Effects of Redox-mediator Electrolyte on the Electrochemical Performance of a Nonaqueous Li-O₂ Battery

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Effects of Redox-mediator Electrolyte on the Electrochemical Performance of a Nonaqueous Li-O₂ Battery

Improving the electrochemical performance of Li-O₂ battery via implementing a soluble catalyst and Nano seed techniques & Studying the fundamental growth and decomposition mechanisms of the cell products.

BY

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<tr>
<td>RM</td>
<td>redox mediator</td>
</tr>
<tr>
<td>CNT</td>
<td>carbon nanotube</td>
</tr>
<tr>
<td>EV</td>
<td>electrical vehicle</td>
</tr>
<tr>
<td>AN</td>
<td>Gutman acceptor number</td>
</tr>
<tr>
<td>DN</td>
<td>Gutman donor number</td>
</tr>
<tr>
<td>ORR</td>
<td>oxygen reduction reaction</td>
</tr>
<tr>
<td>OER</td>
<td>oxygen evolution reaction</td>
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<tr>
<td>GSAS</td>
<td>General Structure Analysis System</td>
</tr>
<tr>
<td>TDPA</td>
<td>tris[4-(diethylamino)phenyl]amine</td>
</tr>
<tr>
<td>CFP</td>
<td>carbon fiber paper</td>
</tr>
<tr>
<td>TEMPO</td>
<td>2,2,6,6-Tetramethyl-1-piperidinyloxy, free radical</td>
</tr>
<tr>
<td>FePc</td>
<td>iron phthalocyanine</td>
</tr>
<tr>
<td>FC</td>
<td>ferrocene</td>
</tr>
<tr>
<td>TTF</td>
<td>tetraethiafulvalene</td>
</tr>
<tr>
<td>MPT</td>
<td>N-methylphenothiazine</td>
</tr>
<tr>
<td>TEGDME</td>
<td>tetraethylene glycol dimethyl ether</td>
</tr>
<tr>
<td>LiTFSI</td>
<td>Bis(trifluoromethylsulfonyl)amine lithium salt</td>
</tr>
<tr>
<td>SEI</td>
<td>solid electrolyte interface</td>
</tr>
<tr>
<td>NMP</td>
<td>1-Methyl-2-Pyrrolidon</td>
</tr>
<tr>
<td>DMC</td>
<td>Dimethyl carbonate</td>
</tr>
<tr>
<td>CV</td>
<td>cyclic voltammetry</td>
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<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscope</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscope</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>FWHM</td>
<td>full width at half maximum</td>
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Energy storage techniques are getting important in meeting the energy structure innovation all over the world. With the fast development and wide implementation of renewable energy resources, it became a hot topic to seek for better energy storage systems to cope the problem of energy fluctuation. Due to the extremely high theoretical energy density and less bulky characteristic, Li-O_2 batteries walked into people’s eyes and attracted a lot of interest for mobile applications.

Redox mediator (RM) worked as a charge transfer intermediate (electron-hole transfer agent) which can lower the energy barrier of decomposing the discharge product, Li_2O_2. Former study indicated Nano seed technique can improve the reversibility of Li_2O_2 and suppress the side reactions with carbon cathode, resulting from their grain refinement function. In our study, through combination of these two promising approaches, the electrochemical performance of the Li-O_2 batteries was significantly improved.

TEMPO was selected as the desirable RM for our Li-O_2 batteries from a group of RMs. And 10 Mm TEMPO was determined to be the optimal concentration for achieving both desirable discharge capacity and superior catalytic efficiency. The rate capability study showed that TEMPO worked more efficient under high current density, demonstrating its fast charge transfer kinetics.

From the pH test and structure analysis of TEMPO, it can be concluded that TEMPO would increase the Gutman donor number (DN) of the electrolyte, which was reported to promote Li_2O_2 generation in the solution. However, the crystallinity and morphology study demonstrated that the discharge product has a smaller domain size as well as particle size after adding TEMPO, indicating that the fast nucleation was induced with the addition of TEMPO, due to the increasing nuclei sites.

¹H-NMR analysis indicated the superior stability of Li-O_2 cells with the addition of TEMPO, as no by-product was detected after cycle. Furthermore, XPS results indicated cell with TEMPO could eliminate the by-products after charge, however, the by-products can still be detected in cell without additive. Additionally, the shift of the binding energy in XPS proved the generation of LiOH through hydrogen abstraction from the electrolyte. Through preloading LiOH and Li_2CO_3 in the cathode, it found the recharging potential perfectly matched to the second platform, indicating that TEMPO was also beneficial for LiOH and by-product decomposition. All these results explained the electrochemical activities during the charge process.

This thesis illustrated that the combination of RM and Nano seed techniques was a promising way to develop high chemical reversibility and low overpotential Li-O_2 batteries. However, the serious hydrogen abstraction from ether-based electrolyte after adding TEMPO was induced by larger exposed surface area of Li_2O_2 in the electrolyte. The hydrogenation can also lead the increasing water evolution after cycle, which might be a trouble for the long-term stability of the Li-O_2 batteries, especially for lithium metal. Therefore, further study on electrolyte selection and lithium metal protection should be continued.

**Keywords:** Redox mediator; Nano seeds; donor number/ acceptor number; growth/decomposition mechanisms; nonaqueous Li-O_2 battery.
1. Introduction

1.1 Why Lithium-O\textsubscript{2} battery

With the booming development of renewable energy and the depletion of primary energy resources, more and more efficient storage systems are required to meet the energy structure innovation in the future. Li-ion battery as a mature rechargeable battery technology has been widely used in cellphones, laptops and even industry. However, its relative low energy density (~300 Wh/kg) limits the application in large-scale energy device, such as electrical vehicles (EV). Subsequently, Li-Air battery as one of the alternatives with superior high energy density (estimated-specific energy density is up to 1700 Wh/kg\textsuperscript{1}) walk into people’s eyes.

![Figure 1-1: Compare theoretical and practical energy density of different types of batteries with gasoline\textsuperscript{1}](image)

As shown in figure 1-1, although theoretical energy density of gasoline is extremely high (~13000 Wh/Kg), the tank to wheel efficiency is only around 12.6\% based on U.S. fleet\textsuperscript{2}, resulting in a practical energy density of gasoline of about 1700 Wh/Kg\textsuperscript{1}. And this practical energy density is at the same level of estimated practical energy density of Li-Air battery\textsuperscript{1}. These factors make Li-Air batteries become an extremely attractive technology especially in transportation. In this thesis, we are involved in Li-O\textsubscript{2} battery system in which the breath-in gas is pure oxygen rather than ambient air. Therefore, the environmental contaminants, such as H\textsubscript{2}O, CO\textsubscript{2} and N\textsubscript{2} are excluded which is necessary for determining the fundamental mechanisms underlying the working performance of Li-O\textsubscript{2} batteries.\textsuperscript{1} The theoretical-specific energy density of Li-O\textsubscript{2} batteries is around 3500 Wh/Kg\textsuperscript{3}. The anode material of Li-oxygen batteries is lithium metal, which is the lightest and most electronegative element in nature\textsuperscript{4}. This makes it a desirable anode material in high capacity storage system. At cathode, oxygen, is abundant in ambient air.

1.2 Different types of Li-O\textsubscript{2} storage systems

Typically, four types of Li-O\textsubscript{2} battery systems are explored as shown in figure 1-2, namely non-aqueous (aprotic), aqueous (protic), solid state and mixed aqueous/aprotic\textsuperscript{1}. The main difference among these four systems...
is the usage of electrolyte, therefore, resulting variations in electrochemical reactions during the energy storage and releasing process. Water is involved in aqueous Li-O₂ battery systems which lead the final discharge product to be LiOH⁵. Since anode material, Li metal is highly active with the appearance of water. Therefore, extra protection on Li metal should be implemented. Nevertheless, this corrosion of the Li-metal anode is a major problem for developing aqueous Li-O₂ batteries. Currently, most reported studies are fulfilled on non-aqueous system for getting better cycling stability and understanding of the fundamental working mechanisms of Li-O₂ cells.

![Figure 1-2: Four architectures of Li-O₂ batteries with lithium metal as anode material – aprotic, aqueous, solid state and mixed aqueous/aprotic](image)

Among these four configurations, only nonaqueous batteries show a promising electrical rechargeability, therefore, attracted the most attention around the world.

### 1.3 Working principle of non-aqueous Li-O₂ batteries

In this thesis, we focus on non-aqueous lithium-oxygen batteries, where the main discharge product is reported to be Li₂O₂ other than LiOH after discharge. Lithium metal was used as the anode. Due to the poor electrical conductivity of Li₂O₂, the highly electronic conductive carbon materials are the most wildly used cathode materials in Li-O₂ batteries. Typically, lithium peroxide is the ideal discharge product, and the net chemical reaction in the cell can be expressed by

$$2Li + O_2 \rightarrow Li_2O_2 \quad \text{(discharge)}$$

This reaction has an equilibrium potential for 2.96 V, which was obtained from the Nernst equation. Although it has a moderate discharge overpotential (≈ 0.4 V), the charge overpotential (≈ 1.5 V) is very large. During discharge, the electrochemical process is charged by the oxygen solubility and activation energy from oxygen gas to oxygen ions in the electrolyte. During charge, the insulating Li₂O₂ mainly corresponds to the high charge overpotential. In some cases⁶⁻⁷, lithium oxide is also detected at deep discharge which is attributed to the further reduction of lithium peroxide.
\[ \frac{1}{2} Li_2O_2 + Li^+ + e^- \rightarrow Li_2O \]

The generation of lithium peroxide can be separated with several one-electron reactions. Oxygen is first reduced to \( O_2^- \), and then generates LiO\(_2\) intermediate combined with lithium ions.

\[ O_2 + e^- \rightarrow O_2^- \]

\[ Li^+ + O_2^- \rightarrow LiO_2 \]

LiO\(_2\) is a vital intermediate which is hardly being in stable state in the Li-O\(_2\) batteries, only a small amount of LiO\(_2\) existing after discharge process.\(^8\) There are two approaches for LiO\(_2\) intermediate transforming to Li\(_2\)O\(_2\) in Li-O\(_2\) cells:

**Solution mechanism:** \( 2LiO_2 \rightarrow Li_2O_2 + O_2 \)

**Surface mechanism:** \( LiO_2 + Li^+ + e^- \rightarrow Li_2O_2 \)

These two pathways correspond to these two different electrochemical mechanisms on the surface of cathode. One is the solution mechanism where two LiO\(_2\) molecules react chemically and splits into lithium peroxide and oxygen gas in the electrolyte. The solution mechanism can be explained by Person’s ‘hard soft acid-base theory’.\(^9\) Many studies\(^{10-11}\) reported the observation of toroidal structure Li\(_2\)O\(_2\) after discharge, and Li\(_2\)O\(_2\) in toroidal shape is known formed via solution mechanism.\(^12\) Another way is LiO\(_2\) electrochemically reacts with lithium ions and electrons, generating Li\(_2\)O\(_2\) on the surface of cathode which is regard as surface mechanism. Li\(_2\)O\(_2\) generated through surface mechanism is amorphous and has thin-film structure with a maximum thickness of around 6-7 nm.\(^13\)

![Figure 1-3: Scheme of Li\(_2\)O\(_2\) generation through solution and surface mechanism in single Li-O\(_2\) cell](image)

Whether the Li-O\(_2\) batteries undergo solution or surface mechanism during discharge is dependent on current density, Gutman donor number (DN) / acceptor number (AN) of electrolyte and solubility of LiO\(_2\) in the solution. Previous researches have proved that at low current density Li\(_2\)O\(_2\) prefers to form via a solution mechanism\(^{14-15}\). The current density would influence the diffusion of oxygen and lithium ions, and solvation of Li\(_2\)O.\(^16\) Aprotic solvent which has high DN or high AN resulting in a better solubility of LiO\(_2\) intermediate\(^{12, 15}\). In high DN/AN
electrolyte, the Gibbs free energy for the dissolved LiO$_2$ in the solution is lower than adsorbed LiO$_2$ on the electrode surface.\textsuperscript{15}

In order to achieve high capacity Li-oxygen battery, surface mechanism is not preferred, because Li$_2$O$_2$ generated via surface mechanism would stick to the surface of the cathode which would block the active sites of the electrode and lead to electrode passivation\textsuperscript{17}. Hence, limiting the discharge capacity and causing the early death and low rate of cells\textsuperscript{13}. On the contrary, solution mechanism can manage higher rate and larger discharge capacity through minimizing the growth of thin film on the surface of electrode. However, surface generated peroxide has more Li defects which could lower the charge overpotential,\textsuperscript{16} and the crystal peroxide from the solution would lead large charge overpotential, due to the poor electronic conductivity and bad contact with the electrode.

1.4 The challenges of Li-oxygen battery

Li-O$_2$ batteries became a hot topic in recent two decades. Many scientific articles have clarified the fundamental mechanism and improved the electrochemical performance of Li-O$_2$ cells. Nevertheless, the challenges of implementing Li-O$_2$ batteries in practice are still not eradicated. The main challenges of Li-O$_2$ batteries are summarized below:

(1) Lithium peroxide as the major discharge product in Li-O$_2$ cells is insulated which has a wide bandgap\textsuperscript{12}, leading a large overpotential during charge process due to the poor electrical conductivity of Li$_2$O$_2$. This internal characteristic of Li$_2$O$_2$ results the poor reversibility and fast capacity fading due to the undecomposed Li$_2$O$_2$ accumulated on the surface and blocked the active sites while cycling. Therefore, it leads low columbic efficiency and short lifetime in Li-O$_2$ cells.

(2) The electrolyte and carbon electrode of Li-O$_2$ batteries are unstable under the attack of several active species O$_2^-$, O$_2$ and Li$_2$O$_2$ in the Li-O$_2$ batteries.\textsuperscript{6,18-19} The high charge potential (up to 4.5 V) would also influence the stability of the electrolyte and carbon electrode. There are always inevitable side reactions\textsuperscript{20-23} in the cell that would result in decomposition of electrolyte with the appearance of Li$_2$O$_2$ and direct contact with lithium metal, leading the generation of ‘cell trash’.

(3) As using lithium metal as anode material, the problem of dendrite formation\textsuperscript{25-26} is well-known to influence the long-term stability and even short-circuit inside the battery, resulting serious safety problem. Furthermore,
Lithium metal is extremely sensitive to air and can easily react with \( \text{O}_2 \), \( \text{H}_2\text{O} \), \( \text{CO}_2 \) and even \( \text{N}_2 \). The gas crossover problem\(^{27}\) makes Li-Air batteries even more challenging in practice.

(4) With high rate, Li-O\(_2\) batteries tend to display surface mechanism and block active sites on the cathode, therefore limiting the discharge capacity. Additionally, the electrolyte and carbon cathode of Li-O\(_2\) cells cannot tolerate really high current density, with which it would like to cause faster electrolyte and carbon electrode decomposition.

Figure 1-4 summarized the main challenges faced by Li-O\(_2\) battery. To estimate whether a battery system is suitable to be implemented in reality, energy density is indeed a core factor, nevertheless, cost, safety and lifetime (measured in years and miles) are also important which are all obstacles for Li-O\(_2\) batteries at present.

1.5 Challenge solving strategies

Due to previously mentioned challenges, the large overpotential during ORR (oxygen reduction reaction) and OER (oxygen evolution reaction) would lead to low energy efficiency and poor round-trip efficiency of Li-O\(_2\) battery. To make breakthrough of these bottlenecks, various approaches were reported. And four major approaches are summarized below.

**Solid catalysts**

At the beginning stage, researchers mainly focused on implementing solid catalyst in the construction of the cathode. Previous studies showed that noble metal\(^{28}\), metal oxides \(^{29}\), carbon nanotubes/nanofibers\(^{30}\), Fe-N/C complexes\(^{31}\), graphene nanosheets\(^{32}\), pyrochlore\(^{33}\), perovskites\(^{34}\) and so on are promising solid cathode catalysts. With the addition of solid catalyst in the electrode, Li-O\(_2\) batteries showed improved performance at beginning, however, since the discharge product Li\(_2\)O\(_2\) is also in solid state, the contact between Li\(_2\)O\(_2\) with the immobile solid catalyst is poor, therefore, during charge process, the decomposition of Li\(_2\)O\(_2\) can only partially benefit from solid catalysts\(^{35}\). Furthermore, with undecomposed discharge product and generated by-product accumulated at the surface of cathode, the immobile solid catalysts are most likely to be covered and therefore lost their catalytic activity after several cycles. These reasons make immobile solid catalysts not a long-term solution for the high overpotential in the Li-O\(_2\) batteries.

