fuels.⁹⁸ Many valuable chemicals are produced by electrochemical reduction of CO₂ in both aqueous and non-aqueous media at metal electrodes. The product selectivity of the direct electrochemical reduction of CO₂ depends on the type of metal electrodes employed in a certain reaction media and the potential applied.^{75, 91, 217} The various cathodic half reactions that involve proton-coupled multi-electron steps during electrochemical reduction of CO₂ yielding CO, formic acid, formaldehyde, methanol and hydrocarbons (methane and ethylene) in aqueous solution (pH 7) at 25 °C and 1 atm. pressure are listed below from Eqn. 7.1 to Eqn. 7.5 along with the equilibrium potentials.^{78, 82}





In non-aqueous solvents such as DMF (N, N'-dimethylformamide) electrochemical reduction of CO_2 at various electrodes involves one electron reduction of CO_2 to an intermediated radical anion (Eqn. 7.6). The standard potential of the $\text{CO}_2/\text{CO}_2^{\cdot-}$ couple is -1.97 V in DMF.⁹⁶ The intermediate radical anion, $\text{CO}_2^{\cdot-}$ combines with another $\text{CO}_2^{\cdot-}$ to form oxalate ($2\text{CO}_2^{\cdot-} + \text{e}^- \rightarrow \text{C}_2\text{O}_4^{2-}$).^{96, 97, 217, 218} $\text{CO}_2^{\cdot-}$ can also combine with CO to form another intermediate $\text{C}_2\text{O}_4^{\cdot-}$ which then takes up an electron to form CO and CO_3^{2-} . The presence of H_2O in the medium can protonate $\text{CO}_2^{\cdot-}$ to form neutral radical ($\text{HCO}_2^{\cdot}$), which then gains an electron to form formate anion HCO_2^- ($\text{HCOO}^{\cdot} \xrightarrow{\text{e}^-} \text{HCOO}^-$).



Many electrodes, including bulk metal electrodes as well as chemically modified electrodes have been evaluated for electrochemical CO_2 reduction in aqueous media, but none of them are practical for widespread CO_2 reduction due to their low catalytic activity and poor stability.^{97, 219} In the literature, metal electrodes are grouped on the basis of the major products formed by the reduction of CO_2 . Hori and co-workers have classified metal electrodes into two groups based the product selectivity in aqueous systems.⁹⁷ Metals such as Au, Ag, Zn, Pd, Ni, and Cd are classed as CO forming and metals such as Pb, Hg, Sn and In as HCOOH -forming metals.

Hydrocarbons (CH_4 and C_2H_4), aldehydes and alcohols are formed in significant amounts and at high rates from CO_2 reduction at metallic Cu cathodes, although at an overpotential of almost 1V.^{78, 220} In non-aqueous media, metals are classified into three groups based on the product selectivity during electrochemical CO_2 reduction:⁸⁴

- (1) Metals such as Cu, Ag, Au, Zn and Sn result in the formation of CO
- (2) Pb, Tl and Hg produce oxalic acid
- (3) At Al, Ga, Fe, Cr, Pd and Cd both CO and oxalic acid are formed

7.1.1. Challenges in CO_2 Electoreduction

Converting CO_2 to other products is challenging because CO_2 is a fully oxidized and extremely stable small molecule. In addition, the products formed from CO_2 reduction are complex molecules.^{74, 82} CO_2 is reduced at high overpotential on most electrocatalysts. The high overpotential observed during CO_2 electrocatalysis is mainly due to the formation of a bent shaped intermediate radical anion ($\text{CO}_2^{\cdot-}$) from a linear CO_2 molecule. This is due to extra energy required for the reorganization of the linear CO_2 molecule to the bent radical anion $\text{CO}_2^{\cdot-}$.⁸² In aqueous electrolytes, the HER from water reduction is thermodynamically favored over CO_2 reduction.^{75, 221} Metals such as Pt, Ti, and Ru etc. possess low hydrogen overpotential and cannot facilitate the reduction of CO_2 while metals such as Au, Ag, and Zn have high hydrogen overpotential and can convert CO_2 at high efficiency. The competing HER during CO_2 reduction in aqueous system can be suppressed using non-aqueous solutions. The electrochemical reduction of CO_2 in common non-aqueous solvents such as DMF, DMSO, MeCN etc. with conventional supporting electrolytes such as tetraethylammonium perchlorate (TEAP) or $[\text{TBA}][\text{PF}_6]$ is advantageous due to the high solubility of CO_2 .^{97, 217, 218}

7.1.2. RTILs as Non-aqueous Media for the Reduction CO₂

A significant amount of interest has been developed recently in the use of RTILs as media for the electrochemical reduction of CO₂.^{75, 77, 80, 83, 86, 91, 222} RTILs are desirable media for CO₂ reduction because of the higher solubility of CO₂ in them, compared to aqueous solutions and conventional organic solvents. CO₂ is remarkably soluble in imidazolium-based ionic liquids.^{91, 133, 223, 224} Blanchard *et al.*,²²⁵ reported the effect of changing cations and anions of the five imidazolium based ILs [bmim][PF₆], [omim][PF₆], [omim][BF₄], [bmim][NO₃] and [emim][EtSO₄] and one pyridinium-based [N-bupy][BF₄] on the IL/CO₂ phase behaviour. They have shown that in all of the ILs, CO₂ dissolves readily in the liquid phase and solubility of the CO₂ depends on the substituent on the cation and nature of the anion of the IL. Also, by addition of CO₂ to the IL phase, the viscosity of the IL decreased and the liquid phase volume expansion was negligible in contrast to the huge expansion in volume observed in conventional organic solvents. Cadena *et al.*,¹³³ conducted a combined experimental and molecular simulation approach to investigate the factor responsible for the high solubility of CO₂ in three pairs of alkylimidazolium-based ILs: (1) [bmim][PF₆] and [bmmim][PF₆], (2) [bmim][BF₄] and [bmmim][BF₄], and (3) [emim][Tf₂N] and [emmim][Tf₂N]. They found that the greatest impact on the solubility of CO₂ in the imidazolium based RTILs was due to the anion. According to molecular modeling study they conducted, CO₂ has shown strong association with the anions of the ionic liquids. Kazarian and co-workers reported that a weak Lewis acid-base interaction exists between the anions of the imidazolium based ionic liquids and CO₂ after investigating the mixtures of CO₂ with [bmim][PF₆] and [bmim][BF₄] using *in situ* attenuated total reflection infrared (ATR-IR) spectroscopy.²²⁶ The role of the anion in absorbing CO₂ was also investigated by Wang *et al.*²²³

using some superbase-derived PILs, and they found that the anion reacts with CO₂ to form liquid carbonates (with imidazole anion) and carbamate (with fluorinated alcohol and phenol-based anions).

The interest in imidazolium based RTILs as reduction media for CO₂ is also due to their ability to act as an efficient co-catalyst that stabilizes the intermediate CO₂^{•-} which survives for longer period than in aqueous and organic media.²²² Therefore, compared to aqueous and other common non-aqueous electroreduction media, high current density, product selectivity and conversion efficiency in the RTILs is expected. Rosen *et al.*⁸⁰ showed that [emim][BF₄] has the ability to form the complex [emim]⁺–CO₂⁻ with CO₂^{•-}. CO₂^{•-} binds strongly enough with the [emim]⁺ to catalyze CO₂ reduction to CO at Ag electrode. They proposed that [emim][BF₄] lowered the energy barrier for the formation of the intermediate radical anion during CO₂ reduction at Pt and Ag. Compton *et al.*⁸³ reported that CO₂ undergoes an irreversible one electron reduction to CO₂^{•-} in [bmim][Ac]. Electrochemical reduction of CO₂ in pure [bmim][PF₆] and in its aqueous mixture to formic acid and formaldehyde were investigated by Yang *et al.*⁷⁵ at boron doped diamond (BDD) electrodes and Cu nanoparticles on BDD electrodes. They reported that the reduction occurred at low overpotentials at BDD electrode when modified with Cu nanoparticles in [BMIm][PF₆]/water mixture and they achieved a high current density (of 5.1 ± 0.1 mA cm⁻² at -1.3 V vs. NHE. Recently, Sun *et al.*⁹¹ highlighted the role of [emim][Tf₂N] as a supporting electrolyte during electrochemical reduction of CO₂ at Pb in acetonitrile. They found that the CO₂ reduction overpotential in acetonitrile solution decreased by 180 mV when [emim][Tf₂N] was used as supporting electrolyte compared to conventional tetraethylammonium perchlorate. They reported that [emim][Tf₂N] also plays a catalytic role in shifting the course of the

reduction pathway. By increasing the concentration of the ionic liquid in TEAP/MeCN solution, the principal product oxalate at Pb electrode switched to CO and an imidazolium carboxylate complex.

7.1.3. Objectives

During the electrocatalytic CO₂ reduction, the change of medium, or the electrode can change the nature of the products generated.¹²⁰ Therefore, for practical application of electrochemical CO₂ conversion technology and to make this process economically viable, it is important to develop an inexpensive and stable electrocatalyst that can bind and activate CO₂ in order to reduce it into useful states at low overpotential and high current densities with maximum output.^{78, 80, 158} In addition, an electrolytic media is needed that can stabilize and favours the formation of the intermediate CO₂^{•-} and can reduce activation energy for the reduction of CO₂ to useful fuel precursors.⁹⁷ Conventional organic solvents such as acetonitrile and dimethylsulfoxide are good for electrochemical studies due to their low viscosities and are employed as electrolytes for the electrochemical reduction of CO₂.^{91, 218, 227} However, due to their volatile nature the electrochemical study in these solvents at wide temperature range is not possible. In addition, conventional organic solvents can vaporize and produce toxic chemicals that can pollute the environment.¹³² Aqueous electrolytes are also employed for CO₂ reduction but hydrogen evolution is one of competing reaction and hence low current density and high overpotential for the reduction is observed at metal electrodes.^{72-74, 228} Compared to conventional toxic and volatile organic solvents, RTILs are less volatile, non-flammable, thermally, chemically and electrochemically stable, and potentially less harmful for the environment.^{91, 222}

In this chapter, RTILs are used as electrolytes for the electrochemical reduction of CO₂ at a variety of metal catalysts including Ag, Cu, Au, Pt and BDD with the aim to drive the reduction at a low overpotential and convert CO₂ to useful products at high conversion efficiency. The main objectives of the study are:

- to design or develop an efficient and inexpensive catalyst that can bind and activate CO₂ in order to facilitate CO₂ reduction and convert it to important carbon-based fuel or fuel precursors at ambient temperature
- to optimize a suitable ionic liquid electrolyte that can stabilize the intermediate radical anion CO₂^{•-} and serve as promoters/co-catalysts for CO₂ activation at low overpotential and high current densities with maximum output
- to explore the role of the imidazolium based ILs as supporting electrolyte during electrochemical reduction of CO₂ in acetonitrile compared to conventional supporting electrolytes.

The RTIL mainly used in the study was [emim][EtSO₄] and we report for the first time CO₂ reduction activities in this imidazolium-based IL at aforementioned catalysts. [emim][EtSO₄] possesses a number of desirable properties such lower viscosity (108 cP) than most imidazolium based RTILs,²²⁹ good thermal and electrochemical stability, and low reactivity with air/water.²³⁰ [emim][EtSO₄] has been used as electrolyte due to the higher CO₂ solubility²³¹ and diffusion rates²³² as well as lower reduction overpotential of CO₂ in this media than in aqueous solutions and common non-aqueous organic solvents.⁷⁵ The solubility of CO₂ in [emim][EtSO₄] is high because the [EtSO₄]⁻ anion has the potential to form a weak complex with CO₂.²²³ The low CO₂ reduction overpotential is expected as the [emim]⁺ cation has the capability to stabilize the intermediate radical anion

by forming an [emim]–CO₂ complex on the electrode surface and lower the activation energy for the reduction of CO₂.^{70, 80}

In most of this study, Ag was used as catalyst for the electrochemical reduction of CO₂. Ag is a cheap, ductile, malleable and easily available metal compared to precious metal catalysts such as Pt.⁷⁴ It is used widely in electrochemistry as a reference and counter electrode, as well as for making other electrodes such as Ag/AgCl, Ag/AgNO₃ etc. It has the lowest resistance and highest thermal and electrical conductivity of all metals⁹⁷ and is expected to be stable under harsh catalytic environments.⁷⁴ It is historically the most active cathode material that has the capability to reduce CO₂ electrochemically to CO selectively at ambient temperature.^{74, 78, 97, 227}

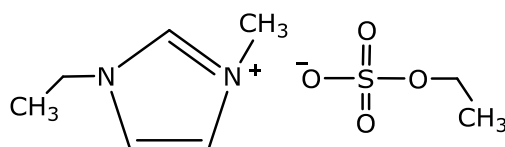
In the study it is found that Au and Ag have the best catalytic behaviour towards electroreduction of CO₂ in [emim][EtSO₄] compared to other catalysts investigated for the reaction. In addition, we observed that the cation of the liquid plays a co-catalytic role during the reduction. Electrochemical investigation of the product formed during CO₂ reduction in [emim][EtSO₄] at Ag catalyst shows that CO is one of the products. It is suggested that optimization of CO₂ conversion technology at Ag electrode to maximize CO production would be beneficial to produce liquid fuels when combined with H₂ via the Fischer-Tropsch process.

7.2. Experimental Section

7.2.1. Reagents and Apparatus

All chemicals were use as received. The RTIL mainly used in this work is [emim][EtSO₄], as shown in Scheme 7.2.1. The other ionic liquids used

were [emim][Tf₂N], [emim][Br] and [empyrr][EtSO₄]. [emim][EtSO₄] was purchased from Merck ($\geq 95\%$) and [emim][Br] from Acros Organics (98%). All of the other ionic liquids were kindly donated by Prof. Peter Licence's ionic liquid research group of the school of Chemistry, University of Nottingham. Other chemicals used were AgNO₃ (Fischer Scientific, analytical reagent grade), ferrocene (Alfa-Aesar, 99.0%), MeCN (BDH VWR prolabo, 99.9%), HClO₄ (Fischer Chemicals, Fischer scientific, UK, 60%) and [TBA][PF₆], (Sigma-Aldrich, 98%). CO₂ (99.5%), N₂ (99.9999%) and Ar (99.995%) were from BOC (Nottingham, UK).



Scheme 7.2.1 Structure of [emim][EtSO₄] used as electrolyte for CO₂ electrochemistry.

