

Polyoxometalates as Redox Mediators for Li – Air Batteries

Jack Castle

Student ID: 14343493

1. Abstract

This report will walk through the process of developing polyoxometalates (POMs) to be used as redox mediators in Li – air batteries. Three POMs; $(\text{TBA})_4[\text{PW}_{11}\text{VO}_{40}]$, $(\text{TBA})_4[\text{PMo}_{11}\text{VO}_{40}]$ and $(\text{TBA})_5[\text{PMo}_{10}\text{V}_2\text{O}_{40}]$ were successfully synthesised and electrochemically characterised. With the redox chemistry of the POMs determined, they were implemented into working cells.

Two of the three POMs resulted in an increase in capacity but had little to no effect on the reduction of the overpotential. One POM was taken forward for testing within a pressure cell, with the resulting data providing information regarding electronic efficiency and side reactions within the cell during the discharge process.

It was determined that in order for POMs to be used as redox mediators, some degree of optimisation will be necessary, more specifically, tuning the redox chemistry to potentials more closely associated with Li_2O_2 oxidation and enhancing the solubility of the compound.

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2. Introduction

2.1 Current Energy Storage Technology

As we continue to work as a planet to reduce our global environmental footprint, the demand for new energy storage technologies will continue to soar. At the current forefront of battery technology manufacturing is the Li – Ion battery. The development of the Li – Ion battery revolutionised the handheld device industry, however, in order to fully utilise the power of portable power storage, for example, for use in cars in place of the traditional combustion engines, we must look for higher energy density alternatives.¹ Research in this field is being driven forward by government led initiatives such as the UK government “The Road to Zero” initiative that plans on ending the production and sale of all new petrol and diesel vehicles in the UK by 2040.² In addition to legislation, they are also providing £246 million for research into next generation battery technology through the Faraday Battery Challenge.²

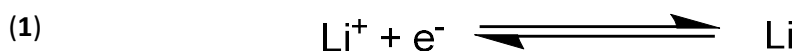
Li – Ion batteries are generally associated with high costs and cell weight. These negatives arise from the materials that are required within the cathode of the cells. The two most common cathode materials are LiCoO_2 and LiMn_2O_4 , both of which use heavier transition metals when compared to the carbon based cathodes of Li – Air and Li – S cells. Whilst cobalt based cathodes have benefits such as good cycling performance, a high discharge voltage and high volumetric capacity, the cobalt itself is a relatively expensive material and the cathodes have been found to have low thermal stability.³ As a result, if we are serious about having a complete reliance on electric powered road vehicles, we must either optimise Li – Ion to reduce cell weight and cost or overcome the problems associated with current Li – Air and Li – S batteries.

2.2 Li – Air

Having been discussed as early as the 1970s, Li – Air batteries were deemed to be too unrealistic at the time due to limitations in dealing with lithium metal, specifically due to its high reactivity which makes it hard to keep the metal surface clean under non-argon atmospheres with Li_2O and Li_3N readily forming under O_2 and N_2 atmospheres. However, in recent years due to advances in materials science, Lithium – Air batteries have picked up interest due to their high theoretical specific energy (3500 Wh kg^{-1}), which is approximately 10 times as large as with Li – Ion batteries⁴. Li – ion batteries rely heavily on Co as a common component of their cathodes. Co has a natural abundance of the 0.0025%⁵ in the Earth's crust and does not exist naturally in its metallic form due to atmospheric oxygen and the chlorine found in sea water. Additionally, the world's leading producer of cobalt is the Democratic Republic of Congo, where its internal conflicts and politics have previously led to instability in the cobalt market resulting in price rises for the material.⁶ Due fact they do not use any comparatively rare transition metals such as Co and make use of naturally abundant oxygen from the atmosphere, Li – Air batteries a very attractive prospect as the next staple battery technology for use in electric vehicles. Generally, Li – Air batteries comprise a Li metal anode, an ionically conductive electrolyte and a porous carbon – based cathode.

The cathode is where the O_2 reduction reaction takes place and so needs to be electrically conductive, porous enough for O_2 diffusion and have a high enough surface area to store a sufficient amount of the discharge product, Li_2O_2 , that corresponds to a large discharge capacity.⁷ The use of O_2 is beneficial as it is essentially a limitless source and produces no carbon based emissions. This not only reduces the environmental impact of the cell but decreases cell weight which is a contributing factor to the high specific energy calculated.⁸

The electropositive nature of alkali metals makes them excellent anode materials due to the ease at which they can lose an electron to an external circuit, or become oxidised. The half reaction for Li metal (1) has a very negative E° value - the most negative of all metallic elements - of -3.04 V vs. standard hydrogen electrode (SHE).⁹



Lithium is widely used for a few reasons such as it being the lightest and the least reactive of the alkali metal series making it the easiest to handle and safest to use within a cell. The low density of lithium metal (0.59 g cm^{-3}) gives it the highest specific capacity known (3860 mA h g^{-1})¹⁰ compared with zinc (820 mA h g^{-1}) and magnesium (2965 mA h g^{-1})¹¹. In the context of this work, LiFePO_4 (LFP) was used as a source of lithium in place of lithium metal as the anode. As this work is a study of the cathodic processes, it was important to eliminate the risk of any side reactions elsewhere in the cell that may have affected any data obtained so the less reactive LFP was substituted in as the anode whilst making little to no difference to the efficiency and working of the cell.

There are three main different categories of electrolyte used in Li – Air batteries. These are; aqueous (*Figure 1*), solid (*Figure 2*) and aprotic (*Figure 3*).

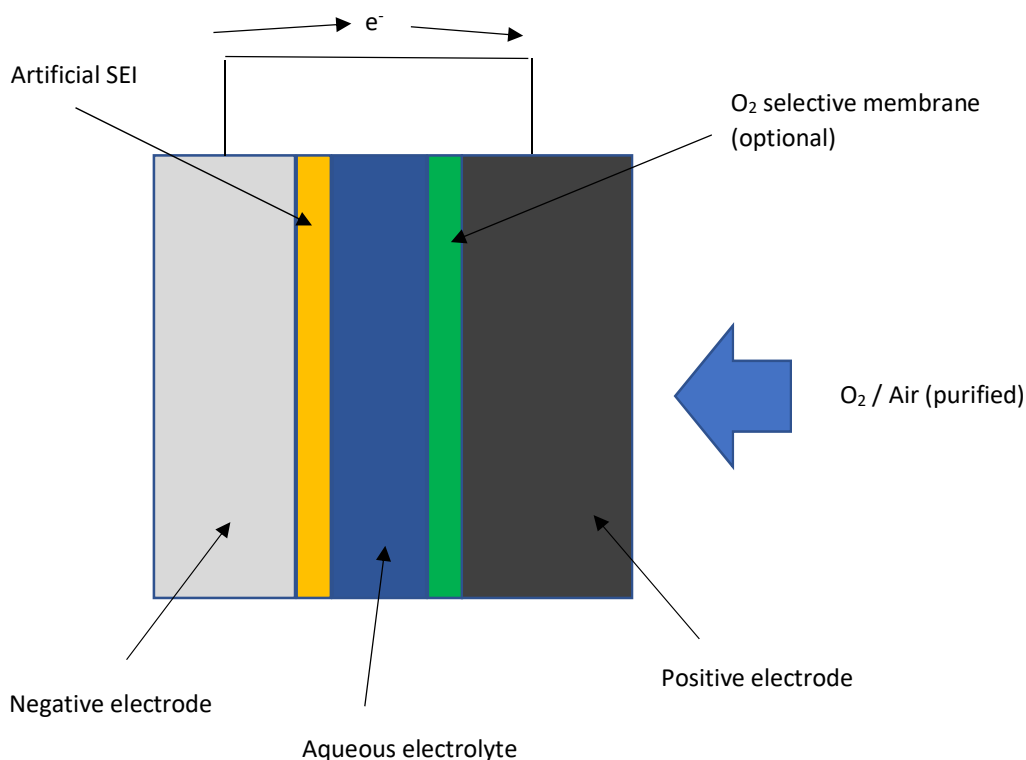


Figure 1 - Schematic showing the structure of a Li – Air cell with an aqueous electrolyte¹²

In the aqueous cells, there is the requirement to have an artificial interface made of lithium conducting ceramic or glass between the electrolyte and the Li metal to avoid the violent reactions that occur when lithium comes into contact with water. At the cathode, Li_2O_2 is still deposited, however cathodic pore clogging does not occur due to the reaction products solubility in water. However, it is also possible for the cathodic reaction to produce LiOH via a $4 e^-$ reduction of oxygen using water, instead of the $2 e^-$ reduction that is usually seen. Despite having a higher practical discharge potential than the aprotic cell¹³ due to the $4 e^-$

reduction that occurs, LiOH is corrosive and will corrode the cell components potentially leading to premature cell death and loss of capacity.

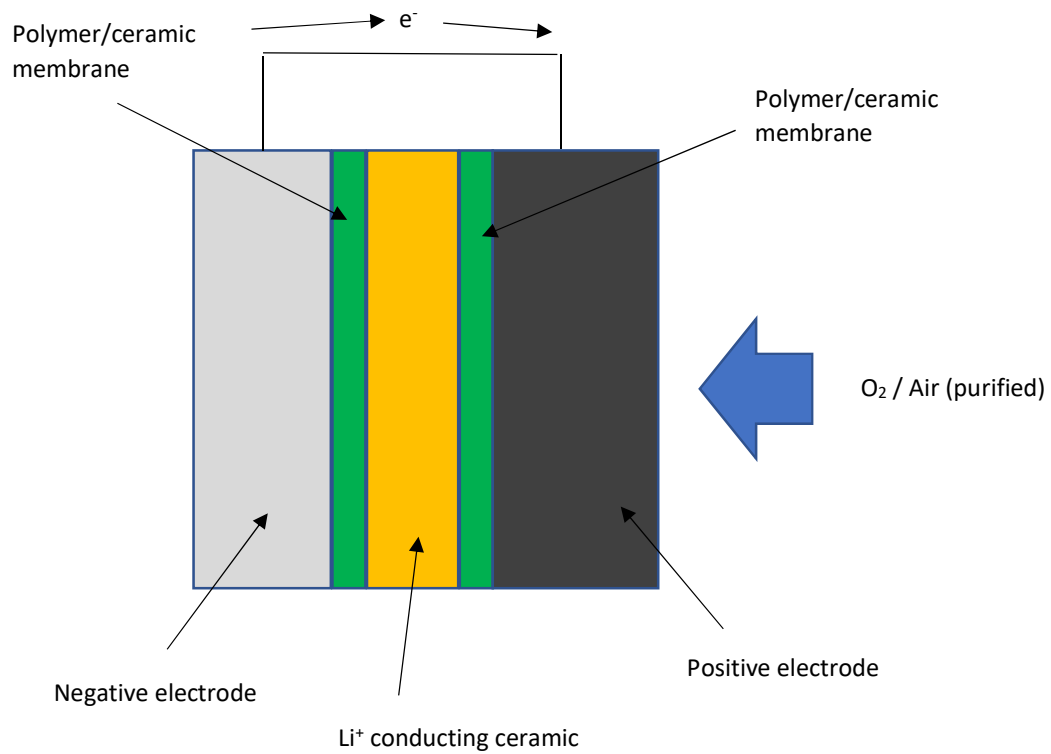


Figure 2 - Schematic showing the structure of a Li – Air cell with a solid electrolyte¹²

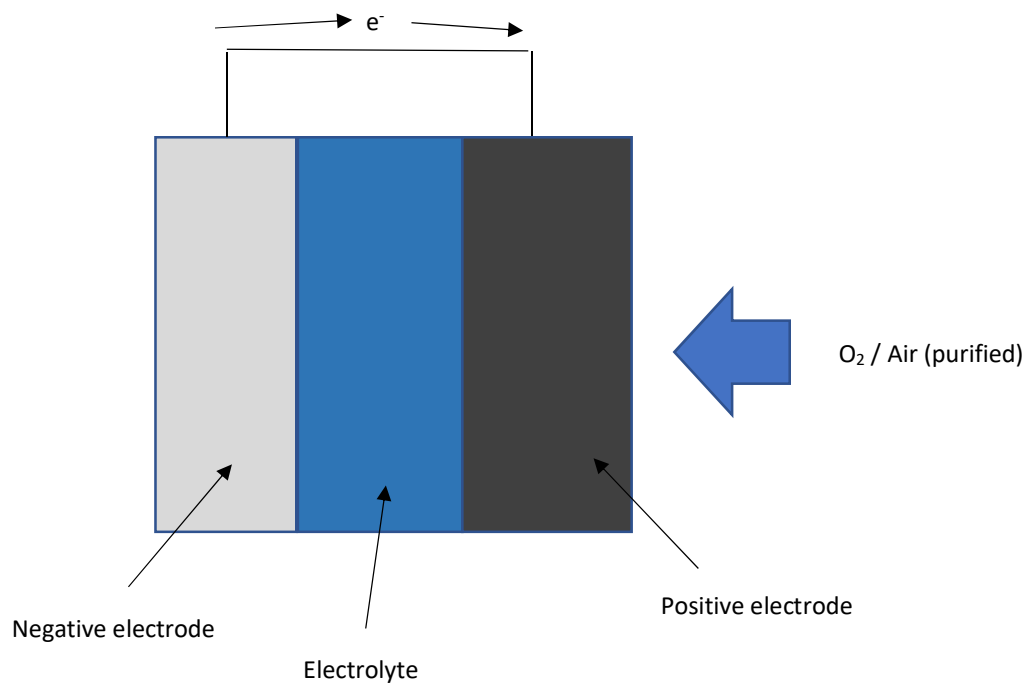


Figure 3 - Schematic showing the structure of a Li – Air cell with an aprotic electrolyte¹²

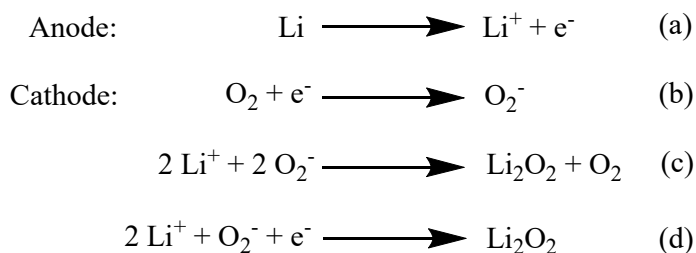
In the case of the solid Li – Air cell, the electrolyte itself is made of ceramic, glass or a glass ceramic. These cells avoid the safety concerns upon rupturing¹⁴ however, the electrolyte itself has relatively poor conductivity compared to the other liquid electrolyte cells.¹⁵

Non – aqueous aprotic electrolyte Li – Air cells are the most widely used cells and are also what is used throughout this work.^{16–19} The solvents used can include carbonates and ethers such as tetraethylene glycol dimethyl ether (TEGDME or tetraglyme). The solvents used generally have very good chemical, electrochemical and thermal stability and should have low viscosity to aid conductivity, minimise water solubility and maximise oxygen solubility.²⁰ Upon addition of the electrolyte to the cell, a spontaneous solid – electrolyte interface (SEI) forms between the surface of the lithium metal and the electrolyte. Whilst this is initially beneficial in both protecting the metal surface and preventing reactions between the highly oxidising lithium and the solvent, over time this can lead to a loss of charge as the SEI continuously reforms.¹ Within the cell, there will also be highly reactive species such as superoxide present that can initiate decomposition of the electrolyte, a problem which is exacerbated with increasing temperature. Ethers like TEGDME are especially stable against nucleophiles such as the superoxide anion intermediate that forms during reaction **2(b)** due to their lack of electron – withdrawing functional groups²¹ making them ideal for use within Li – Air cells. However, in these organic aprotic electrolytes, the Li_2O_2 that is produced during the discharge reaction is not soluble which can lead to a build-up of Li_2O_2 on the surface of the cathode. This leads to a reduction in active surface area, eventual electrode passivation and reduces the conductivity.²² These cells are also prone to ignition upon rupturing due to the flammable nature of the solvents used. In the case of carbonate electrolytes, the Li_2O_2 has been seen to react with the solvent resulting in Li_2CO_3 deposition on the carbon electrode. Li_2CO_3 cannot

be oxidised during charge at potentials < 4 V and so in order to initiate the decomposition of this product, the high potentials needed would also likely lead to the decomposition of the electrolyte and the carbon electrode.²³

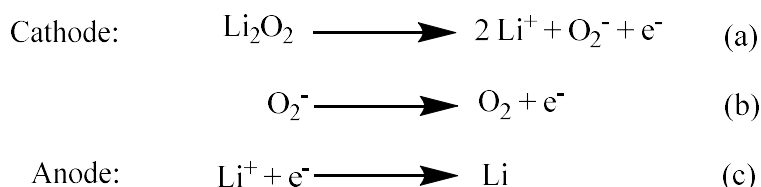
Non – aqueous aprotic Li – Air cells work as a result of two sets of reactions, the discharge reactions **(2)** and the charge reactions **(3)**.