**Soluble catalysts – redox mediator**

To cope with the limitation of immobile catalysts, there came an idea of mobile catalysts which can help the charge transfer not only for Li\(_2\)O\(_2\) generated on the electrode, but also Li\(_2\)O\(_2\) in the solution which is without direct contact with cathode. These diffusible soluble catalysts are added into electrolyte as additives and work as redox mediators (RM) to improve the contact between solid discharge products and the catalysts. Therefore, it can enhance the charge transfer ability of Li\(_2\)O\(_2\) through taking RM as an charge-transfer agent and allow the oxidation of Li\(_2\)O\(_2\) without direct contact with positive electrode\(^{36}\) in charge process. Although known the advantages of solution mechanism in chasing large capacity in discharge, the toroidal Li\(_2\)O\(_2\) is remote from active materials on the cathode\(^{37}\), thus increasing the difficulty in Li\(_2\)O\(_2\) decomposition during charge. To improve the contact between solid discharge products and catalysts, diffusible catalysts are more suitable than immobile catalysts. So far, reported and commonly used redox mediators include TDPA (tris[4-(diethylamino)phenyl]amine)\(^{38}\), TTF (tetraphiafulvalene)\(^{39-40}\), Li\(_2\)TTF\(^{42-43}\), TEMPO\(^{44-45}\) (2,2,6,6-Tetramethyl-1-piperidinyloxy, free
radical), MPT(N-methylphenothiazine)\textsuperscript{46}, FePc (iron phthalocyanine)\textsuperscript{35,47} and FC (ferrocene)\textsuperscript{39}. These redox mediators can effectively decrease the charge potential to 3.3-3.6 V\textsuperscript{49} (with respect of Li/Li\textsuperscript{+}) from higher than 4.5V.

\textbf{Li metal pretreatment}

Pretreating lithium metal with PC (propylene carbonate)\textsuperscript{48-49} solution to generate a thin protected layer on the surface of Lithium metal is the most widely used method to suppress Li dendrite generation in Li-O\textsubscript{2} batteries. Rongrong Miao and coworkers\textsuperscript{50} used dual-salts electrolyte to generate unique solid electrolyte interface (SEI) which can suppress dendrite generation and enhance the crystal growth of Li metal. In some studies, alternatives (especially tin, silicon and their composites) of lithium metal are applied\textsuperscript{51-53} in Li-O\textsubscript{2} battery systems. However, this solution always takes specific capacity as compromise. To generate a SEI protection layer, lithium metal was pretreated with 0.1 M LiTFSI/PC in our study.

\textbf{Cathode reconstruction}

The structure and property of air electrode can influence the rate capability and the morphology of discharge product\textsuperscript{53}. Due to the catalytic activity of the carbon-based materials in ORR, they were commonly used in Li-O\textsubscript{2} batteries.\textsuperscript{54} To improve the electronic conductivity of the electrode and provide more active sites for Li\textsubscript{2}O nucleation\textsuperscript{55}, the surface area of active carbon should be maximized. However, the large carbon surface would accelerate the side reactions in the cell, as increasing the contact area between active species and carbon electrode. For pursuing large-capacity Li-O\textsubscript{2} batteries, the solution growth mechanism should be promoted. Therefore, it should focus on constructing more porous cathode structure to store toroidal Li\textsubscript{2}O\textsubscript{2} generated in the solution. And the microporous structure could also benefit the facile O\textsubscript{2} diffusion. Hence, the design of cathode should be based on the expectation of the cell performance. Currently, most of the cathode reconstruction researches were built on the concept of combining carbon material with solid catalysts.

Although most of Li\textsubscript{2}O\textsubscript{2} can be generated through solution mechanism in high DN/AN solution, the generation of Li\textsubscript{2}O\textsubscript{2} via surface mechanism is inevitable. This resulting Li\textsubscript{2}O\textsubscript{2} on the surface blocks the active sites and reduce the pathways for O\textsubscript{2} gas penetration which would decrease the discharge capacity. Therefore, a concept of ‘Nano seeds’\textsuperscript{56} is introduced in Li-O\textsubscript{2} batteries. Nano seeds, with similar crystal structure as Li\textsubscript{2}O\textsubscript{2}, work as grain-refining agents to induce the formation of Li\textsubscript{2}O\textsubscript{2} crystallite. During discharge, Li\textsubscript{2}O\textsubscript{2} grows along the Nano seeds other than on the carbon surface, since less interfacial energy required, compared with direct growth on the carbon cathode\textsuperscript{56}. During charge, the metal-Li\textsubscript{2}O\textsubscript{2} interface is more stable than carbon-Li\textsubscript{2}O\textsubscript{2} interface, which reduces the parasitic reaction of carbon material at high voltage.

\textbf{1.6 Working mechanism of redox mediator}

In this study, we mainly explored the electrochemical behaviors of solid catalyst combined with soluble catalyst, and how does the catalysts influence structure and property of discharge products and their formation/decomposition mechanism in Li-O\textsubscript{2} batteries.

The working principle of RM can be summarized by three steps\textsuperscript{44}: (1) RMs diffuse onto the surface of cathode and are electrochemically oxidized into RM\textsuperscript{+} during low potential charge process; (2) RM\textsuperscript{+} diffuses to lithium peroxide and helps charge transfer in Li\textsubscript{2}O\textsubscript{2} at higher charge voltage. (3) RM\textsuperscript{+} is reduced back to RM in last step,
and keeps repeating the work during a single charge process. This pathway can be expressed by following reactions

\[ RM \rightarrow RM^+ + e^- \]
\[ Li_2O_2 + 2RM^+ \rightarrow 2RM + 2Li^+ + O_2 \uparrow \text{(chemical oxidation)} \]

RMs keep cycling inside cells during charge process and oxidize Li$_2$O$_2$ repeatedly which promises the working efficiency of RMs. In discharge, RM keeps intact without having electrochemical reactions, unless the voltage drops too low to cause the reduction of RM.

![Figure 1-5: charge process with/without redox mediator](image)

Figure 1-5 illustrates the different charging mechanisms with/without RM. During charging, electrochemical decomposition of peroxide can lead electrolyte to break down as the generation of active species, threatening the stability of electrolyte and carbon \( Li_2O_2 \rightarrow xLi^+ + Li_{2-x}O_2 + xe^- \) \text{(electrochemical oxidation)}. However, RM can decompose peroxide chemically, suppressing side reactions of Li-O$_2$ cells. The implementation of RM does not only decrease the charge overpotential, but can also enhance the lifetime of cell through ensuring the stability of electrolyte.

To determine whether an additive is a suitable RM and to judge the working ability of RMs, several criterions are listed below: (1) the oxidation voltage of RM should be slightly higher than the formation voltage of Li$_2$O$_2$ which could guarantee the discharge capacity of Li-O$_2$ batteries; (2) the working potential of RM should be higher, but close to the equilibrium potential of Li$_2$O$_2$ potential, in order to minimize charge overpotential and improve energy efficiency of cells; (3) RMs should be soluble in the electrolyte and not heavily influence the solubility of oxygen in the solution; (4) RMs should be stable under the working voltage window of cells and under the appearance of active species \( O_2^- \), \( O_2 \) and Li$_2$O$_2$; (5) less likely to react with lithium metal, electrolyte and slow speed to become passivated; (6) have fast charge transfer ability in order to achieve higher rate capacity and energy density.

1.7 Overview of side reactions in Li-O$_2$ batteries

Due to the porous structure and high electrical conductivity of carbon, it is commonly used in Li-oxygen battery as cathode material to achieve larger capacity and good gas diffusion. However, previous studies show that carbon electrode would decompose over 3.5 V to generate Li$_2$CO$_3$ through reacting with Li$_2$O$_2$. And active cell
products would induce electrolyte decomposition during discharge/charge to generate Li$_2$CO$_3$ and Li carboxylate.

Measurements with isotope labeled carbon in the electrode and electrolyte found that during discharge and charge with voltage smaller than 3.5 V, side reactions mainly occurred in the electrolyte. And the quantity of Li$_2$CO$_3$ is highly dependent on the stability of electrolyte. Side reactions in the electrolyte can be expressed by

$$Li_2O_2 \rightarrow xLi^+ + Li_{2-x}O_2 + xe^-$$

$$Li_{2-x}O_2 + electrolyte \rightarrow Li_2CO_3, CH_3COCH_3, LiCOOH, or CH_3COOLi$$

Among all possible organic electrolytes, ether-based electrolyte leads to the lowest generation of by-product in discharge process and which is desired in reversible Li-oxygen battery. Due to its low volatility and superior stability with direct contact of lithium metal and high tolerance of the wide voltage window (2.0 - 4.5 V). Additionally, ether-based electrolyte has less electrophilic carbonyl bonds compared with traditional organic carbonate-based electrolyte, diminishing the attack from nucleophilic species. However, due to ether-based electrolyte has poor anodic stability, it is more likely to decompose at high voltage (>4.5 V). These previous works provide us important information to choose the suitable solvent and working window of the Li-oxygen batteries. In charge process when voltage is higher than 3.5 V, the decomposition of carbon electrode occurs where carbon can chemically react with Li$_2$O$_2$.

$$Li_2O_2 + C + \frac{1}{2}O_2 \rightarrow Li_2CO_3$$

$$2Li_2O_2 + C \rightarrow Li_2O + Li_2CO_3$$

During charging process, Li$_2$CO$_3$, which is in the electrolyte, decomposes and generates at the same time at around 3.5 V, nevertheless, the part which generates on the surface of positive electrode decomposes at higher voltage, around 4.2 V. However, previous study shows that the by-products generated at the surface of cathode cannot completely decompose even under large overpotential, therefore, the accumulation of Li$_2$CO$_3$ with cycling will lead the passivation of positive electrode. With the increasing of cycling number, the generation of Li$_2$CO$_3$ is more likely from the decomposition of carbon electrode other than electrolyte.

Looking into the stability of the electrolyte and carbon cathode is significantly important, as it is one of the core indicators to predict the lifetime of the Li-O$_2$ cells. And the cell stability also plays a significant role in understanding whether RM would influence the occurrence and pathway of side reactions in Li-O$_2$ cells, hence, make effects on the cell performance.

1.8 Highlights of this thesis

So far, there is still debate on the reliability of considering Li-O$_2$ battery as a secondary battery. In this study, the full voltage window was used while testing the cycling performance, which means that all the active sites would be activated after first discharge. However, in previous studies with similar Li-O$_2$ systems, they used capacity restriction while testing the electrochemical performance of cells which leads to questionable results concerning the reversibility of Li-O$_2$ cells.
This is the first time to combine Nano seed concept with RM in Li-O₂ batteries, which is predicted to improve the cell performance under this synergy. As mentioned previously, Nano seed can help improve the reversibility of Li₂O₂ on the surface of cathode, and soluble RM is helpful in improving charge transfer kinetics of Li₂O₂ both in the solution and on the electrode surface.

Previous study about soluble catalysts only focused on the charge process, explaining how RM would improve the decomposition of peroxide. Here, we would like to further study the influence of RMs to the property of electrolyte, hence, clarify their impacts on the growth and decomposition of cell products.

1.9 Research questions and scope of the thesis

The purpose of this thesis is studying the electrochemical performance and working mechanism of Li-O₂ batteries in a redox-mediator electrolyte at different state of discharge/charge. Several research questions are summarized below

(1) What is the most suitable RM for our Li-O₂ battery and its optimal concentration as additive in the electrolyte?

(2) What is the fundamental working principle of RM and how does it influence the electrochemical performance of Li-O₂ cells?

(3) Do RM influence the morphology and crystallinity of cell products during discharge and charge processes?

This thesis is structured as follows: in chapter 2, the methodology will be introduced, where various technical methods applied in this research would be introduced. In chapter 3, the experimental set-up is given. The material preparation is described. Furthermore, the sample preparations for measurement that introduced in chapter 2 will also be described. Result and discussion is in chapter 4, which provides the data analysis and conclusions for each sub-experiment. At end, the conclusions and recommendations are summarized.
Effects of Redox-mediator Electrolyte on the Electrochemical Performance of a Nonaqueous Li-O₂ Battery
2. Methodology

In this section, the theoretical working principle of MACC4000, cyclic voltammetry (CV), X-ray diffraction (XRD), Rietveld refinement, scanning electron microscope (SEM), X-ray photoelectron spectroscopy (XPS) and Nuclear magnetic resonance (NMR) are introduced.

**MACCOR4000**

This is the core method to study the electrochemical performance of the battery. Connect cathode side of cells to pure oxygen before starting MACCOR test. After resting for 5 h, the cells are cycled galvanostatically, which means cycled with a constant current density. (One full cycle is composed by a discharge process to a voltage of 2.0 V and a charge process to a voltage of 4.5 V.) As known the current density, the current would be obtained via multiplying the geometrical area of the cathode (1.26 cm²).

When reaching the equilibrium during rest, MACCOR shows the Open cycle voltage (VOC) of the cell, normally around 2.95-3.15 V, where no electron flow between two electrode as an infinite load resistance connecting to the external circuit. The VOC can be varied to some extent due to the change of thermodynamic force under the variation of environmental factors. When the cell test start, MACCOR provides the online information of the cell emf (electromotive force), and this value can be clarified by the Gibbs free energy of the reactions (ΔG) and the electrode potentials of the two half-reactions:

\[
\Delta G = -nFE = \Delta G^0 + RT\ln \frac{a_R^{v_R}}{a_O^{v_O}} 
\]

\[
E = E^0 + \frac{RT}{nF} \ln \frac{a_O^{v_O}}{a_R^{v_R}} 
\]

In these two equations, \(E\) presents the half-cell potential; \(E^0\) and \(\Delta G^0\) are the standard reaction potential and standard Gibbs free energy respectively, which can be obtained under constant, atmospheric pressure and at room temperature, 298 K; \(n\) stands for the number of electron passed per reaction; \(R\) is gas constant, 8.314 J/mol·K; \(F\) means Faraday constant, indicating the charge of a mole of electrons which is about 96485 C; \(a_R\) and \(a_O\) are the activities of reductant and oxidant in the half reaction, and \(v_R\) and \(v_O\) are stoichiometric coefficients.

\[
E_{\text{rxn}} = E_{\text{cathode}} - E_{\text{anode}} 
\]

Equation 2.2 is known as the famous Nernst equation, with which the redox potentials of the two electrodes can be obtained. Once there is a positive potential difference between cathode and anode, electrons can flow from higher potential to lower potential spontaneously, and the potential difference is regarded as the cell emf, \(E_{\text{rxn}}\), shown in equation 2.3. In Li-O₂ cell, it undergoes a discharge process with a negative Gibbs free energy and a positive cell emf which is defined as a galvanic cell.
CV

Cyclic voltammetry (CV), which is also regarded as the electrochemical spectroscopy, is a popular technology for testing the electrochemical properties of the redox systems. Figure 2-1 illustrates the basic experimental setup of CV. In the obtained CV graph, it shows the relationship between current and potential of the batteries. From the CV curve, not only the redox potential can be determined, but also the information of kinetics of chemical reactions and heterogeneous electrode-transfer reactions can be provided. Therefore, we can use CV to study the redox process unequivocally in Li-O₂ cells and check the reversibility of the redox couples. The information is helpful in analyzing the electrochemical performance of the Li-O₂ batteries.

Figure 2-1: Schematic working theory of cyclic voltammetry (a) Simplified equipment set-up. Where, FG (voltage scan generator), PT (potentiostat), XY (recorder), RE (reference electrode), AE (auxiliary electrode) and WE (working electrode); (b) Illustration of potential sweep. Potential linearly changes within a certain working window. Until reaching the boundaries of set voltage, it changes direction of scanning.

\[ i_p = (2.69 \times 10^5)n^{3/2}AD_0^{1/2}Cv^{1/2} \]  

In the obtained CV curve, the peak current is one of the most important factor. In a Nernstian system, it can be expressed by the Randles-Sevcik equation. As expressed in equation 2.4, the peak current is related to the electron stoichiometry \( n \), electrode surface area \( A \), diffusion coefficient \( D_0 \), species concentration \( C \) and scan rate \( v \). When it reaches the peak current, the maximum amount of electrons are passed. In our CV tests, two-electrode system was used which has no reference electrode, thus the tested current is the net current of the cell under certain potential. And the tested potentials might be slightly different from the real electrochemical potential of the tested species, as it is influenced by the potential of lithium anode.

XRD

X-ray diffraction (XRD) is a fundamental technique for determining the crystal structure, chemical composition and physical properties of materials. Crystal materials are neat arrays of atoms which would have certain distance between diffracting planes. And X-ray waves are regarded as waves of electromagnetic radiation. Once X-ray beam hits crystal materials, the waves would be cancelled one by another in most directions, however, these waves would add together on specific directions. Whether these waves would add or cancel with each
other is dependent on the distance between the nearby diffracting planes (d), incident angle (θ) and wavelength of X-ray (λ)\textsuperscript{13}, and this could be summarized by Bragg’s Law: $2d \sin \theta = n \lambda$, Where, n is any integer. When the waves fulfill the Bragg’s Law, they would sum up and lead peaks at certain angles.

![Figure 2-2: Schematic working principle of reflection and diffraction in crystal material](image)

XRD measurement is based on the observation of scattered intensity while an X-ray beam hitting a sample. In a single material, the intensity varies with the scattered angle, polarization and energy of X-ray beam. Different materials have unique XRD pattern which is the reason for implemented XRD technique in the determination of chemical composition. The height, position and width of the peaks are all important information for determining the characterization of crystalline materials. In our study, the XRD tests of cathodes at different stage of discharge/charge, various current densities and with addition of different types or various concentration of RM were obtained. It would be significant in analyzing the influence of RM to the growth and decomposition of Li\textsubscript{2}O\textsubscript{2}, and also helpful in detecting the generation of by-products inside the cells.