7.2.2. Instrument and Electrodes for Electrochemical Measurements

Cyclic voltammetry, linear sweep voltammetry and chronoamperometry were performed in a three-necked glass cell in a conventional three-electrode arrangement. The working electrodes were a BDD, Au, Pt, Cu and Ag disks of geometrical surface area $7.07 \times 10^{-2} \text{ cm}^2$, $3.14 \times 10^{-2} \text{ cm}^2$, $3.14 \times 10^{-2} \text{ cm}^2$, $3.04 \times 10^{-2} \text{ cm}^2$ and $2.51 \times 10^{-2} \text{ cm}^2$, respectively. The counter electrode used was a Pt (0.5 cm $\times$ 0.4 cm $\times$ 0.1 cm) flag. The ECSA of Pt electrode was $8.95 \times 10^{-2} \text{ cm}^2$, estimated by the electronic charge of hydrogen adsorption/desorption regions using, $210 \mu\text{C cm}^{-2}$ as conversion factor.³ For Au electrode, ECSA was determined by the electronic charge of gold oxides stripping using, $386 \mu\text{C cm}^{-2}$ as the

theoretical charge for a monolayer of gold oxide³ and was $9.5 \times 10^{-2} \text{ cm}^2$. The ECSA of Ag electrode was estimated from the underpotential deposition of lead (Pb_{UPD}) after recording a cyclic voltammogram in a 5 mM $\text{Pb}(\text{NO}_3)_2$ solution in 10 mM KCl + 10 mM HNO_3 ,^{72, 95} (see Figure S 10 in Appendix 1). The charge under the Pb UPD stripping peak at Pb^{2+} concentration of 5 mM or above corresponds to $600 \mu\text{C cm}^{-2} \text{ Ag}$.^{80, 233} The same integrated charge density under the Pb_{UPD} region was used to estimate the ECSA of Cu electrode, from a CV obtained at a Cu electrode (Figure S 11 in Appendix 1) in 5 mM $\text{Pb}(\text{NO}_3)_2$ solution in 10 mM KCl + 10 mM HNO_3 .²³³ The ECSA of Ag and Cu electrodes were estimated to be $4.78 \times 10^{-2} \text{ cm}^2$ and $4.11 \times 10^{-2} \text{ cm}^2$, respectively. The currents in each measurement were normalized to the ECSA for calibration of catalytic activity of the electrodes for the CO_2 reduction in the RTILs. In the case of BDD electrode, the geometric surface area of the electrode was used for calibration of currents for CO_2 reduction in the liquids. The reference electrode was a self-made Ag/Ag^+ reference electrode. The Ag/Ag^+ reference electrode used in pure IL consisted of an Ag wire immersed in 10 mM silver triflate, AgTfO in $[\text{emim}][\text{EtSO}_4]$. When used in MeCN, the Ag/Ag^+ reference electrode composed of Ag wire immersed in 10 mM AgTfO in 0.1 M $[\text{TBA}][\text{PF}_6]/\text{MeCN}$ or 0.1 M $[\text{emim}][\text{EtSO}_4]/\text{MeCN}$.

7.2.3. Construction and Calibration of Ag/Ag^+ Reference Electrodes

Ag/Ag^+ reference electrodes were constructed using a 7.5 cm long glass tube, a 3.2 mm (1/8") porous Vycor frit and a heat-shrink Teflon tubing. The Vycor frit and heat-shrink Teflon tubing was purchased from Gamry instruments, USA. The Vycor tip was placed inside the piece of heat-shrink

tube and held to the glass capillary by sliding the heat shrink Teflon over the end of the glass tube. The Teflon was then gently warmed with a heat gun until the tubing tightened around the Vycor tip and the end of the reference electrode tube. The electrode was then filled with 10 mM AgTfO (Sigma Aldrich $\geq 98.0\%$ (Ag) in [emim][EtSO₄]) and an Ag wire connected to a Teflon top was immersed. In the study that involved MeCN as a main electrolyte, Ag/Ag⁺ reference electrodes were prepared by the same procedure but the Ag wire was immersed in 10 mM AgNO₃ in either 0.1 M [TBA][PF₆]/MeCN or 0.1 M [emim][EtSO₄]/MeCN.

Reference electrode stability is a common issue when using ionic liquids as electrolytes in electrochemistry.^{3, 167} Therefore, the Ag/Ag⁺ reference electrode (Ag/AgTfO in [emim][EtSO₄]) was calibrated against the potential of the ferrocene/ferrocenium redox couple, the IUPAC-recommended redox couple.^{126, 167} Figure S 12 in Appendix 1 show CVs obtained in 5 mM ferrocene solution in [emim][EtSO₄] at Pt and Au electrodes at 100 mV s⁻¹.

The reference electrodes containing 10 mM AgNO₃ in 0.1 M [emim][EtSO₄]/MeCN and 0.1 M [TBA][PF₆]/MeCN were also calibrated versus ferrocene in 0.1 M [TBA][PF₆]/MeCN and 0.1 M [emim][EtSO₄]/MeCN, respectively (Figure S 13 in Appendix 1). The formal potential, $E^{0'}$ (taken as the average of the Fc oxidation peak potential and cathodic Fc⁺ reduction peak potential), was determined in N₂-saturated solution vs. the Ag/Ag⁺ reference electrodes. All potentials are reported versus Fc/Fc⁺ redox couple.

7.2.4. Electrochemical Methods

Prior to use, all the electrodes were polished, sonicated and dried by the procedures described in early sections (Chapter 3). The working, counter and reference electrodes were immersed in the three-necked electrochemical glass cell containing approximately 5 mL of the ionic liquid. Cyclic voltammograms and LSVs were recorded after the solution was bubbled either for 30 minutes with N₂ or Ar to remove dissolved oxygen or for 60 minutes with CO₂ (optimum time of saturation of CO₂ in the IL).

7.2.5. Electrochemical Analysis of the Product of CO₂

Reduction

For the electrochemical analysis of the product formed by the reduction of CO₂ in [emim][EtSO₄], a 3-electrode system was adopted as described above with the addition of Pt as a second working electrode. A 2mm-diameter Pt electrode was used as second working electrode to adsorb CO formed from CO₂ reduction at the Ag working electrode. The experiment was performed using Ag/Ag⁺ reference electrode and Pt flag counter electrode. Chronoamperometry measurements (current-time transient) were carried out by holding the Ag working electrode for 2400 seconds at a -2.33 V vs. Fc/Fc⁺ redox couple in CO₂-saturated [emim][EtSO₄] and also in [emim][EtSO₄]/MeCN. A 2 mm-diameter freshly polished Pt disk electrode (activated in aqueous HClO₄) was held at -0.4 V vs. Fc/Fc⁺ in the same solution for adsorption of the CO forming during the reduction reaction. After the experiment, the Pt electrode was removed from the CO₂/IL system and rinsed with de-ionized water, then immersed in 0.1 M aqueous HClO₄ in a three necked cell to voltammetrically strip any CO adsorbed on the electrode surface.

7.3. Results and Discussion

7.3.1. Effect of CO₂ of the Electrochemical Window of [emim][EtSO₄]

Figure 7.3.1 below shows cyclic voltammograms recorded at a BDD electrode in Ar-saturated [emim][EtSO₄] (saturated for 30 minutes) and then after flushing with CO₂ for 45 minutes. The potential was swept from -2.6 V to +2.6 V vs. Fc/Fc⁺. It is evident from the figure that only charging current flows between -2.31 V and +2.14 V in the solution at BDD in Ar-saturated [emim][EtSO₄].

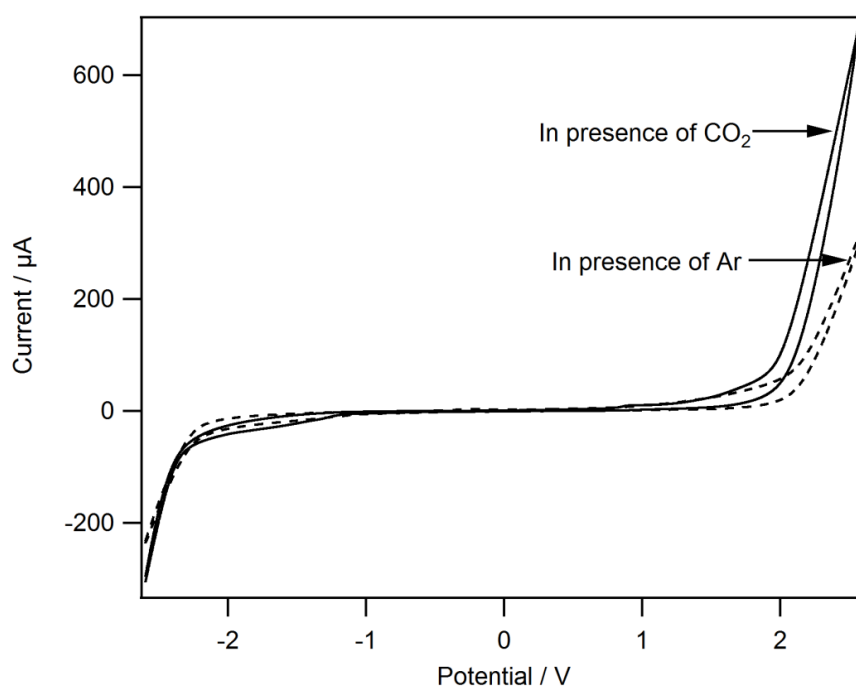


Figure 7.3.1 CVs recorded at 3 mm diameter BDD electrode at a scan rate of 100 mV s⁻¹ in [emim][EtSO₄] after purging with Ar for 30 minutes (dotted line) and then with CO₂ for 45 minutes (solid line) at 25 °C in a potential range from -2.6 V to +2.6 V vs. Fc/Fc⁺ internal reference.

The cathodic potential limit shows the reduction of the [emim]⁺ cation and the anodic potential limit is due to oxidation of the [EtSO₄]⁻ anion

giving an electrochemical window of [emim][EtSO₄] of 4.55 V. In the presence of CO₂, the electrochemical window decreased to 4.38 V, indicating that mass transfer of the cation and anion become faster, presumably due to the decrease in the viscosity of the ionic liquid when CO₂ is bubbled to the IL.²²⁵

7.3.2. Electrocatalytic Reduction of CO₂ in [emim][EtSO₄]

The electrocatalytic reduction of CO₂ was investigated on various electrodes (BDD, Cu, Ag, Au and Pt) in [emim][EtSO₄], as shown in Figure 7.3.2B. We first describe the CO₂ electroreduction activity of polycrystalline Ag using cyclic voltammetry, for general understanding of this electrocatalytic process. Figure 7.3.2A shows the CVs obtained on a 2 mm diameter polycrystalline Ag electrode in the presence and absence of CO₂. The solid black line in the figure shows a CV recorded in blank Ar-saturated [emim][EtSO₄] and the solid red line shows a CV recorded after bubbling with CO₂ for 60 minutes. It is evident from the figure that in the Ar saturated CV, only background charging current flows between -1.5 V and -2.4 V. After -2.4 V, a sharp increase in the reduction current started, which corresponds to reduction of the cation of the IL. In the CO₂ saturated [emim][EtSO₄], a single irreversible broad reduction wave was observed at an onset potential of -2.1 V vs. Fc/Fc⁺, peaking at 2.4 V, after which decomposition of the IL starts. The increase in the reduction current between -2.1 V and -2.5 V is attributed to an irreversible one-electron electroreduction of CO₂ to CO₂^{•-} in the ionic liquid.^{70, 77, 80, 83} The increase in reduction current for CO₂ was also observed during the reverse sweep.

Figure 7.3.2 B shows LSV profiles obtained in CO₂ saturated [emim][EtSO₄] at Ag (red line), Au (black line), Cu (brown line), Pt (green line) and BDD (blue line) electrodes. By comparing the CO₂

electroreduction activity of these electrodes, it was observed that Au and Ag are better for electroreduction of CO₂. At Au and Ag, the onset potential for the reduction was -2.05 V and -2.1 V, respectively, compared to -2.39 V at Cu, -2.4 V at BDD electrode and -2.45 V at Pt.

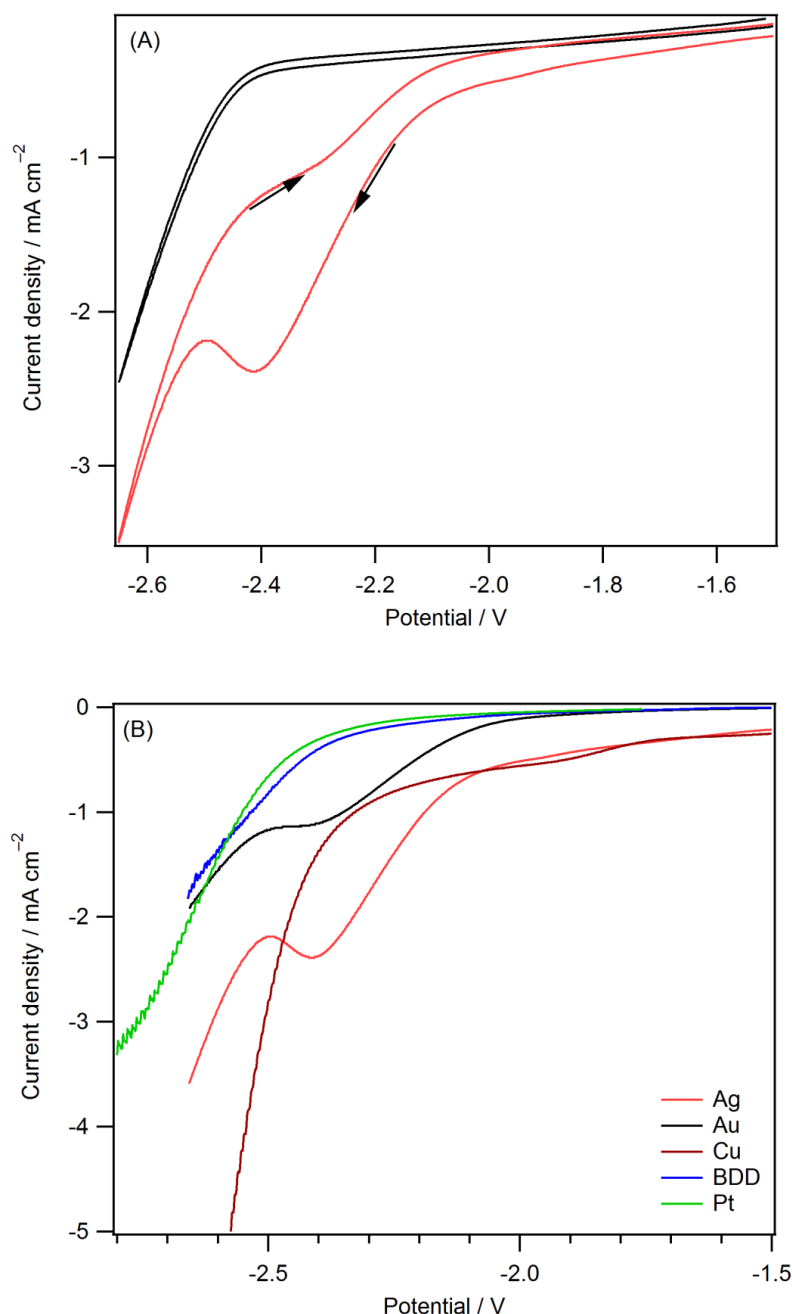


Figure 7.3.2 (A) CVs obtained on Ag electrode at 100 mV s^{-1} in [emim][EtSO₄] at room temperature saturated with Ar for 30 minutes (black line) and then with CO₂ for 60 minutes (red line). The potential was swept from -1.5 V to -2.65 V. (B) LSV profiles showing comparison of the electrocatalytic behaviour of various electrodes for CO₂ reduction in [emim][EtSO₄]. CO₂ was continuously bubbled during the measurements.

Interestingly, BDD, which is a semiconductor electrode obtained by doping diamond films with different concentrations of boron atoms, has shown better electrocatalytic activity for the reduction of CO₂ in the IL than the most widely used Pt catalyst. Although the reduction of CO₂ occurs at about 50 mV earlier at Au catalyst compared to that on Ag catalyst, a higher reduction current density was observed at Ag catalyst than that at Au. Also Ag is much cheaper catalyst than Au. In addition, Ag is found to have known product selectivity that reduces CO₂ mainly to CO.^{69, 70, 72-74, 80, 95, 233} Therefore, Ag was mainly used as catalyst for further investigation of the CO₂ electroreduction in [emim][EtSO₄] and other ionic liquids.

7.3.3. Influence of Temperature on the reduction of CO₂ in [emim][EtSO₄] at Ag catalyst

Figure 7.3.3 shows LSV profiles for CO₂ reduction in [emim][EtSO₄] obtained at 25 °C, 50 °C, 80 °C and 100 °C using polycrystalline Ag. Initially CVs were recorded in the solution in a potential range from -1.8 V to -2.5 V vs. Fc/Fc⁺ and only the cathodic sweeps are shown in the figure. It is evident from the figure that at high temperatures Ag shows better catalytic activity for CO₂ reduction. The onset potential and the reduction peak potential shift toward less positive side. The overpotential for CO₂ reduction in the ionic liquid decreased by ~100 mV and the reduction peak potential shifted from -2.37 to -2.21 V, when temperature was increased from 25 °C to 100 °C, showing better kinetics for the reduction at a polycrystalline Ag electrode. The reduction current density increased significantly with increase of temperature, inset of Figure 7.3.3. At lower temperatures, ILs are more viscous²³⁴ and the viscosity of the IL decreases

with increasing temperature, causing faster mass transport of CO_2 towards the electrode surface.

