The Material Design of Stable Cathodes in Li-Oxygen Batteries and Beyond

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The Material Design of Stable Cathodes in Li-Oxygen Batteries and Beyond

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Advisor: Prof. Dunwei Wang

Non-aqueous Li-O₂ batteries promise the highest theoretical specific energy among all rechargeable batteries. It is the only candidate that can be comparable with the internal combustion engine in terms of gravimetric energy density. This makes Li-O₂ batteries preferable in the application of electric vehicles or drones. However, the materialization of this technology has been hindered by the poor cycling performance. The major reason for the degradation of the battery at the current research stage has been identified as the decomposition of the electrolyte and the cathode. These parasitic reactions will lower the yield of the desired product and induce huge overpotential during the recharge process. By carefully examining the degradation mechanism, we have identified the reactive oxygen species as the culprit that will corrode the cathode and attack the organic solvents. While parallel efforts have been devoted to reduce the reactivity of these species toward electrolyte, the main focus of this thesis is to identify suitable material platforms that can provide optimum performance and stability as cathodes.

A bio-inspired wood-derived N-doped carbon is first introduced to demonstrate the benefit of hierarchical pore structures for Li-O₂ cathodes. But the instability of the carbon cathode itself limits the lifetime of the battery. To improve the stability of carbon, we further introduce a catalytic active surface coating of FeO_x on a three dimensionally ordered mesoporous carbon. The isolation of carbon from the reactive intermediates greatly improves the stability of the cathode. Yet the imperfections of the protection layer on carbon calls for a stable substrate that can replace carbon. TiSi₂ is explored as the candidate. With the decoration of Pd catalysts, the Pd/TiSi₂ cathode can provide extraordinary stability toward reactive oxygen species. But this composite cathode suffers from the detachment of the Pd catalyst. A Co₃O₄ surface layer is further introduced to enhance the adhesion of the catalyst, which doubles the lifetime of the cathode. To achieve a fully stable cathode, Ru catalyst with stronger adhesion on TiSi₂ directly is explored and identified to be robust in the operating conditions of Li-O₂ batteries.

The expedition for stable cathodes in Li-O_2 batteries is expected to provide a clean material platform. This platform can simplify the study in evaluating the effectiveness of catalysts, the reaction mechanism at the cathode and the stability of the electrolyte.

Toward the end of this thesis, an exploration is made to enable rechargeable Mg metal battery with a conversion Br_2 cathode. This new system can avoid the dendritic growth of Li metal by the adoption of Mg as the anode and can promise better cathode kinetics by forming a soluble discharge product.

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List of publications

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Chapter 1. Introduction

Electrical energy storage devices are indispensable nowadays. From the powering of portable electronics to the peak management at grid scale, storing electricity energy in another energy form that can be reversibly extracted is the core responsibility of such devices.^[1-2] Chemical bonds are good candidates for the storage of these energies. The devices that can reversibly convert between electric energy and chemical energy are named rechargeable batteries.^[3] Batteries can be classified by different chemistries at the electrodes. Successful examples are lead-acid batteries, Ni-metal hydride batteries, Li-ion batteries and redox-flow batteries.^[4-5] There are several parameters that are important for the evaluation of the energy storage devices, including gravimetric energy density, volumetric energy density, power density, Coulombic efficiency, round trip efficiency and lifetime. While other parameters can be improved with certain strategies, the energy density of an energy storage device is confined by the chemistries at two electrodes. For most batteries, the energy densities are in the order of $10\sim100$ Wh/kg, which are one order of magnitude lower than internal combustion engines, limiting the electrification of transportation.^[6] Among all the competitors, Li-oxygen batteries offer the highest theoretical energy density that is comparable with gasoline based internal combustion engines.^[7] The development of Li-oxygen batteries is expected to significantly boost the driving range of electric vehicles. However, the development of Li-oxygen batteries faces

critical challenges from the round trip efficiency and stability.^[7] In this dissertation, a comprehensive overview of the current understanding of the Li-oxygen battery system is provided; several experimental approaches to improve the cathode performance are demonstrated as a proof of concept; a frontier work into the battery systems beyond lithium metal is also included.

1.1 The chemistry in Li-O₂ batteries

Batteries, including Li-O₂ batteries, are composed by three major components: the anode, the cathode and the electrolyte.^[3] Redox reactions will take place at the anode and cathode to convert the chemical energy to the electricity. By definition, in the discharge process, oxidation reactions happen on the anode and reduction reactions happen on the cathode. Usually the potential of the redox reactions at the anode is lower than the cathode. This is why the anode is also referred to as the negative electrode while the cathode is referred to as the positive electrode. The difference of potentials between these two electrodes determines the voltage of a certain battery. Once connected by wires to the load, electrons will flow from the anode to the cathode through the out circuit, generating electric current. At the same time, the consumption of reactants and the accumulation of products of the redox reactions will change the equilibrium chemical potentials of the electrodes. If the internal mass transport is not enabled, no voltage or current can be further obtained. This is governed by the Nernst equation. Electrolytes, which are ionically conductive but electronically insulating, can transport the reaction products between two electrodes. This ion transportation allows the continuous operation of the battery by minimizing the internal concentration gradient between the anode and the cathode.

More specifically in Li-O₂ batteries, Li metal serves as the anode with the chemical potential of - 3.0 V vs Standard Hydrogen Electrode (SHE).^[8] This is one of the lowest chemical potential one can achieve from a single metal. For the ease of discussion, unless specified, all the voltage references used in the rest of the dissertation will be based on Li⁺/Li redox pair. This low potential of the anode leads to high battery output voltage, which is one reason why Li metal is desired to be employed as the anode in multiple battery systems.^[9] Additionally, Li⁺ as the charge carrier can provide high energy density ($m_{Li}^+ = 7$ g/mol), high ion diffusion coefficient and abundant intercalation cathode material choices.^[10] These benefits drove the Li-ion battery (LIB) to dominate the electric energy storage applications.

However, the capacity and kinetic limitations of the intercalation chemistry based cathode in LIB can no longer satisfy the increasing need of society. A conversion cathode with much higher energy density and better kinetics is desired to further advance the energy storage technology.^[1] The most promising candidate is the oxygen cathode.^[11] Oxygen as a strong oxidant consists 21% of ambient air. If oxygen can be used as the cathode reactant, there is no need for the battery to carry the intercalation metal oxides to host the Li⁺. This can significantly improve the capacity of the cathode. As can be seen from the comparison below (**Figure 1-1**), the potential of Li-O₂ battery is unsurpassable.



Figure 1-1. The Ragone plot of energy storage devices with typical value of gravimetric energy density and power density.

The chemical reactions on these two electrodes can be summarized as follows (**Figure 1-2**). During discharge process, Li metal will lose 1 e to the outer circuit, get oxidized to become Li^+ , and enter the electrolyte. Meanwhile at the cathode, the electron will be transferred to oxygen molecules and generate superoxides as the intermediate. These superoxide intermediates will be disproportionated by the Li^+ and generate Li_2O_2 as the final discharge product. This electrochemical reaction generates the voltage of 2.96 V (vs Li^+/Li) and has the theoretical energy density of 3505 Wh/kg.^[1] The unbroken O-O bond in the peroxide grants the reversibility to this chemistry. For the recharge process, oxidative potential is applied at the cathode to electrochemically decompose Li_2O_2 into Li^+ and O_2 . Electrons are withdrawn from the peroxides and conducted to the anode, where Li^+ gets reduced to become Li metal. This recharge process removes the insulating

 Li_2O_2 on the cathode surface and regenerates Li metal at the anode. After fully recharge, the battery is ready for the next discharge cycle.



Figure 1-2. The schematic illustration of anode and cathode chemistries in Li-O_2 batteries. Modified with permission from Ref^[7]. Copyright 2011 ACS.

1.2 Major challenges in Li-O₂ batteries

Attracted by the high promising energy density of Li-O₂, researchers have been pursuing the materialization of Li-O₂ battery since 1970s.^[12] The first demonstration of reversible Li-O₂ battery was achieved by Abraham et al in 1996.^[8] Li metal anode, polymer based electrolyte and carbon cathode have been employed. Li₂O₂ was observed as the discharge product which can be removed upon recharge. The studies on Li-O₂ batteries bloomed thereafter.^[7] The challenges identified after three decades of studies can be summarized as follows.