**Rietveld refinement**

The obtained experimental XRD data is always slightly different from the standard XRD pattern, as influenced by the crystallinity and content of the phases. Therefore, in order to get the accurate and detailed crystal information, such as lattice parameter, cell volume and domain size of the cell products, the Rietveld refinement should be implemented. The Rietveld method is based on a least squares approach to refine a theoretical calculated profile until it matches the tested profile\textsuperscript{64}. Through Rietveld refinement the difference between the observed data and calculated data, which is expressed by function M, can be minimized:

$$M = \sum_{i} W_{i} \left( \frac{1}{c} y_{i}^{\text{calc}} - y_{i}^{\text{test}} \right)^{2} \tag{2.5}$$

Where $W_{i}$ is the statistical weight, and c is a scale factor which keeps $y^{\text{calc}} = c y^{\text{test}}$. Theoretically, through applying Scherrer equation, the domain size of Li\textsubscript{2}O\textsubscript{2} can be calculated. The original Scherrer equation was published in 1918, as presented in equation 2.6:

$$B(2\theta) = \frac{k \lambda}{P \cos \theta} \tag{2.6}$$

And the anisotropic domain size can be calculated by:
\[ P = \frac{18000K\lambda}{10\pi(LX-3.168)} \] (2.7)

Where, \( P \) is the mean size of the crystalline domain; \( K \) is the Scherrer constant which is also named dimensional shape factor, 0.89; \( \theta \) is the Bragg angle in degrees; \( \lambda \) is the wavelength of X-ray, 1.5405 Å; \( B \) is the line broadening at half the maximum intensity (FWHM). In our case, as obtained accurate crystal information from the General Structure Analysis System (GSAS) program, the average coherent size is calculated through equation 2.7. Additionally, \( LX \) is the Lorentzian coefficient. To achieve the criteria of fit, \( R \) weighted pattern (\( R_{wp} \)) should be smaller than 5%, which can be obtained from equation 2.8:

\[ R_{wp} = \left\{ \frac{\sum wi(y_{\text{test}} - y_{\text{calc}})^2}{\sum wi(y_{\text{test}})^2} \right\}^{\frac{1}{2}} \] (2.8)

With the implementation of GSAS refinement, the more precise physical properties can be received which provides us important information for analyzing the structure change of products on the surface of cathode under specific conditions.

**SEM**

Scanning electron microscopy (SEM) is a typical technique method to study morphology of the surface of samples and help determine the gain size of crystal species in a sample. As a focused high energy electron beam hit the surface of the specimens, it will generate signals which derives from electron-sample interaction. These signals mainly include: (1) secondary electrons, contributing to the produce of SEM image and show texture on sample, which is regarded as the most important function of SEM technique; (2) backscattered electrons and diffracted backscattered electrons are involved in the determination of orientations and crystal structures of crystals; (3) photons which work as the similar function of X-ray, used for elemental analysis; (4) also heat and visible light.

Here, we mainly use SEM technique to study the morphology of cathodes after operating under different conditions. As known the properties of the electrolyte solution would impact the growth mechanism of peroxide, operating SEM measurements would help study whether the addition of RM would influence the growth of Li₂O₂.

**NMR**

Nuclear magnetic resonance (NMR) is a popular technique which takes an important role in analyzing the structure of molecule, quantitatively analyzing chemical elements, and also play a significant role in biology and life science field. NMR is a promising technique, owning to its fast and accurate characteristics. Nucleons are composited by neutrons and protons which generate small magnetic fields with the cincture of electrons, therefore, leading the quantum property of spin. However, at natural state, the overall spin of the nucleons is zero which is due to the neutralization of magnetism on all directions. The principle of NMR is applying an extra anti-direction magnetic field to the nucleons, which would promote nucleons from low energy levels to high energy levels after absorbing energy from other resources. Once the excited nucleons going back to equilibrium state, it would release energy to the surrounding which can contribute to the energy supply to the
nuclear transition. And only the absorbed energy which matches \( \Delta E = h\nu_0 \), that a magnetic resonance absorption would occur.\(^6^7\) From the result of NMR spectra, important information can be obtained: (1) the position of signals which are represented by chemical shift; (2) relative intensity of signals which is the integration of each peak; (3) Splitting of signals.

As electrolyte decomposition is always a serious problem in Li-O\(_2\) cells, NMR tests would help the study of electrolyte stability in our Li-O\(_2\) cells. Here, \(^1\)H-NMR tests were conducted, since only few milligrams of sample are required, but high accuracy can be guaranteed.

**XPS**

X-ray photoelectron spectroscopy (XPS) is a surface analytical method which can essentially work for areas for some mm\(^2\) and depth for several nanometers. As specific element having a characteristic set of peaks at respect of binding energy, this would help the analyses and identification of chemical bonds on the electrode surface.\(^6^8\)

![Figure 2-3: Working principle of X-ray photoelectron spectroscopy (XPS)\(^6^9\)](image)

Through applying X-ray beams to sample, it can induce the ejection of photoelectrons. As shown in figure 2-3, X-ray photons interact with electron in the K shell, leading the emission of a photoelectron from 1s orbital, while generating a hole in the valence band. Then, the electron from a higher energy level will step back to the 1s orbital and fill the vacancy which would cause either radiationless de-activation process of Auger emission or X-ray fluorescence.\(^7^0\) The binding energy can be calculated with following equation.

\[
E_b = h\nu - E_{\text{kin}} - W_f
\]

Where, \( E_b \) is binding energy; \( h\nu \) is incident photon energy; \( E_{\text{kin}} \) is kinetic energy of photonelectron after emission; and \( W_f \) is work function which stands for the energy requirement for electronic transition between two energy levels. Through XPS techniques we can precisely analyze the species on the cathode surface, in case some products are either amorphous or too less to be detected by XRD and NMR approaches, and also not identical via SEM image.

This chapter describes the basic working principle of the techniques that used in this thesis. In chapter 3, a more detailed experimental design will be introduced.
3. Experimental set-up

3.1 Storyline of experiment

1) Material preparation & cell assembly
   - Anode: Li metal pretreated with PC
   - Electrolyte: 0.5 M LiTFSI/TEGDME + various RMs
   - Cathode: a. Fe$_2$O$_3$/CNT = 300:100; b. CNT/PVDF = 75:25; c. CNT/PVDF with preloaded LiOH or Li$_2$CO$_3$.

2) Selection of redox mediators
   - Electrochemical tests of cells with addition of various RMs, namely TEMPO, TDPA, FePc, Fc and Lil.

3) Concentration optimization
   - Electrochemical tests of cells with different concentrations of TEMPO – 5 mM, 10 mM, 20 mM, 30 mM and 50 mM separately.

4) Electrochemical performance of cells with addition of RM
   - CV tests under Ar / O$_2$ environment
   - Cycling performance with capacity restriction
   - Cycling performance of cells under different current densities

5) Crystallinity and morphology study
   - XRD tests with various operation conditions
   - SEM images for different test conditions
   - GSAS refinement

6) Cell stability after cycle
   - Calculation
   - Cell cycling in closed system & XRD test
   - $^1$H-NMR tests
   - Ex-situ XPS analysis

Figure 3-1: Blocks for illustrating the experimental storyline
3.2 Material preparation and cell assembly

3.2.1 Fabrication of electrodes and electrolyte

**Cathode**

Fe₃O₄ and CNT were dried separately for 24 h in a 65 °C oven before use. Grind the Fe₃O₄/CNT mixture carefully with a ratio of 3:1. Add 3 ml NMP (1-Methyl-2-Pyrrolidon: anhydrous 99.5%, Sigma Aldrich) and transfer the slurry into a ball milling machine. After 4-hour ball milling, the slurry was coated on carbon fiber paper (CFP) and scratched by a doctor blade with a height of 100 µm. The wet electrode layer was dried in a vacuum oven to drive remain water and NMP out.

For preparing CNT/PVDF electrode, PVDF was dissolved in NMP through uniformly stirring. After PVDF completely dissolved in the solution, CNT (with a mass ratio CNT:PVDF=75:25) was added and stirred for 12 hours. The slurry was coated on the CFP and followed by the same steps as preparing the Fe₃O₄/CNT cathode.

For analyzing the decomposition of LiOH and Li₂CO₃ with/without the addition of TEMPO, slurries of CNT/PVDF (75:25) with preloaded commercial LiOH (lithium hydroxide monohydrate, ≥98.0%, Sigma Aldrich) or Li₂CO₃ (lithium carbonate, ≥99.0%, Sigma Aldrich) were prepared in the glovebox, which further coated on the CFP and tried out in the glovebox. All the materials were tried in the oven at 80 °C for two days before use.

**Anode**

Lithium metal was immersed in 0.1 M LiTFSI/PC for around one month, forming a SEI protecting layer on the surface. Afterwards, lithium metal was washed with DMC (Dimethyl carbonate) twice to get rid of extra PC molecules and dried in the anti-chamber.

![Figures 3-2: Lithium metal before and after LiTFSI/PC protection.](image)

Left: before treatment; right: after treatment.

**Electrolyte**

TEGDME (tetraethylene glycol dimethyl ether, Sigma Aldrich) was filtered by molecular sieves to eliminate the pollution of water and other impurities. With LiTFSI (Bis(trifluoromethylsulfonyl) amine lithium salt, Sigma Aldrich), 0.5 M LiTFSI/TEGDME solution was prepared as electrolyte base and combined with different RMs to formulate specific redox-mediator electrolyte. Important characteristics of TEGDME are summarized in table 3-1.
Table 3-1: Important properties of TEGDME$^{58,71}$

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dielectric constant</td>
<td>7.79</td>
</tr>
<tr>
<td>Oxygen solubility</td>
<td>4.43</td>
</tr>
<tr>
<td>DN</td>
<td>16.6</td>
</tr>
<tr>
<td>Viscosity $\eta$</td>
<td>4.05</td>
</tr>
</tbody>
</table>

### 3.2.2 Assemble a battery

Figure 3-3 illustrates the structure of Li-O$_2$ cell in the lab scale. Lithium metal was stuck on the current collector. Use glass fiber as separator to carry electrolyte solution (6 drops, which was added via a pipet) and prevent the short circuit. On the cathode side, Fe$_2$O$_3$/CNT electrode was pasted on the mesh and immersed by 3 drops of the electrolyte.

![Figure 3-3: Schematic illustration of the structure of Li-O$_2$ lab cell](image)

### 3.3 Selection of redox mediators

Based on the former researches, the most suitable RM was selected from TEMPO, TDPA, Fc, FePc and LiI. Various RMs were added into the electrolyte base to prepare electrolytes of 10 mM RM + 0.5 M LiTFSI/TEGDME. Li-O$_2$ cells with different RMs were tested by MACCOR, with a voltage window of 2.0-4.5 V, cathode material Fe$_2$O$_3$/CNT=300:100 and a current density of 0.2 mA/cm$^2$.

### 3.4 Concentration optimization

Six concentration stages of the selected RM were prepared with 0.5 M LiTFSI/TEGDME, namely gradients of 0 mM, 5 mM, 10 mM, 20 mM, 30 mM and 50 mM. And cycling performance was measured with a full voltage window, a current density of 0.2 mA/cm$^2$ and cathode Fe2O3/CNT= 300:100.

Former studies about RMs in Li-O$_2$ batteries only focused on clarifying the working principle of RM during charge process, but not illustrated the impact of RM concentration on the cell performance. The concentration of RM can be important for determining the performance of Li-O$_2$ cells, through influencing the oxygen solubility, electrolyte stability and even impact the catalytic rate while decomposing Li$_2$O$_2$ during charge process.
Table 3-2: Basic information of TEMPO, TDPA, FePc, FC and Li$^{72}$

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Empirical Formula</th>
<th>Molecular Weight [g/mol]</th>
<th>Structural Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEMPO</td>
<td>C$<em>9$H$</em>{18}$NO</td>
<td>156.25</td>
<td><img src="image" alt="TEMPO structure" /></td>
</tr>
<tr>
<td>TDPA</td>
<td>[(C$_2$H$_5$)$_2$NCH$_4$]$_3$N</td>
<td>458.68</td>
<td><img src="image" alt="TDPA structure" /></td>
</tr>
<tr>
<td>FePc</td>
<td>C$<em>{32}$H$</em>{18}$FeN$_6$</td>
<td>568.37</td>
<td><img src="image" alt="FePc structure" /></td>
</tr>
<tr>
<td>Fe</td>
<td>Fe(C$_5$H$_5$)$_2$</td>
<td>186.03</td>
<td><img src="image" alt="Fe structure" /></td>
</tr>
<tr>
<td>Li</td>
<td>LiI</td>
<td>133.85</td>
<td>LiI</td>
</tr>
</tbody>
</table>

3.5 Electrochemical performance of cells with RM

This section included following sub-experiments:

- **CV**: CV tests were conducted with a scan rate of 0.1 mV/s and under Ar/O$_2$ environments to illustrate how the redox reaction of TEMPO would influence the OER of Li-O$_2$ batteries.

- **Capacity restriction**: discharge cells to 500 mAh/g and recharge to 4.5 V/500 mAh/g. This can study how the discharge/charge depth would influence the electrochemical performance.

- **Various current densities**: Li-O$_2$ cells were cycled with different current densities (0.2 mA/cm$^2$ and 0.1 mA/cm$^2$), for illustrating the electrochemical characteristics of RM and the rate capability of Li-O$_2$ cells with additive.

- **Varying cathode composition**: Decrease the content of Fe$_2$O$_3$ in the cathode (Fe$_2$O$_3$/CNT= 9:1, 3:1, 0.5/1 & 100% CNT) or change the carbon resources (Super P) to obtain voltage curves. This was aim to study whether the cathode structure would impact the diffusion of RM in the Li-O$_2$ cells.

3.6 Crystal structure and morphology study

- **XRD**: The crystallinity was studied with ex-situ XRD and GSAS refinement. The cathodes were washed by DMC to move the extra electrolyte and tried in anti-chamber for evaporating DMC. Transfer to the machine with a airtight sample holder. XRD tests were conducted with a Cu K$\alpha$ radiation on a PANalytical X'Pert Pro PW3040/60 diffractometer for a $2\theta$ range of 30-70°. The operating voltage and current were 45 kV and 40 mA, respectively. GSAS refinement was implemented on fitting the obtained XRD patterns, focusing on refining the lattice parameters, peak broadening and crystal anisotropy. The
patterns at the $2\theta$ range of 42.5 and 55.0° were deducted which were corresponds to peaks raised from carbon.

- **SEM**: The texture and morphology of the electrodes were studied with SEM images. Electrodes under different testing points were rinsed by DMC in the glovebox and dried in vacuum condition. Samples were transferred to the SEM machine (JEOL JSM-6010LA) without air leaking. The accelerating voltage of SEM is 10 kV. SEM images were took at different positions and magnifications of a single sample.

3.7 Test the stability of electrolyte

As known the side reactions are always inevitable in Li-O$_2$ cells, it is significantly important to look into the stability of the cells, especially the decomposition of electrolyte and carbon electrode.

- **Calculation**: A rough calculation based on the chemical reactions and mass load of different components was made in advance to estimate the possible severity of side reactions in the battery.

- **Cycle with a closed jar**: An air-tight bottle, which was filled with pure oxygen and with a pressure of 1 atm, directly connected with a Li-O$_2$ cell. Cycle the cell with a full voltage window and current density of 0.2 mA/cm$^2$. After cycle, the cathode was measured via XRD to identify the generation of accumulated by-product.

- **$^1$H-NMR**: Separators and cathodes were took from the tested cell and soaked in D$_2$O (Deuterium oxide) immediately. After completed dissolution, the samples were transferred into NMR tubes and examined by a NMR machine (VNMRS 400) with an external frequency of 400 MHz at 25°C.

- **Ex-situ XPS**: The electrodes were rinsed with DMC and dried in anti-chamber for serval times. XPS measurements were operated with a Al Kα sources from a K-alpha Thermo Fisher Scientific spectrometer at ambient temperature. Here, we mainly focused on Fe 2p, C 1s and O 1s spectrums at different SoC.

This part mainly demonstrated the story line and experimental steps of this thesis. In this coming section, the results of these experiments and data analysis will be provided.
4. Result and discussion

In this chapter, the selection and concentration optimization of RM, and electrochemical performance of the cells were obtained at first. To further study how RM influenced the performance of Li-O₂ cells, the attentions focused on the crystal structure and morphology analysis of the discharge product, and product decomposition mechanism at different stages of charge. At end, the stability of the cell was discussed.

4.1 Cells with different RMs

Figure 4-1 (a) showed the voltage curves of cells with CNT/PVDF (75:25) cathode and without additive, which presented large overpotentials in both discharge/charge processes and poor reversibility. In figure 4-1 (b), it showed the origin voltage curves of Li-O₂ of cell using Fe₂O₃/CNT (300:100) cathode. Due to the implementation of ‘Nano seeds’ meanwhile Fe₂O₃ particles to reconstruct the cathode, the discharge and charge overpotentials decreased to 0.3 V and 1.3 V, respectively.