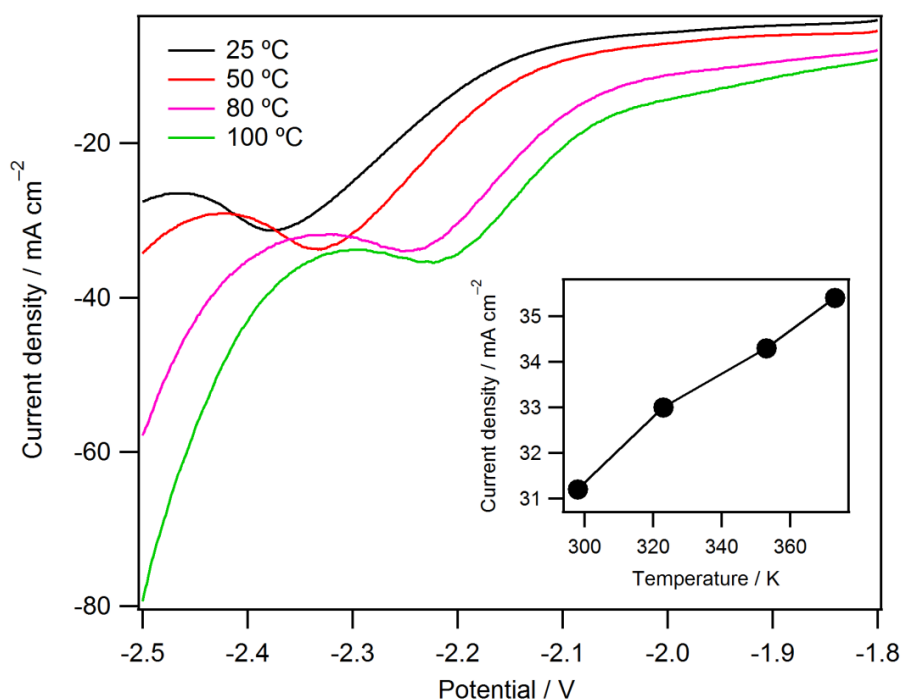


Figure 7.3.3 LSV profiles recorded in CO_2 -saturated $[\text{emim}][\text{EtSO}_4]$ solution at various temperature, 25 °C, 50 °C, 80 °C and 100 °C on a 2 mm diameter Ag electrode at a scan rate of 100 mV s^{-1} in a potential range from -1.8 V to -2.5 V vs. Fc/Fc^+ . Inset: shows a plot of temperature vs current density of the cathodic peak.

7.3.4. Determination of Diffusion Coefficient and Concentration of CO_2

The diffusion coefficient (D) and concentration (C) of CO_2 in $[\text{emim}][\text{EtSO}_4]$ were determined using potential-step chronoamperometry. A chronoamperometric transient was recorded using an Au microelectrode (nominal radius $12.5 \mu\text{m}$) and is shown in Figure 7.3.4 (red line). The potential was stepped from -1.8 V vs. Ag/Ag^+ (-2.05 V vs. Fc/Fc^+) to -2.3 V (-2.55 V vs. Fc/Fc^+) for 10 seconds. The black line in the figure shows the theoretical fitted data using Shoup and Szabo Equation 7.7, which allows determining both D and C of CO_2 simultaneously.^{235, 236}

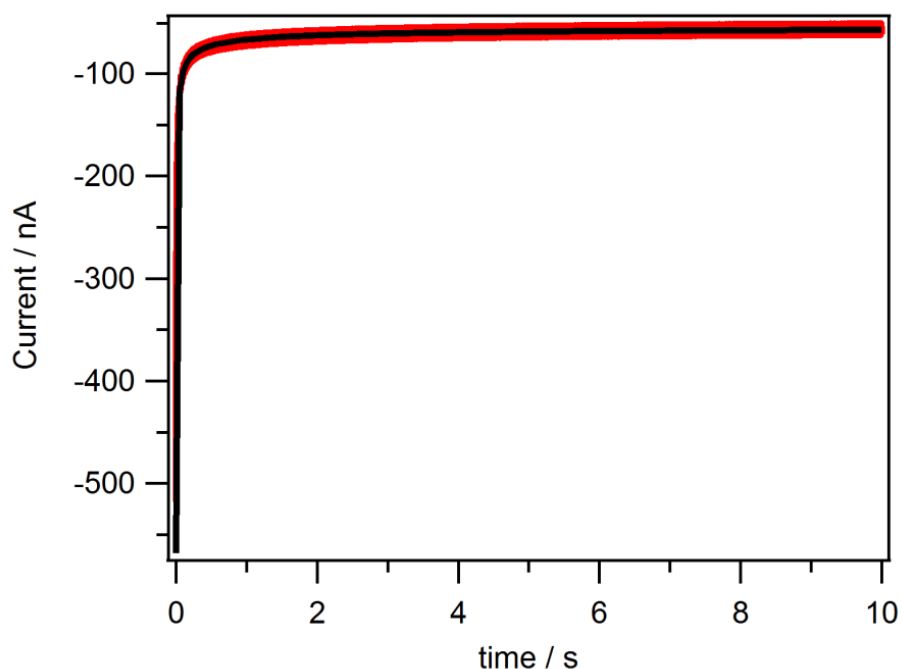


Figure 7.3.4 Experimental (red line) and theoretically fitted (black line) chronoamperometric transients for the reduction of CO_2 in $[\text{emim}][\text{EtSO}_4]$ at room temperature on $15.6 \mu\text{m}$ radius Au electrode. The potential was step from -2.05 V to -2.55 V vs. Fc/Fc^+ for 10 s .

$$i = -4n\text{FDCr} f(\tau) \quad (7.7)$$

where n is the number of electrons involved in the redox process, which is taken as 1 for the reduction of CO_2 to $\text{CO}_2^{\cdot-}$, r is the radius of the Au microelectrode, which was determined using steady state current (Equation 7.8) for oxidation of ferrocene at the microelectrode, i_{ss} (Figure S 14 in Appendix 1).³

$$i_{\text{ss}} = 4n\text{FCD}r \quad (7.8)$$

where i_{ss} was $7.97 \times 10^{-9} \text{ A}$. n is the number of electrons involved in the redox process which is 1 for Fc/Fc^+ redox couple. The concentration, c of

ferrocene solution was $2 \times 10^{-6} \text{ mol cm}^{-3}$. The diffusion co-efficient of Fc/Fc^+ redox couple was $6.7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$.^{3, 237} The actual radius of the Au microelectrode calculated through this experiment was $15.6 \text{ }\mu\text{m}$.

The function $f(\tau)$ in the Shoup-Szabo equation is given by Eqn. 7.9 and the parameter, τ by equation 7.10.

$$f(\tau) = 0.7854 + 0.8863 \tau^{-1/2} + 0.2146 \exp(-0.7823 \tau^{-1/2}) \quad (7.9)$$

$$\tau = 4Dt/r^2 \quad (7.10)$$

The D and C values obtained from theoretical fitted data were $4.61 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ (or $4.61 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$) and $1.9 \times 10^{-5} \text{ mol cm}^{-3}$ (0.019 mol L^{-1}), respectively. The diffusion co-efficient of CO_2 in $[\text{emim}][\text{EtSO}_4]$ ($\eta=108 \text{ cP}$)²²⁷ is comparable to the diffusion co-efficient of O_2 in $[\text{bmim}][\text{BF}_4]$, which was $1.79 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ($\eta=108 \text{ cP}$) measured at $25 \text{ }^\circ\text{C}$ using a $10 \text{ }\mu\text{m}$ diameter Au electrode.²³⁵ The D value for CO_2 in $[\text{emim}][\text{EtSO}_4]$ was higher by two order of magnitude than that observed in $[\text{bmim}][\text{Ac}]$, which was $2.65 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$.²³⁶ This could be due to low viscosity of $[\text{emim}][\text{EtSO}_4]$ in which CO_2 molecules can diffuse faster compared to $[\text{bmim}][\text{Ac}]$ ($\eta=140 \text{ cP}$). However, viscosity could not be the only reason for the high diffusion of CO_2 in $[\text{emim}][\text{EtSO}_4]$. The arrangement of atoms or alkyl groups around central atom in the cation and anion may also play a role. For example, the viscosity of $[\text{bmim}][\text{BF}_4]$, $\eta=108 \text{ cP}$ is same to that of $[\text{emim}][\text{EtSO}_4]$, 108 cP ,²²⁹ and the D value for CO_2 in the latter case is higher by an order of magnitude compared to the former ($7.3 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$).²³⁶

7.3.5. The Role of RTILs as Supporting Electrolyte During Voltammetric Study of CO₂ Reduction in Acetonitrile

The effect of [emim][EtSO₄] as a supporting electrolyte and/or co-catalyst was investigated during CO₂ reduction in conventional organic solvent, acetonitrile compared to a conventional supporting electrolyte, [TBA][PF₆]. Figure 7.3.5 shows cyclic voltammograms measured in MeCN containing (A) 0.1 M [TBA][PF₆] and (B) 0.1 M [emim][EtSO₄] at a 2 mm diameter Ag electrode. The CVs were recorded (A) in a potential range from -1.5 V to -2.52 V and the case of (B) from -1.5 V to -2.54 V at a scan rate of 100 mV s⁻¹ and at a room temperature. Each of the solutions was purged with Ar for 30 minutes in order to remove dissolved oxygen, as oxygen can actively reduce and hinder the main electrochemical process, and CVs were recorded as shown by black lines in Figure 7.3.5 A and B. Then CO₂ was bubbled for 60 minutes into the solutions and CVs were measured at Ag working electrodes as shown by red lines in the Figure.

In the blank (Ar saturated) [TBA][PF₆]/MeCN, only capacitive current flowed from -1.5 V until -2.48 V after which a large reductive current, corresponding to the decomposition of acetonitrile, started flowing. In CO₂ saturated [TBA][PF₆]/MeCN, the current response was different from that in blank solutions. A reduction current started flowing at -2.2 V until -2.48 V. This cathodic reduction wave, which was also observed during the reverse sweep, corresponds to the reduction of CO₂ in the solution. In blank [emim][EtSO₄]/MeCN solution, the background capacitive current flows until, -2.38 V, and no other reduction or oxidation peaks were observed before this potential. After, -2.38 V, the reduction of the solvent took place. In CO₂-saturated [emim][EtSO₄]/MeCN, a sharp increase in the current for the reduction of CO₂ was observed at an onset of -2.0 V.

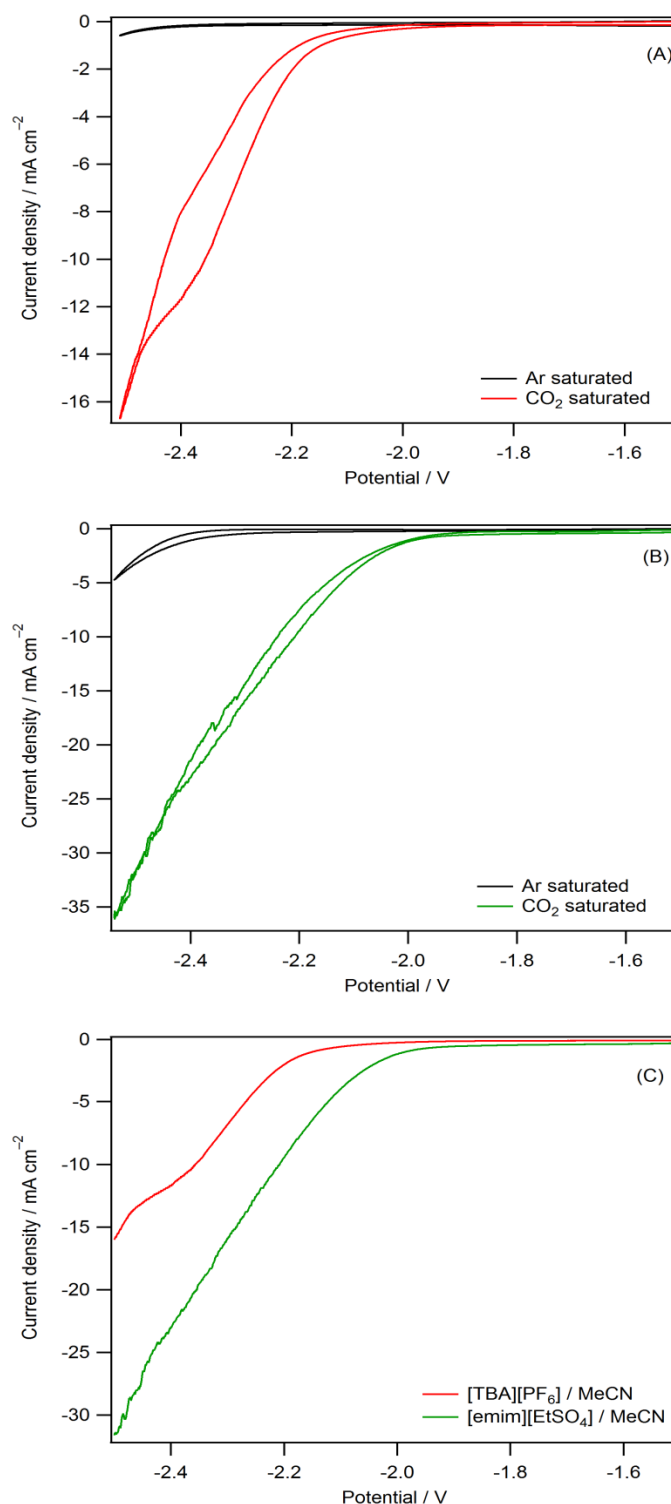


Figure 7.3.5 Cyclic voltammograms recorded at a Ag working electrode in (A) 0.1 M [TBA][PF₆]/MeCN, and (B) 0.1 M [emim][EtSO₄]/MeCN after bubbling Ar for 30 minutes and then CO₂ for 60 minutes in to each solution. Each of the CVs was recorded at a scan rate of 100 mV s⁻¹ and at room temperature. The electrode was swept from an initial potential, -1.5 V to a final cathodic potential, -2.52 V in solution (A) and -2.54 V in solution (B) vs. Fc/Fc⁺ redox couple. (C) Shows comparison of the cathodic sweeps for CO₂ reduction in the two media in the potential range between -1.5 V and -2.5 V.