1.2.1 The overpotential and corrosion of the cathode

The first challenge is the overpotential for the discharge and recharge processes.^[13] The cathode reactions start with the reduction of gaseous oxygen to a solid Li₂O₂. The reaction can only happen when electrons, oxygen and Li⁺ are in close proximity. Electrons are supplied by the solid electrode, Li⁺ ions are supplied by the liquid electrolyte and O₂ comes from the gas phase. Ideally, only this solid-liquid-gas junction named Three Phase Boundaries (TPB) is considered as the active region for Li₂O₂ formation. Realistically, O2 can be dissolved in the liquid electrolyte so the reaction sites can be greatly expanded to the whole cathode surface. The rate determining factor becomes the catalytic activity of the cathode material to reduce the oxygen. The reduction of oxygen has always been a hot topic for its importance in the fields of corrosion preventions, fuel cells and the production of H_2O_2 .^[12,14] The oxygen can be reduced via 1e, 2-e or 4-e process, but none of them is considered as a kinetically facile process. The difficulty increases with the increase of total electrons to be transferred. Catalysts are needed to achieve the selectivity of 2-e process and reduce the overpotential.^[15] Besides the catalytic activity, another source for overpotential is the mass transport limitation.^[16] Both Li⁺ and O₂ in the electrolyte should have sufficient diffusion coefficient to sustain the continuous reaction. This requires the cathode to have adequate porous structures and optimized diffusion length.

In addition to the overpotential during discharge, the recharge overpotential presents even greater challenges. The insulating nature of Li_2O_2 toward both Li^+ and electrons induces high polarization during the recharge.^[17] Also, the electrochemical oxidation of Li_2O_2 relies on the solid-solid contact for the charge transfer. The poor contact between Li_2O_2 and cathode further increases the interfacial resistance. Moreover, carbon is not stable in contact with Li_2O_2 , an even more insulating layer of Li_2CO_3 is formed at the interface (**Figure 1-3**).^[18] The result is the recharge overpotential being more than 1 V for a typical carbon cathode. This high overpotential greatly undermines the roundtrip efficiency and increases the decomposition of both cathode and electrolyte.^[7]



Figure 1-3 Typical overpotential for the cathode reactions and corresponding chemical reactions. Reproduced with permission from Ref. ^[18]. Copyright 2012 ACS.

The last major challenge comes from the contaminations. The idea of Li-air battery is to the take the oxygen directly from the air thus reduces the material to be carried in the battery. However, the ambient air contains abundant gases that are considered as contaminations toward the Li-O₂ battery chemistry. Water, for example, can consist up to 3 % of ambient air. This value is especially high in the rainy days. The H₂O may have profound impact toward the discharge product and intermediates thus need to be eliminated.^[19] Also, CO₂ from the air will inevitably react with the Li₂O₂ and form thermodynamically stable Li₂CO₃.^[20] The buildup of by-product including LiOH and Li₂CO₃ further contributes to the failure of the cathode.

1.2.2 The instability of the electrolyte

The major challenge of the electrolyte comes from instability.^[21] To expand the active region (three phase boundaries), liquid electrolytes are desired. Most of the liquid electrolytes are composed by organic solvents and Li salts. The organic molecules usually have poor anodic stability and suffer from the degradation by reduced oxygen species, such as superoxides, peroxides and molecular oxygen. This will further be elaborated in the next section.

The second challenge of the electrolyte is the balance between the vapor pressure of the solvent and the solubility and diffusivity of O_2 .^[16] Electrolytes with low viscosity and high diffusion coefficient usually possess high vapor pressure. The unique requirement for the oxygen cathode significantly increases head space of the battery. The high vapor pressure of the electrolyte presents challenges for the electrolyte management.

1.2.3 The reactivity and dendritic growth at the anode

Lithium metal as the anode is critical to realize the high energy density of Li-O₂ batteries. The notorious dendritic growth of Li upon plating is limiting the usage of Li metal in all rechargeable Li metal batteries.^[22] Instead of flat and smooth deposition, the growth of Li metal tends to take a branched pathway. The electrochemically deposited Li is known to form needle like dendrites that punctures the separators. Moreover, the dendritic growth of Li will result continuous exposures of fresh Li metal to the electrolyte. This process consumes both the active Li and the liquid electrolyte, leading to the lowered Coulombic efficiency. The situation is further completed by the crossover of oxygen from the cathode in Li-O₂ batteries.^[23]

1.3 Parasitic reactions in Li-O₂ batteries

While kinetic challenges can be optimized by the proper engineering of electrodes, the parasitic reactions and the instability of materials in Li-O_2 batteries is the core problem to be addressed. In this dissertation, we will first examine the origin of parasitic reactions in Li-O_2 batteries and demonstrate several approaches to address the issues.

The reactive oxygen species are abundant in Li-O_2 batteries and play a central role in the electrolyte decomposition, cathode corrosion and synergistic anode degradation.^[24] In the discharge, molecular oxygen is first chemically adsorbed on the cathode surface and receives one electron to be reduced to superoxide (O_2^{*-}). The superoxides can either remain on the surface or be solvated into the electrolyte depending

on the specific solvents or additives.^[25] The superoxide species will further be disproportionated by Li^+ into Li_2O_2 and O_2 , generating the final discharge product as Li_2O_2 . In the recharge process, Li_2O_2 will first be delithiated to superoxide like $Li_{2-x}O_2$. Further oxidation lead to the full decomposition and the release of O_2 , mediated by superoxide, oxygen radicals and singlet oxygen.^[26-28] Thus the ubiquitous presence of reactive oxygen species during the operation of Li-O₂ batteries is obvious.

1.3.1 Parasitic reactions of the electrolyte

The reactive oxygen species will react with the electrolyte from several pathways as summarized in **Figure 1-4**. Four types of parasitic reactions are prominent in Li-oxygen batteries, namely nucleophilic attack, proton mediated degradation, auto-oxidation and acid/base chemistries. Insights into these degradation mechanisms are expected to facilitate future designs of electrolyte that are more resistant to these reactions, leading to the eventual discovery of a desired electrolyte system.



Figure 1-4. Decomposition mechanisms of organic electrolytes in Li-O_2 batteries triggered by reactive oxygen species. Reproduced with permission from $\text{Ref}^{[29]}$. Copyright 2016 Wiley-VCH.

1.3.1.1 Nucleophilic attack

As a negatively charged radical, superoxide (O_2^{\bullet}) may attack positively charged sites on solvent molecules, such as the carbon center of C*=O bonds or the sulfur center of the S*=O bonds.^[30-31] The most well-known example may be organic carbonates. The strongly polarized C=O bonds render the carbon centers positively charged. They are highly susceptible to the nucleophilic attack by superoxide (**Figure 1-5**). ^[32]



Figure 1-5. The nucleophilic attack of ester bonds by superoxide species. Reproduced with permission from Ref^[32]. Copyright 2011 Elsevier.

The reactivity of alkyl carbonates has motivated researchers to seek other electrolyte choices that are less susceptible to nucleophilic attacks. The N in amide (O=C-N) has lower electron negativity than the O (marked by *) in the ester (O=C-O^{*}). As such, the N atom acts as a better electron donating group, making the C center in O=C-N less positive than that in O=C-O. This explains why amide has been considered as a more stable electrolyte toward nucleophilic attacks.^[33] Computational calculations have shown that the free-energy barrier for the nucleophilic attack to amides is indeed greater than DMSO or esters.^[30] It is noted that experimental observations on the stability of amide are not conclusive as conflicting results have been reported.^[34-35]

1.3.1.2 Autoxidation reaction

Ethers might be one of the best nucleophilic-attack-resist solvents due to the lack of C=O bonds. 1,2-dimethoxyethane (DME) and tetra ethylene glycol dimethyl ether (TEGDME) are the most widely used electrolyte for Li-oxygen battery studies presently.^[36-37] However, the well-known autoxidation reaction presents new challenges for ethers,

especially in the oxidative environment of the cathode. The hydrogens on the carbon of the C-O-C bond (α-H) are most susceptible.^[34] The reaction triggered by radicals lead to the polymerization of the solvent and the formation of organic peroxides (**Figure 1-4**).^[38] Not only do the superoxide radicals trigger this reaction, molecular oxygen can also be a major promoter.^[39] The autoxidation was also found in α or β-H position of organic carbonates. The understanding further supports that organic carbonates are poor electrolyte choices for Li-oxygen batteries.^[40] By evaluating the activation free energy required for the uncatalyzed autoxidation in a variety of solvents, computational studies suggest that the auto-oxidation is a general decomposition pathway for Li-oxygen batteries.^[34] Experimentally, ployethers/esters were observed as the decomposition products in ethereal electrolyte, confirming the degradation routes.^[41] Due to the involvement of O₂ in the cathode chemistry, autoxidation of organic solvent is a parasitic reaction that cannot be ignored.