(2)



At the anode, reaction **2(a)** takes place and involves the oxidation of Li. Li⁺ ions diffuse from the anode through the electrolyte towards the cathode. The removed electron travels through the external circuit towards the cathode where it is used to carry out the 1 e⁻ reduction of atmospheric O₂ to superoxide (O₂⁻) as seen in **2(b)**. Two Li⁺ and two O₂⁻ can then undergo a disproportionation mechanism that forms solid Li₂O₂ and O₂ at the cathode surface, shown in **2(c)**. Alternatively, a further reduction of the O₂⁻ can occur to generate the peroxide anion (O₂²⁻) which reacts with two Li⁺ cations to also form Li₂O₂ at the cathode surface, **2(d)**.

(3)



In the case of the charge reaction, most the solid Li₂O₂ found at the cathode is oxidised back to Li⁺ and O₂⁻, shown in **3(a)**. However, not all of the Li₂O₂ is accessible for oxidation, thus

resulting in a compounding pore clogging effect as the cell undergoes further cycling, leading to a loss in conductivity and a decrease in the uptake of oxygen at the cathode during future discharges. Over time, the cathode will become passivated due to the thin film of Li_2O_2 that grows, meaning that all reactivity and function of the cathode is lost and cell death occurs. Meanwhile, at the anode, Li^+ cations are being electrodeposited onto the surface in the form of lithium metal, **3(c)**. However, the lithium is not deposited evenly across the surface and have been found to grow as dendrites that extend into the electrolyte. In the worst case, they will make contact with the cathode leading to a short circuit which could generate enough heat to cause the electrolyte to ignite.¹

Whilst Li – Air cells are an exciting prospect for the future, they have many problems that first need to be overcome before they are viable options for large scale manufacturing. As mentioned, they are intrinsically flawed in the fact that the product, Li_2O_2 , that is responsible for these batteries' high energy, is also the main factor for their failure. On top of this, the increased resistance as a result of the Li_2O_2 is responsible for the large charge overpotential that is observed²⁴, shown in *Figure 4*.

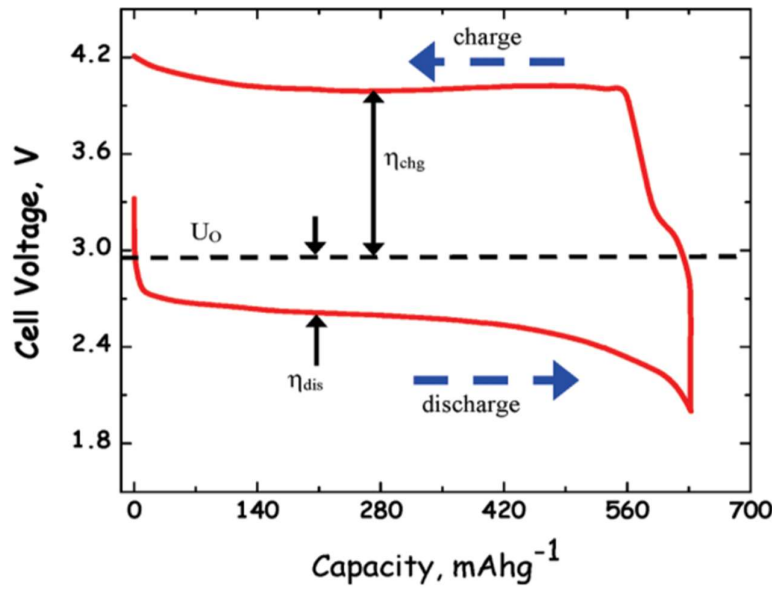


Figure 4 - Discharge / Charge cycle of a Li – Air battery. U_0 is the thermodynamic standard potential of the cell. η_{chg} is the charge overpotential and η_{dis} is the discharge overpotential.²⁴

Li – Air cells have a thermodynamic standard potential, $U_0 = 2.96$ V vs. Li / Li⁺.²⁴ During the discharge, a plateau is observed at approximately 2.7 V vs. Li / Li⁺ with the discharge halting just below 2.1 V vs. Li / Li⁺ as the cathode becomes polarised. As η_{dis} is smaller than U_0 , the discharge provides less energy than thermodynamically expected. On the other hand, η_{chg} is much larger than U_0 meaning that the charge process requires much more energy than thermodynamically expected, thus reducing the overall output and efficiency of the battery.

Battery efficiency can be determined by:

$$(4) \quad \eta_{dis} / \eta_{chg} \times 100$$

In the case of the discharge / charge cycle shown in Figure 4, the cell can be calculated as having an efficiency of 65% ($2.7 / 4.1 \times 100$). This falls far below the value, > 90%, that would be expected of a battery for it to be viable in practical situations.²⁴

2.3 Redox Mediators

A redox mediator is a molecule that is capable of shuttling electrons from an electrode to a substrate and vice versa. In order for a molecule to be a suitable redox mediator, it must be able to be repeatedly oxidised and reduced without any considerable degradation its structure or chemical impact. Ideally, the mediator should be soluble in the electrolyte solution to allow for direct electrochemical contact with the bulk Li_2O_2 . Additionally, the redox mediator must have a redox potential that is more positive than the thermodynamic standard potential for a Li – Air cell (2.96 V)²⁴ but less than the potential measured for the charge reaction (≈ 4 V)²⁴ in order to successfully reduce the charge overpotential that is observed.

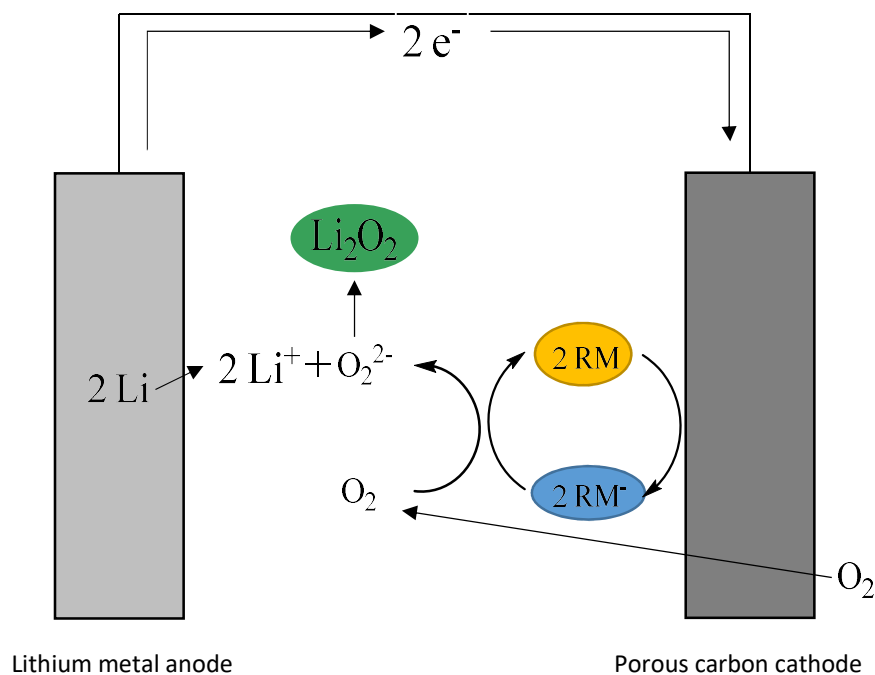
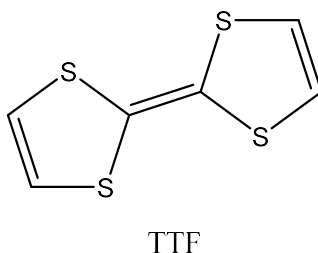


Figure 5 - Diagram showing how a redox mediator promotes Li_2O_2 formation in the electrolyte during the discharge reaction. RM represents redox mediator and $\text{RM}^\bullet$ is the redox mediator in its reduced form.

From the literature²², mediators can be broadly separated into organic mediators and inorganic mediators and then further categorised into oxygen reduction reaction (ORR) mediators (discharge mediators), oxygen evolution reaction (OER) mediators (charge mediators) or dual mediators which can be used for both reactions.

Whilst redox mediators are introduced to improve the cell, there is the chance that additional issues are introduced to an already challenging system.²² Ideally, the mediator should remain localised around the cathode and undergo the reactions with O_2 and Li_2O_2 with the mediator being regenerated each cycle. However, due to a phenomenon known as the shuttle effect, the mediator has a tendency to travel to the anode to complete the regeneration of the mediator, instead of being regenerated as part of the decomposition of Li_2O_2 and regeneration of O_2 .²⁵ This leads to a decrease in battery efficiency and compromises cell cycling performance.²⁶ It is possible to negate this effect by introducing membranes of the sort as seen in the aqueous and solid Li – Air cells which sit between the anode and the electrolyte, however, as previously mentioned, these sorts of barriers negatively impact the cell due to the increase in resistance they cause²⁷. Suitable alternatives include the addition of additives to the electrolyte which promote the formation of an improved SEI upon coming into contact with the anode, with the most common additive being $LiNO_3$.^{28–31}

In 2013, Prof. Peter Bruce and his group reported a new organic OER mediator called Tetrathiafulvalene (TTF).³²



According to Pande and Viswanathan³³, the mediator is positively charged when oxidised and neutral when in its reduced form meaning that the potential of the redox pair can be tuned by using different solvents. This is because the strength of an interaction between a positively charged mediator and the electrolyte is determined by the donor number of the solvent.²⁰

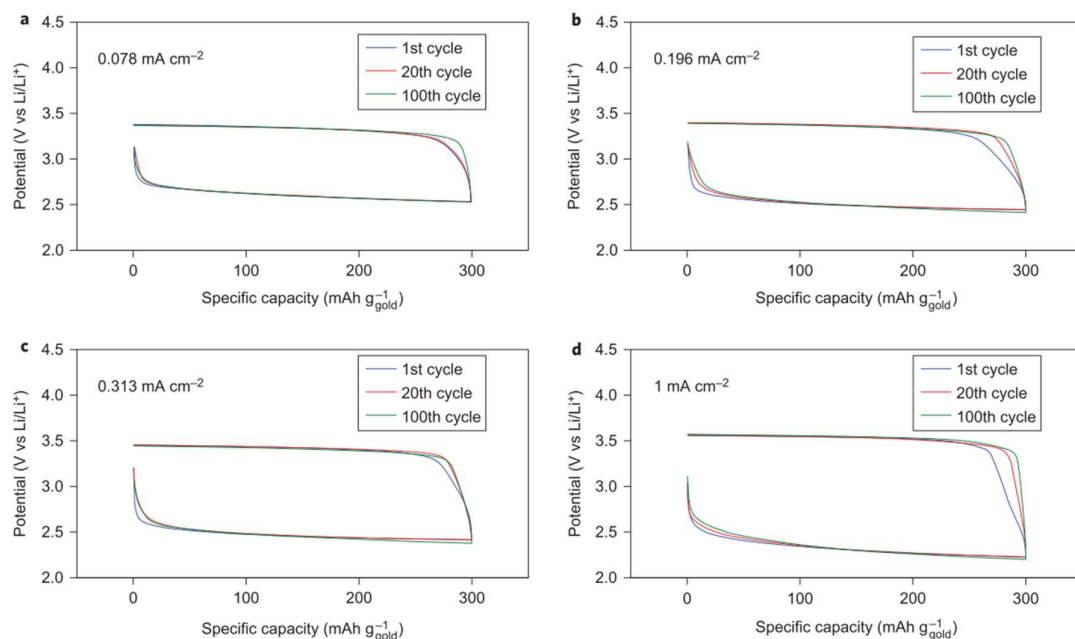


Figure 6 - Cycling stability of Li – Air cells containing TTF as a redox mediator. All four cells used 1 M LiClO₄ with 10 mM TTF in DMSO and a nanoporous gold cathode with LiFePO₄ anode under an O₂ atmosphere.³²

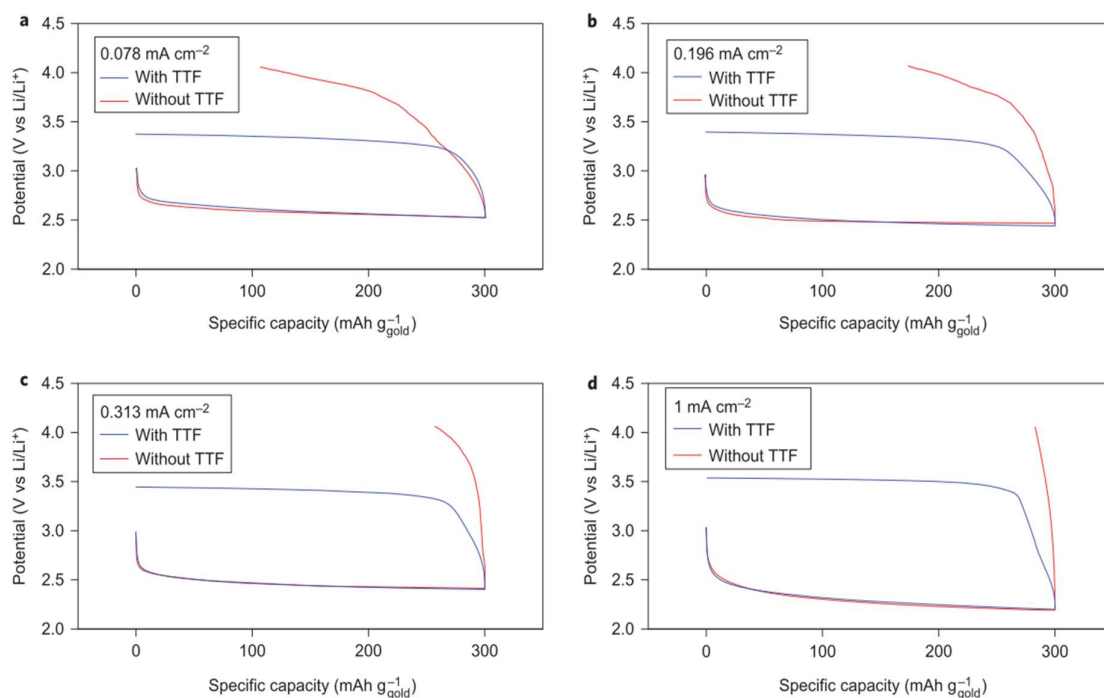


Figure 7 - First cycle discharge / charge curves with (blue) and without (red) TTF acting as a redox mediator. For context, 300 mA h g⁻¹ at gold is roughly equivalent to 3000 mA h g⁻¹ at carbon.³²