The reduction current kept increasing and was also observed during the reverse sweep. This confirms the ability of Ag electrode to reduce CO₂ in acetonitrile using both [TBA][PF₆] as well as [emim][EtSO₄] as supporting electrolytes. However, it is clear from the figure 7.3.5C that the reduction of CO₂ occurs at ~200 mV lower potential using [emim][EtSO₄] as supporting electrolyte in MeCN compared to [TBA][PF₆]. It is found that the composition of an electrolyte can affect the current density, product selectivity and energetic efficiency, during electrochemical CO₂ reduction.^{78,}
⁹¹ The high current density and early onset potential for the reduction of CO₂ in MeCN containing [emim][EtSO₄] at Ag catalyst compared to that in MeCN containing [TBA][PF₆] may be due to the ability of the [emim]⁺ cation to play a co-catalytic role during CO₂ to CO₂^{•-} electron uptake process by stabilizing the intermediate radical anion CO₂^{•-} to form a complex with it.^{70, 77, 80, 81}

7.3.6. The Role of the Cations and Anions of the RTILs on the Electrocatalysis of CO₂ reduction

As mentioned above, [emim][EtSO₄] has an electrocatalytic effect towards CO₂ reduction when used alone as a non-aqueous medium or as a supporting electrolyte in MeCN at a Ag catalyst. This may be due to stabilization of the intermediate radical anion, CO₂^{•-} by the ionic liquid in the reduction process. As mentioned in the introduction section, CO₂ has high solubility in RTILs, and it is found experimentally that the interaction of the anion of the RTILs with CO₂ is responsible.^{70, 80, 223} CO₂ may react with [EtSO₄]⁻ to form a weak Lewis acid-base complex^{70, 223} and if the anion is responsible for the enhanced electrocatalytic reduction of CO₂, then this chemical step will be followed by an electrochemical reduction of

the CO_2 in the complex. In order to verify that whether cation or anion of the RTILs play a role during the electrocatalytic reduction of CO_2 , two experiments were performed. In the first experiment, electroreduction CO_2 was carried out in MeCN containing various RTILs. In the second experiment, CO_2 reduction was performed in various RTILs without MeCN. Figure 7.3.6 displays a linear sweep voltammograms for the reduction of CO_2 in MeCN containing 0.1 M of each of $[\text{TBA}][\text{PF}_6]$ -black line, $[\text{empyrr}][\text{EtSO}_4]$ -red line, $[\text{emim}][\text{EtSO}_4]$ -green line, $[\text{emim}][\text{Tf}_2\text{N}]$ -blue line and $[\text{emim}][\text{Br}]$ -pink line at a Ag working electrode at 100 mV s^{-1} . Initially, CVs were recorded in N_2 saturated and CO_2 saturated MeCN containing 0.1 M of the RTILs, as shown in Figure 7.3.5 A for 0.1 M $[\text{TBA}][\text{PF}_6]/\text{MeCN}$ and Figure 7.3.5 B for 0.1 M $[\text{emim}][\text{EtSO}_4]/\text{MeCN}$, and for 0.1 M $[\text{emim}][\text{Tf}_2\text{N}]/\text{MeCN}$, 0.1 M $[\text{empyrr}][\text{EtSO}_4]/\text{MeCN}$ and 0.1 M $[\text{emim}][\text{Br}]/\text{MeCN}$ are shown in Figure S 15 in Appendix 1. However, only the cathodic sweeps are reported in the potential range from -1.5 V to -2.5 V vs. Fc/Fc^+ for comparison.

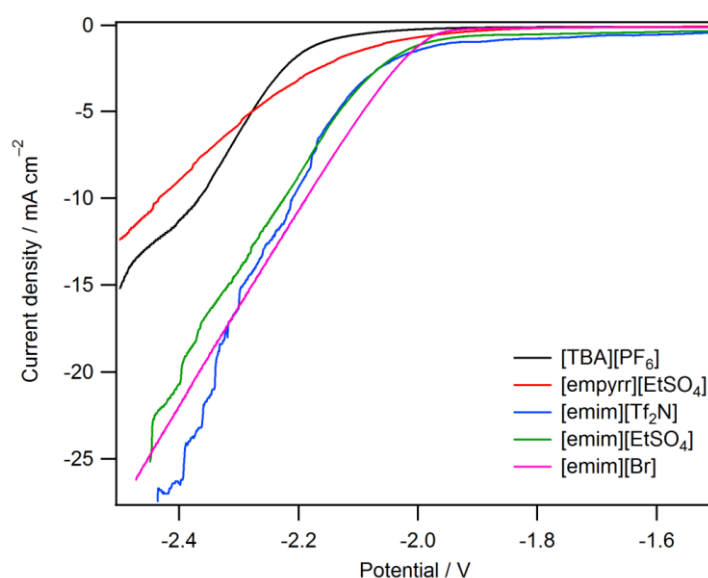


Figure 7.3.6 LSV profiles obtained on a 2 mm diameter Ag working electrode vs. Fc/Fc^+ at a scan rate of 100 mV s^{-1} and room temperature in CO_2 saturated solution of MeCN containing 0.1 M of each $[\text{TBA}][\text{PF}_6]$, $[\text{empyrr}][\text{EtSO}_4]$, $[\text{emim}][\text{Tf}_2\text{N}]$, $[\text{emim}][\text{EtSO}_4]$, and $[\text{emim}][\text{Br}]$ as supporting electrolyte.

Three of the ionic liquids, [emim][EtSO₄], [emim][Tf₂N], and their precursor [emim][Br] have similar cations but different anions. The other two ILs, [emim][EtSO₄] and [empyrr][EtSO₄] possess similar anions but different cations. Generally, it is clear from the figure that compared to [TBA][PF₆], the electrocatalytic reduction of CO₂ at Ag in MeCN is better and starting at lower potential when RTILs were used as supporting electrolytes. This shows that RTILs play catalytic role during the reduction. However, while comparing the catalytic role of the different RTILs towards electroreduction of CO₂, it is found that the overpotential for the reduction of CO₂ in MeCN solution containing 0.1 M [empyrr][EtSO₄] as supporting electrolyte was higher by 80 mV compared to that in MeCN containing [emim][EtSO₄], although both RTILs have similar anion. The reduction of CO₂ also begins at lower potential in the other two imidazolium-based RTILs, [emim][Tf₂N] and [emim][Br] compared to the one with a pyrrolidinium-based cation. This shows that the imidazolium-based RTILs have some co-catalytic role during the reduction of CO₂ at Ag catalyst.^{70, 77, 95, 238} It is suggested by Rosen *et. al.*^{77, 80, 95, 238} that after one electron reduction in imidazolium based RTILs in acidic media, an intermediate complex with [emim]⁺ cation is formed that further results in the formation of CO. The intermediate, [emim]⁺-CO₂ complex, stabilizes the radical anion that is reduced to CO₂ at lower overpotential in the ionic liquid environment. If we consider the effect of the anion here, it is evident from the figure that the onset for the reduction of CO₂ was approximately the same (−2.0 V) in MeCN containing [emim][Tf₂N], 0.1 M [emim][EtSO₄], and [emim][Br] showing that the anion of the RTILs does not play significant role in the reduction process.

The cation-anion effect on electrocatalytic CO₂ reduction was further examined on Ag catalyst in [emim][EtSO₄] and [emim][Tf₂N] without

MeCN. Both of these RTILs contain $[\text{emim}]^+$ cation and different anions. Figure 7.3.7 shows cathodic sweeps for CO_2 reduction in $[\text{emim}][\text{Tf}_2\text{N}]$ and $[\text{emim}][\text{EtSO}_4]$ recorded at a Ag electrode vs. Fc/Fc^+ at 100 mV s^{-1} and room temperature. We can see from the figure that both of the RTILs show similar CO_2 reduction features i.e. the onset potential for the reduction was -2.0 V in both of the RTILs although they have different anions. The onset for the reduction is independent of the anions of the two RTILs. However, the current density corresponding to the reduction CO_2 in $[\text{emim}][\text{Tf}_2\text{N}]$ was higher than that in $[\text{emim}][\text{EtSO}_4]$, probably due to the lower viscosity of the former (27 cP) than the latter (108 cP) which helps in mass transport of CO_2 toward the electrode surface.²²⁹ This confirms that the cation of the ionic liquid, when employed as electrolyte, has a significant role during CO_2 electroreduction and the anion, by contrast, plays no significant role in the reduction process.

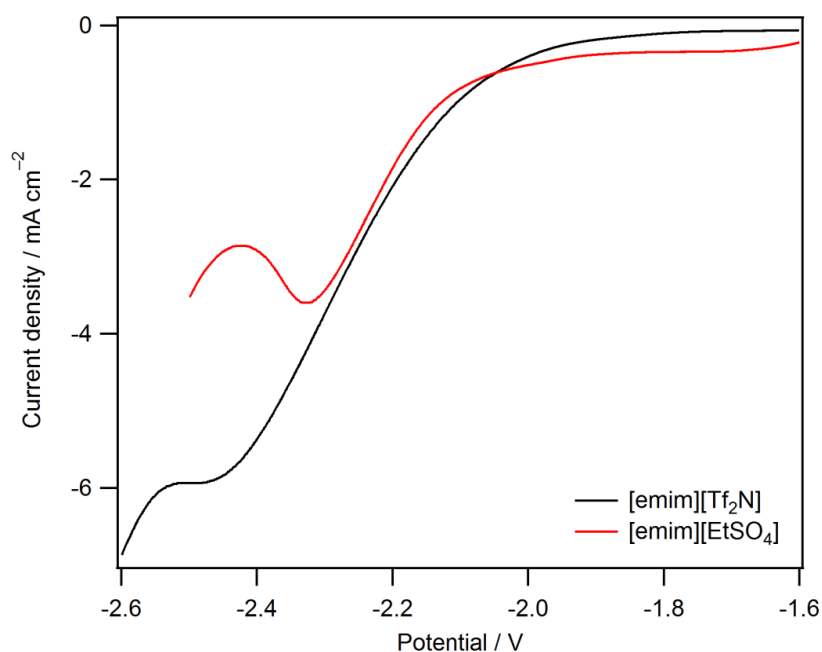


Figure 7.3.7 The LSVs obtained in CO_2 saturated, $[\text{emim}][\text{Tf}_2\text{N}]$ and $[\text{emim}][\text{EtSO}_4]$ on a Ag catalyst at a 100 mV s^{-1} and room temperature in a potential range from -1.6 V to -2.6 V vs. Fc/Fc^+ .

7.3.7. Electrochemical Analysis of the Product Formed

During CO₂ Reduction in [emim][EtSO₄] at Ag

Figure 7.3.8 below represents the result of the experiment, described in the section 7.2.5, which shows cyclic voltammograms recorded at the Pt electrode that was held at -0.4 V vs. Fc/Fc^+ during the course of CO₂ reduction at Ag in [emim][EtSO₄] at 100 mV s^{-1} . A strong oxidative wave, corresponding to voltammetric oxidation of CO, started flowing during the first positive going scan (solid line) at an onset potential of 0.846 V with a peak potential 0.908 V vs. RHE. The adsorbed CO was completely stripped off of the surface of Pt during the first scan, as no CO-oxidation peak was observed in the second scan (dotted line) showing that the surface of Pt was CO-free during the second scan. It is well established that at potentials ≥ 0.85 V (here onset potential of CO oxidation) Pt surfaces oxidize to form PtOH_{ads} in aqueous acid solutions. The surface Pt hydroxide is reduced back to Pt on the reverse scan, as evident from the broad reductive wave in Figure 7.3.8 with a peak potential at 0.75 V. The oxygen containing Pt surface acts as a catalyst to oxidize CO-covered Pt ($\text{Pt}-\text{CO}_{\text{ads}}$) to CO₂ during oxidative sweep by Langmuir-Hinshelwood mechanism.^{3, 239, 240}

Formation of CO from CO₂ reduction in [emim][EtSO₄] at the Ag electrode and its adsorption on and then removal from the Pt surface was reproducible, as a similar kind of behaviour was observed when the experiment was performed again under the same set of conditions but at 50 °C. Also we have shown that CO₂ reduction rate at Ag electrode in [emim][EtSO₄] increased as the overpotential gradually decreased with rising the temperature of the system, probably due to a decrease in viscosity of the liquid with rising temperature. The formation of CO was also detected during electroreduction of CO₂ at Ag in MeCN containing 0.5 M [emim][EtSO₄], see Figure S 16 in Appendix 1.

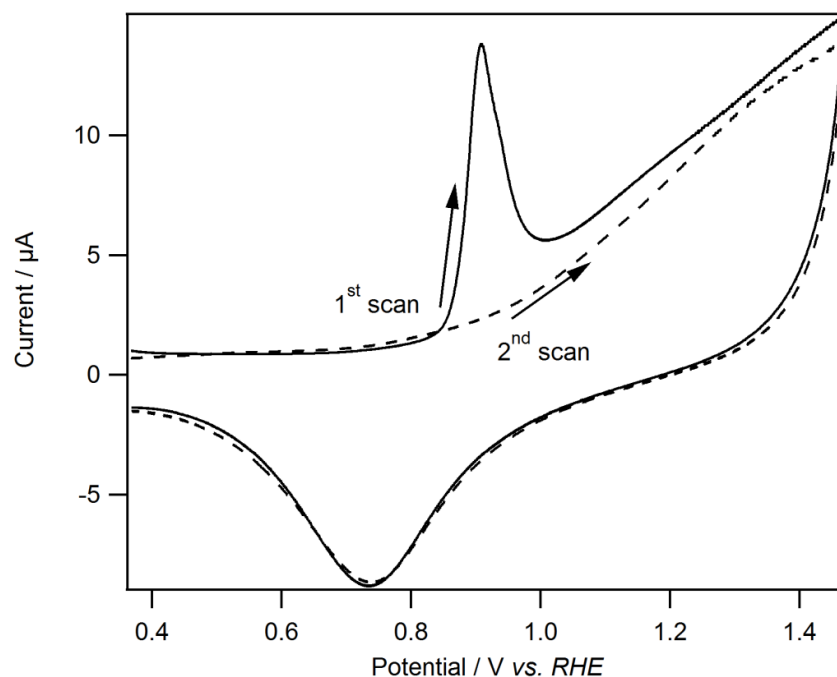


Figure 7.3.8 The cyclic voltammograms on a 2 mm diameter polycrystalline Pt disk (having adsorbed CO) working electrode in a CO-free 0.1 M HClO_4 (aq.) at a 100 mV s^{-1} and 25°C . CO adsorption on Pt was previously established at $-0.4 \text{ V vs. Fc/Fc}^+$ V during electrochemical reduction of CO_2 in $[\text{emim}][\text{EtSO}_4]$ at Ag electrode (held at $-2.33 \text{ V vs. Fc/Fc}^+$ and 2400 seconds). The solid line (—) represents 1st scan where CO stripping occurred and dashed line (---) shows 2nd scan; CO was completely oxidized from Pt surface during 1st scan.

The reduction of CO_2 to CO at Ag cathode involve two steps;⁷⁴ in the first step one electron uptake of CO_2 — to $-\text{CO}_2^{\cdot-}$ and in the second step $\text{CO}_2^{\cdot-}$ anion combine with another CO_2 and an electron to form CO and CO_3^{2-} in non-aqueous media. The optimization of CO_2 conversion at Ag electrode with respect to maximize CO production would be beneficial to produce liquid fuels when combined with H_2 via the Fischer-Tropsch process.⁷⁸ Therefore, from these results a conclusion can be drawn that CO is one of the products formed at Ag electrode from electrocatalytic reduction of CO_2 using $[\text{emim}][\text{EtSO}_4]$ or mixture of $[\text{emim}][\text{EtSO}_4]$ and MeCN as electrolytes. From this analysis we could not detected any other product and detail quantitative analysis of CO and any other gaseous

product forming during the reduction requires further experimentation such as using gas chromatography or IR spectroscopy.

7.4. Conclusions

In this work it is shown that polycrystalline Au and Ag are better catalysts for the electroreduction of CO₂ in [emim][EtSO₄] than Cu, Pt and BDD electrodes. The rate of CO₂ reduction at Ag increases with increasing temperature of the medium. The role of the imidazolium based ionic liquids as supporting electrolyte during CO₂ reduction at a Ag electrode in acetonitrile has been investigated and compared with that of the supporting electrolyte [TBA][PF₆]. It is observed that Ag can reduce CO₂ in acetonitrile at 200 mV lower potential in the presence of [emim][EtSO₄] as supporting electrolyte compared to [TBA][PF₆]. It is found that the reduction of CO₂ in acetonitrile takes place at a lower potential when we used imidazolium-based ionic liquids with [emim]⁺ cation than using pyrrolidinium, [empyrr]⁺ based ionic liquid. It can be concluded that the imidazolium-based ionic liquids both alone and as a supporting electrolyte in acetonitrile, is playing co-catalytic role in the reduction of CO₂ at Ag. In addition, we confirmed that it is the cation not the anion of the imidazolium-based ionic liquids that play a significant catalytic role during electrochemical CO₂ reduction, and responsible for lowering the reduction overpotential. Furthermore, it is found and verified electrochemically that CO is one of the products formed by the electrocatalytic reduction of CO₂ at a polycrystalline Ag electrode both in [emim][EtSO₄] and in the solution of [emim][EtSO₄] in acetonitrile.