1.3.1.3 Acid-base reaction

The acid and base referred here are from the Brønsted definition, which classifies a proton receiver as a base and a proton donator as an acid. In Li-oxygen batteries, the reduction product (Li_2O_2) and intermediate (O_2^-) are both considered as extremely strong base, which may result in the abstraction of protons from aprotic solvent molecules and make them "acidic".

This abstraction of protons on the solvent can be more severe with the existence of a strong electron withdrawing group or the formation of conjugation after the deprotonation.^[42] DMSO is a good example where the S=O group can provide both effects to facilitate the deprotonation of the α -H. As demonstrated by the aging experiment with Li₂O₂ soaked in the DMSO, a significant amount of LiOH was observed (**Figure 1-6a**).^[43] The appearance of H element in the solid product indicates proton abstraction takes place on the DMSO molecule, which is the only proton source. The quantity of LiOH is higher when KO₂ is added to the soaking solution, indicating even stronger deprotonation effect of superoxide species.^[43]



Figure 1-6 a) Li_2O_2 abstracting protons from DMSO molecules generating LiOH. Reproduced with permission from Ref. ^[43]. Copyright ACS. b) Hoffman β -H elimination in PYR₁₄TFSI ionic liquid. Reproduced with permission from Ref. ^[44]. Copyright 2015 ECS.

Another example is the ionic liquid. $PYR_{14}TFSI$ (1-Butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide) is an attractive electrolyte choice owing to its low vapor pressure, wide electrochemical stability window and non-flammable nature.^[26,45] However, the positively charge quaternary N in the PYR cation activates the β -H (H_c and H_d in **Figure 1-6b**) on the carbon second next to the N atom will be activated by strong bases like superoxide species. The deprotonation is accompanied by the removal of alkyl groups and the formation of unsaturated bonds known as the Hofmann β -H elimination.^[44] As a result, the PYR₁₄TFSI could lose its ionic liquid characteristics and trigger more parasitic reactions.^[46]

1.3.1.4 Proton mediated parasitic reaction

The major difference between non-aqueous and aqueous Li-oxygen batteries is the free protons. The introduction of free protons changes the final discharge product from Li_2O_2 to LiOH, which is thermodynamically more stable.^[47] The high electrochemical potential (> 3.4 V) required to decompose LiOH during the recharge process, however, significantly increases the risks of electrochemical oxidation of organic solvent molecules and therefore are undesired.^[48] Moreover, the intermediates in the discharge process with the presence of free protons will behave differently. H⁺ can stabilize the intermediate of nucleophilic attack toward C=O bond by bonding with O, similar to but more effective than the role of Li⁺.^[32] Furthermore, both superoxide and peroxide species can be protonated to generate HO₂ and H₂O₂ species, which are more soluble than their lithium counterparts (i.e., LiO₂ and Li₂O₂, respectively).^[49] The enhanced concentration of reactive oxygen species in the electrolyte greatly increases the chance of previously mentioned parasitic reactions.^[19,50] The high concentration of these species may also induce the crossover of these soluble species from the cathode to the anode, which threaten to compromise the SEI layer and trigger synergistic decomposition of the electrolyte on the Li metal anode.^[51-52] Worse, the decomposition of electrolyte could induce more proton liberation, making this proton mediated decomposition selfcatalyzed.

1.3.2 Parasitic reactions at the cathode

The major location for the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) is the cathode, which is the most vulnerable component toward parasitic reactions induced by reactive oxygen species.^[53] Carbon as the most widely adopted cathode is promising for the following reasons:

1) The catalytic activity of carbon can promote the 2-e reduction of O_2 .

2) The high surface area and conductivity of carbon reduces the overpotential for the ORR reaction.

3) The porosity of carbon provides space for the storage of Li_2O_2 .

4) The gravimetric energy density can be improved by the low density of carbons.

With these desired properties, researchers have successfully demonstrated the prototypical Li-oxygen batteries with high discharge capacity, low discharge overpotential and confirmed the discharge product of Li_2O_2 on carbon cathodes.^[7] However, the carbon cathode was found to be not stable in the operation condition of Li- O_2 batteries.^[54-55] The high applied potentials during recharge further exacerbate the situation. Metal, metal oxide and doped carbon (often in the form of nanoparticles) have been widely explored as co-catalysts in conjunction with the carbon cathode to promote the ORR and OER. These materials have been found to lead to additional parasitic reactions.

1.3.2.1 The corrosion of carbon

The reactive oxygen species can directly react with carbon. For example, the reaction between the discharge product Li_2O_2 and carbon is thermodynamically spontaneous.^[18]

C+Li₂O₂+1/2 O₂=Li₂CO₃
$$\Delta$$
 G= -542.4 kJ/mol (Equation 1-1)
C+Li₂O₂=Li₂CO₃+Li₂O Δ G= -533.6 kJ/mol (Equation 1-2)

This reaction generates Li₂CO₃ on the surface of carbon which will passivate the cathode surfaces and impede the charge transfer. This parasitic reaction has been experimentally quantified by B. D. McCloskey et al.^[56] and visualized by Shao-horn et al.^[57] Superoxide species present even stronger corrosion toward carbon. The process can be illustrated in **Figure 1-7**.



Figure 1-7. The corrosion of carbon during the ORR process generating carbonates and epoxy groups. Reproduced with permission from Ref.^[54]. Copyright 2013 ACS.

The direct reaction between Li_2O_2 and C during discharge only contributes a small fraction of the total carbon corrosion. The majority of carbon corrosion is induced during the recharge process.^[56] The decomposition of Li_2O_2 requires the electrochemical potential of the cathode to be raised above the thermodynamic equilibrium potential. But the poor electrical conductivity of Li_2O_2 and poor solid-solid contact between the Li_2O_2/C requires high polarization to achieve charge transfer.^[58] The actual potential needed (> 4 V vs Li^+/Li) is typically 1 V over the thermodynamic equilibrium potential (2.96 V vs Li^+/Li). The high potential applied makes it possible to directly oxidize carbon in the oxygenated atmosphere, especially after the carbon is "activated" after the discharge process.

$$C + O_2 = CO_2$$
 (Equation 1-3)

P.G. Bruce et al. performed a detailed study of this parasitic reaction and found the stability threshold to be around 3.5 V. Above 3.5 V, significant decomposition of carbon could be confirmed by the generation of ¹³C labelled CO_2 ^[55].

1.3.2.2 Catalysts induced parasitic chemical reactions

Catalysts are introduced to reduce the overpotential of the ORR and OER processes. However, parasitic reactions can often also be promoted at the same times. Pt catalysts in DME electrolyte is a good example.^[59] With the introduction of Pt catalysts, the recharge overpotential was significantly reduced. The electrochemical profile indicates Pt as a good catalyst. However, the examination of gas generation revealed the true reaction to be the decomposition of DME instead of Li_2O_2 (**Figure 1-8**). Theoretical work also confirmed the catalytic effect of Pt toward DME decomposition.^[60]



Figure 1-8. Catalyzed decomposition of DME by the introduction of catalyst including Pt, MnO_2 and Au. a) Electrochemical profile of the discharge and recharge processes. b) Oxygen evolution rate quantified by DEMS. c) CO_2 generation rate quantified by DEMS. Reproduced with permission from Ref ^[59]. Copyright 2011 ACS.