As presented in figure 4-2, the discharge voltage plateau maintained at 2.7 V with the addition of RMs, which proved that the working region of RMs were at charge process. Among these RMs, TEMPO maintained the highest discharge capacity which was about 1050 mAh/g, nevertheless, FePc caused the most serious capacity fading which was only around 700 mAh/g after the first cycle. However, compared with the cell without additive, the discharge capacity of cells with TEMPO decreased to some extent at start-up region. And this was explained by salt out effect of TEMPO which meant the reduction of oxygen solubility in the electrolyte.

During charge process, there were two visible voltage plateaus in cells with the addition of TEMPO, FePc and LiI. Among these three RMs, TEMPO achieved the lowest charge overpotential (~0.74 V) and longest first charge plateau. However, cells with FePc only decreased the charge potential to around 4.0 V; the addition of LiI can only maintain very limited working range which was around one third of the whole charge capacity. The addition of TDPA and FC did not make obvious changes on the charge profiles, which might be attributed to their slow charge transfer kinetics, being influenced by the ionic strength of the electrolyte.
Figure 4-2: Voltage curves of cycling cells with different RMs, a current density of 0.2 mA/cm² and cathode material Fe2O3/CNT = 300:100. (a) various electrolyte solution, the sequence from left to right – TEMPO, FePc, Fc, TDPA and Lil; (b) 10 mM TEMPO; (c) 10 Mm TDPA; (d) 10 Mm FePc; (e) 10 Mm Fc and (f) 10 mM Lil.

Additionally, the molecular size and mass of RMs might be a factor of their working performance, as shown in the Stokes-Einstein equation:

$$D_{AB} = \frac{2kT}{b\eta_B}(\frac{N_A}{V_A})^{1/3}$$

This equation illustrates the diffusion coefficient of diffusing species A in a vicious liquid B. Where, T is the temperature; b is the size-dependent constant which increases with molecule sizes; $N_A$ is the Avogadro constant, $V_A$ is the molar volume of the diffusing species and $\eta_B$ is the liquid viscosity. As listed in table 3-2, heavier RMs presented poor performance which demonstrated slower diffusion rate compared with lighter RMs, namely TEMPO and Lil.

As shown in figure 4-3, compared to the origin cell, the cells with TEMPO showed the superior cycling stability and cell capacity. On the contrary, the capacity fading became even faster after adding FePc, FC and Lil in the electrolyte. This result led to the question of their fitness of being used as soluble catalysts in Li-O₂ cells. The most possible reason was these RMs would threaten the electrolyte and electrode stability, hence, studying how the RM would impact the properties of the electrolyte was significant.
Result and discussion

Through this comparison, the cell with addition of TEMPO showed the best performance, no matter in specific capacity, catalytic activity or cycling stability. An increase in capacity was found after around 35 cycles in cell with TEMPO which was explained in the following part.

4.2 Concentration optimization

Previous studies did show the superior performance of TEMPO in enhancing the charge transfer ability of peroxide. Apart from this, as an additive in the cells, it can also impact the oxygen solubility and the properties of the electrolyte. The reversible processes of oxygen reduction can be separated into four individual reactions:\textsuperscript{15}

\[
\begin{align*}
    O_2(\text{Gas}) & \rightleftharpoons O_2(\text{Solution}) \\
    O_2(\text{Solution}) + Li_{\text{(Surface)}} & \rightleftharpoons O_2^-(\text{Solution}) + Li^+(\text{Solution}) \\
    O_2^-(\text{Solution}) + Li^+(\text{Solution}) & \rightleftharpoons LiO_2(\text{Surface}) \\
    LiO_2(\text{Surface}) & \rightleftharpoons O_2(\text{Gas}) + Li_{\text{(Surface)}}
\end{align*}
\]

As the equilibrium of the first equation shift to the left due to the salt-out effect of TEMPO, the equilibrium of the rest reactions will also be influenced. The third reaction is simply the transform between LiO\(_2\) in the solution and on the surface of the cathode. The shift of this reaction would also promote the direction of peroxide growth to either the solution mechanism or the surface mechanism. And the extent of the impact might be a function of TEMPO concentration, as TEMPO would influence the oxygen solubility.
Figure 4-4: Voltage curves of cycling cells with different TEMPO concentration, a current density of 0.2 mA/cm² and cathode material Fe₂O₃/CNT = 300:100. (a) No additive; (b)5 mM TEMPO; (c)10 mM TEMPO; (d) 20 mM TEMPO; (e) 30 mM TEMPO and (f) 50 mM TEMPO.

As presented in figure 4-4 and figure 4-5(a), the discharge capacity declined with increasing TEMPO concentration. Furthermore, faster capacity fading was detected in cells with high TEMPO concentrations (≥20mM). However, cells without or with low TEMPO content (≤10 mM) maintained relatively stable discharge capacity. The support information of this result can be found in table appendix A.

Two charge plateaus were obtained in all cells with TEMPO. With cycling processing on, the relative length of the first charge plateau declined which was clearly shown in cell with low TEMPO concentration (5 mM), suggesting that TEMPO might be gradually deactivated after cycle.

Figure 4-5(c) showed the columbic efficiency of cells with different TEMPO concentration. The columbic efficiency increased with raising TEMPO concentration which was attributed to the oxidation of TEMPO. However, the columbic efficiency was significantly higher than 100% which would reduce the round-trip efficiency of the Li-O₂ batteries. The relative length of the first charge plateau increased with raising TEMPO concentration, as TEMPO oxidized at the end of the first charge plateau before the potential reached to the second charge plateau. To study the working efficiency of TEMPO, the ratios of the capacity located on the first charge plateau (excluding the oxidation capacity of TEMPO) and the discharge capacity were calculated and listed in appendix A. These ratios indicated moderated concentrations of TEMPO, 10 -20 mM, can lead the longest relative length of the first charge plateau.
4.3 Electrochemical performance of cells with addition of RM

4.3.1 Cyclic voltammetry analysis

Other than cycling performance, it is significant to understand the redox behavior of TEMPO with/without the appearance of \( \text{O}_2 \) and working potential of OER with/without TEMPO. This would help to explain how TEMPO electrochemically impacted the cell performance.

In figure 4-6(a), it showed the electrochemical behavior of cell without additive. The cathodic peak indicated the reduction of oxygen, while the main anodic peak, started from around 4.2 V matched with the voltage of the charge plateau, presenting the oxidation of the discharge product. There was a sloppy region starting from
around 3.1 V, indicating the OER of the surface Li$_2$O$_2$, which was easier to be decomposed compared with crystal Li$_2$O$_2$.

The insert CV image in figure 4-6(b) represented the redox reactions for the cell with TEMPO under Ar environment which showed two pairs of redox couples. The anodic peak starting from around 3.5 V showed the oxidation of TEMPO, while the cathodic peak presented the reduction of TEMPO$^+$. The half-way potential, $E_{1/2}$ indicated the formal potential of TEMPO was 3.75 V, which matched to the voltage of the first charge plateau.

Under oxygen environment, as shown in figure 4-6(b), the cathodic peak began to appear at the potential of 3.0 V, resulting from ORR. During OER, three anodic peaks were obtained. The small peak at the range of 3.0 -3.3 V represented the oxidation of the surface Li$_2$O$_2$. Compared with the cell with no additive, although the integrated area under the cathodic peak was significant larger than it in cell with TEMPO, the area under the small anodic peak (from 3.0 to 3.4 V) was clearly much smaller than it in cell without TEMPO. Thus, we can conclude the addition of TEMPO would suppress the generation of surface peroxide. Then, it is followed by the main anodic peak which corresponded to the decomposition of the crystal peroxide. The main peak was located at the potential range of 3.5 -4.2 V which shifted to the lower potential with respect of the cell with no additive and perfectly matched with the working window of TEMPO, indicating that TEMPO did enhance the charge transfer of Li$_2$O$_2$. When the applied voltage was higher than 4.2 V, another anodic peak, corresponding to reaction on the second charge plateau appeared. This distinguish peak with respect of the main anodic peak should own to the decomposition of cell products other than peroxide. And later XRD test also proved this speculation.

![Figure 4-6: Cyclic Voltammetry for cells with/without TEMPO and under Ar/O$_2$ environment. (a) no additive; (b) with 10 mM TEMPO, with a scan rate of 0.1 mV/s and cathode Fe$_3$O$_4$/CNT=300:100. The insert figures are](image-url)
the enlarged CV curves for cells under Ar environment; (c) anodic and cathodic peak currents of 10 mM TEMPO; (d) the reversibility of TEMPO under Ar environment.

The ratio of the anodic \( i_{p,a} \) and cathodic \( i_{p,c} \) peak currents, and the repetitivity of the CV curves can illustrate the reversibility of TEMPO. The current peaks of TEMPO under Ar environment were highlighted in figure 4-6(c), with which it obtained \( i_{p,a}/i_{p,c} \approx 0.95 \). Cell with 10 mM TEMPO was cycled under Ar environment as shown in figure 4-6(d), which indicated a desirable repetitivity. These results indicated TEMPO’s superior electrochemical reversibility and fast charge-transfer kinetics.

In figure 4-6(d), the variation of the anodic current while cycling was due to the change of the ‘decaying’ background which was induced by the electrolyte molecule polarization. Therefore, the deactivation of TEMPO that discovered in the previous section should blame to the nucleophilic attack of \( O_2^- \) or coverage by cell products during cycling, other than reaction with Li metal. Following experiments will explain the deactivation mechanism of TEMPO.

### 4.3.2 Electrochemical performance under capacity restriction

To study the influence of discharge depth on the cell performance, a capacity restriction (500 mAh/g) was set. However, Figure 4-7(a) still performed two charge plateaus and the relative length of the first charge plateau kept intact compared to cells cycled with full voltage window. This result can point out: (1) the appearance of the two charge plateaus were not related to the state of discharge; (2) the capacity that located on the second charge plateau was a scale of time when the same current density was applied.

Notably, difference in voltage curves were found when the cell did not have voltage setting during charge. In figure 4-7(b), no capacity degradation on the first charge plateau was observed when the cell was without voltage setting. This result led a speculation – TEMPO still tried to help the decomposition of discharge product at the end of charge process, therefore closely attached to the surface of cathode. However, when the voltage was forced to reach 4.5V, the carbon and electrolyte decomposition was accelerated, leading the generation of by-products, commonly Li$_2$CO$_3$. These by-products would gradually block active sites on the cathode and also cover TEMPO which was stuck at the electrode surface. The overpotential of the first charge plateau kept increasing while cycling which also indicated the generation of by-products. By-products would precipitate and accumulate on the cathode surface during charge and reduce the electrical conductivity of cathode and limit the heterogeneous kinetics, resulting in a raising overpotential during cycle.
Figure 4-7: Cycling performance with capacity restriction, 10 mM TEMPO and a current density of 0.2 mA/cm². (a) discharge to 500 mAh/g and charge to 4.5 V; (b) discharge to 500 mAh/g and recharge to 500 mAh/g, without voltage restriction.

Nevertheless, the cell without voltage limitation showed a constant end of charge potential for more than 40 cycles, shown in figure 4-8. However, the voltage increased to 4.7 V after 50 cycles which was high enough for Li₂CO₃ decomposition. Hence, all TEMPO would be released back to the solution at the end of charge and lead a stable catalytic performance in the cell.

Figure 4-8 cycling performance of Li-O₂ cells - Test time vs. Voltage - with discharge/charge capacity restriction (500 mAh/g) , 10 mM TEMPO, a current density of 0.2 mA/cm² and cathode material Fe₂O₃/CNT=300:100.

4.3.3 Cell performance as a function of current density

Rate capability is a significant criteria to show the ability of cell to achieve high power density and superior cell stability. Furthermore, current density can influence the growth mechanism of peroxide. And the current density might influence the catalytic activity of TEMPO. To support this assumption, electrochemical performance of cells with different current densities were measured.

Figure 4-9: Cycling performance as a function of current density. (a) 0.2 mA/cm² and (b) 0.1 mA/cm², without voltage restriction, with a capacity restriction of 0.5 mAh and 10 mM TEMPO.
With a smaller current density, the changes in charge profiles and TEMPO catalytic efficiency became more obvious while cycling, indicating the variations of reaction pathways. This result can be explained by TEMPO’s fast charge-transfer kinetics. And the overall reactions were summarized by following reactions:

\[
\text{TEMPO} \rightarrow \text{TEMPO}^+ + e^-
\]

\[
\text{Li}_2\text{O}_2 + 2\text{TEMPO}^+ \rightarrow 2\text{Li}^+ + 2\text{TEMPO} + \text{O}_2 \uparrow \text{(chemical oxidation)}
\]

\[
\text{Li}_2\text{O}_2 \rightarrow x\text{Li}^+ + \text{Li}_{2-x}\text{O}_2 + xe \text{ (electrochemical oxidation)}
\]

Known TEMPO’s fast charge-transfer characteristic from the previous CV tests, the electrochemical oxidation of TEMPO had a faster speed than chemical reaction where peroxide reacted with TEMPO. Therefore, chemical oxidation was the limited step during OER. At high rate, there was a higher reaction rate of chemical oxidation process, which can be explained by the Arrhenius equation:

\[
k = A \exp \left( -\frac{E_a}{RT} \right)
\]

Where, \(A\) is frequency factor; \(E_a\) is the activation energy; \(R\) is the gas constant; \(T\) is temperature; \(n\) is the number of electrons involved in the reaction. With large current density, the frequency of attempts on surmounting the energy barrier is higher which means a larger frequency factor. Therefore, reaction constant is larger under large current density. This indicated a faster cycling rate of TEMPO with a large current density. On the contrary, at low rate, the reaction speed of chemical OER decreased and TEMPO accumulate in the cell, resulting the limited current density from TEMPO oxidation. Therefore, \(\text{Li}_2\text{O}_2\) would undergo electrochemical decomposition to provide extra electrons, leading the generation of active species, \(\text{LiO}_2\), and threaten the cell stability. Hence, the best overall cycling performance was achieved with a large current density.

Furthermore, side reactions can be suppressed with a high current density, since when the voltage was higher than 3.5 V\textsuperscript{22}, both the CNT and electrolyte would not be stable. In this case, higher current density can minimize the reaction time to undergo side reactions. On the contrary, the electrode and electrolyte would stay longer under high charge potential at low rate, accelerating the formation of by-products. As shown in figure 4-9, the end of charge voltage increased faster under small current density which reached 4.75 V after 50 cycles. However, in cell with larger current density, it raised to 4.75 V after 100 cycles. This also indicated the high current density would mitigate chemical instability.

In summary, a higher current density would improve the catalytic efficiency of TEMPO and the electrochemical performance of Li-O\textsubscript{2} batteries. The fast charge-transfer characteristic of RM was a desirable feature, not only because it improved the energy efficiency of cells, but also because it was a promising property for pursuing large power Li-O\textsubscript{2} batteries and shorter charging period.

4.3.4 Cell performance as a function of cathode structure

Hee-Dae Lim and his co-workers\textsuperscript{57} illustrated that the structure of the cathode would influence the diffusion of soluble catalysts which can hinder the charge transfer of RMs to peroxide. Therefore, this led our question
of whether the working performance of TEMPO and the appearance of the second charge plateau were dependent on the structure of the cathode in our case. If the second charge plateau was induced by the cathode structure, the relative length of the second charge plateau would change after varying Fe$_2$O$_3$ content or changing the carbon resources.

Figure 4-10: voltage profile using different cathode materials. (a) different ratio of Fe$_2$O$_3$/CNT; (b) comparison between CNT and Super P, with 10 mM TEMPO.

Figure 4-10 showed the voltage curves of cells with different recipes of cathode materials. 4-10(a) illustrated the relationship between Fe$_2$O$_3$/CNT ratio and the shape of voltage curves. The results indicated the variations of Fe$_2$O$_3$/CNT compositions significantly impacted the cell capacities, as Fe$_2$O$_3$ is much heavier than CNT. However, the shapes of the voltage profiles did not change after altering the compositions.

In figure 4-10(b), the cell which took SuperP as carbon resources showed much smaller discharge capacity, since CNT has much higher surface/volume ratio and high porosity which can provide better electrical conductivity, more active sites and larger space to store the discharge products. However, the shape of potential curves still kept intact after changes.

These results demonstrated the second charge plateau was not induced by the cathode structure in our case and TEMPO can freely diffused to any location to react with peroxide. Furthermore, it indicated the combination of CNT and Fe$_2$O$_3$ is a promising strategy, as the large surface area of CNT can make sure more Fe$_2$O$_3$ particles expose to the surface and avoid peroxide thin film to block the active carbon sites.