Further studies should focus on detailed product analysis using gas chromatography to evaluate the faradaic and energetic efficiency, for the reduction of CO₂ at a Ag electrode in both [emim][EtSO₄] as well as in

acetonitrile containing [emim][EtSO₄] as a supporting electrolyte. In addition, further study will focus on exploration of other inexpensive and robust metal catalysts/co-catalysts systems and/or modification of Ag catalysts with other metals/metal oxides for the conversion of CO₂ to useful carbon based fuels and fuel precursors in the IL promoters at a low energy cost and high conversion efficiency.

Chapter 8: Final Conclusions and Future Outlook

8.1. Final Conclusions

The work discussed within this Thesis provided an insight into the electrocatalysis of some important redox processes using ionic liquid as electrolytes.

The study began with a detailed investigation of the electrochemical behaviour of Pt in a series of protic ionic liquids ([dmea][TfO], [dema][TfO] and [dema][Tf₂N]). It was found that the trace H₂O is not an innocent spectator and its oxidation leads to the formation of stable oxide films on Pt surface while in contact with the PILs. The oxidation of Pt surfaces in the PILs was confirmed by using voltammetry and XPS techniques. The extent of oxidation and surface charge density values under the Pt-oxides reduction peaks increased upon an increase of water contents in the PILs. The polarization potential, concentration of H₂O in PILs and temperature of the liquids all had a significant effect on the growth of thick oxide films at Pt in the liquids and a significant increase in the oxide film thickness and oxide stripping charges were observed, when the oxide films were grown at higher polarization potentials, high water contents and elevated temperatures. At low oxidizing potentials, PtO was formed but when the potential was increased, a thicker film of PtO₂ was grown on the top of PtO at elevated temperatures, as is evident from the XPS analysis of the Pt surface after polarization in [dema][Tf₂N] at 2.3 V and 100 °C.

An investigation of the oxide growth mechanism reveals that the initial growth of the Pt oxide species (sub-monolayer and a monolayer) follows direct logarithmic growth kinetics, and after which the oxide

formation follows inverse logarithmic kinetics in the PILs. The mechanism of this Pt oxidation in PILs and the resulting composition of the Pt surface appeared to undergo a similar mechanism to that of Pt oxidation in aqueous acid. However, a noticeable difference between the two electrolytes was that the potential at which the surface oxidation of Pt starts; 0.75 V in aqueous acid and positive of 1.0 V in the PILs.

The reactivity analysis revealed that the surface oxides formed at Pt play a pivotal role during the electrooxidation of hydrazine, formic acid, and ethanol and dimethyl ether. It was observed that the residual surface oxides at Pt, left over after the activation of the electrode at high positive potentials, enhanced hydrazine oxidation with the onset potential shifted to less positive values in [dmea][TfO] and [dema][TfO], while in [dema][Tf₂N], the electrode appeared to be activated prior to performing any potential sweeps. In addition, it appears that the reaction between adsorbed oxides and hydrazine depends on the amount of the residual oxides on the surface during potential cycles. These results are basic investigation that would be helpful in the understanding of the surface electrochemistry of hydrazine in ionic liquid electrolytes.

The electrochemical oxidation HCOOH in PILs at Pt, Au and Pd electrocatalysts revealed some very interesting results. Our results signify that in contrast to aqueous media, oxidation of HCOOH at Pt catalyst in PILs occurs mainly by dehydration plus CO_{ads} oxidation at a potential that coincides with the onset of the formation of Pt surface oxides. The rate of HCOOH oxidation in the PILs increased and overpotential decreased by increasing the anodic potential limits and water content of the liquids. It was also found that at lower potentials some intermediate species stick to the catalyst surface that passivated the catalyst with respect to HCOOH oxidation in the PILs causing a high overpotential. The identity of the

poisoning intermediates is not clearly established during electrochemical investigation but we suggest that these adsorbed species could be mainly CO_{ads} in the ionic liquids similar to that observed in aqueous systems.¹⁸⁵ By comparing the catalytic activity of the three catalysts used for the oxidation of formic acid in PILs, it was found that Pd catalyst showed higher catalytic activity at a lower potential for the process than that at Pt and Au electrocatalysts. The overall activity of the three catalysts investigated for the electrooxidation of HCOOH in the PILs was $\text{Pd} > \text{Pt} > \text{Au}$.

The electrocatalytic role of the trace water is also dominant during electrooxidation of ethanol and dimethyl ether in the ionic liquid, $[\text{dema}][\text{TfO}]$. It is found that the Pt surface get poisoned by the adsorbed CO-like intermediates during ethanol and DME oxidation in $[\text{dema}][\text{TfO}]$. The surface oxides that are formed at Pt by the oxidation of trace water in the liquid removes these adsorbed intermediates through a bifunctional surface reaction (Langmuir-Hinshelwood mechanism), in a similar manner to that observed in conventional aqueous electrolytes. From the study we conclude that similar to EtOH oxidation in aqueous media, two oxidation peaks during positive going potential sweep and a re-oxidation peak during reverse sweep can be obtained. However, the oxidation current is lower in comparison with that in aqueous media which is also evident from the higher activation energy values, (24 kJ mol^{-1} for 1st oxidation peak and 19 kJ mol^{-1} for the 2nd oxidation peak) in contrast to the activation energy observed in aqueous media, (22.1 kJ mol^{-1} and 13.5 kJ mol^{-1}).⁵⁵ In addition, due to a very low content of H_2O in $[\text{dema}][\text{TfO}]$, a higher overpotential was observed for oxidation of ethanol and or DME than in aqueous electrolytes. The oxidation current increased and overpotential decreased as temperature of the liquid was increased. This study also gave

a basic insight to the mechanism ethanol and DME oxidation reaction in ionic liquid environment.

To conclude further, it is suggested that the trace water, often found in trace quantity in PILs, cannot be ignored when studying electrocatalytic reactions in the protic ionic liquid electrolytes. The oxidation of water in PILs to cover Pt surfaces with oxides can hinder or facilitate various electrocatalytic processes.

Finally we investigated electrocatalytic reduction of CO_2 at various electrocatalysts in aprotic room temperature ionic liquids. In this work it is shown that polycrystalline Au and Ag are better electrocatalysts for the reduction of CO_2 in $[\text{emim}][\text{EtSO}_4]$ than Cu, Pt and BDD electrodes. The rate of CO_2 reduction at Ag increases with increasing temperature of the medium. The role of the imidazolium based ionic liquids as supporting electrolyte during CO_2 reduction at a Ag electrode in acetonitrile has also been investigated and compared with that of the commercial supporting electrolyte, $[\text{TBA}][\text{PF}_6]$. It is observed that Ag can reduce CO_2 in acetonitrile at 200 mV lower potential in the presence of $[\text{emim}][\text{EtSO}_4]$ than in the presence of $[\text{TBA}][\text{PF}_6]$. Reduction of CO_2 in acetonitrile takes place at a lower potential when using imidazolium-based ionic liquids with $[\text{emim}]^+$ cation than using pyrrolidinium, $[\text{empyrr}]^+$, based ionic liquid showing that the imidazolium-based ionic liquids is playing co-catalytic role in the reduction of CO_2 at Ag. In addition, we confirmed that it is the cation not the anion of the imidazolium-based ionic liquids that play a significant catalytic role during electrochemical CO_2 reduction and is responsible for lowering the reduction overpotential. Furthermore, it is found electrochemically that CO is one of the products formed by the electrocatalytic reduction of CO_2 at a polycrystalline Ag electrode both in $[\text{emim}][\text{EtSO}_4]$ and in the solution of $[\text{emim}][\text{EtSO}_4]$ in acetonitrile.

8.2. Future Work

As discussed in this Thesis, many surface chemical reactions, such as the ORR, the oxidation of hydrazine and small organic molecules are structure sensitive and their rate could be controlled by the strength of the binding energy of the reactant molecule with the catalytic surface by changing the interatomic distance of the electrocatalysts, the composition of the electrocatalyst, the surface area, and the electronic configuration of the material.^{241, 242} Based on these assumptions, my future work will include the following.

8.2.1. ORR at Pt alloys in PILs

The ORR is important in H_2 - O_2 fuel cells and the rate of ORR is very slow. One of the reasons attributed to the slow kinetics of this important reaction is blockage of the Pt electrocatalyst surface by oxide species formed in aqueous electrolytes. The surface oxides at Pt cathode can modify the electrocatalytic activity of the Pt catalysts by consequent detachment or dissolution of the Pt nanoparticle electrocatalysts, affecting the durability of the catalyst, the mechanism and kinetics of ORR and consequently the performance of the fuel cell.^{14, 34, 35, 172} In protic ionic liquids the oxidation of Pt due to trace water is found to occur at potentials positive of 1.0 V so Pt electrocatalysts surfaces are free of surface oxides nearer the thermodynamic potential than in aqueous media. In addition, the rate of ORR can be enhanced by carrying out the reduction at high temperatures, which is possible in protic ionic liquids due to their high thermal stabilities. To demonstrate the effect of surface oxides formed at Pt in PILs on the electroreduction of O_2 and the effect of temperature on this reaction, an

initial investigation of the ORR was carried out at Pt electrocatalysts in [dmea][TfO] (Figure 8.2.1).

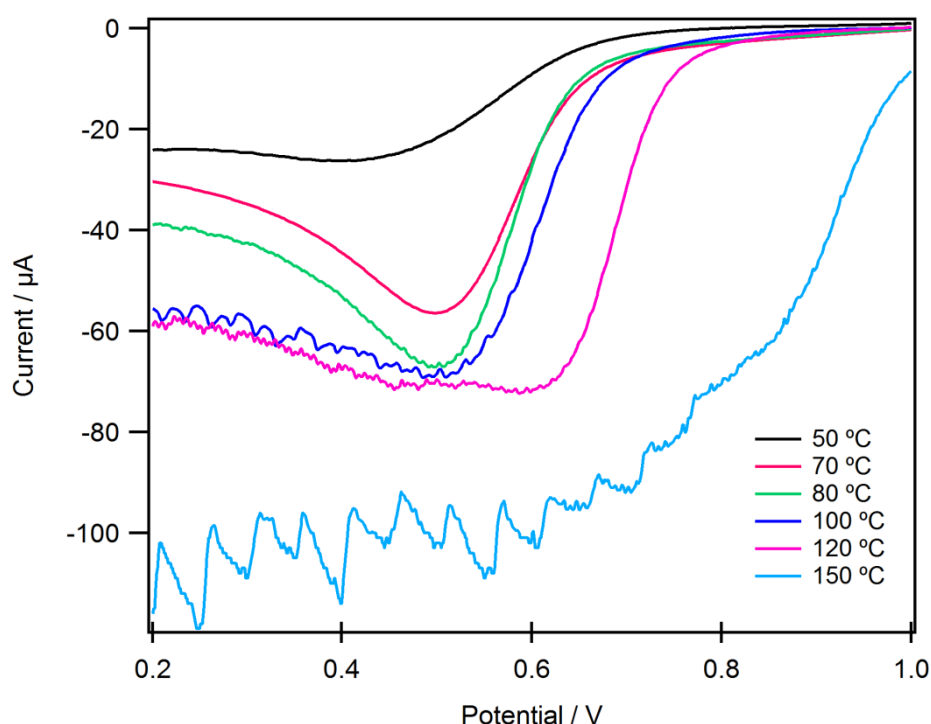


Figure 8.2.1 Hydrodynamic ORR polarization voltammograms at a 2 mm diameter Pt disk electrode at 50 mV s^{-1} and a range of temperatures 50 °C, 70 °C, 80 °C, 100 °C, 120 °C and 150 °C in O_2 -saturated [dmea][TfO].

The figure shows that ORR starts at potentials when oxides are removed from the surface of the electrode. The rate of ORR increased with rising temperature and a transformation in the shape of voltammogram from a peak-shaped response to a well-defined limiting current was observed. It was observed that as temperature increased the ORR proceeded faster, which was evident from shifting the entire ORR wave towards less negative potential. Consequently, it is likely that the best electrocatalysts for use in PIL electrolyte fuel cells will be those that bind oxide species weakly. The use of Ni and Co alloys with Pt as electrocatalyst for ORR reaction will be a better option. Therefore, one of my future works will focus on using Ni-Pt and Co-Pt alloys for ORR in protic ionic liquids at

high operation temperatures to explore the possibility of enhancing the kinetics of this important reduction reaction.

8.2.2. Formic Acid Oxidation in PILs at Alloys

The inclusion of readily oxidised metals such as Pd, Ru to the Pt catalyst to form bimetallic catalysts may aid in reducing the overpotential for HCOOH oxidation. These metals can provide synergetic effect to Pt, which can orient the catalysts in favor of the oxidation of HCOOH through the direct dehydrogenation path at lower potentials.^{54, 192} Therefore our future work will also focus on making this alloy and exploring this possibility.

8.2.3. Ethanol Oxidation in PILs at Sn-Pt Bimetallic Catalysts

For facile electrocatalytic oxidation of ethanol, an active electrocatalyst is required that helps in C-C bond breaking, can promote direct dehydration of EtOH, and form earlier surface adsorbed oxygen species that can help in the removal of catalyst's poisoning species such as CO_{ads}. The catalyst poisoning can be overcome by modifying the Pt surface with another metal to increase its coverage in adsorbed OH species coming from water that are necessary for the oxidation of CO-like adsorbed species that comes from EtOH dissociation. It is found that adding Sn to Pt surface to form a bimetallic catalyst have shown the best results and undergo EtOH oxidation at much lower potentials due to facile formation of OH_{ads} at lower potentials on Sn compared to bare Pt.²¹⁵ Therefore, my future work will also include making Sn-Pt alloy catalyst for the electrocatalytic oxidation of EtOH using PILs as supporting electrolytes that could be a promising electrode/electrolyte combination for the development of direct ethanol fuel cells.

8.2.4. Analysis of the DME Oxidation Intermediates in PILs

We observed through electrochemical measurement the formation and adsorption of some unknown potential-dependent intermediates during DME electrocatalysis at Pt in a protic ionic liquid. The identity of these intermediates should be explored in our future work using FTIR spectroscopy.

8.2.5. Product Analysis and Exploration of Electrocatalysts for CO₂ Electroreduction in RTILs

In future work, in addition to above, a detailed product analysis for the reduction of CO₂ at a Ag electrode in both [emim][EtSO₄] as well as in acetonitrile containing [emim][EtSO₄] as a supporting electrolyte using gas chromatography (GC) to evaluate the faradaic and energetic efficiency is recommended. Also, further study should focus on exploration of other inexpensive and robust metal catalysts/co-catalysts systems and/or modification of Ag catalysts with other metals for the conversion of CO₂ to useful carbon-based fuels and fuel precursors in the IL promoters at a low energy cost and high conversion efficiency.