Transitional metal oxides, such as Fe₂O₃, MnO₂, Co₃O₄, Cr₂O₃ and RuO₂ are also popular catalyst candidates.^[37,61-64] While these metal oxides do facilitate the ORR or OER processes, the change of discharge product is a concern. One frequently observed phenomenon is the change of oxygen reduction process to the undesired 4-e process, generating Li₂O or LiOH, especially when H₂O was involved.^[65] This deviation from 2-e process reduces the reversibility and increases the over potential. Product detection will be necessary to confirm there is no parasitic reaction of 4-e O₂ reduction when introducing new catalysts. Also, newly formed lithium oxides or peroxides may be incorporated into the transition metal oxide (MO_x), generating the Li_xM_yO_z.^[66] The involvement of these transition metal oxides in the ORR process could change the reaction completely. First, these metal oxides can no longer be considered as a catalyst because of their participation in the reaction. Second, the phase change accompanied by the Li₂O incorporation results in the cracking, dissolution and detachment of transition metal oxides that reduce the reversibility of the cathode.^[27]

Another emerging catalyst choice is the soluble catalyst, often referred to as the redox mediator. Redox mediators could limit the recharge voltage at their redox potential by being oxidized from the reduced form to oxidized form ($RM \rightarrow RM^+$). This can prevent the risk of parasitic reaction triggered by high potential. The oxidized form of redox mediator is expected to chemically oxidize Li_2O_2 and regenerate the reduced form ($2RM^+$ + $Li_2O_2 \rightarrow 2RM + 2Li^+ + O_2$) ^[67]. Potential parasitic chemical reactions can originate from two aspects. The first is the chemical stability of the redox mediator molecules themselves. Redox mediators usually contain organic ligands or conjugated bonds. All the parasitic reactions to the organic molecules discussed in **Chapter 1.3.1** can also be applied here. The second origin of parasitic reactions is the poor selectivity of redox mediators to oxidize Li_2O_2 . For example, LiI and LiBr have both been proposed as the redox mediator.^[68-69] Their oxidized form, I_3^- and Br_3^- , are known to be corrosive toward

metal current collectors. Their reaction with the solvent molecules and polymer separators has also been noted.^[70-71] Compatible cell components have to be used to eliminate these potential parasitic reactions.

1.3.3 Parasitic reactions on the anode

Due to the low equilibrium electrochemical potentials, Li metal can react with almost all known liquid electrolyte to produce a surface layer often broadly referred to as the solidelectrolyte-interface (SEI).^[72] The SEI layer has proven critical to the success of Li-ion batteries. Notwithstanding, it presents significant challenges for Li-O₂ battery operations. Not only does the formation process consume the Li metal and the liquid electrolyte, the fragile spontaneous passivation layer is also not mechanically strong enough to ensure complete protection for the lithium anode during plating. As a result, dendrites are often observed, which would expose more fresh lithium to the liquid electrolyte to further induce parasitic chemical reactions between Li and the electrolyte. The most immediate measurable effect is the worsening Coulombic efficiency (<<100%).^[73] The dendritic growth is also the best known reason that leads to safety failures of Li batteries, including Li-ion batteries. In the case of Li-oxygen battery, the situation is further complicated and worsened by the crossover of reactive soluble oxygen species.^[23]

1.3.3.1 Corrosion of the Li metal

When DMSO, DMA, acetonitrile or water are in contact with Li metal, no stable SEI can be formed, leading to the continuous corrosion. This is due to the high solubility of the electrolyte decomposition products.^[74] For electrolytes that are more compatible with Li anode, including ethers and organic carbonates, insoluble decomposition product is anticipated to make the corrosion self-limiting.^[72] However, this meta-stable SEI still can be compromised by the dendritic growth of Li. Fresh Li surfaces are always expected to evolve during the charging step of Li-oxygen batteries, resulting in the continuous consumption of active anode material. As observed in literatures, repeated cycling of Li metal in TEGDME resulted in the darkening of the Li surfaces and eventually the loss of all Li metal.^[51] This phenomenon is universal in many secondary battery systems with Li metal as anode, including Li metal-ion battery, Li-S battery, Li-redox flow battery etc.^[1,75] Strategies to protect Li metal by incorporating robust artificial SEI are promising to mitigate the dendritic growth and corrosion of Li.^[9]



Figure 1-9 Spontaneous formation of SEI layer and its protection effect of Li against electrolyte and oxygen. The composition and morphology of SEI on Li metal could be changed by the involvement of O_2 . Reproduced with permission from Ref. ^[29]. Copyright 2016 Wiley-VCH.

1.3.3.2 Synergy between oxygen and the SEI formation

One thing special about Li-oxygen batteries is the ubiquitous presence of O_2 in the cell. The porous polymer separators used in the testing cell allow free travel of oxygen to

the anode. The introduction of oxygen to the anode surface may have profound impact toward the SEI formation (Figure 1-9) and the impacts may be negative or positive depending on the specific electrolyte system.^[23,29] On one hand, the oxygen will get reduced on the surface of Li, generating superoxide, peroxide and oxide species.^[76] They are passive in nature to shut down further reaction between O2 and Li. However, as we discussed in Chapter 1.3.1, they are reactive toward the liquid electrolyte via multiple potential reaction pathways. This may initiate the decomposition of electrolytes and in return release free protons to weaken the passivation layers.^[76-77] On the other hand, oxygen can help the formation of a better SEI layer on Li in some instances. For example, in an ionic liquid (N1114TF2N) base electrolyte, the introduction of oxygen to the electrolyte results in the reduction of SEI thickness by 67% together with lower interfacial resistance. The anode coulombic efficiency was also improved by 10% compared with the anode in Ar atmosphere, indicating a more effective SEI was formed $[^{[78]}$ From this perspective, the parasitic reaction that O_2 involved here offers positive impact on the overall stability of the anode.

1.4 Summary

The fundamental reason for the poor cycling lifetime of Li-O_2 batteries is the rich parasitic reactions on the cathode, in the electrolyte, and at the anode. At the current stage of study, the parasitic reactions that result in the instability of cathode are the most prominent. The rest of this dissertation will be focusing on this important topic. With the help of relatively stable ether based electrolyte, we are seeking to find truly stable cathodes. The stable cathode can in return provide a clean platform to identify better electrolytes. Novel electrode structures, new materials choices, and effective protection approaches that can improve the cathode stability will be presented. Toward the end of this dissertation, a battery system with better promised kinetics and reversibility will also be proposed and explored.

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Chapter 2. A wood derived N doped carbon cathode for Li-O₂ batteries

Carbon is a promising material as the oxygen cathode in non-aqueous Li-O₂ batteries.^[1] Its high porosity, high conductivity, light weight and good catalytic activity contribute to the desired cathode performance. Among them, the porous structure of carbon is especially important.^[2] In Li-O₂ batteries, the transportation of Li⁺ and oxygen limits the maximum current density and obtainable capacity.^[3] Adequate ion and gas transport channels via interconnected pores can facilitate the mass transportation.^[4-5] Inspired by the transportation of water and dissolved mineral in plants through Xylem and Phloem,^[6] the hierarchical pore structure of the wood could be a good template for the cathode of Li-O₂ batteries.



Figure 2-1 Scheme of wood-derived N doped carbon as the cathode in Li-O₂ batteries.

In collaboration with Prof. Zhu from Northeastern University, we carbonized the wood harvested from yellow pine and took advantage of the existing pore structure from the wood. Free-standing binder-free carbon cathodes were obtained. With further activation by N atom doping via a facile gas phase reaction, the wood derived N doped carbon (wd-NC) exhibit significantly improved cathode performance. In this chapter, the structural and chemical properties of wd-NC as the cathode for Li-O₂ batteries were explored. An overall energy efficiency of 65 % and cycle number over 20 at 70 % depth of discharge was demonstrated. The discharge product was also confirmed to be Li_2O_2 . This presents a new way of fabricating free-standing and binder-free cathode in a regenerable way.