4.4 Crystallinity and morphology study

This section is aim to illustrate the growth and decomposition mechanisms of cell products through crystallinity and morphology studies. At start, the basic crystal information of Li$_2$O$_2$, Fe$_2$O$_3$, as well as the inference of the impacts of RM on the growth of peroxide were provided. Then, it was followed by the sub-experiments: (1) discharge product with different current density; (2) discharge product with different TEMPO concentration; (3) change of crystallinity at various SoC; (4) crystallinity after cycle, and (5) discharge products before and after adding TEMPO with a simplified cathode.
Figure 4-11 (a), (b) showed the standard XRD pattern for Li$_2$O$_2$ and Fe$_2$O$_3$. The space groups for Li$_2$O$_2$ and Fe$_2$O$_3$ were $P6_3/mmc$ (194) and $R-3c$ h (167) separately. In the TEM image of iron oxide shown in figure 4-11 (c), the location of dark points stood for the position of iron atom, as it had high electron density surrounded the nuclei and would be more likely to rebound the electron beams and decrease the transmission rate of electron to the collector. Therefore, it marked the sum of d-spacing for 10 parallel crystal planes in different directions, obtaining the d-spacing on the two dimensions is 0.274 and 0.364 nm, separately. The shorter dimension of Fe$_2$O$_3$ matched to the d-spacing of Li$_2$O$_2$ at (100) which is 0.272 nm. This close crystal relationship was the origin reason for the preferential growth of peroxide along the inter planar of iron oxide. However, since the inter d-spacing for (104) and (110) of Fe$_2$O$_3$ was close to the spacing of Li$_2$O$_2$ at (100) and (101), it can easily lead the peak overlap at small angle, as shown in figure 4-11 (a)(b). This problem was more serious when Li$_2$O$_2$ faces the peak broadening problems. In the XRD experiments, we mainly focused on faces (100), (101) and (104) which showed the most distinguishable peaks for lithium peroxide.

Figure 4-11: Crystal characteristics for Li$_2$O$_2$ and Fe$_2$O$_3$. (a), (b) Standard power X-ray diffraction patterns for Li$_2$O$_2$ and Fe$_2$O$_3$, respectively; (c) TEM of Fe$_2$O$_3$ powder.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Representatives</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>High AN</strong> Lewis acid</td>
<td>chemical species with an empty orbital, which is capable of accepting an electron pair</td>
</tr>
<tr>
<td></td>
<td>H$^+$, Me$_3$B</td>
</tr>
<tr>
<td><strong>High DN</strong> Lewis base</td>
<td>chemical species with a filled orbital containing an electron pair which is not involved in bonding</td>
</tr>
<tr>
<td></td>
<td>OH$^-$, NH$_3$</td>
</tr>
</tbody>
</table>
As known the DN and AN played key roles in determining the growth mechanism of Li$_2$O$_2$, understanding the influence of TEMPO on the DN/AN of the electrolyte became a starting point to study how TEMPO would impact the growth of peroxide. Table 4-1 summarized the determinations of Lewis acid/base and their relationship with DN/AN. It indicated that there is a close relationship between pH and DN/AN, since proton is a typical Lewis acid, however, hydroxide is a strong Lewis base. pH tests of electrolyte with/without TEMPO were listed in table 4-2 which showed that both electrolytes are acidic, however, the pH increased after adding TEMPO, indicating the alkaline trait of TEMPO.

The structural formula of TEMPO in table 3-2 demonstrated that only hydrogen, carbon, nitrogen and oxygen atoms involved in the molecule. The electrons in outer orbital of carbon and hydrogen atoms were all bonded which showed neither Lewis acid nor Lewis base characteristic. Nevertheless, oxygen and nitrogen atoms contained electron lone pairs which would undeniably increase the DN of the electrolyte. Incorporating with the alkaline characteristic of TEMPO, it can conclude that TEMPO would increase the DN of the electrolyte.

<table>
<thead>
<tr>
<th>Table 4-2: pH tests of electrolyte with/without TEMPO</th>
</tr>
</thead>
<tbody>
<tr>
<td>No additive</td>
</tr>
<tr>
<td>pH 1</td>
</tr>
<tr>
<td>pH 2</td>
</tr>
<tr>
<td>pH 3</td>
</tr>
<tr>
<td>Overall</td>
</tr>
</tbody>
</table>

As confirmed that TEMPO would raise the DN of the solution, it will promote solution mechanism for peroxide generation in Li-O$_2$ batteries. This conclusion was supported by the SEM images in figure 4-12, which showed the morphology of discharged cathodes with different TEMPO concentrations. It was easy to find that more toroidal-shaped peroxide appeared in the solution after increasing TEMPO concentration and all the cells had similar discharge capacity. This meant more peroxide generated through solution mechanism, indicating the increase of electrolyte DN.

**Figure 4-12: SEM of cathodes after discharge with different TEMPO concentration.** (a) with no additive, discharge capacity: 1.7 mAh; (b) with 5 mM TEMPO, discharge capacity: 1.5 mAh; (c) with 30 mM TEMPO, discharge capacity: 1.6 mAh, with a current density of 0.2 mA/cm$^2$.

**4.4.1 Discharge product with different current density**
XRD patterns in figure 4-13 (a) only detected the generation of lithium peroxide after discharge, and there was no observation of Li$_2$O or Li$_2$CO$_3$ which were reported by other researches. Therefore, Li$_2$O$_2$ was regarded as the main discharge product in our Li–O$_2$ batteries. The peaks which corresponded to Li$_2$O$_2$ phase became more distinguishable under smaller current density, indicating a better peroxide crystallinity at low rate.

![XRD patterns](image)

**Figure 4-13: XRD patterns for cathodes after discharging with different current density 10 mM TEMPO.** (a) XRD patterns with a current density from 0.2 mA/cm$^2$ to 0.02 mA/cm$^2$; (b) XRD pattern after refinement without LiOH phase; (c) XRD pattern after refinement with LiOH phase and a current density of 0.02 mA/cm$^2$.

As marked in figure 4-13(a), there was a distinguishable peak at 32.5 deg with a current density of 0.02 mA/cm$^2$ which was not detected under other current densities. This could be attributed to the variation of lattice strain of Li$_2$O$_2$ or the involvement of a new phase. However, the extra peaks were detected in the refined XRD pattern as shown in figure 4-13(b). Therefore, we can conclude that other chemical product would generate during discharge except Li$_2$O$_2$.

Former study$^{75}$ demonstrated that the appearance of Li$_2$O$_2$ would cause the dehydrogenation from ethers. As active species such as O$_2^-$ would attack ether electrolyte and abstract hydrogen from the solution and generate $H_2O$. And this would further lead the formation of water and lithium hydroxide. Therefore, we speculated LiOH would be the new phase detected under small current density. Figure 4-13 (c) showed the refined XRD pattern with LiOH phase, and clearly the extra peaks were perfectly fitted. As shown in figure 4-14, the (101) facet of LiOH was close to the (100) facet of Li$_2$O$_2$, and its (110) facet was overlapped with Fe$_2$O$_3$’s (110) facet, which caused the difficulties in further analyzing their phase change at different states.
Crystal information of Li$_2$O$_2$ obtained from GSAS refinement was summarized in Table 4-3. With the variation of current density, there was no obvious relationship between the variations in lattice parameters and current density. Nevertheless, there was an increase in coherently scattering domain size as reducing the current density. This concluded that superior crystallinity was achieved through promoting solution mechanism.

Figure 4-14: Power X-ray diffraction pattern of LiOH from Pearson’s Crystal data.

Figure 4-15: Morphology of cathode surface after discharge with different current density and 10 mM TEMPO. (a) and (b) 0.2 mA/cm$^2$; (c) and (d) 0.05 mA/cm$^2$; (e) and (f) 0.02 mA/cm$^2$. 
Table 4-3: Crystal information for Li$_2$O$_2$ after discharge with different current density and 10 mM TEMPO.

<table>
<thead>
<tr>
<th>Current density [mA/cm$^2$]</th>
<th>a [Å]</th>
<th>c [Å]</th>
<th>volume [Å$^3$]</th>
<th>Lx</th>
<th>Domain size [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.20</td>
<td>3.13578±0.0011</td>
<td>7.59829±0.0158</td>
<td>64.705±0.121</td>
<td>81.0917±2.1104</td>
<td>10.0810±0.2730</td>
</tr>
<tr>
<td>0.10</td>
<td>3.13735±0.0007</td>
<td>7.62771±0.0096</td>
<td>65.021±0.071</td>
<td>77.6172±1.2498</td>
<td>10.5515±0.1771</td>
</tr>
<tr>
<td>0.05</td>
<td>3.13617±0.0005</td>
<td>7.64205±0.0086</td>
<td>65.094±0.062</td>
<td>61.2718±1.1964</td>
<td>13.5198±0.2784</td>
</tr>
<tr>
<td>0.02</td>
<td>3.13688±0.0006</td>
<td>7.59413±0.0102</td>
<td>64.715±0.074</td>
<td>52.9807±1.3848</td>
<td>15.7701±0.4384</td>
</tr>
</tbody>
</table>

* ALL the refinements finished with the Rwp < 2%.

Figure 4-15 showed the high resolution SEM images for the cathode surface with different discharge current densities. The density of discharge products and their particle size increased with decreasing current density. With the rate lowered to 0.02 mA/cm$^2$, the famous toroidal-shaped peroxide was detected. If looking into the toroidal peroxide, it will find each toroidal particle was stacked by several thin flakes, illustrating the growth mechanism of crystal peroxide to some extent. Namely, Li$_2$O$_2$ flakes were generated at the beginning stage. Then, pill together to construct more crystallized toroidal structure.$^{76}$ The particle size can be a scale of time, as longer discharge time was consumed under small current density.

In summary, Li$_2$O$_2$ was determined as the main discharge product. Small current density led Li$_2$O$_2$ to obtain a larger domain size as well as particle size. LiOH was detected by XRD after discharge under small current density.

4.4.2 Crystallinity under different TEMPO concentrations

Previous section illustrated how TEMPO concentration would influence the electrochemical performance of Li-O$_2$ cells. To further study the impact of TEMPO on the growth mechanism of Li$_2$O$_2$, the crystalline and morphology studies were processed on cells with the addition of different TEMPO concentrations.

Figure 4-16: XRD patterns and SEM for cathodes after discharging with different TEMPO concentrations. (a) XRD patterns with various TEMPO concentrations; (b) SEM without additive and; (c) SEM with 10 mM TEMPO;
(d) SEM without 30 mM TEMPO and (e) SEM without 50 mM TEMPO with a current density of 0.05 mA/cm².

**Particle size**

Figure 4-16 showed the XRD patterns of cathode after discharging with different TEMPO concentration. The concentration of TEMPO would not change the type of main discharge product, as lithium peroxide was always the only discharge product observed from XRD.

Comparing SEM images in figure 4-16 (b) to (e), peroxide in cell without additive showed more obvious toroidal structure. The cells with TEMPO generated more flake-shaped products but few toroidal particles. Coherent with previous discussion, the density of the particles, corresponding to the discharge product, on the surface of the electrode increased with increasing TEMPO concentration. However, particle sizes were slightly decreased. All these results pointed out TEMPO might induce the fast nucleation of Li₂O₂ by increasing the nuclei sites in the solution, resulting in a decreasing particle size but increasing particle density.

**Domain size**

There was no significant difference in the XRD patterns or the refinement results in cell with different TEMPO concentration, as the domain size of peroxide might be influenced by the Nano seeds, which might hide the impact of TEMPO on the crystallinity of peroxide. To minimize this influence, a simplified cathode with CNT:PVDF= 75:25 was used in the further study. As shown in figure 4-17, the XRD pattern of cell with 10 mM TEMPO showed a serious peak broadening compared to the cell without additive, indicating the peroxide was tend to be less crystallized after adding additive. This was coherent to the reducing domain sizes and lattice parameters of peroxide in cell with 10 mM TEMPO. Same experiments were processed to ensure the accuracy of the conclusion, which also shown the same result.

**Figure 4-17: XRD patterns after refinement.** (a)No additive (Rwp = 1.70%); (b)10 mM TEMPO (Rwp = 1.20%) , with cathode material CNT:PVDF= 75:25 and a current density of 0.2 mA/cm².

In figure 4-17(b), the (100) facet of Li₂O₂ shifted to the left. According to the previous observation of LiOH after discharge and the refinement result, we can predict TEMPO would trigger the generation of LiOH. Here, we can speculate the amount of LiOH generated during discharge might be a function of Li₂O₂ particle size, since the smaller Li₂O₂ particle size can lead a larger exposed surface area in the electrolyte which can accelerate the dehydrogenation with a larger contact area.
Table 4-4: Crystal information for Li$_2$O$_2$ after discharging with/ without TEMPO

<table>
<thead>
<tr>
<th>Number</th>
<th>a [Å]</th>
<th>c [Å]</th>
<th>volume [Å$^3$]</th>
<th>Lx</th>
<th>Domain size [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>No additives</td>
<td>3.1364±0.0002</td>
<td>7.6703±0.0039</td>
<td>65.342±0.034</td>
<td>41.5437±0.3485</td>
<td>20.4700±0.1859</td>
</tr>
<tr>
<td>TEMPO</td>
<td>3.1267±0.0006</td>
<td>7.3720±0.0111</td>
<td>62.461±0.118</td>
<td>70.4163±1.2584</td>
<td>11.6814±0.2186</td>
</tr>
</tbody>
</table>

In summary, Nano seeds could maintain the Li$_2$O$_2$ domain size at a certain magnitude. TEMPO would decrease the particle size as well as the domain size of Li$_2$O$_2$. Since TEMPO increased DN of the solution and induced fast Li$_2$O$_2$ nucleation in the electrolyte by adding extra nuclei sites, thus, more small peroxide particles would exist in the solution and significant increase the contact surface between peroxide and electrolyte, resulting more serious hydrogen abstraction. Later XPS analysis would support this conclusion.

4.4.3 Different state of discharge and charge

In figure 4-18, the continuous growth of peroxide can be found from the variation of the XRD peaks, especially at (101) facet during discharge process.

![Figure 4-18: Cells at different states of discharge/charge.](image)

Figure 4-18: Cells at different states of discharge/charge. XRD patterns with corresponding testing points shown in the voltage curve, with cathode Fe$_2$O$_3$: CNT = 300:100 and a current density of 0.2 mA/cm$^2$. 


At the beginning of charge process, the peaks corresponding to \( \text{Li}_2\text{O}_2 \) phase kept intact which indicated the decomposition of amorphous and less crystalline \( \text{Li}_2\text{O}_2 \). As the amorphous peroxide was regarded to break down at low potential (3.0 ~ 3.2 V) which were reported in previous research\(^{77}\) and also supported by our CV results. After that the intensity of \( \text{Li}_2\text{O}_2 \) peaks reduced, indicating their gradual de-crystallinity while recharging the cell. When the cell was recharged to the end of the first charge plateau (“charge to 2.0 mAh), there was no longer observation of peroxide which meant that peroxide was cleared out from the battery and the decomposition of other chemical species led the appearance of the second charge plateau.

The chemical species decomposed at higher charge potential can be either by-products, such as lithium carbonates/lithium carboxylates or lithium hydroxide as mentioned in previous sections. With the appearance of oxygen and other nucleophilic species, \( \text{Li}_2\text{O}_2 \) batteries would undergo various side-reactions and generate several by-products, namely \( \text{H}_2\text{O}, \text{CO}_2, \text{HCO}_2\text{Li} \) and \( \text{CH}_3\text{CO}_2\text{Li} \). And the appearance of \( \text{H}_2\text{O} \) can lead the reaction with \( \text{Li}_2\text{O}_2 \) and generate \( \text{LiOH} \). Therefore, studying side reactions in \( \text{Li}_2\text{O}_2 \) cells played an significant role to reveal \( \text{Li}_2\text{O}_2 \) batteries’ working mechanism which will be provided in section 4.5.

### 4.4.4 After several cycles

Comparing figure 4-19(a) to figure 4-13, the \( \text{Li}_2\text{O}_2 \) peaks did not appear after the second discharge no matter in high/low rates. In 4-19(b) and (c), the SEM images of the cathode after the first discharge and the second discharge also demonstrated the significant reduce of the amount of toroidal peroxide after the 2\textsuperscript{nd} discharge. The discharge products after the 2\textsuperscript{nd} discharge turned to be irregularly shaped which could be the semi-crystal peroxide. Although there is no distinguishable \( \text{Li}_2\text{O}_2 \) peaks in XRD patterns, the visible toroidal particles in the SEM image indicated the generation of crystal peroxide. However, the strong \( \text{Fe}_2\text{O}_3 \) intensity would hinder the observation of weak peroxide peaks. Additionally, the discharge capacity was increased via reducing the current density.

Furthermore, table 4-5 showed the crystal information obtained from GSAS refinement which demonstrated a decrease in domain size after the 2\textsuperscript{nd} discharge with both current densities. And there were expansions of peroxide unit cell after the 2\textsuperscript{nd} discharge. As clarified by Swapna Ganapathy and her colleagues\(^{56}\), the surface area is closely related to the magnitude of lattice parameters. The expansion of unit cell volume can be explained by the increased surface/volume ratio in smaller peroxide domain which had a larger surface area after the 2\textsuperscript{nd} discharge and therefore, increased the surface energy of the crystalline. Notably, although particle size and domain size are different, we always find the consistency between these two parameter in our study.