In the work published by Bruce et al.,³² they found that cells containing TTF could be cycled 100 times with very little degradation in performance (Figure 6) whilst significantly reducing the overpotential during the charge process (Figure 7).³² As seen in Figure 7, the addition of TTF certainly reduces the charging potential in all four experiments. Not only this, but the redox mediator actually enables the cell to be charged at much higher current densities as shown in cells (c) and (d). Additionally, it can be seen that the TTF has no contribution to the capacity of the cell as it acts solely as an electron – hole shuttle between the cathode surface and Li₂O₂ (Figure 8).^{32,34}

Further work by Zhang et al.³⁵ concluded that with the addition of LiCl as the electrolyte in a cell containing TTF, the mediator was kept in close proximity to the cathode surface. As the TTF is oxidised in the presence of Cl⁻, it begins forming TTF⁺ Cl_x⁻ as a solid that coats the cathode that prevents the shuttle effect from occurring.^{22,35}

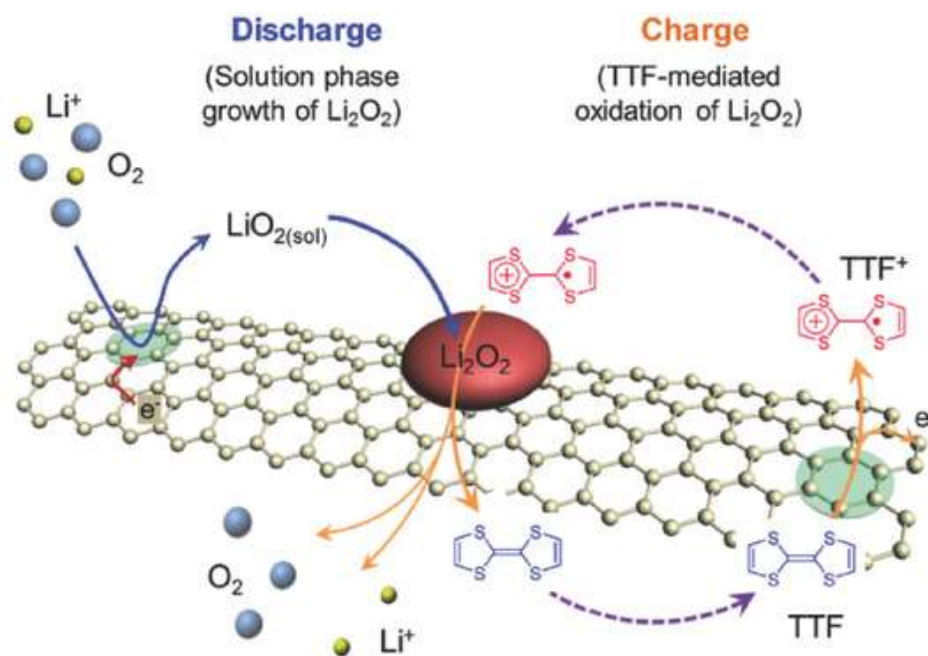


Figure 8 - Illustration of how TTF mediates the OER in Li – Air cells.³⁴

Another example of an OER redox mediator is 2,2,6,6- tetramethylpiperidinyloxy (TEMPO). In work by Janek et al.,³⁶ they showed that the N – O bond in TEMPO can reversibly undergo a one electron oxidation to an oxoammonium cation at 3.74 V vs. Li / Li⁺.^{22,36}

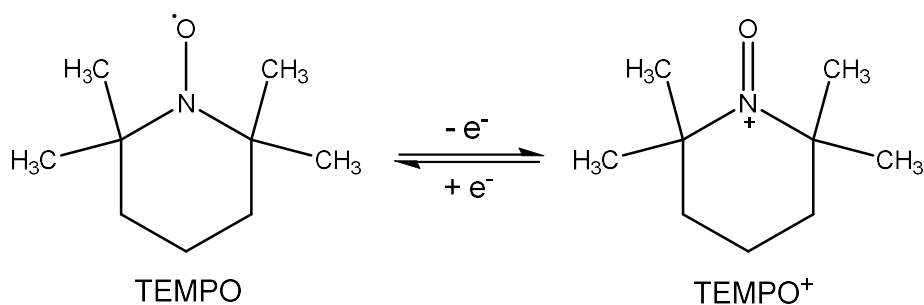


Figure 9 - Schematic showing the change in structure of TEMPO upon being oxidised and reduced.³⁶

The studies by this group showed that the oxidation of TEMPO during the charging of a cell occurs with minimal side reactions, as shown by the ratio between the number of moles of

electrons to moles of oxygen produced, which ideally should equal or be close to $2 e^- / O_2$. In the case of TEMPO, a value of $2.01 e^- / O_2$ was obtained as shown in *Figure 10*.³⁶

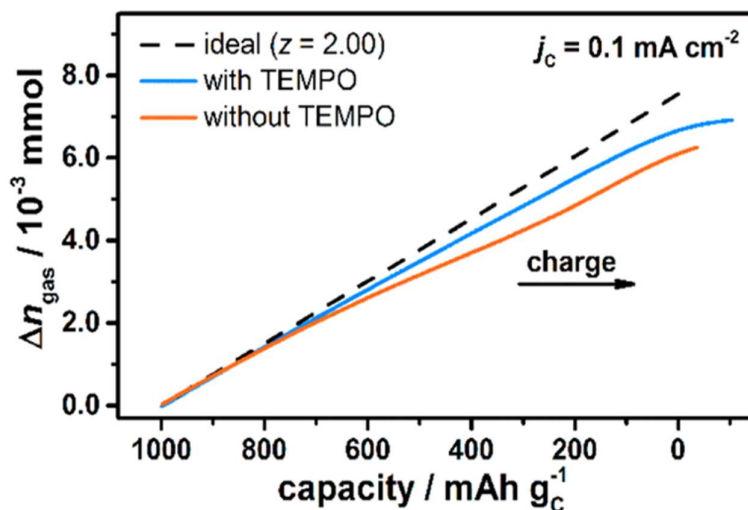


Figure 10 - Plot showing the number of moles of gas vs capacity for a cell with 10 mM TEMPO and 0.1 M LiTFSI in diglyme using a Ketjenblack cathode.³⁶

Figure 9 shows that in the presence of TEMPO, the charge reaction lies much closer to the desired ratio of $2 e^- / O_2$. During the charge reaction, the TEMPO diffuses to the cathode surface where it gets oxidised to TEMPO⁺. The TEMPO⁺ then diffuses to the Li₂O₂ and oxidises it, with the TEMPO⁺ being simultaneously reduced back to TEMPO.³⁶ This cycle is represented visually in *Figure 11*.

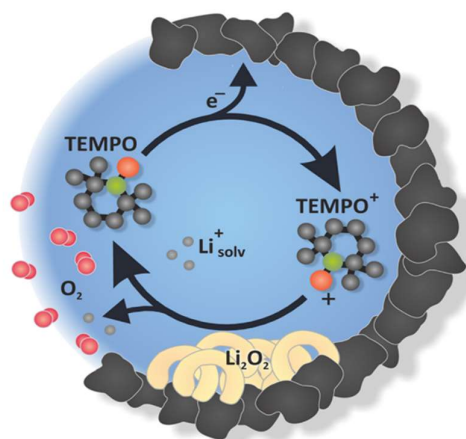


Figure 11 - Proposed cycle of TEMPO/TEMPO⁺ in a Li - Air cell during charging.³⁶

From the data obtained in the work by Janek et al., it can be seen that TEMPO does successfully reduce the overpotential in the cell both during the first cycle (Figure 12a) and the full cycle (Figure 12b). However, the addition of TEMPO in the full cycle cell leads to a loss of capacity compared to the full cycle cell without TEMPO. They suggest that the decrease in capacity is due to the second reduction step from superoxide to Li₂O₂.³⁶

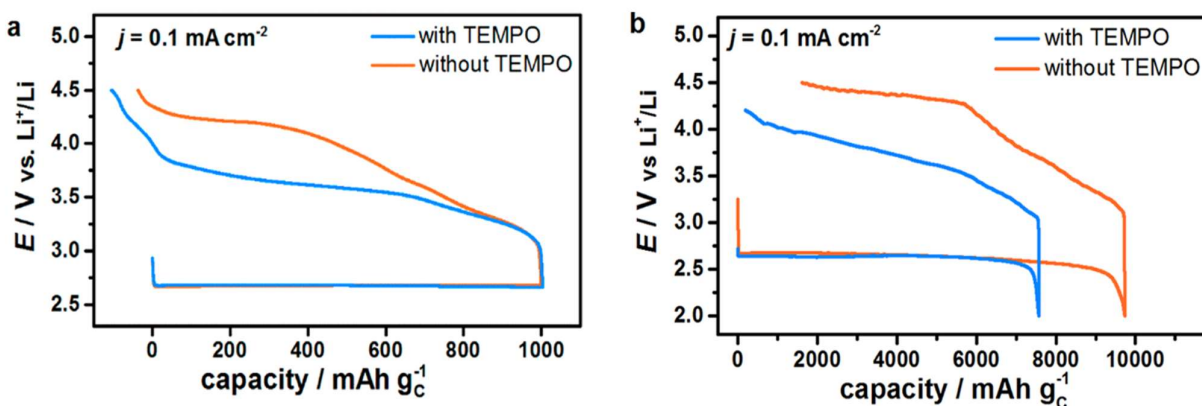


Figure 12 - (a) First cycle discharge / charge plot for Li - Air cell with 10 mM TEMPO (blue) and without TEMPO (orange) and (b) Full cycle discharge / charge plot for Li-Air cell with 10 mM TEMPO (blue) and without TEMPO (orange).³⁶

In the case of TEMPO, the degree of reduction in the overpotential is dependent on the redox potential of the nitroxide group. This potential for modification could allow the opportunity for a more effective TEMPO – based OER mediator. Work by Hase et al.³⁷ has shown that the

presence of a methoxy group in place of one of the methyl groups lowers the nitroxide redox potential to a value of 3.5 V vs. Li / Li⁺³⁷ down from 3.74 V vs Li / Li^{+22,36} seen with unmodified TEMPO.

One of the most studied groups of organic ORR mediators are quinones^{22,38,39} (*Figure 13*).

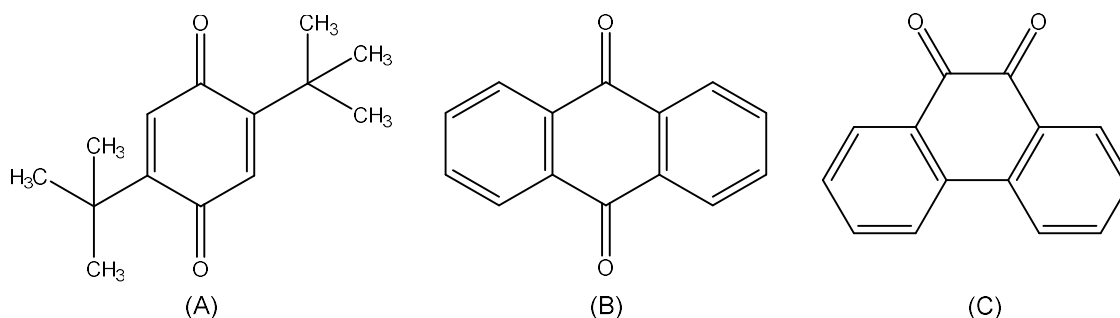


Figure 13 - Three examples of quinone – based molecules from the literature.^{22,39} (A) = 2,5-di-tert-butyl-1,4-benzo-quinone (DBBQ), (B) = 9,10-anthraquinone (AQ), (C) = 9,10-phenanthrenequinone (PAQ).

These molecules specifically act as discharge mediators and have promise due to their preferential reduction of oxygen to superoxide. A quinone with a more positive oxidation potential than the potential for O₂ to Li₂O₂ leads to the ORR still proceeding, albeit without any solid Li₂O₂ formation or deposition on the electrode surface.²² As stated by Bruce et al.,⁴⁰ when using DBBQ, the superoxide intermediate is never formed and is replaced with LiDBBQO₂. Li₂O₂ is found to form as toroids (doughnut like shapes) instead of forming as the thin film on the electrode surface as would normally be expected.⁴⁰ Shown in *Figure 14*, the LiDBBQO₂ intermediate is lower energy than the usual superoxide intermediate that forms. This increase in stability of the intermediate is the energetic driving force behind the preferred alternative reaction route. The introduction of DBBQ to the cell results in a massive increase in capacity at a variety of current densities, shown in *Figure 15*. For example, a cell discharged at 0.1 mA cm⁻² without DBBQ had a capacity of approximately 11 mAh m⁻² whereas

with DBBQ, the cell discharged at the same current density had a capacity of nearly 450 mAh

m^{-2} .⁴⁰

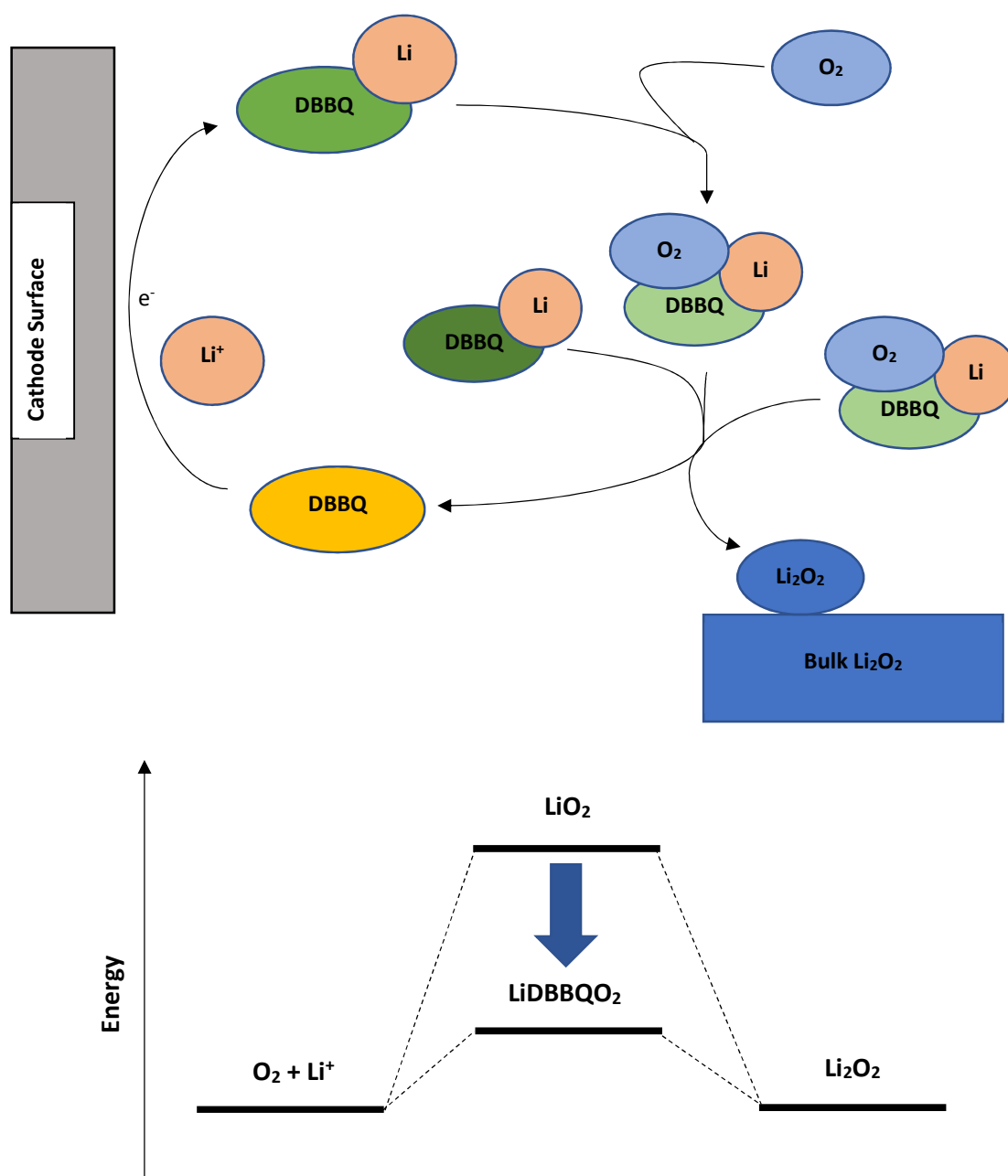


Figure 14 - Illustration of the cyclical reaction involving DBBQ (top). Energy diagram showing the difference in energy between the intermediates in cells with DBBQ (LiDBBQO_2) and without DBBQ (LiO_2) present (bottom).⁴⁰