2.1 Methods

2.1.1 Material preparation

The pristine wood was harvested from yellow pine and cut into rectangular thin sheets. The carbonization was carried out in two steps. The wood was first baked at 240 °C for 12 h in ambient air to drive out the moisture and small organic molecules. The resulting sample was then transferred to a tube furnace with Argon atmosphere for full carbonization. The tube was maintained at 760 torr with the Ar flow of 30 sccm (Standard Cubic Centimeter per Minute). The temperature of the furnace was ramped from room temperature to 900 °C with the speed of 10 °C/min and held at 900 °C for another 2 h to obtain wood-derived carbon (wd-C). For wood-derived N-doped carbon

(wd-NC), the carbonization and N doping were carried out simultaneously with anhydrous NH₃ as the reaction gas (Airgas, 75 sccm, 760 torr) at 800 °C for 2 h. The wd-NC was prepared at 800 °C but not 900 °C because carbon was found to react severely with NH₃ at 900°C. Before transferring the resulting samples into the glovebox (Mbraun, MB20G, with O₂ and H₂O concentrations < 0.1 ppm), the wd-C and wd-NC were further vacuum dried at 150 °C for at least 12 h in the antechamber. All carbon samples were used directly without further processing. The free standing cathodes have the areal density of 19 mg/cm² at the thickness of 1 mm.



Figure 2-2. The illustration of carbonization and N-doping processes for the wood.

2.1.2 Material characterization

Scanning electron microscopy (SEM) was collected on a JEOL 6340F microscope operated at 15 kV. Raman spectra were acquired using a micro-Raman system (XploRA, Horiba) with an excitation laser of λ =532 nm. The surface area and pore volume information was obtained by N₂ adsorption/desorption experiments carried out on an

automatic gas sorption analyzer (Autosorb iQ, Quantachrome) at 77 K. For XPS analysis of the carbon electrode after Li-O₂ operations, the cell was transferred to an O₂-tolerant Ar-filled glove box (H₂O level < 0.1 ppm, MBraun), where it was disassembled to extract the cathodes. The cathodes were further washed with pure anhydrous dimethoxyethane (DME, anhydrous grade, Sigma-Aldrich) 3 times to remove trapped salts. Afterwards, the cathode was vacuumed to remove solvents and then transferred to the XPS (K-Alpha, Thermo Scientific) vacuum chamber with minimal exposure to ambient air (< 1 min). Xray diffraction data was obtained on a PANalytical X'Pert Pro diffractometer with airtight sample holder without exposing the sample to ambient air. Mechanical test was performed with a Discovery HR-1 hybrid rheometer. All samples tested were of the same dimensions (9mm×8mm×3mm)

2.1.3 Electrochemical characterization

LiClO₄ (99.99%, battery grade, Sigma-Aldrich) was first baked at 130 °C in the antechamber of the glovebox and then dissolved in DME to form a 0.1 M electrolyte solution. Customized SwagelokTM type cells were assembled in the glove box with Li metal (380 μ m in thickness, Sigma-Aldrich) as the anode, 2 pieces of Celgard 2400 films as the separator, and 0.1 M LiClO₄ (100 to 200 μ L) as the electrolyte. The assembled batteries were then transferred to the O₂-tolerant Ar-filled glove box, where O₂ (ultrahigh purity, Airgas) was purged into the cell to replace Ar. Electrochemical characterization was conducted using an electrochemical station (Biologic, VMP3).

2.2 Results and discussions



2.2.1 Physical appearance and mechanical properties

Figure 2-3 Appearance of the wood-derived N doped carbon cathode and the mechanical test performance in comparison with wd-C and Vulcan carbon.

The carbon obtained in the above mentioned method maintained the structural integrity of the original wood. As well known, wood is a good structural material that can be applied as the frame in the constructions. This mechanical strength is closely related with the unique microstructure of aligned fibers. Upon carbonization, the fibers composed by cellulose were dehydrated to become carbon. As we observed, during the first step of baking at 240 °C, 67 % of weight was lost. This lost is mainly contributed by the moisture in the wood and small organic molecules. In the second step, another 50 % weight loss was observed on wd-C which represents the dehydration of cellulose to form carbon. The average resulting weight of wd-C is 17 % of the original wood while the wd-NC is 11% of the original wood. The significant loss of weight is expected for the full carbonization.

To demonstrate the mechanical strength of the samples after significant weight loss, compression test was carried out to compare the maximum stress the samples can undertake. Three samples were chosen for comparison: wd-C, wd-NC and Vulcan carbon powders bonded by 5 % PVdF binders. The Vulcan carbon was selected to represent widely used particulate carbon cathodes reported in literatures.^[7] Three samples were prepared into the same size and subjected to the compressions tests. As can be seen in **Figure 2-3b**, wd-NC possesses higher mechanical strength than wd-C and Vulcan carbon bonded by PVdF. Further interpretation of the data in **Figure 2-4** can help to give a better understanding of its mechanical property. The wd-NC can hold up to 800 kPa pressure without crushing. This strength ensures wd-NC to withstand the pressure applied during the assembly of the battery. The small displacement at same stress indicates that wd-NC is relatively stiff, which usually lead to brittleness.



Figure 2-4 Raw data of mechanical stress test for wd-NC, wd-C and Vulcan carbon samples. The sudden drop of the curves stands for the physical crush of the sample

2.2.2 Microstructures and pore structures

The microstructure of the carbon was examined by the SEM. The carbon sample was composed by the vertically aligned channels derived from the porous structure of woods. The diameters of the channels are in the range of 10-50 μ m both in wd-C and wd-NC. These channels at micron-meter scale are considered as the facile transportation pathways for Li⁺ and O₂. On the side of the walls, smaller inter-channel pores with the diameter under 2 μ m can provide additional diffusion pathway. In case the terminals of one channel were clogged, Li⁺ and O₂ can still enter this channel from the adjacent channels.



Figure 2-5 SEM images showing the microstructure of wd-C and wd-NC samples. (a) &(b) Top view of wd-C and wd-NC, respectively. (c) The hierarchical pore structure of wd-NC. (d) The inter-channel pores on the walls of wd-NC.

The difference between wd-NC and wd-C hides in the pores that can't be easily visualized. N₂ adsorption and desorption measurement was employed to reveal the detailed pore structure and surface area. The isothermal adsorption and desorption curve indicate significantly higher surface area of wd-NC sample vs wd-C sample. The normalized surface area for wd-NC is 745 m²/g while wd-C is only 75.5 m²/g. The pore volume of wd-NC is also 10 times higher than wd-C. The majority of the pores measured here are micropores (d < 2 nm). The detailed comparison was listed in **Table 2-1**.

 Table 2-1 Summary of BET surface area and pore volume for wd-NC, wd-C and Vulcan carbon sample.

	BET surface area	Micro pore	Total pore volume
Sample	(m²/g)	volume (cm ³ /g)	(cm³/g)
wd-C	75.5	0.035	0.035
wd-NC	745	0.22	0.36
Vulcan			
XC72	254 ^[8]		0.174 ^[8]



Figure 2-6 N_2 adsorption-desorption isothermal data indicating significantly higher surface area of wd-NC sample vs wd-C sample.

The enlarged surface area and pore volume can be explained by the activation effect of NH_3 during the N doping process. NH_3 can react with carbon to form CH_4 and N_2 .^[9] This corrosion of carbon can create more micropores and enlarge the surface area of carbon. The knock-off of carbon can also induce the N doping on carbon, which will be proved later.

2.2.3 Chemical composition

The chemical composition of the wd-C and wd-NC was examined by Raman and XPS. Raman spectroscopy is a good method to examine the degree of carbonization and characterize the structure of carbon. By comparing three samples, we conclude the carbonization of both wd-C and wd-NC is complete (**Figure 2-7**). The pristine wood contains large amount of organic component which results in the featureless fluorescence response in the Raman spectrum. After carbonization, wd-C and wd-NC samples both exhibit distinct carbon peaks. The vibration mode at ~1330 cm⁻¹, known as the D band, corresponds to the sp³ hybridized carbon introduced by defects or heteroatom doping. The peak at the Raman shift of ~1590 cm⁻¹ represent the sp² hybridized graphitic carbon. ^[10] The intensity between the D band and G band can help to estimate the crystallinity of the carbon.^[11] The slightly higher D/G ratio of wd-NC than wd-C reflects the doping of N in the carbon.