After the first cycle, the stability of electrolyte was influenced by the appearance of the active species to some extent, leading the generation of electrolyte fragment. This would increase the impurity of the solution which can impact the solubility of \( \text{LiO}_2 \) and vary the nucleation pathway of the discharge products in the electrolyte. Therefore, during the second discharge process, the change in the crystallinity and morphology of the discharge products can be explained by the fast nucleation of the discharge products.
Result and discussion

Figure 4-19: Crystallinity and morphology of cathode after the second discharge. (a)XRD patterns of cells at different current densities; (b) (c) SEM images of the cathode after the 1<sup>st</sup> and 2<sup>nd</sup> discharge, respectively, with a current density of 0.2 mA/cm<sup>2</sup> and 10 mM TEMPO.

Table 4-5: Crystal information for Li<sub>2</sub>O<sub>2</sub> after the first and second discharge

<table>
<thead>
<tr>
<th>Current density [mA/cm&lt;sup&gt;2&lt;/sup&gt;]</th>
<th>Number</th>
<th>a [Å]</th>
<th>c [Å]</th>
<th>volume [Å&lt;sup&gt;3&lt;/sup&gt;]</th>
<th>Lx</th>
<th>Domain size [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1&lt;sup&gt;st&lt;/sup&gt; discharge</td>
<td>3.1358±0.0011</td>
<td>7.5983±0.0158</td>
<td>64.705±0.121</td>
<td>81.0917±2.1104</td>
<td>10.0810±0.2730</td>
</tr>
<tr>
<td></td>
<td>2&lt;sup&gt;nd&lt;/sup&gt; discharge</td>
<td>3.1418±0.0013</td>
<td>7.5989±0.0177</td>
<td>64.957±0.135</td>
<td>93.2961±2.3802</td>
<td>8.7159±0.2302</td>
</tr>
<tr>
<td>0.1</td>
<td>1&lt;sup&gt;st&lt;/sup&gt; discharge</td>
<td>3.1374±0.0007</td>
<td>7.6277±0.0096</td>
<td>65.021±0.071</td>
<td>77.6172±1.2498</td>
<td>10.5515±0.1771</td>
</tr>
<tr>
<td></td>
<td>2&lt;sup&gt;nd&lt;/sup&gt; discharge</td>
<td>3.1474±0.0023</td>
<td>7.6132±0.0305</td>
<td>65.314±0.231</td>
<td>108.857±4.0856</td>
<td>7.4327±0.2873</td>
</tr>
</tbody>
</table>

Notably, disappearance of Li<sub>2</sub>O<sub>2</sub> peaks can also lead by the peak shift. As the position of Fe<sub>2</sub>O<sub>3</sub> and Li<sub>2</sub>O<sub>2</sub> XRD peaks were so close, the shift of the peaks will cause the overlap of these two phases. However, the increase of the unit cell volume indicated the peak should shift to smaller angle other than larger angle where Fe<sub>2</sub>O<sub>3</sub> peaks appeared. To further check the change of crystallinity and morphology while cycling, several discharged cells with cathode CNT/PVDF= 75:25 to exclude the influence of Fe<sub>2</sub>O<sub>3</sub> were tested by XRD. As expected, the peroxide XRD peaks shifted to the left with increasing unit cell volume and reducing domain size. And the peak broadening became more serious after serval cycles which cannot be refined after the 3<sup>rd</sup> discharge. The detailed information can be found in appendix C.

In summary, these results indicated that the crystallinity and anisotropy of peroxide was continuously decreasing with unit cell expansion while cycling.
4.5 Cell stability

The stability of electrolyte was considered to be one of the largest challenges to achieve high performance Li-O\textsubscript{2} cells, as the electrolyte was hard to achieve superior stability under the wide potential window, with the contact of lithium metal and appearance of active discharge species. And as mentioned in last section, studying the side reactions in the cell was also inevitable for understanding the growth and decomposition mechanism of cell products for further developing the cell performance. This section was consisted by (1) calculation of side reactions with the worst case; (2) cell cycling with pure oxygen gas supplied by a closed jar, followed with XRD test after cycle; (3) NMR tests at different SoC and after cycle; (4) ex-situ XPS semi-quantitative analysis.

4.5.1 Calculation of side reactions with the worst case

The decomposition of by-products at high charge potential was regarded as a possible reason for the appearance of the second charge plateau. To quantify the possibility of this assumption, the worst scenario was implemented in the calculation, namely the decomposition of all CNT, TEGDME and LiTFSI in a single cell. And here we assumed all the by product was Li\textsubscript{2}CO\textsubscript{3} (transferring two moles of electrons via decomposing per mole of by-products, \(2Li^++2e \rightarrow 2Li; \ CO_2^2- \rightarrow CO_2 + \frac{1}{2}O_2 + 2e\)) and no generation of LiRCO\textsubscript{3} or HCOOLi, since through this way the maximum electron-transfer ability of by-products can be obtained.

The average discharge capacity of Li-O\textsubscript{2} cells while using Fe\textsubscript{2}O\textsubscript{3}/CNT= 300:100 cathode was around 2.5 mAh when the mass of activated material on the cathode was around 2.5 mg including Fe\textsubscript{2}O\textsubscript{3}. The capacity of the second charge plateau was about 40% of the total discharge capacity, thus, roughly 1.0 mAh per cycle. In case of obtaining 1.0 mAh, the amount of Li\textsubscript{2}O\textsubscript{2} required was

\[
n_{Li_2O_2/mAh} = \frac{3.6 \text{ C/mAh}}{1.6 \times 10^{-10} \text{C} \times N_A \times n} = 1.868 \times 10^{-5} \text{ mol} \tag{4.6}
\]

Where

- \(N_A\) is the Avogadro constant, 6.022 \times 10^{23}.
- \(n\) is the stoichiometric of electron number involved in the chemical reaction, 2.

Decomposition of CNT

The mass of CNT was one fourth of the total mass of activated material, 0.625 mg. Therefore, 5.208 \times 10^{-5} mole of carbon contained in each cathode, taking the molar mass of carbon as 12 g/mol. The possible reaction of carbon with the appearance of Li\textsubscript{2}O\textsubscript{2} can be expressed by

\[
Li_2O_2 + C + \frac{1}{2}O_2 \rightarrow Li_2CO_3
\]
Therefore, the stoichiometric among Li$_2$O$_2$, carbon and Li$_2$CO$_3$ is 1, namely $n_{Li_2O_2/mAh} = n_{carbon/mAh} = n_{Li_2CO_3/mAh}$. Through applying $N_{CNT} = \frac{n_{carbon}}{n_{Li_2O_2/mAh}}$, it can obtain that all the CNT can meet 3 cycles of the carbon requirement for the second charge plateau, ($N_{CNT} = 3$).

**Decomposition of electrolyte**

When considering the decomposition of electrolyte in the Li-O$_2$ batteries, both solvent and solute should be considered. In our cell, TEGDME (CH$_3$O(CH$_2$CH$_2$O)$_4$CH$_3$) and 0.5 M LiTFSI (CF$_3$SO$_2$NLiSO$_2$CF$_3$) were used as solvent and solute, respectively. The volume of electrolyte adding into each battery was 0.25 mL. And the concentration of LiTFSI was 0.5 mol/L, therefore the total amount of Li$_2$CO$_3$ that can be generated through decomposing LiTFSI in the battery was $1.25 \times 10^{-4}$ mol, using the same stoichiometric as CNT decomposition. 2.5 cycles was obtained for the carbon demand of the second charge plateau, ($N_{LiTFSI} = 2.5$).

The density of TEGDME was 1.009 g/ml and the molecular weight was 222.28 g/mol. Therefore, the solvent can generate $1.1348 \times 10^{-3}$ mole of Li$_2$CO$_3$ in each cell which meant the solvent can supply the carbon demand for by-products for around 61 cycles ($N_{TEGDME} = 61$).

Through the chemical reaction based calculation, we can confirm that the second charge plateau was impossible only led by the decomposition of by-products, as the cells can run more than 70 cycles without significant capacity fading.

Table 4-6: Maximum obtainable cycles as a function of decomposition components

<table>
<thead>
<tr>
<th>Components</th>
<th>Number of cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_{CNT}$</td>
<td>3.0</td>
</tr>
<tr>
<td>$N_{LiTFSI}$</td>
<td>2.5</td>
</tr>
<tr>
<td>$N_{TEGDME}$</td>
<td>61.0</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>66.5</strong></td>
</tr>
</tbody>
</table>

**4.5.2 Pure oxygen gas supplied from a closed jar**

In previous electrochemical tests, the Li-O$_2$ cells were attached to oxygen channels which were connected by a external pipeline. If impurity gas was generated during cycle, the cell could outlet the evolved gas back to the external container and release the impact of side reactions on the cell performance. To exclude the influence of this factor, a closed jar filled with pure oxygen and 1 atm pressure was directly connected with a cell. The system set-up was shown in figure 4-20(a).

The Electrochemical performance shown in figure 4-20(b) and (c) had no significant change compared with cells connected with normal oxygen channels. Furthermore, the stable performance also indicates no significant gas evolution other than oxygen while cycling. Similar calculation as made in last section was processed here, taking the second charge plateau attributed to the by-products decomposition as prerequisites. The
result demonstrated the mole ratio between CO₂ and O₂ would be around 11.3% at the end of the 37th cycle (cell death since being touched). This high concentration of the impure gas would be high enough to influence the cell’s electrochemical performance and cause the observation of Li₂CO₃. Fortunately, the stable cell performance proved that there were no serious side reactions in our Li-O₂ batteries.

![Figure 4-20](image)

**Figure 4-20: Electrochemical performance and XRD pattern of cell cycled in a closed jar.** (a) model of the closed system; (b) voltage curves; (c) cycling performance; (d) XRD of cathode after cycle, with cathode Fe₄O₉/CNT=300:100, 10 mM TEMPO and a current density of 0.2 mA/cm².

XRD pattern in figure 4-20(d) showed that no crystal by-product accumulated at the surface of the electrode after cycle. And Fe₄O₉ achieved desirable stability, as no peak broadening after cycle. However, there was a decrease in intensity, which might own to the reduction of Fe₄O₉ by some active species in the cell.

### 4.5.3 NMR tests at different SoC and after cycle

XRD can only be used to detected crystal species and cannot provide information for amorphous products. And SEM images can provide useful morphological information, but cannot used to determine the chemical species. Therefore, we implemented liquid NMR technique to further explore the chemical species appeared in the system and study the stability of Li-O₂ batteries. The tests were processed at different cell states, namely after discharged to 2.0V, recharged to 4.0 V, 4.5 V and after cycle. As NMR analysis was highly dependent on the content of the sample involved in the test, ¹H-NMR which only required 0.5 mg sample was conducted.

The results were shown in figure 4-21. HOD signal was used for the calibration which was located at 4.64 ppm, and the rest of the ¹H-NMR spectrums were attributed to TEGDME. The signals appeared at 3.65 to 3.48 ppm and 3.25 ppm represented to two different groups of hydrogen atoms in TEGDME. The methyl-group hydrogen atoms in TEGDME which marked with red color in the figure 4-21, have a larger shielding factor compared with the one marked in blue, resulting a smaller chemical shift. Hydrogen atoms which marked with blue were close to their neighboring hydrogen atoms, leading the frequent jump of magnetic nuclei within the slightly different environments. This chemical exchange and conformational conversion led the broadening of peaks, ²⁹
therefore caused the amalgamate of the proton signals. However, this would not influence the analysis of by-products. As reported in many studies, lithium formate (at chemical shift of 8.43 ppm) and lithium acetate (at chemical shift of 1.89) which separated from the signals raised from TEGDME, were observed in ether-based electrolyte after discharge to 2.0 V.

**Figure 4-21:** \(^1\)H solution NMR spectrums of cathode and separator at different SoC with 10 mM TEMPO. (a) pristine, \(^1\)H NMR for the electrolyte; (b) cell discharge to 2.0 V; (c) cell recharge to 4.0 V; (d) cell recharge to 4.5 V, all cells with a discharge capacity around 1.8 mAh. Both cathode and separator were extracted with 1 ml D\(_2\)O, and test operated with an applied frequency of 400 MHz.

The values on the top of the peaks were the ratio of integral area under each peak, with which the relative atom contents under different environment can be obtained, as the area was proportional to the number of spin. Compared with the pristine sample, there was no significant change in area ratios and no observation of new signals at different SoC. Notably, previous studies only immersed cathode, but without separator in D\(_2\)O which even minimize the content of by-products, but still detected strong peaks for lithium formate and lithium acetate. This indicated the suppression of side reactions in our Li-O\(_2\) cells with the contributions of either Nano seed or soluble additive.

\(^1\)H-NMR tests for cells without TEMPO after discharge to 2.0 V and charge to 4.5 V also demonstrated the promising electrolyte stability during the first cycle, as no by-product was detected. More information of the NMR results can be found in appendix E. Additionally, the poor electrochemical performance of cell with TEMPO when using CNT:PVDF as cathode material also demonstrated the significant role of Fe\(_2\)O\(_3\) in enhancing the stability of Li-O\(_2\) battery, as presented in appendix E. This illustrated that Nano seed played a more important role in enhancing the stability of the ether-based electrolyte, compared with soluble additive.
Effects of Redox-mediator Electrolyte on the Electrochemical Performance of a Nonaqueous Li-O₂ Battery

Figure 4-22: ¹H solution NMR spectrum of cathode and separator after cycle with/without TEMPO. (a) cell cycled with 10 mM TEMPO; (b) cell cycled without TEMPO. ¹H NMR (400 MHz, D₂O), result with δ ppm: 4.64 (s), 3.65-3.48 (m), 3.25 (s) and 8.32 (s). Insert figure in (b) is the magnified image for the chemical shift of lithium formate. Tests were conducted after 10 cycles, in case the electrolyte would meet severe evaporation after long-term cycle.

However, the NMR signals are highly dependent on the content of species in the solution. When the content of by-product was too low, no chemical shift can be obtained. Thus, cells were tested by ¹H-NMR after cycle, as predicting by-products would accumulate in the cells while cycling. However, still no by-products were detected in cell with addition of TEMPO, shown in figure 4-22. However, a small peak corresponding to lithium formate signal (δ ppm: 8.32) was detected in cell without additive after cycle. It indicated that TEMPO further suppressed the side reactions in the cell during cycle.

To sum-up, no by-products were detected by ¹H-NMR after cycle in cell with TEMPO, which showed the superior stability of our Li-O₂ batteries. The ¹H-NMR results indicated the co-work of Nano seeds and TEMPO was a promising approach to achieve superior performance Li-O₂ batteries.

4.5.4 Ex-situ XPS semi-quantitative analysis

XPS tests were conducted to semi-quantitatively analysis the appearance of chemical species with the implementation of TEMPO at different SoC to illustrate the chemical reactions underneath the electrochemical performance.

The XPS peaks were fitted with XPSpeak 4.1, based on Gaussian-Lorentzian function. Shirley was selected as the background type, and the Lorentzian-Gaussian ratio was set to be 30%. The focus points of XPS analysis were marked in figure 4-23.
Figure 4-23: Schematically illustration of XPS testing points. Cell with TEMPO: discharge to 2.0 V, recharge to 3.8 V and 4.3 V, respectively; cell with no additive: discharge to 2.0 V and recharge to 4.5 V, with a current density of 0.05 mA/cm$^2$.

Table 4-7: Summary of XPS peak assignments

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Chemical bond</th>
<th>Binding energy [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>O 1s</td>
<td>α-Fe$_2$O$_3$</td>
<td>O-Fe=O</td>
</tr>
<tr>
<td></td>
<td>Li$_2$O$_2$/FeOOH</td>
<td>Li-O-O-Li/O=Fe-O-H</td>
</tr>
<tr>
<td></td>
<td>LiOH</td>
<td>Li-O-H</td>
</tr>
<tr>
<td></td>
<td>carboxylate/carbonates</td>
<td>C=O</td>
</tr>
<tr>
<td></td>
<td>LiN(SO$_2$CF$_3$)$_2$</td>
<td>S=O</td>
</tr>
<tr>
<td></td>
<td>TEGDME</td>
<td>C-O</td>
</tr>
<tr>
<td>C 1s</td>
<td>CNT</td>
<td>C-C</td>
</tr>
<tr>
<td></td>
<td>TEGDME</td>
<td>C-H</td>
</tr>
<tr>
<td></td>
<td>CNT/TEGDME</td>
<td>C-O</td>
</tr>
<tr>
<td></td>
<td>DMC</td>
<td>RO-C=O</td>
</tr>
<tr>
<td></td>
<td>carboxylates</td>
<td>O=C=O</td>
</tr>
<tr>
<td></td>
<td>Li$_2$CO$_3$ (carbonate)</td>
<td>CO$_3$</td>
</tr>
<tr>
<td></td>
<td>LiN(SO$_2$CF$_3$)$_2$</td>
<td>CF$_2$</td>
</tr>
<tr>
<td></td>
<td>LiN(SO$_2$CF$_3$)$_2$</td>
<td>CF$_3$</td>
</tr>
</tbody>
</table>

Table 4-7 summarized the assignments for each chemical bond and their corresponding binding energy. This summary was based on the former XPS studies about Li-O$_2$ batteries$^{75}$, LiTFSI electrolyte$^{80}$, Fe 2p spectra$^{81}$ and metal oxides$^{82}$. The C-C bonds in CNT with a binding energy of 284.48 eV was used to calibrate all the spectra.