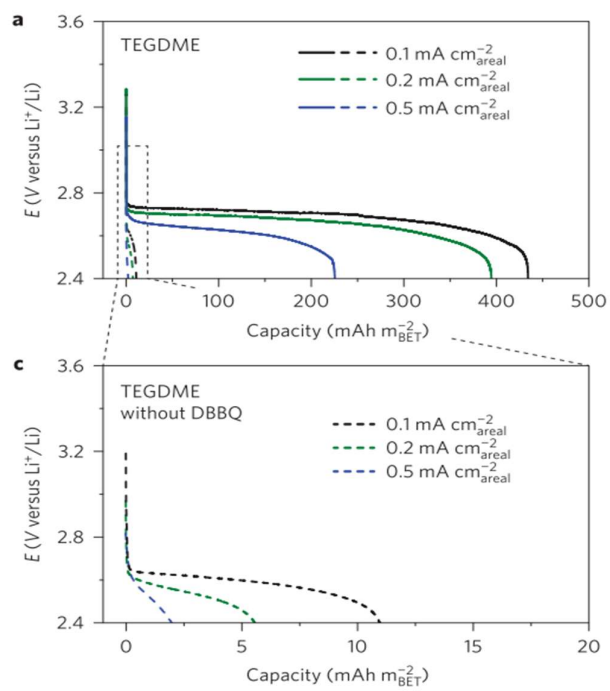


Figure 15 - Discharge curves of a Li - Air cell with a gas diffusion layer (GDL) cathode using 1 M LiTFSI in TEGDME with DBBQ (solid lines) and without DBBQ (dashed lines).⁴⁰

2.4 Polyoxometalates

Polyoxometalates (POMs) are a large group of compounds that comprise clusters of group 5 and 6 transition metal oxides in their highest oxidation states with the general formula $\{MO_x\}_n$ where most commonly, $M = Mo, W, V$.⁴¹ The metal oxide fragments self – assemble to form large clusters and can be classified as i) isopolyoxometalates (*Figure 16 (a) and (b)*), consisting solely of metal oxide clusters in varying numbers and ii) heteropolyoxometalates (*Figure 16 (c) and (d)*) which self – assemble around central heteroatom such as phosphorus or silicon.⁴² The sheer variety of POMs that can be made is demonstrated in *Figure 17*.

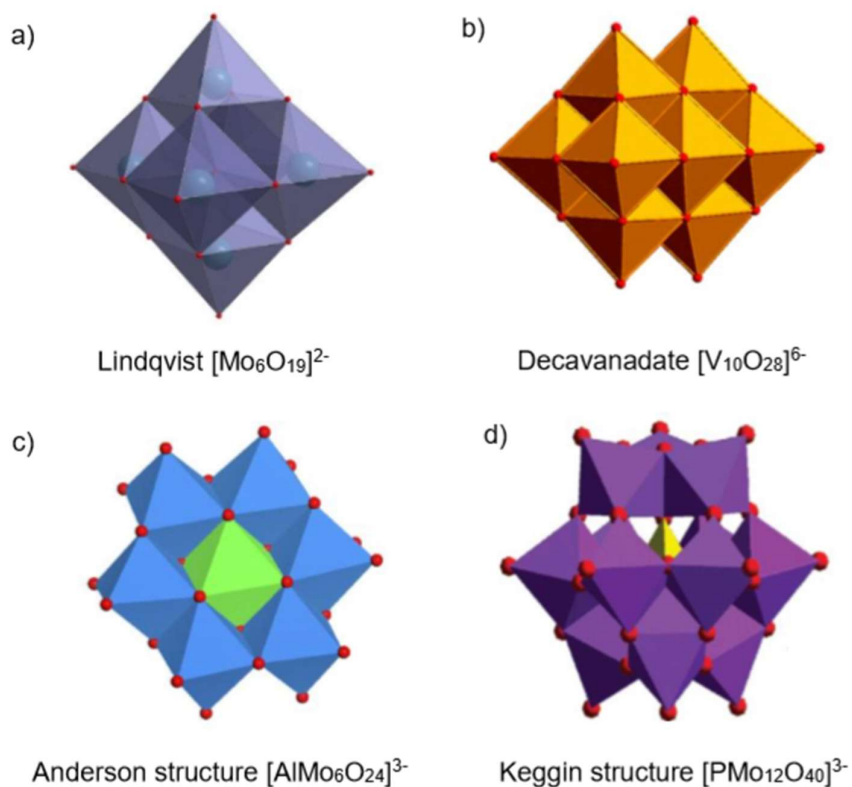


Figure 16 - Examples of isopolyoxometalates (a)⁴³ and (b)⁴⁴ and heteropolyoxometalates (c)⁴⁵ and (d).⁴⁶

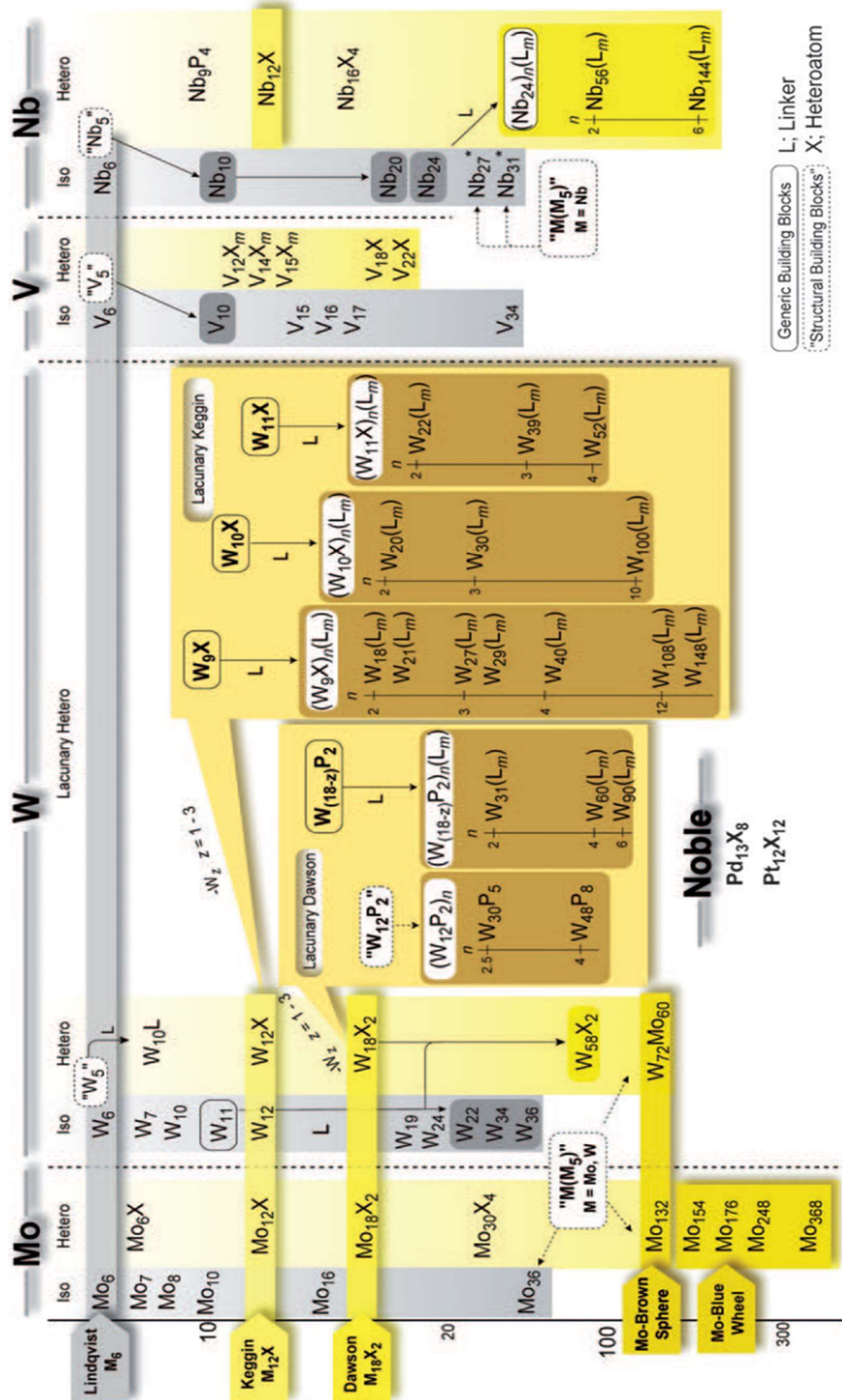


Figure 17 - Schematic showing the classification of POMs.⁴¹

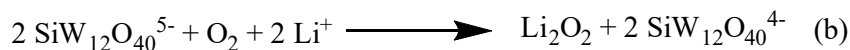
In recent years, POMs have garnered increased attention due to how variable their properties can be. They can have multiple, multi – electron redox processes and are able to undergo rapid electron transfers without any loss to structure.⁴⁷ By substituting individual metal atoms for different metal atoms or by altering the central heteroatom, it is possible to alter their redox potentials, thermal stability and conductivity of the POM. In addition to this, it has also been found that exchanging the counterion associated with the POM can alter the electrochemical properties of the molecule.⁴⁸ Due to their tunability, there is genuine interest in their role as catalysts for a variety of applications ranging from the decontamination of water⁴⁹ to their use in selective hydroxylation⁵⁰ and epoxidation⁵¹ reactions. For example, POMs can be used to support a catalyst material such as gold nanoparticles that are able to catalyse the epoxidation reactions of olefins as reported by Tebandeke et. al⁵². Additionally, POMs can be modified by removing a metal oxide cluster or by adding organic groups to create sites that can catch and coordinate heavy metal atoms making them useful in the process of water decontamination. Most appropriately to this work, their ability to accept and donate multiple electrons without any negative impact to structure or reactivity makes them fantastic electron shuttles for use in electrocatalysis.

2.5 POMs as Redox Mediators

The main reason behind the thinking of using POMs as redox mediators is their tuneable and multiple redox processes and their increased chemical and structural stability compared to organic redox mediators. In work by Homewood et al.,⁵³ they indicated that the Keggin POM $\text{SiW}_{12}\text{O}_{40}^{4-}$ can be implemented in Li – Air cells to increase their discharge capacity and potential by facilitating the reduction of O_2 to O_2^- away from the cathode surface, thus

initiating the formation of Li_2O_2 in the electrolyte instead.⁵³ In their work, they put forward the proposed reaction mechanism.

(5)



In reaction 5(a), the POM undergoes a single electron reduction at the cathode surface. The reduced POM then diffuses to the electrolyte where two reduced POM molecules reduce O_2 via a single electron reduction to O_2^- followed by another single electron reduction to O_2^{2-} , which then combines with two Li^+ cations to form Li_2O_2 and the original POM species, shown in 5(b).⁵³ The data presented by Homewood et al.⁵³ is shown in Figure 17.

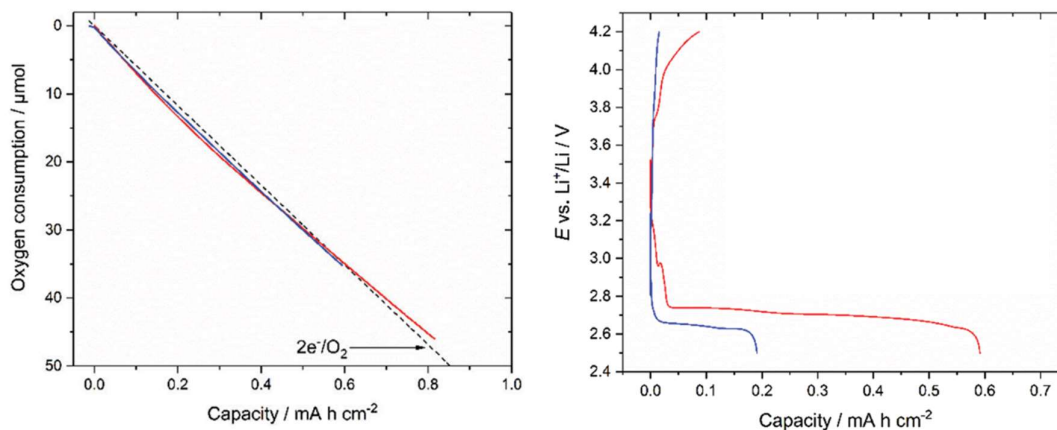


Figure 18 - (a) Plot showing the ratio of the number of moles of O_2 to the number of electrons during discharge with the POM (red) and without the POM (blue). The dashed line indicates the ideal $2\text{e}^-/\text{O}_2$ ratio. (b) shows the charge / discharge curves for a Li – Air with (red) and without (blue) POM. Both cells contained 50 mM $\text{TBA}_4\text{SiW}_{12}\text{O}_{40}$ with 1 M LiTFSI in DMSO using a carbon cloth cathode.⁵³

The data presented shows that the addition of the POM to the cell results in a significant increase in the capacity of the cell, with very little deviation from the ideal ratio of e^- / O_2 meaning that there are very few side reactions taking place during discharge. However, the POM used has no effect on the overpotential of the cell during charging⁵³ but does bring the

discharge potential more positive and closer to the thermodynamic potential at 2.96 V vs. Li / Li⁺.²⁴ In order for this POM to be able to act as a dual mediator for both the charge and discharge processes, it would need to have a redox process at a potential more positive than 2.96 V vs Li / Li⁺ in order to successfully catalyse the decomposition of the Li₂O₂. This could theoretically be achieved by substituting one of the tungsten atoms in the POM with another metal that has a more positive redox potential, such as vanadium or molybdenum.^{54–56} The idea of modifying the redox potentials of the POMs was used in this project.