The N doping was further confirmed by the XPS, in which the N 1s signal can definitively prove the incorporation of N in the carbon lattice. Further deconvolution of the N 1s signals reveals the chemical environment of the N bonding. The most prominent form of the N appears to be pyridinic N with the binding energy of 398.2 eV. This N on the six-member ring of carbon was identified to further activate carbon for the ORR. As shown by Guo et al, the carbon next to the pyridinic N facilitates the adsorption of O_2 which is the first step of the ORR.^[12-13] A secondary component of the N signal is the pyrrolic N at 400.7 eV.^[14] This is consistent with the N substituting the O on the 5-membered ring in the precursor.



Figure 2-7 Raman and XPS characterization confirming the carbonization and N doping of wd-NC (a) The two Raman peaks corresponding to the D band at \sim 1330 cm⁻¹ and G band at \sim 1590 cm⁻¹ of carbon are prominent for both wd-C and wd-NC samples. (b) XPS spectrum of C 1s signal for wd-NC sample. (c) XPS spectrum of N 1signal for wd-NC sample.

2.2.4 Electrochemical performance

The electrochemical activity of wd-C and wd-NC as the cathode of Li-O_2 batteries were further examined. Li was used as the anode and DME/0.1M LiClO₄ was employed as the electrolyte. With the same sample size and mass loading, wd-NC exhibits 5 times higher discharge capacity and lower overpotential for both discharge and recharge. The increase of capacity can be explained by the difference in the pore volume. The discharge product, Li_2O_2 , is a solid. Generally the porosity of the cathode determines the maximum amount of discharge product can be hosted in the cathode. Due to the insulating nature of Li_2O_2 and the non-aqueous electrolyte we employed in our system, Li_2O_2 was mainly formed through the surface pathway. Thus only micropores and mesopores will contribute to the total capacity. The higher total pore volume (mainly micropores, **Table 2-1**) of the wd-NC results in the higher capacity than wd-C.



Figure 2-8 Voltage profiles of wd-NC and wd-C as cathodes with the same current density of 0.08 mA/cm^2 (4 mA/g). Compared with wd-C, the average roundtrip overpotential of wd-NC decreased from 1.65 V to 0.75 V and the areal capacity increased by 5 times.

The overpotential of wd-NC was also smaller than wd-C. The discharge potential of wd-NC plateaus around 2.7 V while the wd-C plateaus around 2.55 V. This can be understood from two aspects. First, the surface area of wd-NC is much higher than wd-C, which enables higher exchange current. Second, the N atoms doped in wd-NC effective promoted the conductivity and the ORR activity. The average recharge overpotential was also decreased significantly for the wd-NC compared with wd-C. This was understood by the morphological and compositional change of discharge product. A more intimated contact with less Li₂CO₃ passivation layer between Li₂O₂ and the cathode was expected to be formed during the discharge process as a result of the improved ORR activity. This intimate contact in turn reduces the charge transfer resistance in the recharge process. Also, there might be more superoxide components in the discharge product formed in the discharge process on wd-NC. This enrichment could be a result of stabilization effect brought by the N atoms.



Figure 2-9 Rate capability and cycling performance of wd-NC. (a) With the current density increased from 0.04 mA/cm^2 to 0.20 mA/cm^2 , the discharge voltage plateau decreased from 2.75 V to 2.40 V, and the charge voltage plateau increased from 3.3 V to 4.4 V, indicating N doping facilitates the ORR kinetics more effectively than it does the OER. (b) Galvanostatic cycling tests under a constant current density of 0.08 mA/cm^2 and 70% depth of full discharge (Absolute capcity each cycle: 1.5 mAh). The average voltages and energy efficiency for each cycle was

plotted against the cycle number. The energy efficiency decreased from 70% to 60% after 5 cycles and remained stable onward.

Due to the better normalized capacity and kinetics, the following studies will be only focused on wd-NC samples. The overpotentials at different current densities were further explored for the evaluation of rate performance. With the current ramping from 0.04 mA/cm^2 to 0.2 mA/cm^2 , the average overpotential only increased from 200 mV to 560 mV for the discharge process. For the average recharge overpotential, the change is more significant with more than 1 V of increase. This further highlights the intrinsic difficulty of the OER process in Li-O₂ batteries compared with the ORR process.



Figure 2-10 The structure of wd-NC after long cycles till cell failure. The porous structure of the wood-derived carbon cathode was clogged by the accumulation of by-products and undecomposed products, which ultimately led to the battery's failure.

With the capacity limited to 70 % depth of discharge, we cycled the battery with wd-NC cathode to evaluate the long term stability. While the voltage profile for discharge is relatively stable across the first 20 cycles, a sharp increase of average recharge overpotential was evident. This is again related with the intrinsic instability of

carbon material in the Li-O₂ battery operation conditions. Upon repeated cycles, the accumulation of Li_2CO_3 by-product and undecomposed Li_2O_2 will lead to the final failure of the battery. This can be reflected by the SEM image taken after the prolonged cycling, in which significant amount of byproduct was found to clog the majority of the channels (**Figure 2-10**).

2.2.5 Product confirmation

Microscopic evidence was first provided by SEM. The surface of pristine wd-NC was smooth and clean as show in **Figure 2-11a**. After discharge, Li₂O₂ particles were observed to accumulate both inside the pores and on the surface of the carbon walls (**Figure 2-11b**). After full recharge, those particles were removed to reveal the original clean surfaces (**Figure 2-11c**).



Figure 2-11 SEM image confirming the formation and decomposition of Li₂O₂.

To confirm the electrochemical behavior and the morphological change we observed above indeed represent to the formation and decomposition of Li_2O_2 , spectroscopic measurement was performed to identify the discharge product. XRD was first utilized for its unambiguousness. Three stages of wd-NC cathode were examined by

X-ray diffractometer with Cu-K α radiation. The bare wd-NC carbon was featureless in the scanned region between 30 ° and 44 ° except for the declining slope on the low angle resulted by the carbon substrate. The discharge sample clearly exhibited the diffraction peak of Li₂O₂ at 34.8 ° (2 0 1) and 22.8 ° (2 0 0) respectively (JCPDS 74-0115). There is a separate peak at 31.5 ° which is close but not identical to the peak at 31.8 ° (0 0 2) of Li₂CO₃. It was hypothesized to be to the superoxide component that contributes to the favored recharge behavior on wd-NC.^[15-16] Another possibility was the solvation effect of electrochemical grown Li₂CO₃.^[17] After recharging, all prominent peaks were removed leaving only the sloping from carbon on the data. This removal of discharge product was further confirmed by XPS. Both the Li 1s and O 1s signal convey the same message that Li and O containing compounds were formed on the discharged sample and removed after recharge. The high sensitivity of XPS can still pick certain amount of Li and O residue, which can be ascribed to the inevitable accumulation byproducts. These byproducts are low in quantity and poor in crystallinity thus undetectable in the XRD.



Figure 2-12 Spectroscopic detection of Li_2O_2 . (a) X-ray diffraction patterns, (b) XPS spectra of Li 1s signals and (c) XPS spectra of O 1s signals of wd-NC before discharge (bare), after the 1st cycle discharge (discharged) and the 1st cycle recharge (recharged).

2.3 Conclusions

In summary, we have investigated a new nitrogen-doped free-standing porous carbon material as a promising cathode material for Li-O₂ battery. This material takes advantage of the spontaneously formed hierarchical porous structure derived from wood. The structure is expected to facilitate both mass transport and discharge product storage. Moreover, we introduced heteroatom (N) doping to further improve the catalytic activity of the carbon cathode for lower overpotential and higher capacity. We have unambiguously confirmed the initial electrochemical process to be the desired reactions

of Li_2O_2 formation and decomposition. The free standing nature and mechanical strength of wood derived carbon makes it possible to eliminate the need for additional current collector and binders, improving the overall energy density and reducing possible parasitic chemical reactions. Also, the renewability of wood with this unique structure could potentially provide a cost-effective route as porous electrode for large-scale mass production.