**Fe 2p spectra**
Fe 2p spectra was presented in figure 4-24. The pristine Fe 2p, which was attributed to Fe₂O₃, was split into Fe 2p₁/₂ and Fe 2p₃/₂ envelopes, with binding energies of 724.7 eV and 711.2 eV, respectively. And the Fe 2p₃/₂ envelope was corresponding to a high-spin Fe cation from the compounds which was regarded as the main peak in most Fe 2p XPS studies.¹¹

![Fe 2p spectra](image)

**Figure 4-24:** XPS patterns of Fe 2p spectra of cathode after being discharged/charged to certain potential with/without TEMPO. Figures from (a) to (c) showed the pristine and discharged cathodes (with/without TEMPO); figures from (d) to (f) presented the results from the recharged cathode.

After discharge to 2.0 V, the surface of Nano seeds were all covered by the discharge products in cell with TEMPO, as no observation of Fe cation signal on the surface. In cell without TEMPO, the Fe 2p peaks became less distinguish, however, this meant the Fe₂O₃ sites were only partially occupied after full discharge. And the shape of the main peak changed in the cell without TEMPO after discharge. This might be attributed to the reduction of iron oxide with the appearance of active species.

During recharge process, the Nano seeds were gradually recovered from the cathode surface while decomposing the discharge products. This indicated the superior reversibility of Nano seeds in the Li-O₂ batteries. However, the Fe 2p spectra of cell recharged to 4.5 V had no difference compared with pristine cathode which seemed not possible if it was reduced during discharge. And this might be induced by the individual difference.
of the cells. To further study the reduction of Fe$_2$O$_3$ with the appearance of active species in order to clarify the working mechanism of Fe$_2$O$_3$ in energy preference aspect, XPS test can be conducted after cycle.

**C 1s spectra**

In figure 4-25(c), the cells without RM generated both lithium carbonate and carboxylate while discharging, as the $\text{–C=O/CO}_3$ peak located between the binding energy of $\text{–C=O}$ and $\text{–CO}_3$ respectively. However, there was still a residual peak for $\text{–C=O/CO}_3$ after cell recharge to 4.5 V, as shown in figure 4-25(f). This indicated that by-product cannot be completely cleared out from the cells without TEMPO during charge. In cells with TEMPO, there were appearances of $\text{–CO}_3$ peaks after discharge to 2.0V and recharge to 3.8 V, indicating the generation of lithium carbonate during both discharge and recharge process.

![C 1s spectra](image)

**Figure 4-25:** XPS patterns of C 1s spectra of cathode after being discharged/charged to certain potential with/without TEMPO. Each peak corresponds to: C-C from CNT; C-H from TEGDME; C-O from CNT/TEGDME; CF$_2$ and CF$_3$ from LiTFSI; O=–C-OR from DMC (residue after rinsing); CO$_3$ from lithium carbonate and C=O from lithium carboxylate. Their specific binding energy can be found in table 4-7.

However, the $\text{–CO}_3$ peak disappeared when cell with TEMPO recharged to 4.3 V. This demonstrated that TEMPO not only can benefit the charge transfer in peroxide, but can also promote the decomposition of by-
products, therefore enhance the lifetime of the Li-O₂ batteries. And the addition of TEMPO changed the pathway of side reactions in the cell which suppressed the generation of lithium carboxylate during discharge.

The peak corresponding to carbonate in cell recharge to the end of the first plateau, 3.8 V, increased significant during charge, representing that more serious side reactions took place under high voltage. However, the by-product completely decomposed at the end of charge, indicating the second charge plateau was partially resulted from by-product decomposition, since previous discussions has already denied the second charge platform was totally imputed on side reactions.

When cell discharged to 2.0 V with TEMPO, the disappearance of –C-C, corresponding to CNT, was due to the precipitation of peroxide from the solution. As TEMPO increased DN of the solution, there was more peroxide generating through solution mechanism with respect of cell without TEMPO. And the testing depth of XPS technique is only several nanometers. The solution peroxide with the domain size larger than 10 nm, covered the electrode surface after discharge, as the solution peroxide cannot distinguish Nano seeds and CNT.

**O 1s spectra**

The O 1s spectra in figure 4-26 showed three peaks at the binding energy of 532.5 eV, 531.5 eV and 530.0 eV in pristine electrode, generating from LiTFSI, FeOOH and Fe₂O₃ respectively. And ether functional group at the binding energy of 533.6 eV was corresponds to TEGDME. After discharge to 2.0 V, the peak at the binding energy of 531.5 eV slightly shifted to the higher binding energy, resulting from the generation of lithium carboxylates/carbonates and Lithium hydroxide with the binding energy of 532.2 and 531.8 eV respectively. And it was undeniable that Li₂O₂ was the main discharge product, as shown in pervious XRD tests. However, due to the same binding energy of Li₂O₂ and FeOOH in O 1s spectra, it is hard to quantize peroxide generated during discharge.

Known from previous C 1s spectra, larger amounts of by-products were generated in cell without TEMPO than in cell with additive after discharge. This conclusion was drew from the peak areas of the by-products and their discharge capacities. (Two cells had similar discharge capacity, 2.3 mAh for cell with TEMPO and 2.1 mAh for cell without additive.) Hence, if lithium carboxylate/carbonate was the main factor of peak shift at the binding energy of 531.5 eV, it would impact more on the cell without additive. Clearly, this was conflict with the obtained result. Therefore, we can conclude that carboxylate/carbonates were the minority compared with lithium hydroxide, and the shift of the peak was mainly own to the generation of LiOH after discharge. The larger binding energy shift in cell with TEMPO, from 531.5 eV to 531.8 eV, indicated more LiOH generated with the addition of TEMPO. When the cell with TEMPO recharged to 3.8 V, the peak slightly shift back, however, still maintained a binding energy of 531.8 eV. Therefore, we can predict that LiOH and by-product still attached to the electrode surface at the end of the first charge plateau. However, which of these two components was the main contributor of the second charge plateau was still questionable, as more by-products generated at higher potential.
Figure 4-26: XPS patterns of O 1s spectra of cathode after being discharged/charged to certain potential with/without TEMPO. Each peak is attributed to: Fe-O and FeOOH from iron oxide; S=O from LiTFSI; C-O from TEGDME; Li-O-O-Li and Li-OH represented lithium peroxide and lithium hydroxide, respectively, and C=O from lithium carbonate/carboxylate. The binding energy of Li$_2$O$_2$ was the same as its for FeOOH, namely 531.5 eV.

And the variation in Fe-O intensity at different SoC was in line with previous discussion for Fe 2p spectra. Decreasing Fe-O intensity while discharge, and gradually recovered during recharge. This demonstrated the repeatable cycling mechanism with this cathode structure, and indicated Fe$_2$O$_3$ with CNT was a promising cathode recipe for the secondary Li-O$_2$ batteries.

It was worthy to mention that the XPS tests were carried on the cathode worked with small current density (0.05 mA/cm$^2$). Based on the fast charge transfer characteristic of TEMPO, we believe even better cell stability can be obtained with a higher current density.

4.5.5 LiOH and Li$_2$CO$_3$ decomposition with TEMPO

Other research reported that the lithium carbonate was predicted to decompose at the range of 4.38-4.61 V, and the decomposing voltage for lithium hydroxide was even higher, 4.67-5.02 V.$^{73}$ In our cells, a much lower voltage, 3.8-4.3 V, was obtained at the second charge plateau, demonstrating that TEMPO would benefit the decomposition of Li$_2$CO$_3$ and LiOH. This can be illustrated by following chemical reactions:
2TEMPO$^+$ + 2LiOH $\rightarrow$ 2TEMPO + 2Li$^+$ + H$_2$O + $\frac{1}{2}$O$_2$↑

2TEMPO$^+$ + Li$_2$CO$_3$ $\rightarrow$ 2TEMPO + 2Li$^+$ + CO$_2$↑ + $\frac{1}{2}$O$_2$↑

To further support this result, cathodes (CNT/PVDF = 75:25) with preloaded LiOH or Li$_2$CO$_3$ were implemented in the oxygen-free cells. As shown in figure 4-27 (a) and (c), there were clear differences in charge profiles between cells with/without TEMPO. The first charge plateaus of cells with TEMPO indicated the oxidation of TEMPO at the potential of 3.75 V. LiOH can be decomposed with the addition of TEMPO, achieving a stable voltage plateau at 4.3 V which perfectly matched with the second charge plateau of our Li-O$_2$ cells. Cell without additive showed a dramatic voltage jump to 4.5 V. This indicated TEMPO can undeniably enhance the charge transfer in LiOH.

Figure 4-27: Voltage curves and XRD patterns for cells recharged with preloaded LiOH or Li$_2$CO$_3$. (a) charge curves for decomposing LiOH with/without TEMPO; (b) XRD patterns for recharged cathodes with LiOH; (c) charge curves for decomposing Li$_2$CO$_3$ with/without TEMPO, and (d) XRD patterns for recharged cathodes with Li$_2$CO$_3$, with a current density of 0.1 mA/cm$^2$ and cathode CNT/PVDF = 75:25.

Figure 4-27 (c) showed the XRD patterns for the recharged electrodes with preloaded LiOH. Clearly, the cell with TEMPO had a significant weaker intensity and the peaks at (201) and (211) facets disappeared after recharge to 4.5 V. However, there was no obvious peak broadening at facets (101) and (110). Furthermore, there was no obvious change in XRD patterns for cell without additive. As listed in table 4-8, the lattice parameters and unit-cell volume for LiOH in battery recharged with TEMPO were increased compared with LiOH in the pristine electrode and cell without additive. And the domain size of LiOH in the cell with TEMPO was the smallest among the three results in table 4-8.
This result indicated the outer-surface LiOH was decomposed with the appearance of TEMPO which would enlarge the exposed surface of LiOH crystalline, therefore the volume of the unit cell expanded by the increasing surface energy.

Table 4-8: Crystal information from GSAS refinement for recharging preloaded LiOH

<table>
<thead>
<tr>
<th>Number</th>
<th>a [Å]</th>
<th>c [Å]</th>
<th>volume [Å³]</th>
<th>Domain size [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>pristine LiOH</td>
<td>3.5483±0.0001</td>
<td>4.3502±0.0004</td>
<td>54.771±0.007</td>
<td>69.2982±1.0849</td>
</tr>
<tr>
<td>recharge with TEMPO</td>
<td>3.5617±0.0003</td>
<td>4.3756±0.0010</td>
<td>55.507±0.019</td>
<td>67.5156±1.9128</td>
</tr>
<tr>
<td>recharge without additive</td>
<td>3.5507±0.0001</td>
<td>4.3544±0.0004</td>
<td>54.898±0.007</td>
<td>68.9176±0.9529</td>
</tr>
</tbody>
</table>

As shown in figure 4-27(c), the second charge plateau of Li$_2$CO$_3$ decomposition in cell with TEMPO was sloppy which not matched with the relative steady second charge platform in the Li-O$_2$ batteries. This demonstrated that lithium carbonate was not the main contributor for the second charge plateau in the Li-O$_2$ cells, as compared with hydroxide. It is interesting to find that in cell with high TEMPO concentration (30/50 mM) showed a sloppier second charge plateau after cycle, indicating more serious side reactions in cells with plethora of TEMPO. From figure 4-27 (b), no obvious change in XRD pattern was found after recharging the preloaded Li$_2$CO$_3$ no matter with/without TEMPO. Therefore, we can conclude only amorphous Li$_2$CO$_3$ can be decomposed with the appearance of TEMPO. Table 4-9 listed the crystal information of Li$_2$CO$_3$. The volume expansions of the unit cells were detected after charge. In cell with TEMPO, an increased Li$_2$CO$_3$ domain size was detected, indicating the crack formation for releasing the decomposing stress.

Table 4-9: Crystal information from GSAS refinement for recharging preloaded Li$_2$CO$_3$

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>pristine Li$_2$CO$_3$</td>
<td>8.3551±0.0006</td>
<td>4.9719±0.0003</td>
<td>6.1940±0.0003</td>
<td>233.732±0.028</td>
<td>46.2483±0.6411</td>
</tr>
<tr>
<td>recharge with TEMPO</td>
<td>8.3589±0.0007</td>
<td>4.9748±0.0004</td>
<td>6.1965±0.0004</td>
<td>234.071±0.036</td>
<td>51.0260±1.0015</td>
</tr>
<tr>
<td>recharge without additive</td>
<td>8.3624±0.0008</td>
<td>4.9767±0.0004</td>
<td>6.2011±0.0004</td>
<td>234.436±0.036</td>
<td>46.7888±0.8512</td>
</tr>
</tbody>
</table>

It was undeniable that the properties of the commercial and electrochemical generated LiOH and Li$_2$CO$_3$ can be different to some extent. However, we believe that the highly crystalline commercial products were more difficult to be decomposed, due to the poorer charge transfer ability and lack of defects.

4.6 Experimental summary

In this section, summaries for TEMPO’s working performance and the growth/decomposition mechanisms of cell products in the Li-O$_2$ batteries were summed up.

4.6.1 Working performance of TEMPO
The overall performance of TEMPO was desirable. However, the major problem was its poor long-term stability. This instability can be the result of: (1) TEMPO was reduced to TEMPO\(^{-}\) after discharge potential drops to 2.3 V, which was an irreversible process; (2) TEMPO might be instable with the appearance of active species, as the reversibility of TEMPO/TEMPO\(^{+}\) was desirable under Ar environment; (3) TEMPO can be consumed by lithium metal when the SEI broke down after cycle; (4) it might be passivated by the coverage of the by-products. Reasons (2) and (4) were the most possible factors in our case.

<table>
<thead>
<tr>
<th>Criteria</th>
<th>Evaluation</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charge transfer ability</td>
<td>Good</td>
<td>fast charge transfer - as higher the current density, better the catalytic performance</td>
</tr>
<tr>
<td>Stability</td>
<td>Bad</td>
<td>superior reversibility as shown in CV results; lose catalysis activity after around 40 full cycles.</td>
</tr>
<tr>
<td>Working potential</td>
<td>Moderate</td>
<td>(~3.75) V, which significant reduced the charge overpotential, but still far from the equilibrium potential, 2.96 V.</td>
</tr>
<tr>
<td>Solubility in the electrolyte</td>
<td>Good</td>
<td>completely soluble</td>
</tr>
<tr>
<td>Influence on the oxygen solubility</td>
<td>Moderate</td>
<td>salt-out effect slightly reduced the oxygen solubility</td>
</tr>
</tbody>
</table>

The influence of TEMPO on the growth mechanism of discharge product was mainly attributed to the increasing DN and nuclei sites in the electrolyte. The reasons for this conclusion were summarized below: (1) from TEMPO’s structure and pH, it concluded TEMPO increased the number of electrons pairs which were not involved in bonding; (2) in the CV test, the integrated area corresponding to the amorphous Li\(_2\)O\(_2\) decomposition significantly decreased after adding TEMPO, indicating the promotion of solution mechanism; (3) From SEM images and GSAS refinement results, we detected the higher particle density, but smaller particle/domain sizes of the discharge products after adding TEMPO.

### 4.6.2 Mechanism summary

Based on the experimental results, the working mechanisms of Li-O\(_2\) batteries with/without RM under full working window were summarized in figure 4-28 and figure 4-29, respectively.

During discharge, the major difference between cells with and without TEMPO was the cell with TEMPO would accelerate the abstraction of hydrogen atoms from the electrolyte and trigger the generation of water. The appearance of water in the electrolyte led the reaction with peroxide/superoxide, generating amorphous lithium hydroxide at end. This conclusion was supported by the following results: (1) Under small current density, LiOH was detected from XRD; (2) In O 1s XPS result, the shift of the binding energy indicated the generation of LiOH, and (3) Through preloading commercial LiOH in the cathode mixture and charge the cell with 10 mM TEMPO, a stable charge plateau at 4.3 V was obtained which perfectly matched with the second charge plateau of the Li-O\(_2\) batteries.
During charge process, with the appearance of TEMPO, \( \text{Li}_2\text{O}_2 \) was more likely to process chemical decomposition with less generation of active intermediate. Furthermore, benefited from the fast charge transfer of TEMPO which narrowed the energy barrier of \( \text{Li}_2\text{O}_2 \) decomposition, the overpotential of the charge process...
was significant reduced. With these two reasons, side reactions were suppressed during charge process. However, LiOH and Li$_2$CO$_3$ had even larger bandgaps compared to Li$_2$O$_2$, resulting higher overpotential at the second charge plateau in cell with TEMPO. Fortunately, there was no observation of accumulated by-product at the end of the first charge and after cycle from the results of $^1$H-NMR and XPS tests. Nevertheless, by-product was detected at the end of the first cycle with XPS, and after 10 cycles with $^1$H-NMR in cell without additive. These results point out that moderate concentration of TEMPO could also benefit the decomposition of by-products, hence achieving longer lifetime without fast cathode passivation. However, this has to take larger overpotential as a sacrifice.