3. Project Aims

The aim of this project is to develop a group of POMs that can work as redox mediators in Li – air cells to increase the discharge capacity and reduce the charge overpotential of the cell. This will be achieved by synthesising POMs based around the Mo_{12} and W_{12} Keggin structure (*Figure 15d*) that have been modified by the substitution of V into the POM framework with the hope that there will be redox processes that overlap well with the potentials of oxygen reduction and Li_2O_2 oxidation in non – aqueous media. By varying the base metal of the POM (W and Mo) and the number of vanadium atoms in the POM, the redox chemistry of the POM will be shifted. These shifts and the overlap with the Li – air reactions will be characterised using cyclic voltammetry.

Each POM will initially be characterised using cyclic voltammetry, ^{31}P NMR, infra – red and UV – Vis spectroscopy. With the POMs characterised, suitable candidates will be implemented into cells for galvanostatic measurements to look for any impact the POMs may have on the capacity and the overpotential of the cell with the best performing POM being used for pressure measurements. Using the pressure data, the ratio of number of moles of electrons to the number of moles of oxygen consumed / generated will be calculated to measure the efficacy of the cell, compared to a cell containing no POM.

Additionally, after discharging the POM containing cells, the cathodes will be removed without exposure to atmospheric air and SEM and FT – IR of the cathodes will be carried out. The SEM will provide the ability to detect any formation of Li_2O_2 clusters on the electrode surface compared to the thin film of peroxide that would be expected with the unmediated cell. The FT -IR data will give important information about both the presence of the peroxide and whether any electrolyte decomposition is present, suggested by any presence of a C=O band on the spectrum.

4. Experimental

All solvents and reagents were purchased from Sigma Aldrich, Fischer Scientific or Acros Organics and were used without any further purification. 100 mesh per inch stainless steel AISI316L woven mesh was purchased from Advent Research Materials. ^{31}P NMR was carried out using a Bruker Ascend 400 NMR Spectrometer. IR spectroscopy measurements were taken using a Bruker Alpha FT-IR with an ATR attachment.

4.1 Synthesis of $(\text{TBA})_4[\text{PW}_{11}\text{VO}_{40}]$ (I)

$\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (7.88 g, 23.9 mmol) and Na_2HPO_4 (0.307 g, 2.16 mmol) were dissolved in stirred deionised water (40 °C). The solution was then heated (85 °C) for 1 h. The solution was adjusted to pH 4.8 using concentrated HNO_3 then stirred for 15 mins and then cooled to room temperature. Once cooled, acetone (200 mL) was added. The solution was then evaporated under reduced pressure to yield $\text{Na}_7[\text{PW}_{11}\text{O}_{39}]$ (8.30 g) as a powder. The collected powder was suspended in acetonitrile and was added to excess tetra-n-butylammonium bromide (TBABr) (5.00 g) dissolved in deionised water (60 mL) at pH 4.8. A cloudy precipitate formed and was collected and dried via suction filtration to yield $(\text{TBA})_4\text{H}_3[\text{PW}_{11}\text{O}_{39}]$ (8.28 g, 105 %) as a white powder. $(\text{TBA})_4\text{H}_3[\text{PW}_{11}\text{O}_{39}]$ (1.94 g, 0.531 mmol) was dissolved in acetonitrile (50 mL). NaVO_3 (0.0647 g, 0.531 mmol) was dissolved in stirred, hot (80 °C) deionised water (20 mL). Once dissolved, the NaVO_3 solution was acidified to pH 4.8 which turned the solution a bright orange colour. The orange solution was added dropwise to the acetonitrile solution. Upon complete combination of the solutions a yellow colour was observed and a yellow precipitate formed. The yellow solid was collected via suction filtration and washed with water (2 x 20 mL) and ethyl acetate (2 x 20 mL) to yield the final product as a fine yellow powder (1.15 g, 58 %). The final product was dissolved in acetonitrile and left to crystallise

uninterrupted in a cool, dark cupboard to yield bright yellow crystals. ^{31}P NMR – 400 MHz @ 298 K (δ , DMSO – d_6) ppm: -15.34. IR (ATR) cm^{-1} : 2950 (C-H stretch, w), 1075 (P-O_a stretch, s), 950 (W=O_d stretch, s), 800 (W-O_b-W, b).

4.2 Synthesis of (TBA)₄[PMo₁₁VO₄₀] (II)

Na₂HPO₄ (0.350 g, 2.47 mmol) and NaVO₃ (0.300 g, 2.46 mmol) were dissolved in stirred, hot (80 °C) deionised water (50 mL). Once the colourless solution had cooled, it was acidified with concentrated H₂SO₄ (approx. 5 mL) until the solution was a red colour. Na₂MoO₄·2H₂O (6.65 g, 27.5 mmol) was dissolved in deionised water (50 mL) and was added to the red solution, which turned the solution orange. To the orange solution, more H₂SO₄ (25 mL) was added and stirred vigorously for 15 mins. After stirring, excess TBABr (5.00 g) was added and a clumpy precipitate formed. The precipitate was filtered and dried via suction filtration and the orange solid was washed with deionised water (3 x 20 mL) and diethyl ether (3 x 20 mL) to yield a fine, light orange powder as the final product (3.93 g, 58 %). The final product was dissolved in acetonitrile and left to crystallise uninterrupted in a cool, dark cupboard to yield bright orange crystals. ^{31}P NMR – 400 MHz @ 298 K (δ , DMSO – d_6) ppm: -3.85. IR (ATR) cm^{-1} : 2950 (C-H stretch, w), 1050 (P-O_a stretch, s), 925 (Mo=O_d stretch, s), 750 (Mo-O_b-Mo, b).

4.3 Synthesis of (TBA)₅[PMo₁₀V₂O₄₀] (III)

Na₂HPO₄ (0.370 g, 2.61 mmol) and NaVO₃ (1.01 g, 8.28 mmol) were dissolved in stirred, hot (80 °C) deionised water (50 mL). Once the colourless solution had cooled, it was acidified with concentrated H₂SO₄ (approx. 5 mL) until the solution was a dark red colour. Na₂MoO₄·2H₂O (5.99 g, 24.8 mmol) was dissolved in water (50 mL) and was added to the red solution, which turned the solution orange. To the orange solution, more H₂SO₄ (20 mL) was added and stirred vigorously for 15 mins. After stirring, excess TBABr (5.00 g) was added and a clumpy

precipitate formed. The precipitate was filtered and dried via suction filtration and the orange solid was washed with deionised water (3 x 20 mL) and diethyl ether (3 x 20 mL) to yield a fine, dark orange powder as the final product (1.1 g, 14 %). The final product was dissolved in acetonitrile and left to crystallise uninterrupted in a cool, dark cupboard to yield dark brown crystals. ^{31}P NMR – 400 MHz @ 298 K (δ , DMSO – d_6) ppm: -4.11. IR (ATR) cm^{-1} : 2950 (C-H stretch, w), 1050 (P-O_a stretch, s), 900 (Mo=O_d stretch, s), 750 (Mo-O_b-Mo, b).

4.4 Reference Electrode and Electrolyte Preparation

All glassware used was washed with acetone and Milli-Q water and was dried in a ThermoScientific VACUTherm oven (vacuum oven) at 60 °C for 3 h. The three POMs were dried under vacuum in a Büchi Glass Oven B-585 (Büchi tube) at 80 °C for 3 days to ensure complete dryness before being transferred into the glovebox. Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and TBAPF₆ were dried in a similar manner, however at a higher temperature of 120 °C. TEGDME was distilled and subsequently dried using molecular sieves. The glassy carbon (GC) working electrode was first washed with acetone and Milli-Q water, then polished using a slurry of 0.3 μm alumina powder with Milli-Q water, then was washed again with more Milli-Q water before the electrode was dried in a vacuum oven at 60 °C under vacuum for 1 h. The platinum wire (Pt) counter electrode was washed with acetone and then Milli-Q water, before being annealed over a flame and then placed in a vacuum oven at 60 °C under vacuum for 3 h.

The LiFePO₄ (LFP) reference electrode was made by spreading a putty consisting Super P Carbon, LiFePO₄ and 10% PTFE in water solution, in a 8:1:10 weight ratio respectively onto stainless steel mesh. To the combined materials, a minimum amount of IPA was added to bind the mixture. The putty was then spread onto the end of a thin strip of stainless-steel mesh

with dimensions 5 mm x 150 mm. The end of the mesh was folded back on itself, encasing the spread putty between two layers of mesh. The folded tip was then pre-charged in a solution of glacial acetic acid (1.5 mL) and H_2O_2 (3.6 mL) in Milli-Q water (250 mL) for 12 h. The pre-charged LFP was washed with ethanol and then water before being dried under vacuum in Büchi tube at 120 °C for 12 h. Once transferred inside the glovebox, the LFP mesh was then housed inside a pipette with a glass frit in the end that was held in place by heat shrink wrap. The pipette was then filled enough to cover the LFP putty, with a solution of 1 M TBAClO_4 and 0.1 M LiClO_4 in DMSO and a length of copper wire was tightly wrapped around the opposite end of the steel mesh. When not being used, the reference electrode was stored in a tall vial with a small amount of the reference solution in the bottom.

4.5 Cyclic Voltammetry Experiments Under N_2

All preparation of solutions and experiments were carried out inside a MBraun MB200B Eco glovebox under an N_2 atmosphere and measurements were taken using a BioLogic BP-300 potentiostat. Using the dried LiTFSI, four solutions of 0.25 M LiTFSI in tetraethylene glycol dimethyl ether (TEGDME) were made, with stirring. To three of these solutions, one of the three different dried POMs was added to make a POM concentration of 10 mM. Overnight stirring and heating at 40 °C was required for the POM to dissolve. At this point, there were four different solutions; 0.25 M LiTFSI in TEGDME, 0.25 M LiTFSI with 10 mM **(I)** in TEGDME, 0.25 M LiTFSI with 10 mM **(II)** and 0.25 M LiTFSI with **(III)** in TEGDME. A small amount of a solution (3 mL) was measured into the glass cell and the dried GC working electrode, Pt counter electrode and the prepared LFP reference electrode were secured in place, ensuring that enough of each electrode was submerged in the solution and that none of the electrodes were in contact with one another. The resistance of the solution was accounted for by running

an electrochemical impedance measurement, with the result being used as the IR correction value. Measurements for each solution were then taken between 2 V and 4.5 V vs. Li/Li⁺ with a scan rate of 100 mV s⁻¹.

4.6 Cyclic Voltammetry Experiments Under O₂

All preparation of solutions and experiments were carried out inside a MBraun MB200B Eco glove box under an N₂ atmosphere and measurements were taken using a BioLogic BP-300 potentiostat. Using the dried LiTFSI, four solutions of 0.25 M LiTFSI in TEGDME were made, with stirring. To three of these solutions, one of the three different dried POMs was added to make a POM concentration of 10 mM. Overnight stirring and heating at 40 °C was required for the POM to dissolve. At this point, there were four different solutions; 0.25 M LiTFSI in TEGDME, 0.25 M LiTFSI with 10 mM **(I)** in TEGDME, 0.25 M LiTFSI with 10 mM **(II)** and 0.25 M LiTFSI with **(III)** in TEGDME. A small amount of a solution (3 mL) was measured into the 5-necked glass cell and the dried GC working electrode, Pt counter electrode and the prepared LFP reference electrode were secured in place, ensuring that enough of each electrode was submerged in the solution and that none of the electrodes were in contact with one another. The resistance of the solution was accounted for by running an electrochemical impedance measurement, with the result being used as the IR correction value. With the electrodes in place, a gas bubbler and an outlet line were fitted in the two remaining slots of the flask. They were then connected to an external gas line that used N5 purity O₂ stored outside the glovebox. Once connected, the solution was bubbled with O₂ for 10 mins, ensuring the bubbling was halted before the measurement was taken. Measurements for each solution were then taken between 1 V and 5 V vs. Li/Li⁺ with a scan rate of 100 mV s⁻¹.

4.7 Preparation of Materials for Galvanostatic Cycling of Li – Air Cells

Super P carbon was used as the cathode material in the cells. The super P was mixed with 10 % PTFE solution in a 9:1 ratio with minimum IPA acting as a binder again. The stainless steel mesh was punched into 12 mm wide disks and washed with acetone and Milli-Q water, with the disks subsequently dried in a vacuum oven at 60 °C for 12 h. The super P putty was then spread onto the stainless steel disks with a mass loading of approximately 4 mg cm⁻². The coated steel disks were then dried in a Büchi tube under vacuum at 120 °C for 12 h. Glass fibre separators were purchased from GE Healthcare and then punched into 12 mm disks without any washing and were dried in a Büchi tube under vacuum at 300 °C for 12 h. Free-standing LFP was used as the anode in the cells. The LFP was made using the same method as the reference electrode, however, instead of being spread onto stainless steel mesh, the putty was rolled to a thickness of 350 µm using a mechanical roller. The rolled LFP was then cut into 12 mm disks using lever-action punch. The LFP disks were then pre-charged in a solution of glacial acetic acid (1.5 mL) and H₂O₂ (3.6 mL) in Milli-Q water (250 mL) for 15 mins. The pre-charged LFP disks were then washed with Milli-Q water and dried in a Büchi tube under vacuum at 120 °C for 12 h.

Cell housing components were purchased from Swagelok. Any metal components of the cell were washed with hot soapy water, followed by acetone, followed by Milli-Q water and were then dried in a vacuum oven at 60 °C for 3 h. Finally, 0.025 mm thick PTFE film was cut into strips with dimensions 25 mm x 40 mm. The PTFE was washed and dried using the same method as the metal parts but in a separate beaker to avoid any crumpling of the film. Inside the glovebox, four solutions of 0.25 M LiTFSI in TEGDME were made, with stirring. To three of these solutions, one of the three different dried POMs was added to make a POM

concentration of 10 mM. Overnight stirring and heating at 40 °C was required for the POM to dissolve. At this point, there were four different solutions; 0.25 M LiTFSI in TEGDME, 0.25 M LiTFSI with 10 mM **(I)** in TEGDME, 0.25 M LiTFSI with 10 mM **(II)** and 0.25 M LiTFSI with **(III)** in TEGDME.

4.8 Galvanostatic Cycling of Li-Air Cells

All cells were prepared inside an MBraun MB200B Eco glovebox under an N₂ atmosphere. All measurements were carried out outside the glovebox on the bench using an Ivium OctoStat30. The PTFE film was wrapped around the central part of the cell to reduce the risk of shorting. The cell was constructed by sandwiching 1 x LFP disk, 2 x GFS and 1 x Super P on mesh disk between a solid steel rod and the hollow steel tube responsible for oxygen delivery to the electrodes. Before the electrodes were encapsulated, 200 µL of electrolyte solution was added. The hollow tube was then carefully inserted, avoiding any crumpling of the PTFE film, into the cell and tightened in place to ensure no leakage was possible. The whole cell was then connected to a gas line fitted with N5.0 purity O₂. The cell was purged with O₂ for approximately 5 mins before being sealed off to any external atmosphere. The cells were then removed from the glovebox and connected to the Octostat. All cells were set up to record a 1 h open cell potential (OCV) measurement before they started discharging and charging. The cells were set up to discharge at one of three current densities (50 µA cm⁻², 100 µA cm⁻², 200 µA cm⁻²) and a potential limit of -1.2 V was established. The cells were charged at the same current densities and had a potential limit of 1 V.