Further efforts to improve the cell performance can be anticipated by protecting the carbon and increase the pore volume at the micropore and mesopore scale. This approach will be demonstrated in the next chapter.

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Chapter 3. The protection of carbon cathode

Carbon is not stable in the operation condition of Li-O₂ batteries.^[1-2] As observed in the previous chapter, although the carbon cathode can indeed enable right cathode reactions during the initial cycles of Li-O₂ batteries, the corrosion of carbon inevitably results in the accumulation of Li_2CO_3 .^[3-4] This limits the life time of carbon based Li-O₂ batteries.^[5] The instability of carbon originates from the attack by reactive oxygen species and the high applied potential during the recharge.^[6] In this chapter, we tend to address the stability of carbon from these two aspects.

For the corrosion of carbon by reactive oxygen species including superoxides, peroxides or singlet oxygens, the direct contact between carbon and these species are necessary.^[1,7] If physical isolation can be achieved between these reactants, the reaction is expected to be minimized.^[8] Based on this understanding, we proposed to a thin layer of coating to conceal the carbon. This coating should be conductive and thin to minimize extra resistant and weight. Catalysts that can promote the ORR should be further incorporated to compensate the loss of catalytic activity from carbon.

To minimize the electrochemical oxidation of carbon at high potential, lower recharge overpotential is desired.^[2] To achieve this goal, promoter for Li_2O_2 decomposition should be incorporated.^[9-10] As to the way of introducing this promoter, the thin film coating serves this purpose best. The promoters are usually metal or metal

oxides which can be easily fabricated into the thin film form.^[11] Moreover, the conformal coating on the cathode surface can ensure the continuous contact between Li_2O_2 with the cathode, maximizing the promotion effect. These thoughts can be reflected in the following illustration (**Figure 3-1**).



Figure 3-1 Rational design of protected carbon cathodes by a conformal thin film coating of OER catalysts.

Experimentally, we employed the atomic layered deposition (ALD) to achieve this conformal thin coating. The unique layer-by-layer growth mechanism of ALD provides an ideal approach toward the tuning of the thickness, coverage and composition of the coating. For the material choices, iron oxide was selected as the thin film for its good film quality and catalytic activity; Palladium was selected as the ORR catalyst for its highest activity; Three-dimensionally ordered mesoporous (3DOm) carbon was chosen as the substrate for its functionalized surface and enlarged mesopore volume. Overall, this approach was demonstrated to significantly reduce the corrosion of carbon and improve the lifetime of the carbon cathode by 4 times, which will be detailed in this chapter.

3.1 Methods

3.1.1 Material synthesis

The 3DOm carbon was prepared and provided by our collaborator Prof. Wei Fan from University of Massachusetts, Amherst. ^[12-13] A precursor solution made of furfuryl alcohol and oxalic acid with a weight ratio of 200:1 was impregnated within silica colloidal crystal templates composed of highly monodisperse 12 or 35 nm silica nanoparticles (SNPs). The resulting samples were heated to 70 °C for 2 days to polymerize furfuryl alcohol, followed by heating at 200 °C in flowing N₂ for 3 h to cure the polymer, and then heated at 900 °C for an additional 2 h to carbonize the samples. The SNPs were dissolved in 6 M KOH solution at 150 °C for 2 days to yield 3DOm carbon replica. The resulting carbon material was then thoroughly washed with 70 °C deionized water until the resulting solution was near neutral. Finally, the 3DOm carbon was dried at 70 °C for 24 h.

Carbon and polytetrafluoroethylene (PTFE) were mixed in isopropyl alcohol (IPA) with a mass ratio of 8:2. The mixture was dispersed by sonication and coated on the Ni. The electrode was further dried in vacuum oven overnight to remove the residual solvent.

The growth of FeO_x has been reported by us previously.^[14-16] The as-prepared carbon electrode was placed in the ALD (Savannah 100, Cambridge Nanotech) chamber and heated to 180 °C. Iron *tert*-butoxide (Fe₂(^tBuO)₆) and water were employed as precursors at 120 °C and 25 \mathbb{C} , respectively. Each cycle of the growth followed the repeated sequence of 3 s Fe precursor pulse, 60 s adsorption, 90 s purging by N₂; 0.05 s pulse of water, 60 s reaction, and another 90s for purging by N₂. A typical growth lasts 50 cycles to yield desired coating of FeO_x of ca. 2.5 nm in thickness.

Pd nanoparticles were deposited in a Savannah S100 ALD system (Ultratech). The growth temperature was 250 °C, with $Pd(hfac)_2$ (Palladium(II) hexafluoroacetylacetonate, 60 °C) and formalin (37 wt% in H₂O, 25 °C) as precursors. Each cycle consisted of 5 repeated pulse/purge sub-cycles of $Pd(hfac)_2$ and formalin for sufficient surface adsorption in the high aspect ratio 3DOm carbon.



Figure 3-2. Three stages of material synthesis: a) SEM image of closed packed silica as the templates. Reproduced with permission from Ref ^[13]. Copyright 2008 NPG. b) Scheme of 3DOm carbon after the removal of silica bead templates. C) Scheme of 3DOm carbon coated by FeO_x and decorated by Pd via ALD.

3.1.2 Electrochemical characterization

LiClO₄ in dimethoxyethane (0.1 M) was used as purchased from Novolyte (BASF) with water level <10 ppm. Tetraethylene glycol dimethyl ether (TEGDME, \geq 99%, Sigma-Aldrich) was first stored over freshly activated 4 Å molecular sieves and then distilled. The distilled TEGDME was stored over molecular sieves before usage. LiClO₄ (99.99%, Battery grade, Sigma-Aldrich) was further baked at 130 °C in a vacuum oven within the glove box and mixed with TEGDME to generate the 1 M solution. Customized Swagelok type cells were assembled in the glove box (H₂O and O₂ levels < 0.1 ppm, MBraun) with Li metal as the anode, Celgard 2400 films as the separator, 0.1 M LiClO₄ in DME or 1.0 M LiClO₄ in TEGDME as the electrolyte. Batteries were studied using potentiostats (VMP3, Bio-Logic).

For DEMS characterization, the cell was first discharged in TEGDME under pure O_2 to a given capacity. Due to the high vapor pressure of DME, TEGDME was utilized here as the electrolytes to enable the on-line detection at nearly vacuum. TEGDME is less stable as DME thus the overall measured degree of decomposition is expected to represent the upper limit of what can be achieved in the DME cell. The discharged cell was then evacuated for 5 h to remove O_2 . For *in situ* analysis, the cell was connected to the mass spectrometer under vacuum with a dry rotary pump (nXDS 10i, Edwards) as the differential pump. The cell was wired to a potentiostat (609D, CH Instruments) for galvanostatic recharging, while gas content was analyzed using a customized mass spectrometer with quadrupole mass analyzer (Microvision 2, MKS). Every MS scan was

collected from 28 to 44 amu within 3 s to give both the desired time resolution and accuracy.

3.1.3 Material characterization

SEM images were taken on a JEOL 6340F microscope and TEM were performed on a JEOL 2010F microscope operated at 200 kV. X-ray diffraction measurements were performed on PANalytical X'Pert Pro diffractometer with Cu Kα radiation. The cell was first transferred to an O₂-toleranted Ar-filled glove box and disassembled inside to extract the cathode, which was rinsed with pure anhydrous DME (Sigma-Aldrich) for 3 times to remove remaining salts. An airtight sample holder with an X-ray transparent Kapton film window was used to transfer the sample and carry out XRD characterizations without exposing the sample to the ambient air. Surface analysis was carried out using a K-Alpha XPS (Thermo Scientific). The sample was also washed by DME with the same procedure as described above and mounted on the sample stage with a short exposure to the ambient air (typically <5 min) before entering the load lock. Raman spectra and mapping were acquired using a micro-Raman system (XploRA, Horiba) with a 532nm laser excitation. The N₂ adsorption/desorption experiments were carried out on an automatic gas sorption analyzer (Autosorb iQ, Quantachrome) at 77 K. The pore size distribution and cumulative pore volume were obtained by applying a built-in quenched state density functional theory (QSDFT) adsorption model with cylindrical/spherical configuration for carbon (ASiQwin v3.0, Quantachrome).