Appendix 1: Supporting Figures

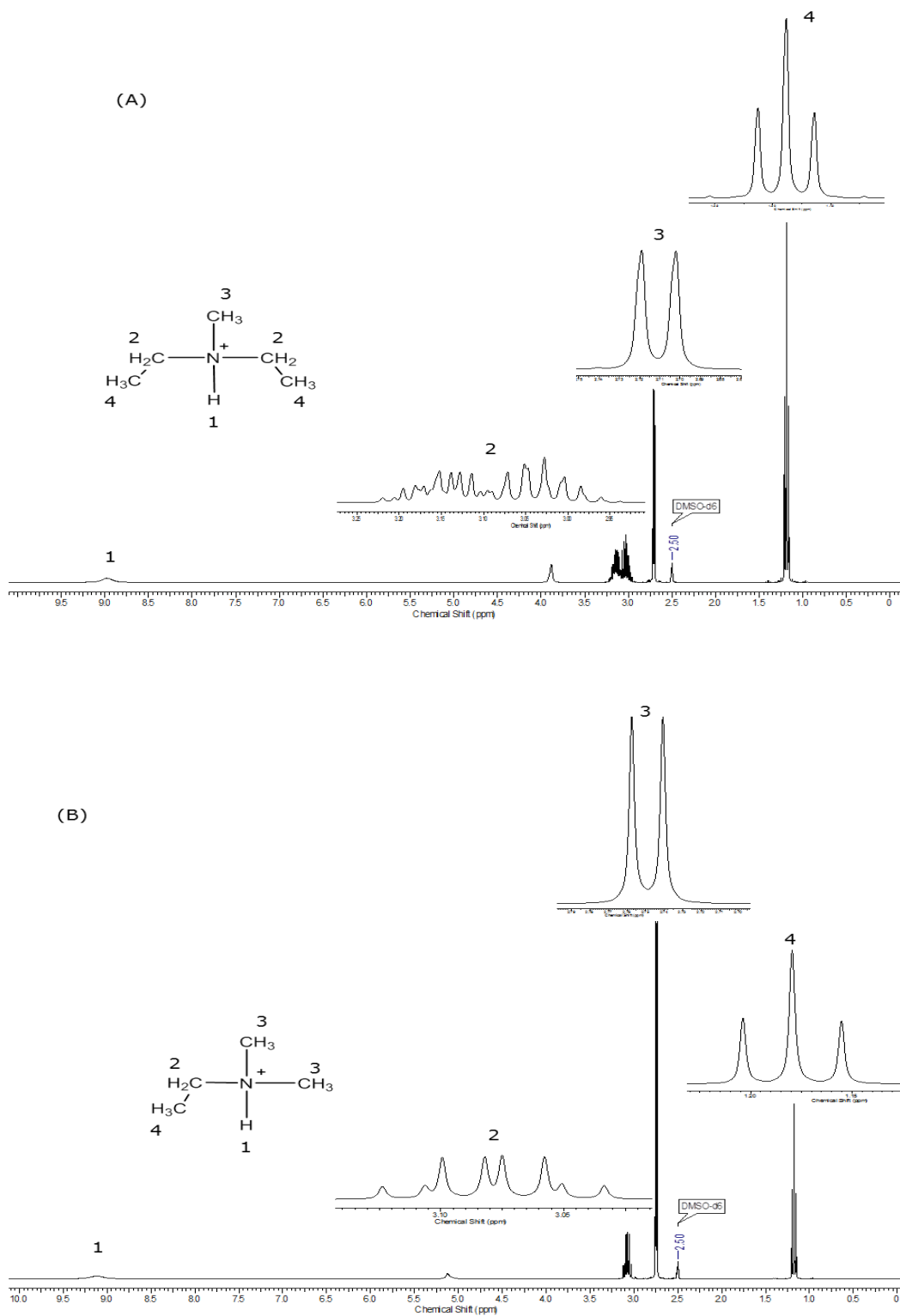


Figure S 1 ^1H NMR of (A) [dema][Tf₂N] and (B) [dmea][TfO].

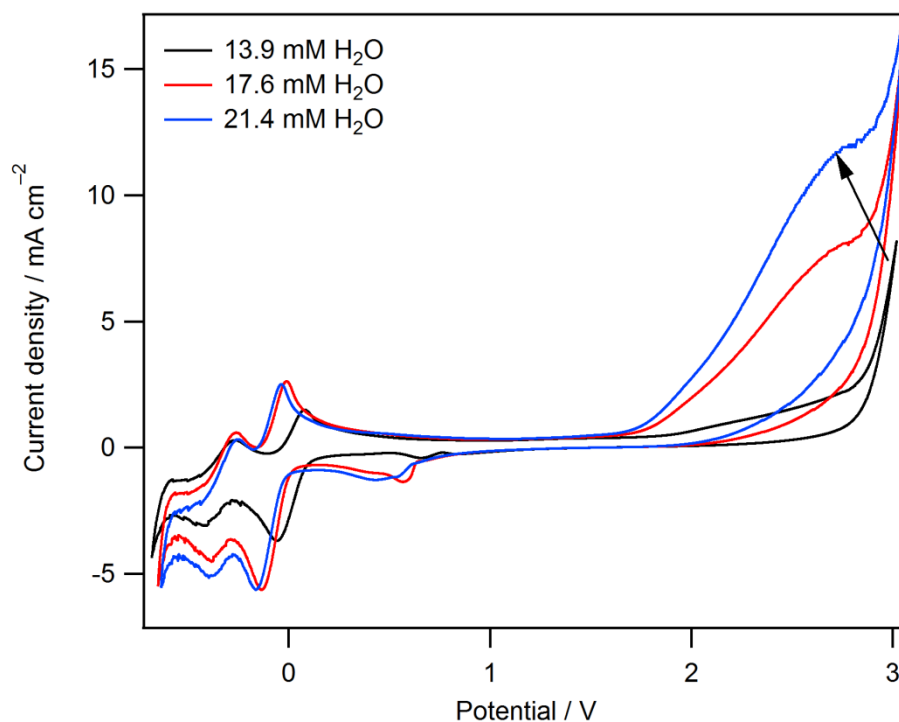


Figure S 2 CVs at 2 mm diameter Pt disk electrode vs. Pd-H at 50 mV s^{-1} and at 50°C obtained after deliberate addition of water to vacuum dried samples of $[\text{dmea}][\text{TfO}]$ showing the effect of water concentration on the electrochemical window of the PIL.

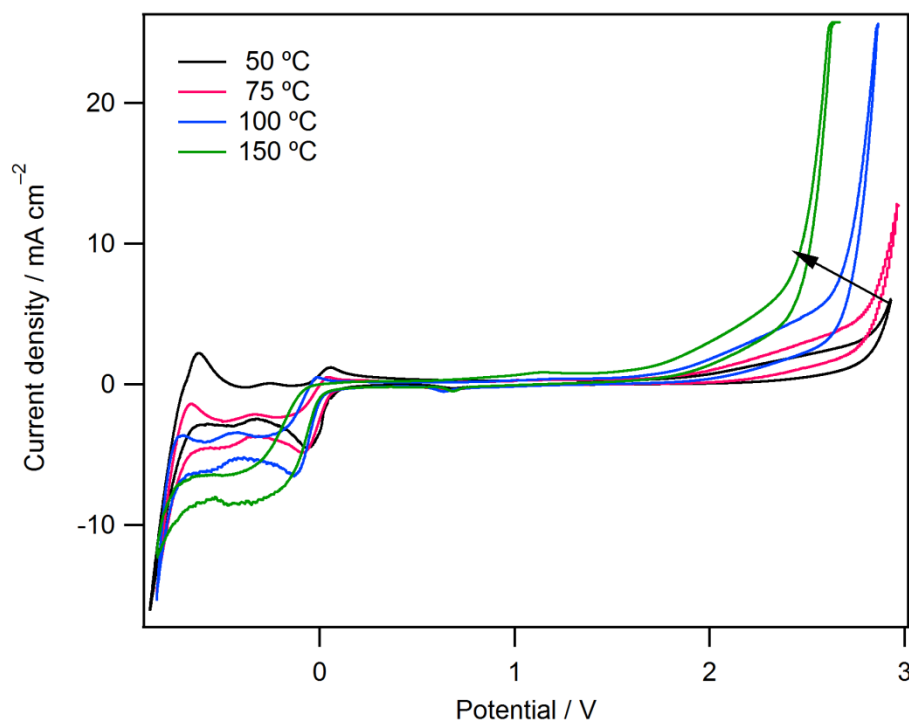


Figure S 3 CVs at 2 mm diameter Pt disk electrode vs. Pd-H at a scan rate 50 mV s^{-1} in vacuum dried blank $[\text{dmea}][\text{TfO}]$ at different temperatures (50°C , 75°C , 100°C and 150°C).

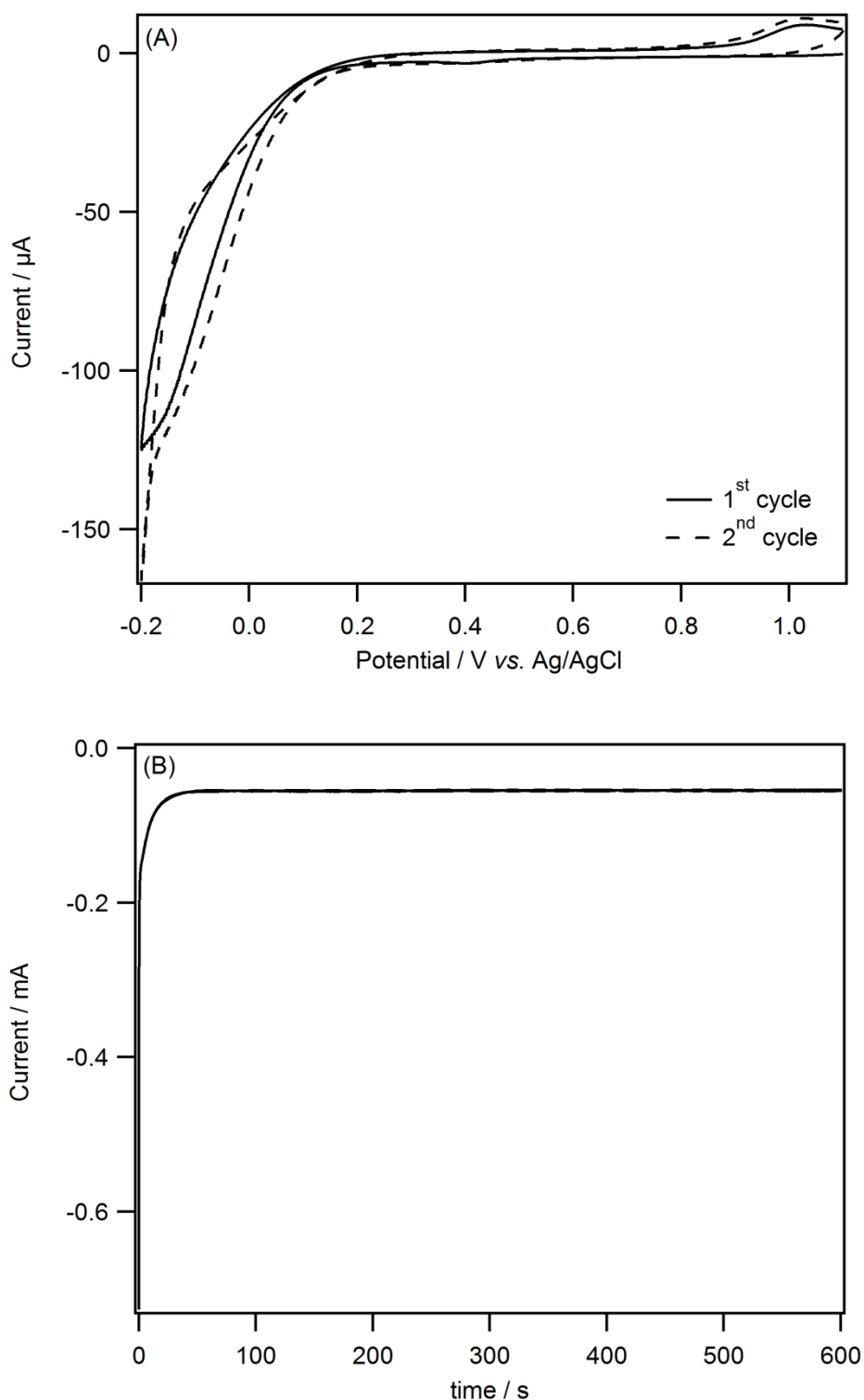


Figure S 4 (A) CV at 3 mm diameter GC disk electrode vs. Ag/AgCl at a scan rate of 100 mV s^{-1} in 0.1 M HCl containing $5 \text{ mM H}_2[\text{PtCl}_6] \cdot 6\text{H}_2\text{O}$ at room temperatures by scanning the electrode potential from initial 1.1 V to -0.2 V . (B) Chronoamperometric curve obtained at a 3 mm diameter GC electrode vs. Ag/AgCl for electrodeposition of Pt from $5 \text{ mM H}_2[\text{PtCl}_6] \cdot 6\text{H}_2\text{O} + 0.1 \text{ M HCl}$ by stepping the potential from 0.5 V to -0.2 V for 600 s .

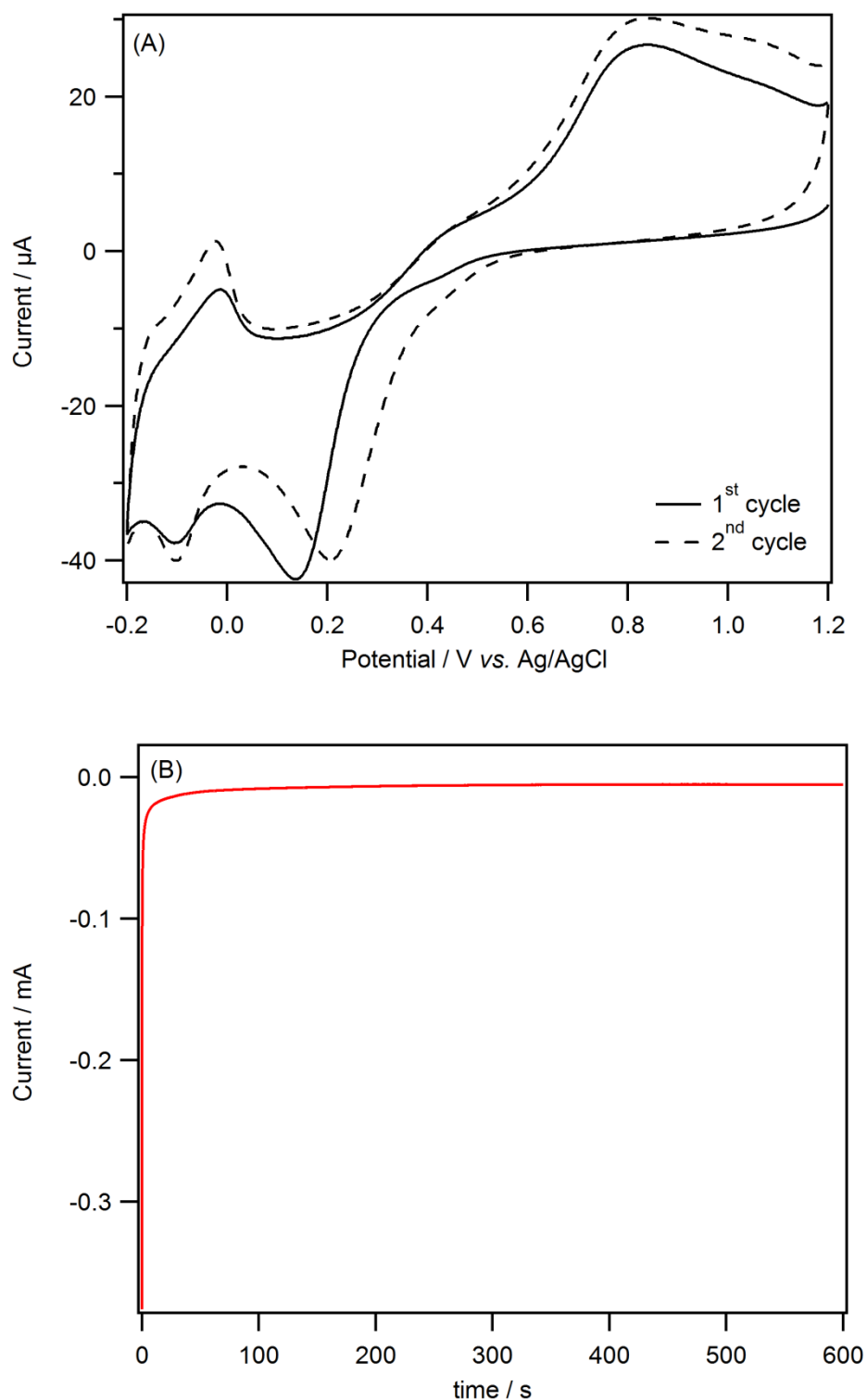


Figure S 5 (A) CV at 3 mm diameter GC disk electrode vs. Ag/AgCl at a scan rate of 100 mV s^{-1} in $0.1 \text{ M H}_2\text{SO}_4$ containing 1 mM PdCl_2 at room temperatures by scanning the electrode potential from initial 1.2 V to -0.2 V . (B) Chronoamperometric curve obtained at a 3 mm diameter GC electrode vs. Ag/AgCl for electrodeposition of Pt from the same solution by stepping the potential from 0.5 V to -0.2 V for 600 s .