4.9 Preparation for Galvanostatic Cycling of Li-Air Cells with Pressure Sensor Measurements

Super P carbon was used as the cathode material in the cells. The super P was mixed with 10 % PTFE solution in a 9:10 ratio with minimum IPA acting as a binder again. The stainless steel mesh was punched using a levered punch into 24 mm wide disks and washed with acetone and Milli-Q water, with the disks subsequently dried in a vacuum oven at 60 °C for 12 h. The super P putty was then spread onto the stainless steel disks with a mass loading of approximately 4 mg cm⁻². The coated steel disks were then dried in a Büchi tube under vacuum at 120 °C for 12 h. Glass fibre separators (GFS) were cut with a hand punch into 24 mm disks without any washing and were dried in a Büchi tube under vacuum at 300 °C for 12 h. Free-standing LFP was used as the anode in the cells. The LFP was made using the same method as the reference electrode, however, instead of being spread onto stainless steel mesh, the putty was rolled to a thickness of 350 µm using a mechanical roller. The rolled LFP was then cut into 24 mm disks using a hand punch. The LFP disks were then pre-charged in a solution of glacial acetic acid (1.5 mL) and H₂O₂ (3.6 mL) in Milli-Q water (250 mL) for 15 mins. The pre-charged LFP disks were then washed with Milli-Q water and dried in a Büchi tube under vacuum at 120 °C for 12 h.

Cell housing components were both purchased from Swagelok. Any metal components of the cell were washed with hot soapy water, followed by acetone, followed by Milli-Q water and were then dried in a vacuum oven at 60 °C for 3 h. Finally, 0.127 mm thick PTFE film was cut into strips with dimensions 20 mm x 75 mm. The PTFE was washed and dried using the same method as the metal parts but in a separate beaker to avoid any crumpling of the film. Inside the glovebox, four solutions of 0.25 M LiTFSI in TEGDME were made, with stirring. To three of these solutions, one of the three different dried POMs was added to make a POM

concentration of 10 mM. Overnight stirring and heating at 40 °C was required for the POM to dissolve. At this point, there were four different solutions; 0.25 M LiTFSI in TEGDME, 0.25 M LiTFSI with 10 mM **(I)** in TEGDME, 0.25 M LiTFSI with 10 mM **(II)** and 0.25 M LiTFSI with **(III)** in TEGDME.

4.10 Galvanostatic Cycling of Li-Air Cells with Pressure Sensor Measurements

All cells were prepared inside an MBraun MB200B Eco glovebox under an N₂ atmosphere. All measurements were carried out outside the glovebox using an Ivium OctoStat30 wired into in a LabCold incubator at 20 °C. The PTFE film was wrapped around the bottom half of the cell to reduce the risk of shorting. The cell was constructed by sandwiching 1 x LFP disk, 2 x GFS and 1 x Super P on mesh disk between the inside of the bottom half of the cell and two stainless steel rings. Before the electrodes were encapsulated, 800 µL of electrolyte solution was added. The oxygen delivery components were then placed on top of the steel rings, avoiding any crumpling of the PTFE film and was then tightened in place to ensure there was no leakage neither in nor out. The whole cell was then connected to a gas line fitted with N5.0 purity O₂. The cell was purged with O₂ for approximately 10 mins before being sealed off to any external atmosphere. The cells were then removed from the glovebox and connected to the Octostat. The pressure sensor was connected to the Octostat and its parameters were set according to the range of the sensor. All cells were set up to record a 10 h open cell potential (OCV) measurement before they started discharging and charging. The cells were set up to discharge at one of three current densities (50 µA cm⁻², 100 µA cm⁻², 200 µA cm⁻²) and a potential limit of -1.2 V was established. The cells were charged at the same current densities and had a potential limit of 1 V. After the cell had cycled, the pressure cell was calibrated to calculate the head space within the cell.

5. Results and Discussion

Three POMs were successfully synthesised, $(\text{TBA})_4[\text{PW}_{11}\text{VO}_{40}]$, $(\text{TBA})_4[\text{PMo}_{11}\text{VO}_{40}]$ and $(\text{TEA})_5[\text{PMoV}_2\text{O}_{40}]$ following the methods mentioned previously. The compounds were characterised by ^{31}P NMR spectroscopy which in the case of each POM, presented a single sharp peak indicating a single phosphorus environment located at the centre of each POM molecule. The two molybdenum-based POMs, $(\text{TBA})_4[\text{PMo}_{11}\text{VO}_{40}]$ (-3.85 ppm) and $(\text{TEA})_5[\text{PMoV}_2\text{O}_{40}]$ (-4.11 ppm) have chemical shifts just over 10 ppm more positive than $(\text{TBA})_4[\text{PW}_{11}\text{VO}_{40}]$ (-15.34 ppm). This is due to there being much less electron density surrounding the central phosphorus atom with the Mo POMs vs. the W POM, resulting in more deshielded P nuclei in the Mo POMs. Some smaller signals were also observed close the main peak, however, after recrystallisation of the POM, the subsidiary peaks were much less apparent suggesting that these peaks could likely be attributed to phosphorus containing impurities such as fragmented metal oxide assemblies that were removed during the recrystallisation process.

Attenuated Total Reflectance (ATR) infra – red spectroscopy was used to provide confirmation of the presence of the important bonds associated with POMs. Based on the IR spectrum (*Figure 19*), there is a small shift between the $\text{W-O}_d\text{-W}$ (800 cm^{-1}) and $\text{Mo-O}_d\text{-Mo}$ (750 cm^{-1}) bending modes. This shift is due to the fact that the W-O bond is stronger than the Mo-O bond.

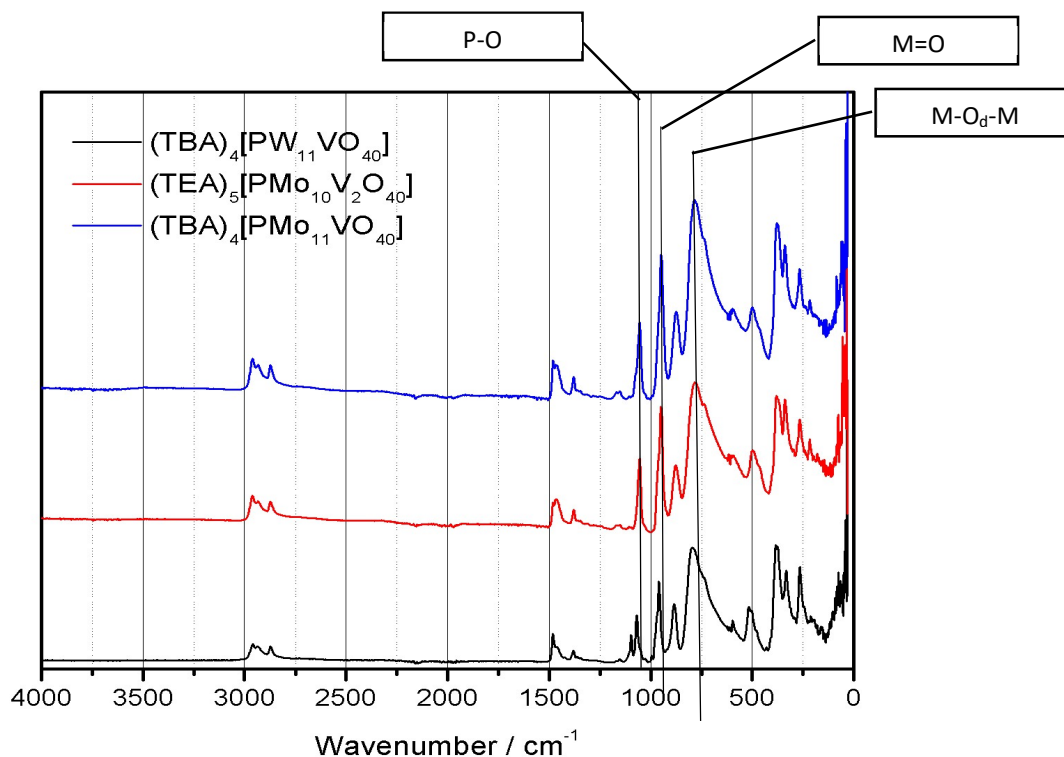


Figure 19 - ATR FT - IR spectra of the three POMs synthesised with the notable POM peaks highlighted

Ideally, it would have been appropriate to characterise the POMs further through the use of mass spectrometry. However, due to restrictions put in place by the analytical services team that specifically state TBA salts cannot be put through the electrospray ionisation MS (ESI-MS) meant that this method was not possible to be used in this case. They have found that the TBA counterion has a tendency to linger in the machine and potentially contaminate further samples taken, which is not a huge problem for other POM measurements due to the POMs having such high molecular weights but can become particularly problematic for other researchers who may want characterise their organic compounds.

5.1 Electrochemical Characterisation

Before implementing the POMs into live cells, it was important to understand if they would be suitable candidates to mediate the ORR and OER reactions. To do this, cyclic voltammetry was carried out on all three of the POMs. The system that was used involved 0.25 M LiTFSI in TEGDME as the electrolyte with a glassy carbon working electrode, a platinum wire counter electrode and an LFP reference electrode. Below (Figure 20) is the CV of LiTFSI under N_2 and under O_2 .

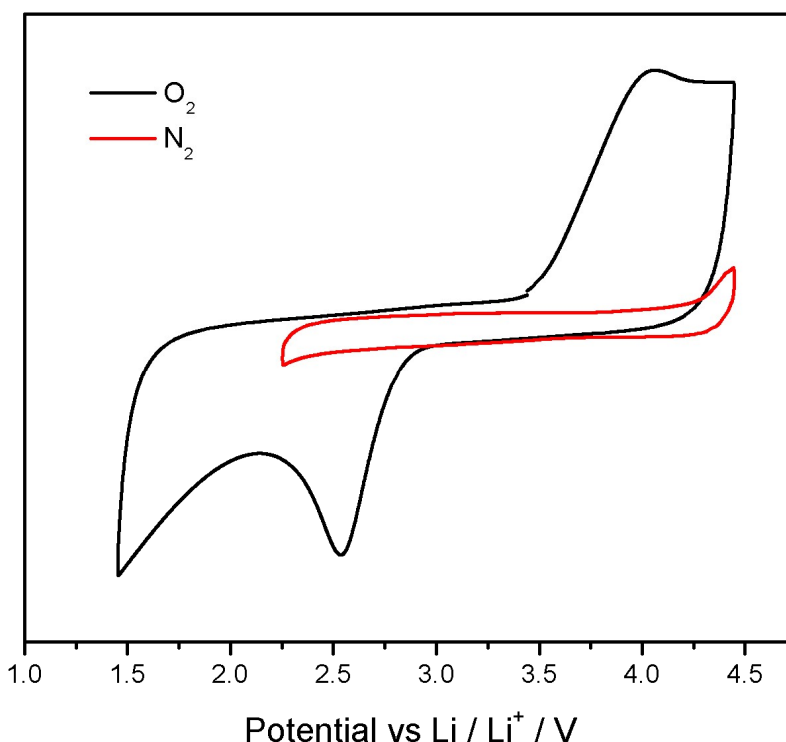


Figure 20 - CV of 0.25 M LiTFSI in TEGDME under O_2 (black) and under N_2 (red) at glassy carbon with a scan rate of 100 mV s^{-1} .

Under these conditions, it can be seen that O_2 undergoes a $1 e^-$ reduction to O_2^- at approximately 2.5 V. The O_2^- then combines with Li^+ ions at the cathode surface to form Li_2O_2 via reaction 2(c). The oxidation reaction of the peroxide occurs at approximately 4 V and is dependent on the reduction process. With further cycling, the oxygen reduction peak decreases in size and the peroxide peak grows. Eventually the electrode surface will become

passivated due the loss of active surface area as a result of the build-up of electronically insulating Li_2O_2 , causing the oxygen reduction peak to no longer be visible. With the knowledge that the two fundamental peaks in Li – air occur at 2.5 V and 4 V, the POMs were screened just outside this range to determine if there was any suitable overlap between POM processes and the reduction and oxidation processes observed in *Figure 20*.

The synthetic method for the Mo – based POMs used was based on the method used by Tsigdinos et al.,⁵⁷ with modifications being made. Instead of forming the free acid POMs, the method was modified to yield the TBA or TEA salts of the POMs. This was done to aid the solubility of the POMs in the organic solvents used for the cells in this project. Both $(\text{TBA})_4[\text{PMo}_{11}\text{VO}_{40}]$ and $(\text{TEA})_5[\text{PMo}_{10}\text{V}_2\text{O}_{40}]$ fully dissolved in TEGDME, however the solubility of $(\text{TBA})_4[\text{PW}_{11}\text{VO}_{40}]$ was limited, even after stirring for a week at 40 °C. Fortunately, a high concentration of POM in solution was not required due to the cells only needing catalytic quantities of POM and because of this, each POM was made to a 10 mM solution. Using the solutions made, CVs of the POMs were obtained (*Figure 21 - 23*).

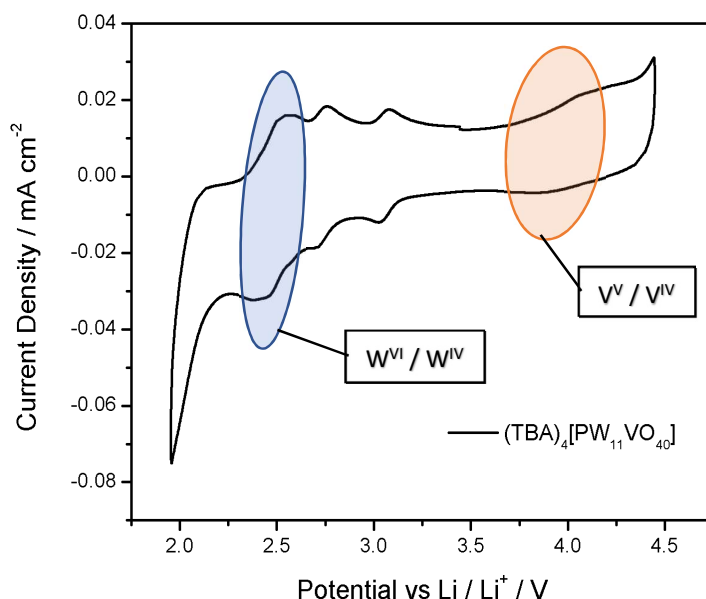


Figure 21 - CV of 10 mM $(\text{TBA})_4[\text{PW}_{11}\text{VO}_{40}]$ with 0.25 M LiTFSI in TEGDME. Ovals are used to highlight the W and V redox processes of interest.