![Figure 4-30: Schematic illustration of cell capacity as a function of water content.](image)

The evolution of water in the cell would also influence the DN/AN of the electrolyte, as H$_2$O was determined to have high AN$^{12}$ which can enhance the dissolution of $O_2^-$ in the electrolyte, and thus further promote the solution mechanism. And this would be the reason for an increase in capacity after 35 cycles in cell with 10 mM TEMPO, as shown in figure 4-30. However, when water content kept increasing during cycle, it would cause the cell moisture over the tolerance of lithium metal, therefore, leading the fast capacity fading.
5. Conclusions & Recommendations

5.1 Conclusions

The purpose of this thesis is to study how redox mediator (RM) would influence the electrochemical performance of a nonaqueous Li-O₂ battery, and further investigate the reaction mechanism on the surface of the electrode. The main purpose of adding RM is in order to decrease the charge overpotential. Fe₂O₃ nanoseeds can remarkably enhance the cell stability which was proved by the previous research in our group. In this thesis, through combining TEMPO redox mediator and Fe₂O₃ nanoseeds, the electrochemical performance of the Li-O₂ batteries was significantly improved.

We implemented electrochemical study to investigate cell capacity, reversibility and lifetime. The electrochemical performance, potential sweep method, X-ray diffraction, high resolution images (SEM & TEM), ¹H-NMR and XPS tests were processed to reveal the working mechanism of Li-O₂ batteries with RM. The conclusions are listed as below:

- With the TEMPO additive, the charge performance of Li₂O₂ batteries followed two combination reactions. Firstly, TEMPO oxidized into TEMPO⁺ at surface of the electrode. Secondly, TEMPO⁺ chemically reacted with Li₂O₂ and processed the formation of Li⁺ and O₂. With this process, the charge potential was lowered from 4.3 V to 3.75 V and the generation of nucleophilic species (LiO₂) was largely avoided.

- As the TEMPO redox mediator added into the electrolyte, two charge plateaus appeared on the charge curve. The first plateau corresponding to the chemical reaction between TEMPO and Li₂O₂. The second plateau may correspond to the chemical reaction between TEMPO and by-products, such as LiOH and Li₂CO₃, etc.

- TEMPO could also influence the discharge performance of Li-O₂ batteries, which was ignored by other reports. (a) TEMPO increased the Gutman donor number (DN) of the electrolyte and promoted solution mechanism of Li₂O₂; (b) TEMPO accelerated the hydrogen abstraction from TEGDME and promoted the generation of LiOH; (c) TEMPO added the nuclei sites in the electrolyte which decreased the crystallinity of the discharge products.

- The moderate concentration (10 mM) of TEMPO, associated with Fe₂O₃ nanoseeds decorated cathode can enhance the cycling stability, suppress side reactions and reduce charge overpotential in Li-O₂ batteries under the fast charge transfer characteristic of TEMPO. The combination of soluble additive and Fe₂O₃ nanoseeds can be a promising pathway to develop high efficiency and long lifetime Li-O₂ batteries.
Answer the main research questions:

(1) What is the most suitable RM for our Li-O₂ battery and its optimal concentration as additive in the electrolyte?

Based on the former studies, several promising RMs (TEMPO, TDPA, FC, FePc and LiI) were selected as candidates for Li-O₂ batteries. According to compare their cycling stability, overpotential and cell capacity, TEMPO was considered as the most suitable RM in this case. However, other RMs either threatened the cycling stability or did not decrease the charge overpotential. Cell with addition of 10 mM TEMPO achieved 70 cycles under full voltage window (2.0 – 4.5 V) without serious capacity fading (~1000 mAh/g), and more than 100 cycles with capacity restriction of 0.5 mAh. After adding TEMPO, charge overpotential for the first charge plateau was 0.5 V lower than without additive, but no change in discharge profile was detected. The superior cycling performance under full voltage window demonstrated the active sites in the cathode are reversible, proving the reliability of regarding Li-O₂ cell as a secondary battery.

Different TEMPO concentrations were added in the electrolyte. However, due to the salt-out effect of TEMPO on oxygen, the discharge capacity decreased linearly with increasing TEMPO concentration. As TEMPO concentration increased, the first charge plateau was shortened and the cumblic efficiency was much higher than 100% in Li-O₂ batteries, which meant the energy efficiency decreased. To achieve both desirable cell capacity and energy efficiency, moderate TEMPO concentration, 10 mM, was determined to be the optimal concentration in the Li-O₂ batteries.

(2) What is the fundamental working principle of RM and how does it influence the electrochemical performance of Li-O₂ cells?

From the cyclic voltammetry results, the formal potential of TEMPO was found to be 3.75 V under Ar environment. This voltage met the OER peak under O₂ environment. The OER cathodic peak shift to lower potential after adding TEMPO, indicating TEMPO worked as a charge transfer carrier for the decomposition of Li₂O₂.

The performance of TEMPO was influenced by current density, due to its fast charge transfer kinetic. A higher current density can enhance the kinetic energy of the reaction, leading a faster recycle speed of TEMPO in the cell. Under a smaller current density, the chemical decomposition was slowed down, limiting the reduction of TEMPO⁺ which further accelerated the electrochemical decomposition of Li₂O₂. Therefore, the cells performed better with larger current density, for these two factors: (1) TEMPO was more effective at high rate, suppressing the electrochemical decomposition of Li₂O₂, and (2) the generation of by-product would be a scale of time with the appearance of the nucleophilic species.

XRD and ¹H-NMR analysis demonstrated that no accumulated by-products were detected in cells with additives. However, lithium formate was found in cells without additive after cycle through ¹H-NMR. Furthermore, the XPS results proved that TEMPO would promote the generation of LiOH during discharge. Particle size as well as domain size of Li₂O₂ decreased after adding TEMPO, as TEMPO would increase the nucleation sites for the solvated LiO₂. Therefore, the larger Li₂O₂ surface area resulted in the hydrogen abstraction and promoting the generation of LiOH. Additionally, lithium carbonate/carboxylate was detected by XPS. However, with TEMPO, the by-products were eradicated at the end of charge. Both ¹H-NMR and XPS analysis showed TEMPO
can scissor side reactions and keep ‘cleaner’ cathode surface. These results showed the potential of implementing RM in Li-Air system which uses atmosphere air as breathing-in gas, having much higher contents of H$_2$O and CO$_2$.

(3) Whether RM would influence the morphology and crystallinity of cell products during discharge and charge?

Morphology of cell products was studied by SEM technique. Toroidal shape peroxide was observed after discharge. As the concentration of TEMPO increased, more peroxide particles appeared after discharge, proving the conclusion that TEMPO can increase DN of the solution, hence, promote solution mechanism. Smaller domain size as well as particle size was observed after adding TEMPO, because the additive led the fast nucleation, through increasing the nuclei sites in the solution.

Ex-situ XRD results showed the continuous decreasing crystallinity of Li$_2$O$_2$ during charge process, and no peroxide was observed at the end of the first charge plateau. However, LiOH and Li$_2$CO$_3$ were detected by XPS at the end of the first charge plateau. Additionally, recharging cell with preloaded LiOH and Li$_2$CO$_3$ proved TEMPO’s capability of decomposing LiOH and Li$_2$CO$_3$. This explained the decomposing mechanism at the second charge plateau.

5.2 Recommendations

Studies in this thesis clearly improved the cell performance and provided useful information to clarify the fundamental mechanism beneath the electrochemical performance of the Li-O$_2$ batteries. To strengthen the credibility of the results and further improve the battery performance, several recommendations were summarized below:

(1) **Suitable electrolyte:** due to the superior stability under wide working window and with the appearance of nucleophilic species, ether-based electrolytes were regarded as the suitable solvent for Li-O$_2$ cells. Although the soluble catalysts can significantly minimize the voltage window, they would also accelerate the abstraction of hydrogen from ether, therefore, ether based electrolyte might not be the best choice with the implementation of RM. Other promising solvent can be DMSO, DMA and Me-Im, which have higher DN and less likely to have facile dehydrogenation.

(2) **In-situ analysis other than ex-situ:** Li-O$_2$ cells are sensitive to water and oxygen. To study the growth or decomposition mechanism of cell product, it is better to apply in-situ analysis, such as Operando XRD for obtaining crystal information, and in-situ XPS to study the generation of chemical species at the surface of cathode. In this way, deviation derived from external factor and individual difference can be minimized. And the relaxation of the unit cell before XRD measurements will also cause the inaccurate of the obtained crystal information.

(3) **Protection of lithium metal:** Although lithium metal was protected with LiTFSI/PC, the results demonstrated the protection of the artificial SEI was still limited, as black oxidized spots were found on lithium
metal surface after reopen the cycled batteries. The protected layer most likely decomposed upon the reaction on lithium metal surface. Therefore, implementing a more stable protection approach, such as lithium-ion selected membrane or solid-liquid electrolyte would be promising to achieve long-life Li-O₂ batteries.

(4) Neutron diffraction: Unlike XRD, neutron diffraction can determine the location of H atom in the crystal structure, and provide reliable crystal information at high 2θ value. These features can provide us useful information to explain how the abstracted hydrogen atom from the electrolyte would influence the structure and property of the cell products.
Acknowledgement

Having no idea about researches behind batteries, except the importance of battery technologies for our daily life, I started the study in Sustainable energy technology (SET). Witness and participate in a fantastic energy structure innovation is a dream for most ‘SETers’. Energy storage, taking a role of ‘trouble solver’ in this energy evolution, undeniably requires more researches for development.

Firstly, I would like to thank my supervisor Marnix Wagemaker who gave us great lectures in course ‘Sust. Hydrogen and Elec. Energy Storage’. Through taking the lecture, it stimulated my inherent motivation on working on battery researches. During the project, Marnix helped me to explore the interesting approaches to overcome the research barriers without adding any pressure. This promoted me to enjoy working in the labs and find the real interest in seeking for the truth.

As an inexperienced student stepped into a totally unfamiliar field, I am lucky to meet my daily supervisor, Zhaolong Li, who guided me to use every single equipment, taught me loads of lab skills and encouraged me to think more independently. Thank Zhaolong a lot for never giving me up, even after I ruined his precious sample and always asked silly questions. As a scientist ‘grown’ in the lab, I saw how many efforts and enthusiasm that Zhaolong put on research, which always inspired me during my whole graduation project.

Furthermore, I would like to thank Swapna for every small discussions and instruction. Frans, thank you for keeping the lab in order and your kind help for every requirement. Additionally, I have to thank my ‘battery friends’, Ivan, Eveline, Intan, Loic, Santhosh and more others, for the days we discussed about our ‘battery babies’ and the great time we spent together.

At end, thank for my family, who spiritually supported me all the time, without you I cannot be the place I am.

Hope this thesis would not be the end, but the start of thinking.

Sincerely,

Zhimin Zhou

Reactor Institute of Delft

28/03/2018
### Appendix A:

**Table appendix A: Cycling performance of Li-oxygen cells with different TEMPO concentration** – in case to compare the capacity fading speed and the relative length of the first charge plateau

<table>
<thead>
<tr>
<th>TEMPO concentration</th>
<th>A-Discharge capacity [mAh/g]</th>
<th>B-Capacity of the first charge plateau exclude oxidation capacity of TEMPO [mAh/g]</th>
<th>Ratio (B/A)</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1st cycle</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 mM TEMPO</td>
<td>712.49</td>
<td>399.77</td>
<td>0.56</td>
<td></td>
</tr>
<tr>
<td>10 mM TEMPO</td>
<td>821.66</td>
<td>641.15</td>
<td>0.78</td>
<td></td>
</tr>
<tr>
<td>20 mM TEMPO</td>
<td>922.36</td>
<td>690.76</td>
<td>0.75</td>
<td></td>
</tr>
<tr>
<td>30 mM TEMPO</td>
<td>887.11</td>
<td>619.86</td>
<td>0.70</td>
<td></td>
</tr>
<tr>
<td>50 mM TEMPO</td>
<td>849.33</td>
<td>623.34</td>
<td>0.73</td>
<td></td>
</tr>
<tr>
<td><strong>3rd cycle</strong></td>
<td></td>
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<td></td>
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<tr>
<td>5 mM TEMPO</td>
<td>856.15</td>
<td>507.75</td>
<td>0.59</td>
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</tr>
<tr>
<td>10 mM TEMPO</td>
<td>889.62</td>
<td>616.11</td>
<td>0.69</td>
<td>Start-up</td>
</tr>
<tr>
<td>20 mM TEMPO</td>
<td>921.83</td>
<td>632.51</td>
<td>0.69</td>
<td></td>
</tr>
<tr>
<td>30 mM TEMPO</td>
<td>968.23</td>
<td>583.85</td>
<td>0.60</td>
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<tr>
<td>50 mM TEMPO</td>
<td>875.16</td>
<td>465.63</td>
<td>0.53</td>
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<tr>
<td><strong>5th cycle</strong></td>
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<tr>
<td>5 mM TEMPO</td>
<td>749.42</td>
<td>438.7</td>
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<td>851.33</td>
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<td>755.4</td>
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<td>731.84</td>
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<tr>
<td><strong>10th cycle</strong></td>
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<tr>
<td>5 mM TEMPO</td>
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<tr>
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<td>746.34</td>
<td>439.56</td>
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<td>696.36</td>
<td>440.02</td>
<td>0.63</td>
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<tr>
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<td>345.35</td>
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<tr>
<td>5 mM TEMPO</td>
<td>804.46</td>
<td>102.93</td>
<td>0.13</td>
<td></td>
</tr>
<tr>
<td>10 mM TEMPO</td>
<td>874.01</td>
<td>466.14</td>
<td>0.53</td>
<td></td>
</tr>
<tr>
<td>20 mM TEMPO</td>
<td>658.93</td>
<td>390.25</td>
<td>0.59</td>
<td></td>
</tr>
<tr>
<td>30 mM TEMPO</td>
<td>590.89</td>
<td>303.99</td>
<td>0.51</td>
<td></td>
</tr>
<tr>
<td>50 mM TEMPO</td>
<td>551.07</td>
<td>293.73</td>
<td>0.53</td>
<td></td>
</tr>
</tbody>
</table>

*the red block showed the highest discharge capacity among all the concentration gradients; the yellow blocks illustrated the decreasing discharge capacity as a function of TEMPO concentration; the blue blocks indicated the highest ratios of the first charge plateau which demonstrated the working range of TEMPO.*
Effects of Redox-mediator Electrolyte on the Electrochemical Performance of a Nonaqueous Li-O₂ Battery

Appendix B:

Figure appendix-B1: XRD patterns after GSAS refinement of cells discharge to 2.0 V with different current densities and 10 mM TEMPO. With \( R_{wp} < 2\% \).
Appendix C:

Figure appendix C: Crystallinity and morphology of cathode after discharge for different cycles. (a) XRD patterns of cells at different cycles of discharge; (b) SEM image for pristine cathode; (c) SEM image after the first discharge; (d) SEM after the second discharge; (e) SEM after the fifth discharge with cathode CNT:PVDF= 75:25, a current density of 0.2 mA/cm$^2$ and 10 mM TEMPO.

<table>
<thead>
<tr>
<th>Number</th>
<th>a [Å]</th>
<th>c [Å]</th>
<th>volume [Å$^3$]</th>
<th>Lx</th>
<th>P [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>the 1$^{st}$ discharge</td>
<td>3.1267±0.0006</td>
<td>7.3720±0.0111</td>
<td>62.461±0.118</td>
<td>70.4163±1.2584</td>
<td>11.6814±0.2186</td>
</tr>
<tr>
<td>the 2$^{nd}$ discharge</td>
<td>3.1378±0.0009</td>
<td>7.8129±0.0164</td>
<td>66.622±0.153</td>
<td>80.8665±1.1581</td>
<td>10.1103±0.1507</td>
</tr>
</tbody>
</table>

*the XRD patterns for the 3$^{rd}$ and 5$^{th}$ cycles shown in figure appendix C cannot be refined, due to the serious FWHM broadening.
Appendix D:

Figure appendix D: Cyclic voltammetry for cell with different TEMPO concentration under Ar environment.
Appendix E:

Figure appendix E1: $^1$H solution NMR spectrum of cathode and separator after discharge to 2.0 V and recharge to 4.5 V without TEMPO. $^1$H NMR (400 MHz, D$_2$O), result with $\delta$ ppm: 4.64(s), 3.65-3.48 (m), 3.25 (s) and 8.32 (s). No extra peak for by-product was obtained.

Figure appendix E2: cycling reversibility with a current density of 0.2 mA/cm$^2$, 10 mM TEMPO and cathode material PVDF:CNT = 25:75.
Appendix F:

![Graphs showing electrochemical performance of Li-O\textsubscript{2} batteries with Super P as carbon resources.](image)

**Figure appendix F:** Electrochemical performance of Li-O\textsubscript{2} batteries with Super P as carbon resources. (a) voltage profile; (b) cycling performance. The cell capacity firstly increased and reached the maximum capacity at around 40 cycles, then dramatically dropped down. This result was coherent to the final conclusion of this thesis that moisture content increased while cycling, which enlarged AN in the solution and promoted the solution mechanism to achieve a larger capacity. When the water content was higher than the maximum tolerance of lithium metal, the cell death fast came to the end.


72. SIGMA-ALDRICH.