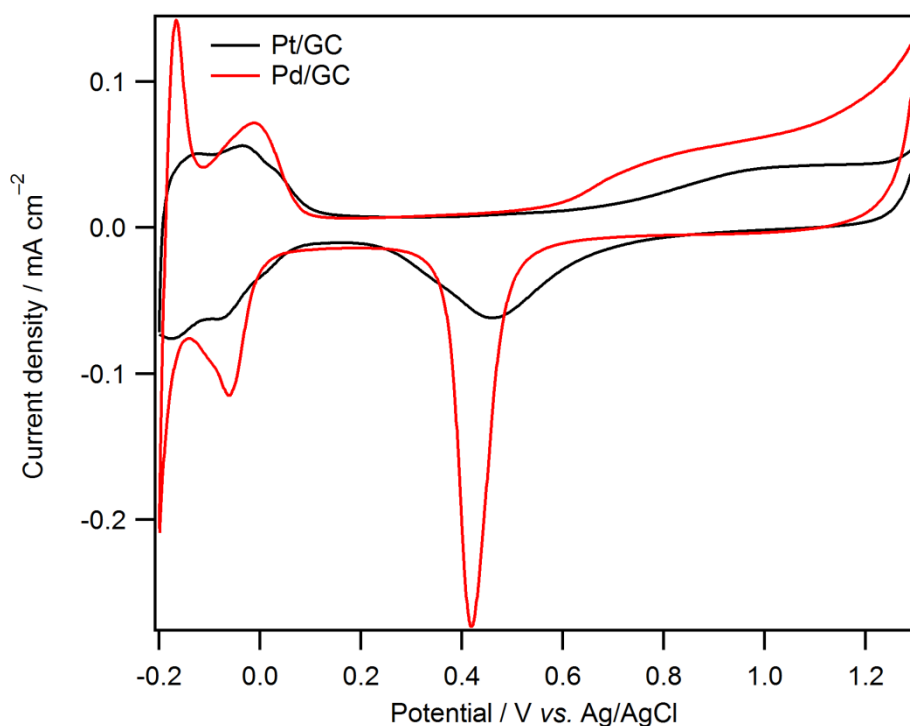


Figure S 6: Cyclic voltammograms obtained at Pt/GC and Pd/GC catalysts at 50 mV s⁻¹ vs. Ag/AgCl in N₂-saturated 0.1 M HClO₄ (aq.) at room temperature.

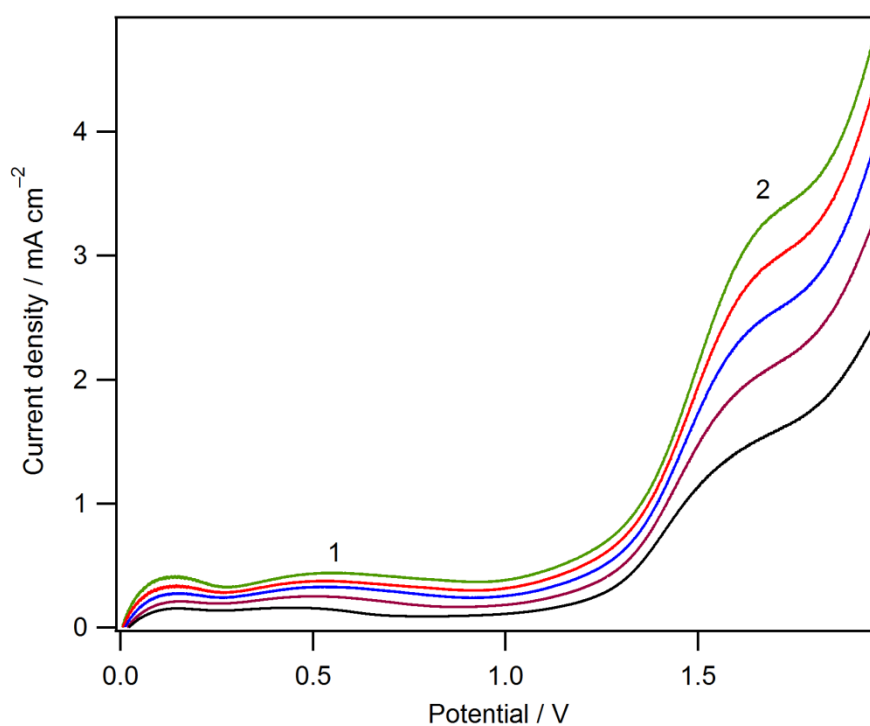


Figure S 7 Cyclic voltammograms showing the effect of scan rate (from top to bottom 500, 400, 300, 200 and 100 mV s⁻¹) on the electrooxidation of 0.5 M HCOOH in [dema][TfO] at a 2 mm diameter Pt disk electrode.

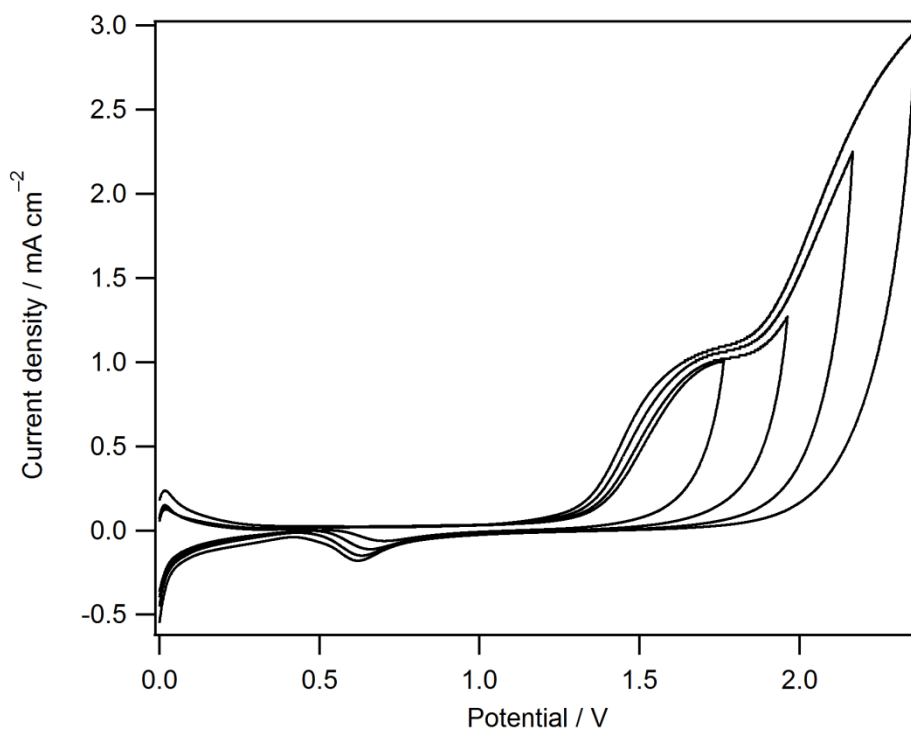


Figure S 8 CVs showing effect of the anodic reversal potential on the electrooxidation of 0.5 M HCOOH in [dema][TfO] obtained at Pt wire (3 mm diameter was the exposed surface of the wire) at 50 mV s^{-1} and 25°C . The potential was scanned from -0.035 V (shown from 0.25 V) and switched back at upper potential limits 1.75 V , 1.95 V , 2.15 V and 2.35 V .

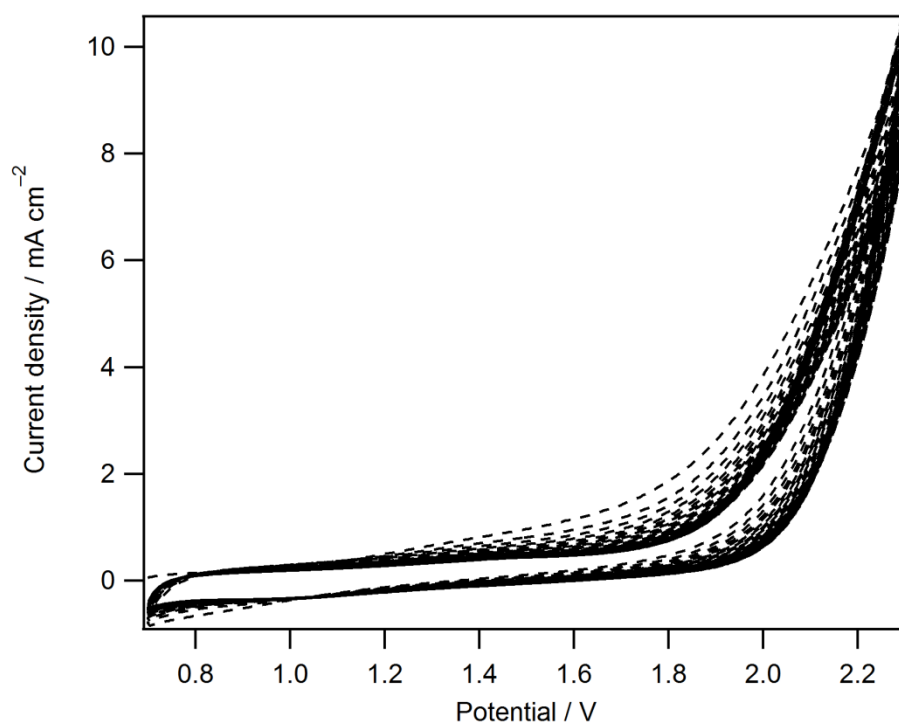


Figure S 9 CV profiles on a 2 mm diameter Pt in DME saturated [dema][TfO] solution at room temperature. The electrode was cycled fifty cycles in a potential range between 0.7 V and 2.3 V at 500 mV s^{-1} .

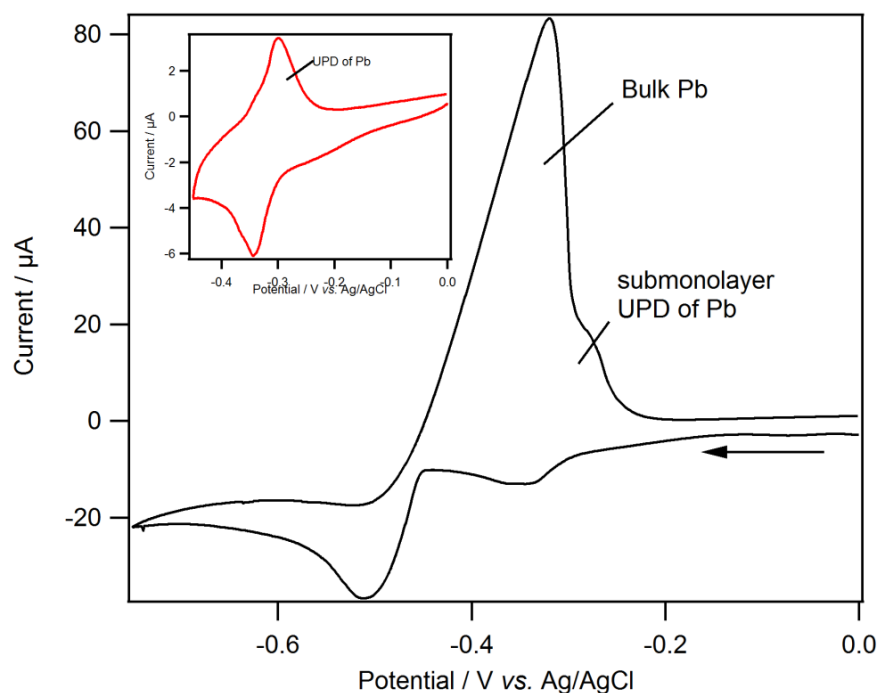


Figure S 10 Cyclic voltammogram on a Ag electrode obtained at a sweep rate of 10 mV s^{-1} in a $5 \text{ mM Pb(NO}_3)_2$ solution in $10 \text{ mM KCl} + 10 \text{ mM HNO}_3$ in a potential range from 0.0 V to -0.75 V , showing the UPD and bulk deposition of Pb. Inset: shows only the Pb UPD region. The arrow shows the direction of the scan.

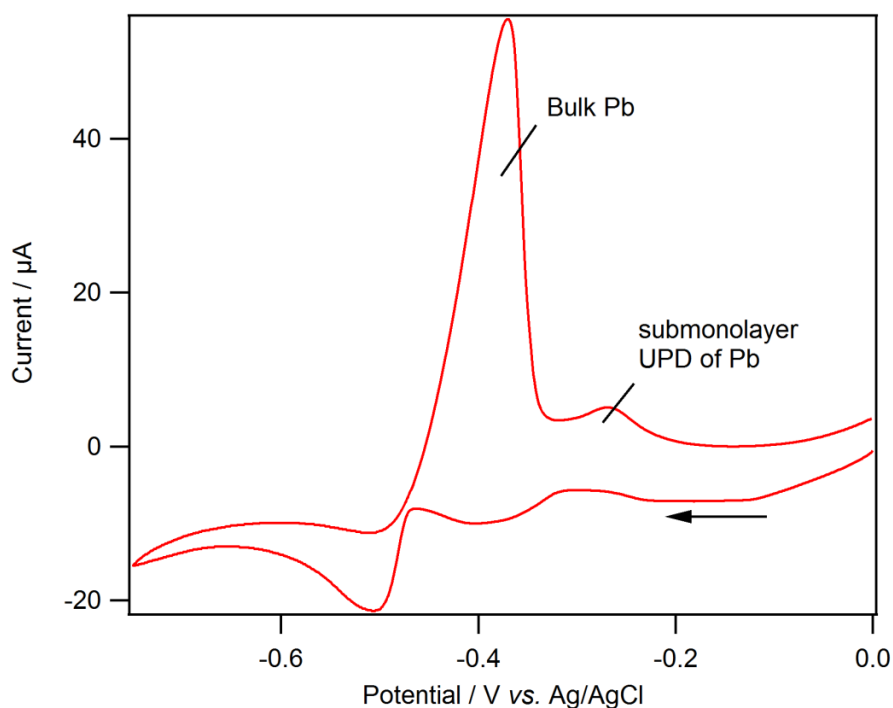


Figure S 11 Cyclic voltammogram recorded at a 2 mm Cu electrode at 10 mV s^{-1} in a $5 \text{ mM Pb(NO}_3)_2$ solution in $10 \text{ mM KCl} + 10 \text{ mM HNO}_3$ in a potential range from, 0.0 V to -0.75 V , showing the UPD and bulk deposition of Pb. The arrow shows the direction of the scan.