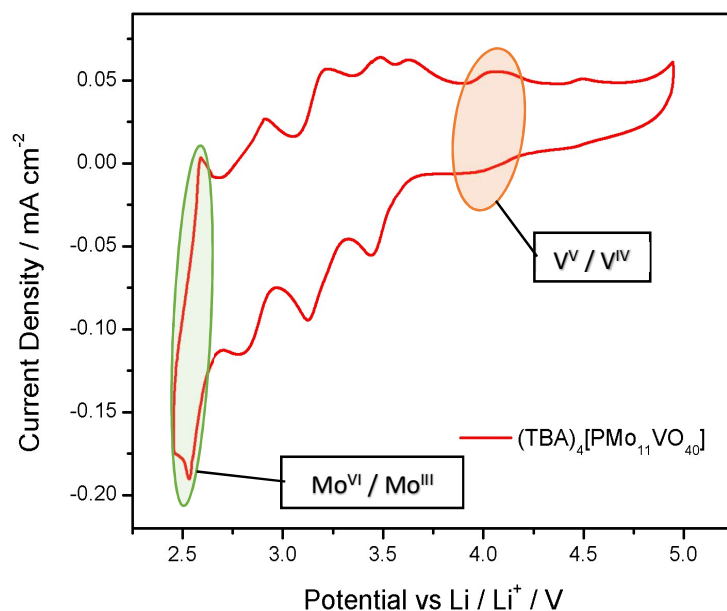


Figure 22 - CV of 10 mM $(\text{TBA})_4[\text{PMo}_{11}\text{VO}_{40}]$ with 0.25 M LiTFSI in TEGDME. Ovals are used to highlight the Mo and V redox processes of interest.

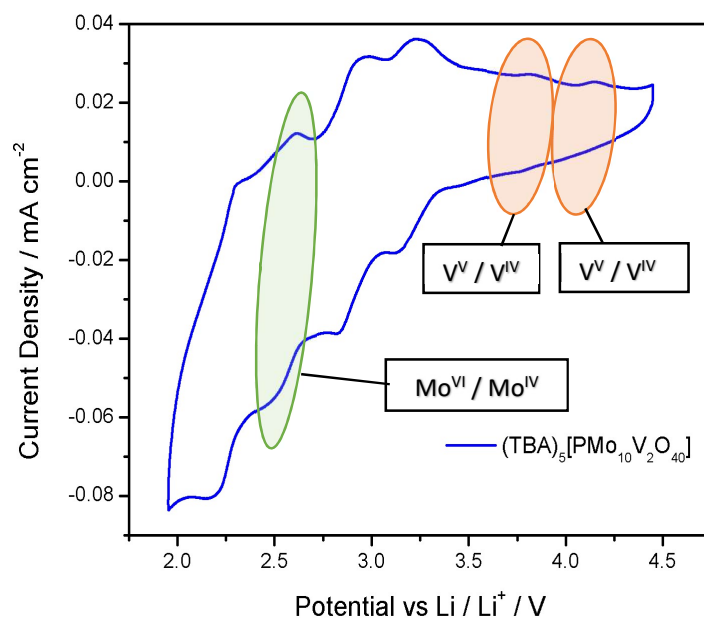


Figure 23 - CV of 10 mM $(\text{TBA})_5[\text{PMo}_{10}\text{V}_2\text{O}_{40}]$ with 0.25 M LiTFSI in TEGDME. Ovals are used to highlight the Mo and V redox processes of interest.

From the three CVs presented, all of the POMs appear to have at least quasi – reversible redox processes in the regions that would be ideal. Quasi-reversible refers to the nature of the process and means that whilst the process appears to visibly be reversible, the peak to peak

separation is greater than 57 mV meaning the process is technically irreversible.⁵⁸ In the case of $(\text{TEA})_5[\text{PMo}_{10}\text{V}_2\text{O}_{40}]$, the two processes observed sit either side of 4 V, however, despite the second V^{IV} oxidation lying closer to 4 V, the process is not reversible and therefore has no use in the electron shuttling nature of the POM. Below is a direct comparison of each POM with the CV of LiTFSI under O_2 .

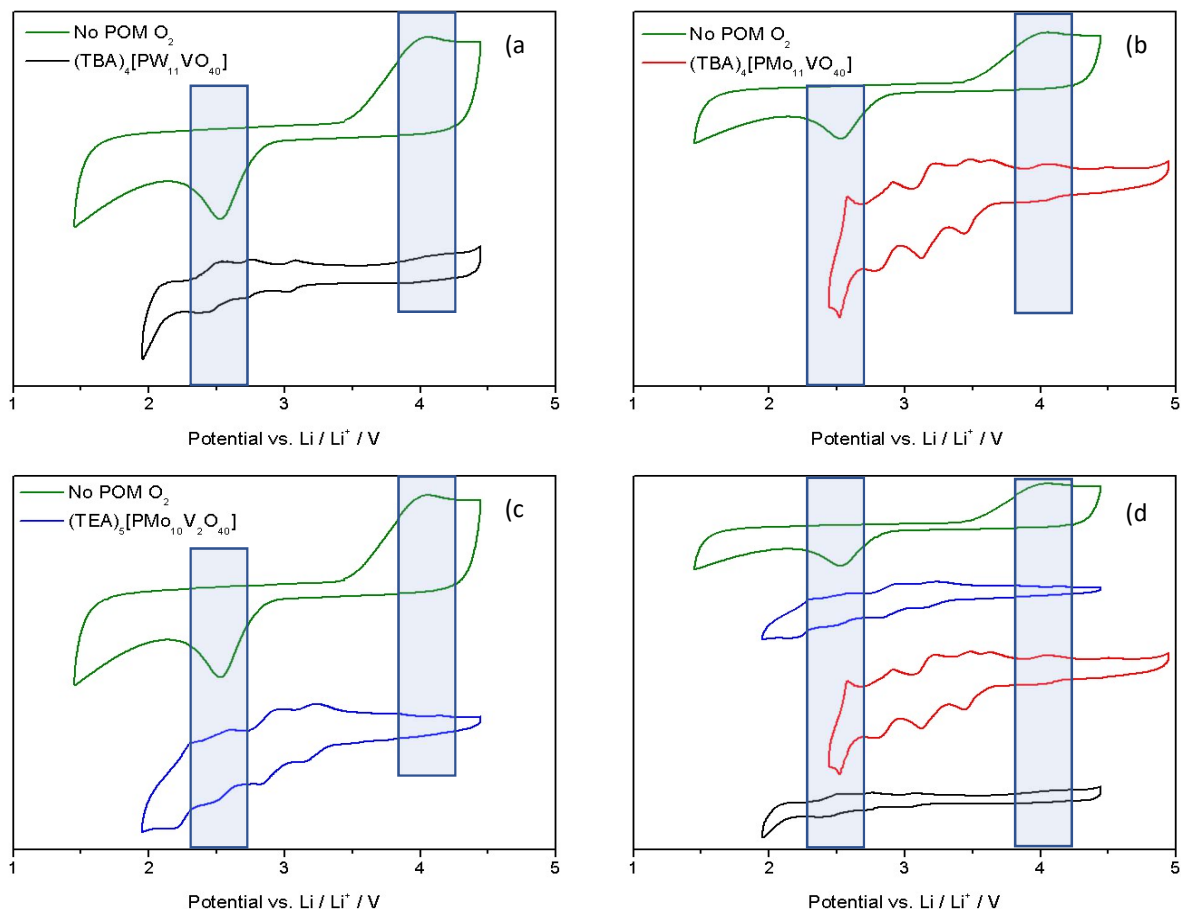


Figure 24 - CV of (a) $(\text{TBA})_4[\text{PW}_{11}\text{VO}_{40}]$, (b) $(\text{TBA})_4[\text{PMo}_{11}\text{VO}_{40}]$, (c) $(\text{TEA})_5[\text{PMo}_{10}\text{V}_2\text{O}_{40}]$ under N_2 with the CV of LiTFSI under O_2 overlaid. (d) Comparison of (a), (b) and (c). Blue boxes indicate potentially overlapping processes.

Once the POMs are aligned with the O_2 LiTFSI CV, it becomes very clear that all three POMs have potential as ORR mediators as shown in Figure 24 (d). In addition to this, there was shown to be potential for OER mediation as well, however, the POM redox chemistry around 4 V was not as well aligned with Li_2O_2 oxidation and was much less defined. CVs of the POMs

were then obtained in the presence of O_2 to ascertain whether or not the POM could facilitate the ORR and OER at shifted potentials. In the first negative scan, the POM peaks are observed but quickly fade during the second cycle due to the passivation of the working electrode by Li_2O_2 , indicated by the growing peak that is associated with the oxidation of Li_2O_2 .

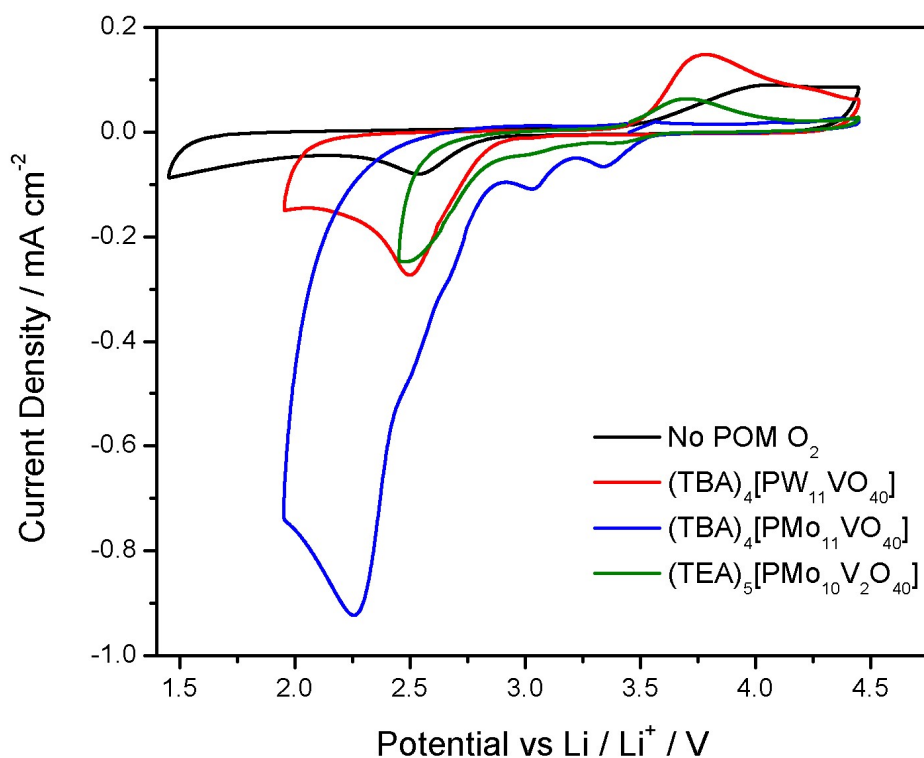


Figure 25 - CVs of all POMs under O_2 . 10 mM POM with 0.25 M LiTFSI in TEGDME

The introduction of $(TBA)_4[PMo_{11}VO_{40}]$ results in a negative shift in the potential at which O_2 is reduced by comparison to the discharge potential shown in *Figure 4*, which gives the discharge plateau at about 2.7 V. This negative shift in potential could possibly be attributed to a further POM redox process at 2.25 V that was outside of the scanned range shown in *Figure 22*. The peak associated with the reduction of O_2 may still be present at 2.5 V, as there appears to be a shoulder on the large peak at 2.5 V but the additional POM peak which was not initially detected could overlap and mask the O_2 reduction peak. In order to confirm this, a repeat of the CV shown in *Figure 22* between 2 V and 5 V would be necessary. Despite the

O₂ reduction peak being mostly covered by the larger POM peak at 2.25 V there is still a noticeable increase in the magnitude of the oxygen reduction process compared to O₂ reduction in the experiment using no POM, suggesting that this POM can sufficiently catalyse the oxygen reduction reaction. Despite this, if this POM was to facilitate O₂ reduction at this lower potential in an actual cell then we would see a further deviation from the thermodynamic standard potential (2.96 V vs Li / Li⁺), thus resulting in a lower round trip efficiency of the cell. The other two POMs, (TBA)₄[PW₁₁VO₄₀] and (TEA)₅[PMo₁₀V₂O₄₀] show no shift in the potential associated with the ORR but do still show an increase in magnitude of the peak at 2.5 V compared to the peak at 2.5 V for no POM. They do exhibit a shift in the potential of Li₂O₂ oxidation from 4 V to about 3.5 V. These combined results suggest that they have functional potential as both discharge and charge mediators and if they behaved the same way in a live cell, they would effectively reduce the overpotential observed during the charging process leading to a greater round trip efficiency. With this information, all three POMs were taken forward for use in live cells in galvanostatic cycling experiments.

5.2 Galvanostatic Cell Cycling

With the POMs characterised, they were incorporated into live cells. Using the same 0.25 M with 10 mM POM electrolyte, the cells were cycled between 2.25 V and 4.45 V vs Li / Li⁺. Super P carbon on stainless steel mesh was used as the cathode with an LFP anode. Firstly, it was important to gain an understanding of the sorts of potentials and capacities that are associated with unmediated, live cells. Under the conditions mentioned above, a cell containing no POM was discharged and then charged at a current density of 0.1 mA cm⁻².

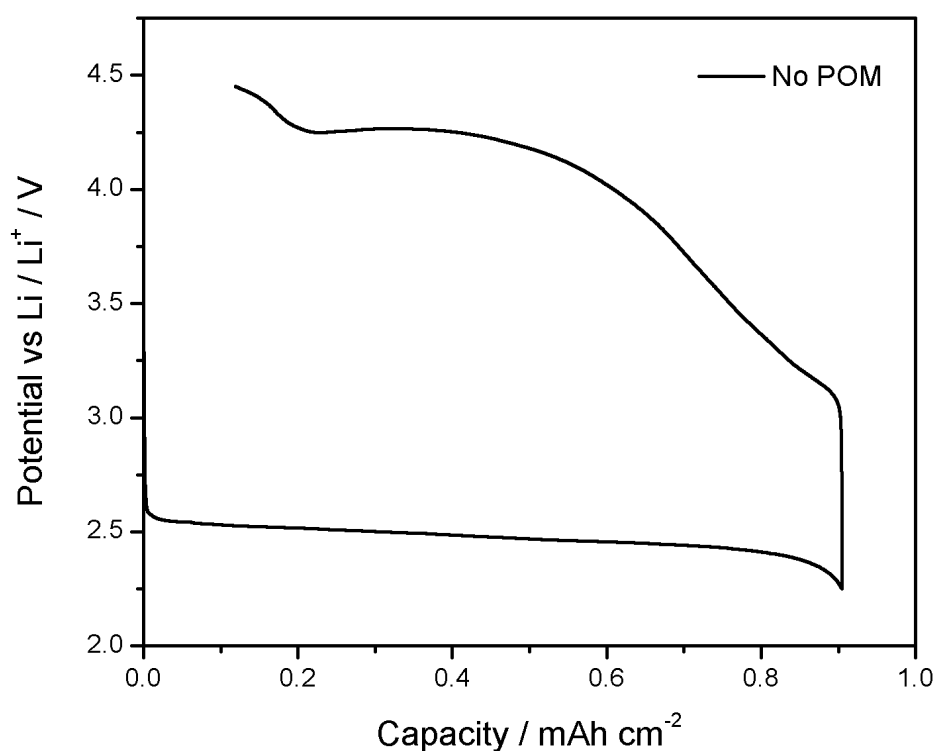


Figure 26 - Capacity plot of cell containing no POM with 200 μ L of 0.25 M LiTFSI in TEGDME.