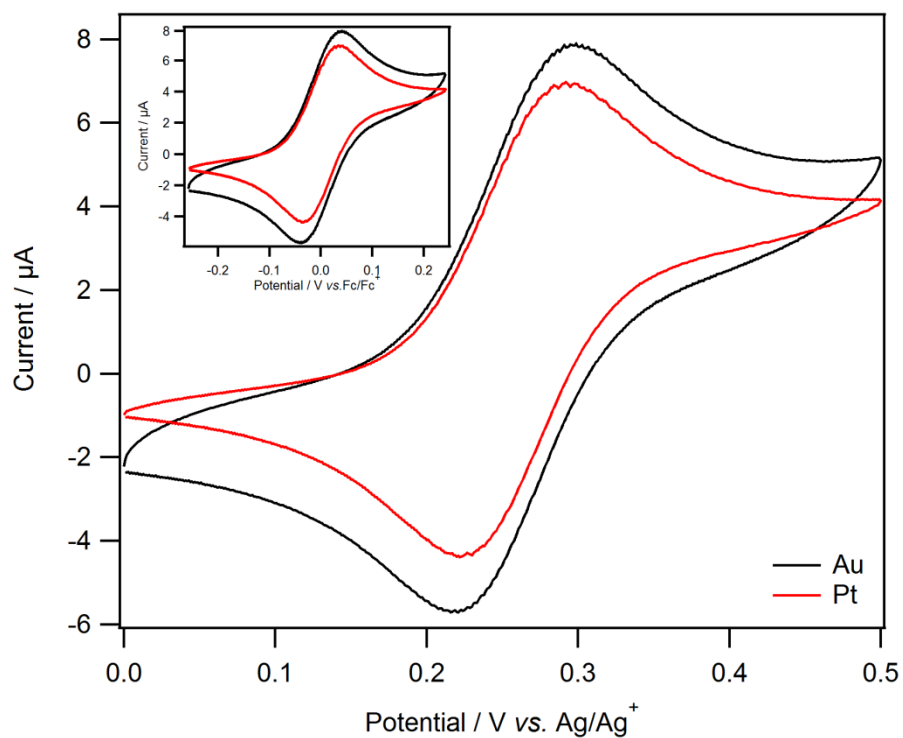


Figure S 12 Cyclic voltammograms at a 2 mm diameter Pt (red line) and a 2 mm diameter Au (black line) disk electrodes at a scan rate of 100 mV s^{-1} and 25°C in 5 mM ferrocene solution in $[\text{emim}][\text{EtSO}_4]$ in a potential range between 0.0 V and 0.5 V vs. Ag/Ag^+ . Inset: shows CVs adjusted vs. Fc/Fc^+ redox couple.

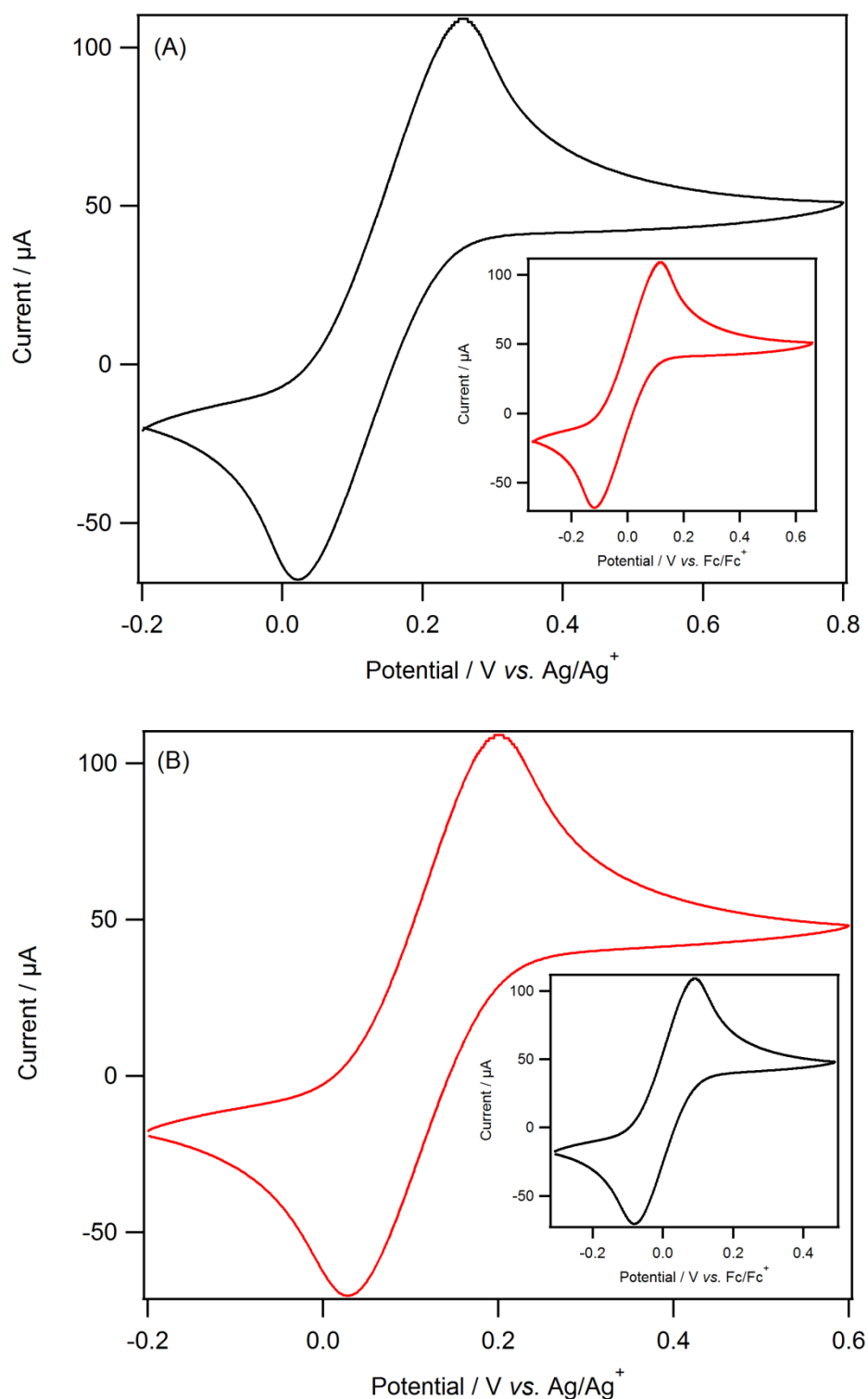


Figure S 13 CVs obtained at 3 mm diameter GC electrode vs. Ag/Ag^+ at a scan rate of 100 mV/s and 25 °C in a solution of (A) 0.1 M $[\text{emim}][\text{EtSO}_4]$ and (B) 0.1 M $[\text{TBA}][\text{PF}_6]$ in MeCN containing 5 mM ferrocene. The formal potential was 0.14 V in the case of (A) and (B) 0.11 V for Fc/Fc^+ redox couple Inset: in each case shows CVs after adjusting the potential scale in each case vs. Fc/Fc^+ .

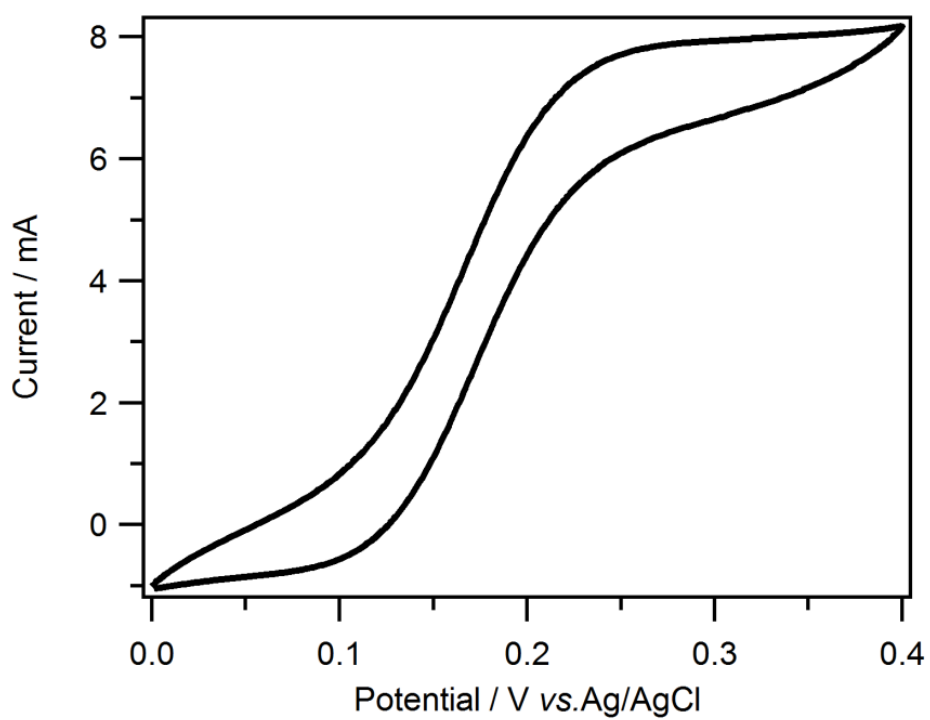


Figure S 14 CV obtained in, 0.1 M KCl (aq.) containing 2 mM ferrocene at a, 25 μm diameter Au electrode at a 5 mV s^{-1} .

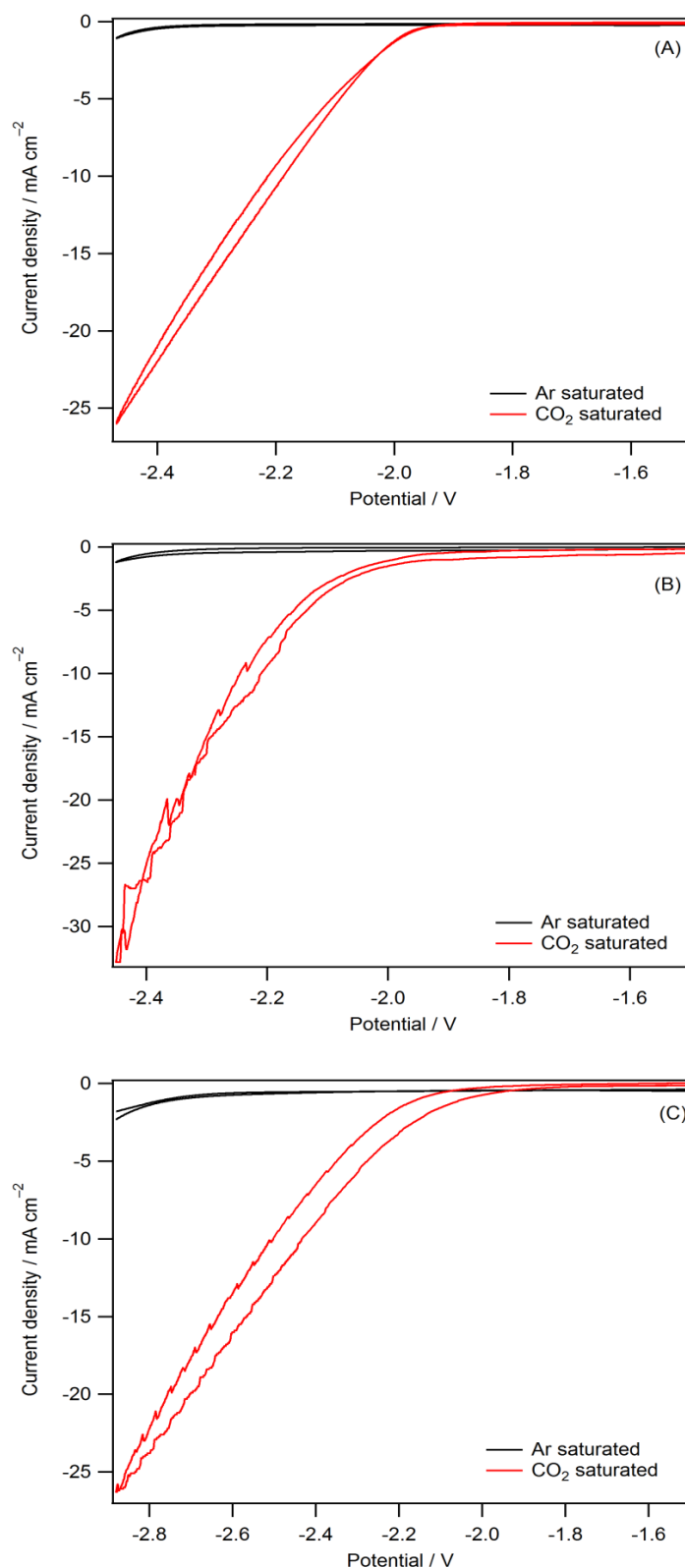


Figure S 15 CVs recorded on a Ag working electrode at a 100 mV s^{-1} in MeCN containing 0.1 M of (A) [emim][Br]/MeCN, (B) [emim][Tf₂N]/MeCN and (C) [empyrr][EtSO₄]/MeCN after bubbling Ar for 30 minutes (blank lines) and then CO₂ for 60 minutes (red lines) in of the solution. The potential of the working electrode was swept from an initial value, 1.5 V to, -2.47 V in (A), -2.45 V in (B) and -2.9 V in the case of (C) vs. Fc/Fc⁺.

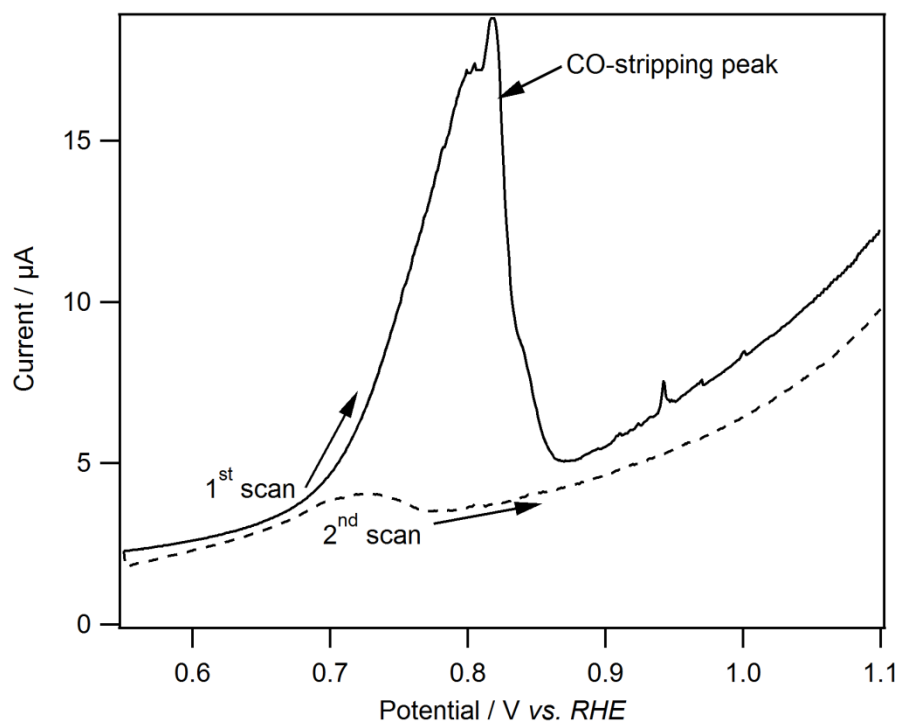


Figure S 16 The forward anodic sweeps, (solid line shows 1st and dashed line 2nd scan), for CO stripping from a 2 mm diameter polycrystalline Pt disk electrode in a CO-free 0.1 M H₂SO₄ (aq.) at a 100 mV s⁻¹ and 25 °C. CO adsorption on Pt was previously established in 0.5 M [emim][EtSO₄] + MeCN solution during electrochemical reduction of CO₂ at Ag electrode.

Appendix 2: List of Publications

From this Thesis

1. D. A. Walsh, A. Ejigu, **S. Muhammad** and P. Licence, "The Formation and Role of Oxide Layers on Pt During Hydrazine Oxidation in Protic Ionic Liquids", *ChemElectroChem*, 2014, 1, 281-288.

From Other Projects

2. **S. Muhammad**, S. T. Hussain, M. Waseem, A. Naeem, J. Hussain and M. Tariq Jan, "Surface charge properties of zirconium dioxide", *Iranian Journal of Science & Technology*, 2012, A4, 481-486.

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