The above figure shows the characteristic discharge plateau at approximately 2.7 V and has a capacity of 0.9 mAh cm⁻². As expected for an unmediated cell, the high overpotential during charge can also be seen. All further data obtained from these type of measurements will draw comparisons with this plot as the baseline measurement. Upon adding the POMs to the electrolyte of the cells, we would hope to see an increase in discharge capacity compared and a decrease in the overpotential when compared to *Figure 26*. This comparison can be seen in *Figure 27*.

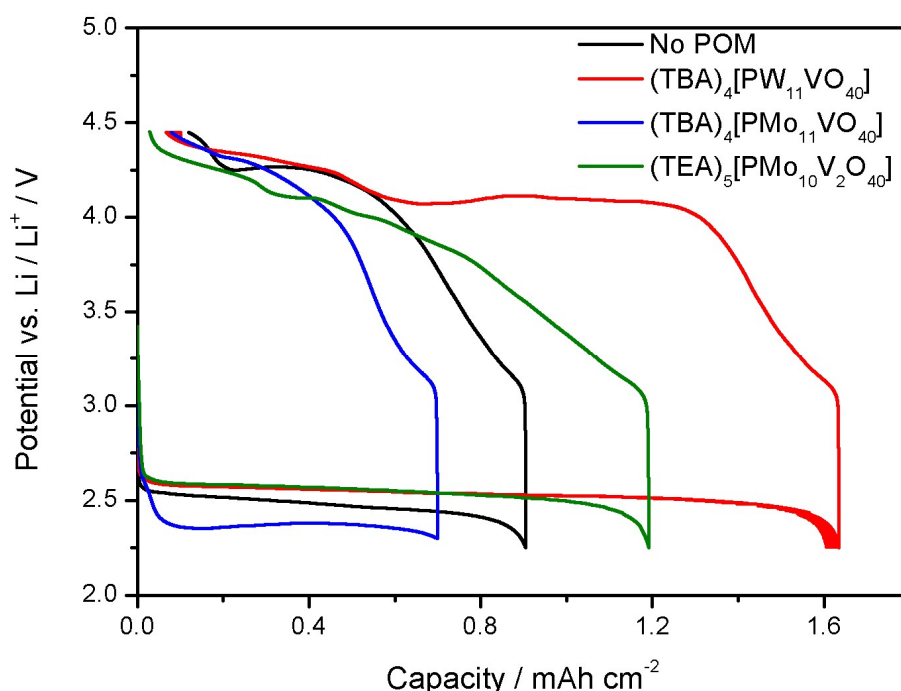


Figure 27 - Capacity plots of all POMs compared to the cell run without any POM.

Upon looking at *Figure 27*, it becomes immediately clear that (TBA)₄[PMo₁₁VO₄₀] behaves in a similar manner to how it affected the reduction of O₂ that was shown in the cyclic voltammetry with a decrease in the ORR potential compared to the no POM cell. Not only is this less efficient, a decrease in capacity is also observed with no notable impact on the overpotential. Despite this, other experiments (*Figure 28*) performed at lower current densities suggested that this POM had promise as an ORR mediator showing a fairly large

increase in capacity from 0.9 mAh cm⁻² to 1.35 mAh cm⁻² although this result was not reproducible in several attempts.

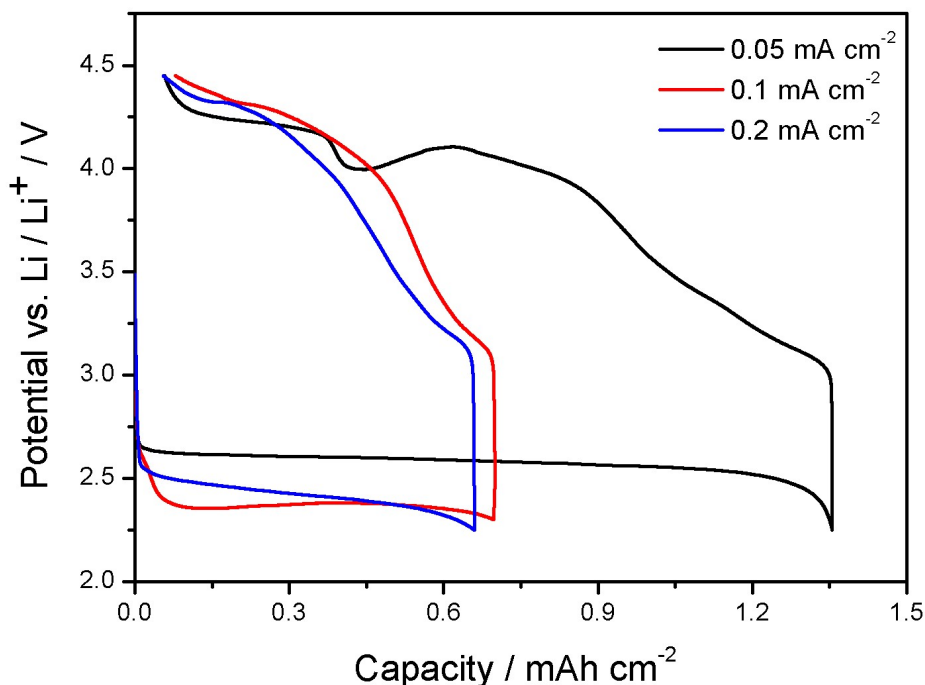


Figure 28 - Comparison of cells containing (TBA)₄[PMo₁₁VO₄₀] at different current densities. The cell contained 200 μ L 10 mM POM with 0.25 M LiTFSI in TEGDME at a super P carbon cathode.

At 0.1 mA cm⁻² and 0.2 mA cm⁻², the POM hinders the capacity. It is possible that the higher currents are causing the POM to initiate decomposition of the TEGDME solvent leading to the formation of Li₂CO₃, an insoluble by-product that also has insulating properties. The presence of Li₂CO₃ would decrease the active surface area of the cathode that is available to be able to reduce the POM and also potentially blocks the pores of the cathode where the Li₂O₂ is stored leading to the decrease in capacity.

Both (TBA)₄[PW₁₁O₄₀] and (TEA)₅[PMo₁₀V₂O₄₀] show an increase in capacity showing 1.6 mAh cm⁻¹ and 1.2 mAh cm⁻² respectively. (TEA)₅[PMo₁₀V₂O₄₀] also appears to show some degree of reduction in the overpotential with the majority of the charge reaction occurring under 4 V. Whilst the shallowing of the charge profile is wanted, the degree to which the overpotential

is reduced does not improve the viability of the cell significantly. Based on the data presented, none of the POMs synthesised have the ability to reduce the overpotential of the cell. As a result, the POM that was taken forward to pressure measurements was $(\text{TBA})_4[\text{PW}_{11}\text{VO}_{40}]$ due to it having the largest benefit to the capacity of the cell.

5.3 Galvanostatic Pressure Cell Measurements

Using 10 mM $(\text{TBA})_4[\text{PW}_{11}\text{VO}_{40}]$ with 0.25 M LiTFSI in TEGDME once again, pressure cell measurements were taken alongside a control cell without any POM. The pressure cells were discharged and charged at 0.1 mA cm^{-2} . The discharge / charge curves for these two pressure cell measurements are shown in *Figure 29*.

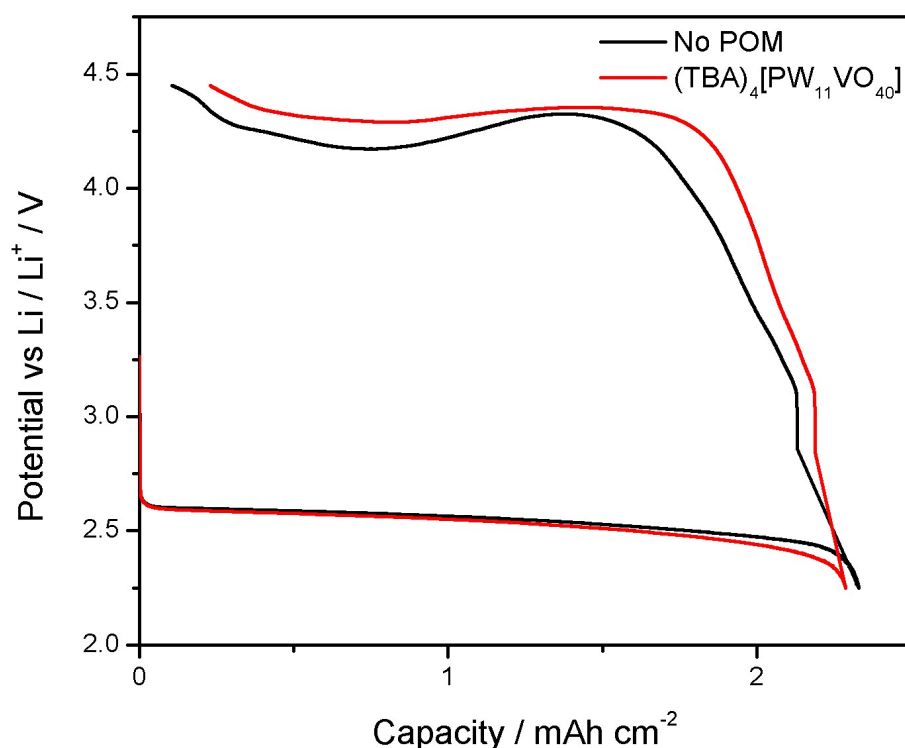


Figure 29 - Discharge / charge plot for the two pressure cell measurements taken. 800 μL 10 mM POM with 0.25 M LiTFSI in TEGDME at super P carbon.

The presence of the POM in this case results in a very slight decrease in the capacity of the cell, on the contrary to what was previously observed in the smaller cells. The benefit of running these experiments with a pressure sensor connected is that it allows for pressure changes within the cell during the discharge and charge to be monitored and recorded. Using the data obtained, it is possible to gain an understanding of the electrochemical efficiency of the cell by calculating the ratio of the number of moles of e^- passed to the number of moles of O_2 consumed or produced during cycling. In an ideal world, the ratio should be equal to 2 and means that within the cell during the discharge all of the electrons passed are being used for the reduction of O_2 and not side reactions.

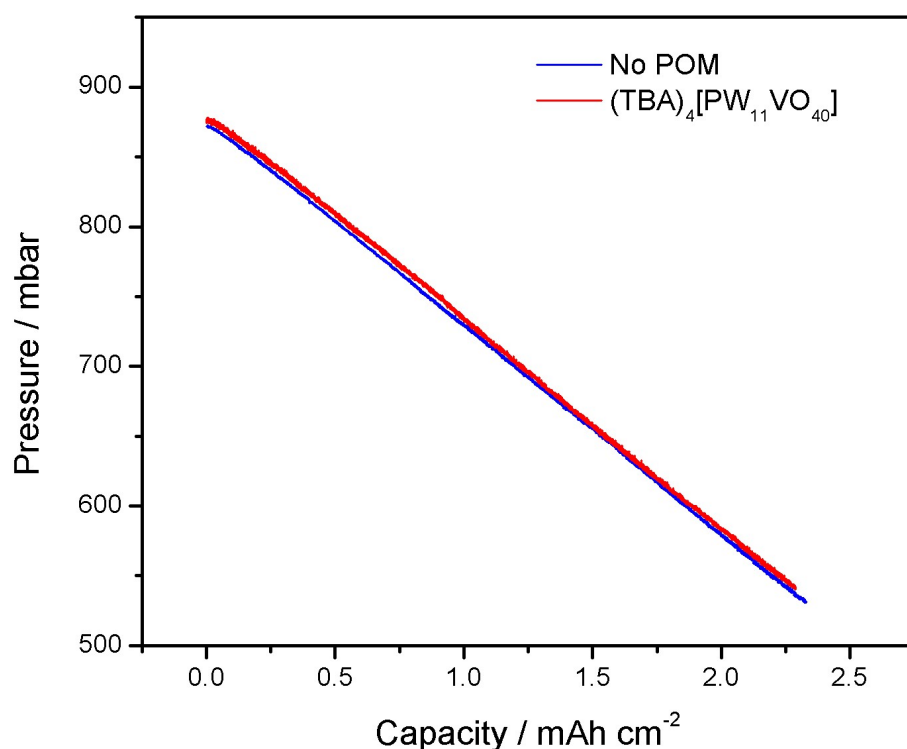


Figure 30 - Plot showing the ratio of the number of moles of e^- passed during discharge to the number of moles of O_2 consumed during discharge for the two cells shown in Figure 29.

From the data obtained, a value of 2.004 was calculated for the cell without any POM and 2.069 for the cell containing the POM. This difference, despite being small indicates that there is some degree of decomposition as a result of the POM being present.

The comparison of the data collected from the live cell experiments suggests some inconsistencies. Further work will be required to fully understand the role of POMs as redox mediators in Li – air batteries.

6. Conclusion

To conclude, of the three POMs synthesised, the POM with the most potential for use in Li – air cells as a redox mediator for the oxygen reduction and oxygen evolution reactions is $(\text{TBA})_4[\text{PW}_{11}\text{VO}_{40}]$.

The electrochemical data obtained showed that the POM had redox processes at suitable potentials to mediate both the reduction of O_2 and Li_2O_2 and the enhancement of the discharge reactions was supported by the galvanostatic cycling data that was obtained. It is worth noting that whilst this POM had limited solubility in TEGDME, there was still positive data obtained suggesting that were the POM fully soluble in the electrolyte used, even further improvements to capacity could be observed. However, in the pressure cell, the POM showed a slight decrease in capacity. This is more likely an accurate representation of the actual POM behaviour due to the pressure cells being generally more reliable and reproducible. In addition to this, the interpretation of the pressure data showed that the presence of the POM does result to a degree of decomposition during discharge, evidence for which could be further obtained through the use of SEM and FT-IR post – mortem analysis of the cathodes.

Based on the electrochemical data combined with the evidence of POM function obtained from the galvanostatic cycling experiments, in order to facilitate the oxidation of Li_2O_2 to help reduce the overpotential it may be necessary to modify this POM to have more prevalent redox chemistry at more positive potentials, around 4 V vs Li / Li^+ . This could be achieved by substituting more vanadium atoms into the POM in place of tungsten atoms. However, this could also lead to the weakening of the POM structure as you introduce more vanadium atoms which would reduce the rigidity of the POM that results from the strong W-O bonds.

7. Future Work

To take this work further, it would be necessary to elucidate the presence of any possible decomposition products such as Li_2CO_3 via means of SEM and FT-IR before deciding if a POM has real world potential in cells. For example, under FT-IR, if there was any solvent based decomposition products such as carbonates, the spectrum would be expected to have a sharp peak at approximately 1700 cm^{-1} which corresponds to the C=O bond. FT – IR could also be used to probe the cathode surface as a means of detecting Li_2O_2 , which has corresponding peaks within the fingerprint region. By using SEM, it would be possible to obtain high resolution images of the cathode surface at a magnification that allows the visualisation of any bulk Li_2O_2 deposits such as toroids.

It may also be necessary to modify the $(\text{TBA})_4[\text{PW}_{11}\text{VO}_{40}]$ to enhance its redox chemistry at more positive potentials and also, its solubility. The logical progressions from the current POM would be $(\text{TBA})_5[\text{PW}_{10}\text{V}_2\text{O}_{40}]$ and $(\text{TBA})_6[\text{PW}_9\text{V}_3\text{O}_{40}]$ if the current trend holds, which should result in POM redox chemistry at more positive potentials opening the opportunity for possible dual-mediation of both the ORR and OER.

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