3.2 Results and discussion

3.2.1 Mesopores in 3DOm carbon and its influence on battery

performance

Choosing 3DOm carbon as the substrate mainly bases on two considerations. First, the surface of 3DOm carbon contains rich functional groups. This functionalized surface enables further functionalization of the surface by providing the anchoring groups. Second, the pore diameter of the 3DOm carbon is well-defined and controlled by the diameter of silica bead templates. Mesopores were considered as the most useful pores in terms of the capacity.^[17] In this chapter, 3DOm carbon with 35 nm pore diameter was mainly studied. The pore diameter was confirmed by the N₂ adsorption and desorption measurement. As shown in **Figure 3-3b** the pore size distribution proved that the majority of the pore volume was contributed by the mesopore region and the pore are narrowly distributed between 30-35 nm. This narrow distribution simplifies the further study of the surface coating thickness and the discharge product distribution. Thus 3DOm carbon is considered as a great platform to study the protection of carbon.



Figure 3-3 N₂ adsorption and desorption measurements and pore size analysis. a) Isotherm curve b) Pore size distribution c) cumulative pore volume



Figure 3-4 Discharge and recharge curve for super P carbon Vulcan XC 72 and 35nm 3DOm carbon

Galvanostatic discharge and recharge was performed to evaluate the cathode performance (**Figure 3-4**). The total capacity and overpotential performance of 35 nm 3DOm carbon was first measured and compared with other commercially available carbon including Super P and Vulcan XC72. At the same current density (200 mA/g), 3DOm carbon exhibits lower overpotential and higher capacity. The low overpotential for discharge can be explained by the higher normalized surface area, which increases the active sites and reduces the local current density.^[18] In addition, the low recharge overpotential can be explained by the confinement effect of Li₂O₂ achieved by the rigid pore with diameter of 35 nm. The pore size of the carbon limits the particle size of Li₂O₂.



Figure 3-5 Scanning electron micrographs of 3DOm carbon surfaces at different stage of discharge and recharge.

This was further evidenced by the distribution of discharge product with the depth of discharge. At the initial stage of discharge (0-4000 mAh/g), the porous structure of 3DOm carbon on the surface can be clearly observed (**Figure 3-5**). This indicates that the growth of Li_2O_2 was mainly inside the pores. Only toward the end of discharge (>5000 mAh/g), Li_2O_2 began to cover the surface with small grains. At the end of discharge, relatively dense film was formed on the surface of carbon chunk. It can be imagined that carbon is acting as a porous core while Li_2O_2 grows as a shell that is rooted inside the pores. Compared with a large free standing Li_2O_2 toroid, the 35 nm pores of 3DOm carbon compartmentalize Li_2O_2 into numerous small particles and provide a facile charge transport pathway on the carbon walls.



Figure 3-6 TEM characterizations of (a) pristine Pd/FeO_x modified 35 nm 3DOm carbon and (b) fully discharged Pd/FeO_x modified 35 nm 3DOm carbon samples.

TEM images help to further illustrate this perception. The pristine carbon before discharge is featured by micron-sized hollow particles with ordered pore structure (**Figure 3-6a**). After the discharge operation, the pores of carbon were filled by Li_2O_2 which homogenized the contrast of TEM images (**Figure 3-6b**). Upon irradiation by the electron beam, Li_2O_2 will be burned off, revealing the ordered carbon core. (Inset of **Figure 3-6b**)



Figure 3-7 Pore size distribution of fresh and discharged 35 nm 3DOm carbon electrode.

Even stronger evidence was provided by the pore size analysis of the carbon cathode before and after the discharge. As shown in **Figure 3-7b**, the volume of the pore with diameter around 30 nm significantly decreased. This is direct evidence that the formed Li_2O_2 is occupying the mesopores.^[17] The integration of the pore volume

indicates that 50 % of the total pores are utilized to store Li_2O_2 (Figure 3-7c). This is explained by the bottle neck effect that the clogging of small pore opening will lead to the incomplete usage of inner pore volumes.^[19]

3.2.2 The coating of FeO_x and Pd on 3DOm carbon

Atomic layered deposition was employed to deposit FeO_x as the catalytic active protection layer. The deposition result can be visualized by TEM images. As shown in **Figure 3-8**, before the deposition, carbon walls with low contrast can be identified by their circular shape and well-defined diameter. After the deposition of 50 cycles of FeO_x , a relatively dense film composed by the granular particles with high contrast can be observed. Further deposition of Pd (also by ALD) introduces small particles that were decorated on the FeO_x surfaces. The elemental confirmation of FeO_x and Pd was provided by XPS which will be shown later in this chapter.



Figure 3-8 TEM images of a) pristine carbon, b) after ALD of FeOx and c) after the ALD of both FeOx and Pd

The uniform deposition of FeOx within the pores of 3DOm carbon was further confirmed by the pore size analysis. As illustrated in **Figure 3-9a**, the coating of FeO_x

with thickness *r* should uniformly shrink the pore diameter of the 3DOm carbon by 2*r*. This was indeed observed in the pore size distribution data in **Figure 3-9b**. The growth rate of FeO_x by ALD was typically 0.5~0.6 Å/cycle. 50 cycles' growth of FeO_x in ALD results in about 2.5 nm film deposition, which leads to the pore diameter of the 3DOm to uniformly shrink by 5 nm. This indicates the conformal deposition of FeO_x on the carbon, which is critically to isolate the electrolyte from the carbon surfaces.



Figure 3-9 A) Illustration of the deposition of FeO_x and Pd on 3DOm carbon b) The pore size distribution before and after the deposition of FeO_x on 3DOm carbon

Electrochemical data was provided to evaluate the effects of the coating toward the overpotential and lifetime. To eliminate the difference in total capacity, all the comparison was made by discharging the cathodes to the same depth of discharge at the same current density (200 mA/g, normalized to the total mass of active materials). The overpotential for discharge can be ranked with the following order: FeO_x/C > Pd/FeO_x/C > C > Pd/C. This is consistent with the fact that FeO_x is not a good ORR catalyst while Pd is one of the best ORR catalysts. The loading of Pd on FeOx can help to correct the ORR activity loss to some degree. The overpotential for recharge also matches the prediction well with the order of: C > Pd/C > FeO_x/C \approx Pd/FeO_x/C. The promotion effect of FeO_x toward Li₂O₂ decomposition is evident and will not be compromised after the addition of Pd nanoparticles. Further, the cycling performance was also investigated with the capacity limitation of 500 mAh/g at the current density of 200 mA/g. The addition of FeO_x significantly improved the lifetime by 4 folds, leading to 68 cycles' operation over 650 h.



Figure 3-10 a) The comparison of overpotential between different cathodes at the same current density (200 mA/g_{total}). b) The comparison of cycling lifetime with the same current density (200 mA/g_{total}) and discharge capacity (200 mAh/g_{total}).

To prove that the electrochemical profile correlates to the desired cathode reaction of Li_2O_2 formation and decomposition, product detection was performed by XRD and XPS. Similar with the wd-NC, the discharged carbon cathode exhibits distinct diffraction pattern of Li_2O_2 (**Figure 3-11a**). The peaks are relatively broad indicating the small domain size that is confined by the pore size of 3DOm carbon. Upon recharge, no peak for Li_2O_2 or Li_2CO_3 was observed, indicating the removal of all crystalline products. Worth noting, after 60 cycles of repeated discharge and recharge, the cathode can still give distinct diffraction pattern for the Li_2O_2 after discharge with no observable Li_2CO_3 peaks. This helps to highlight the stability improvement of the cathode. O 1s peaks of the XPS data also provide similar conclusions (**Figure 3-11b**). The discharged cathode shows significantly increased oxygen contents on the surface that can be ascribed as Li_2O_2 based on the chemical shift (light blue colored peak, ~ 532 eV). This content can be fully removed to resume the original feature of O 1s spectrum that is generated by the FeO_x coating.



Figure 3-11 Product detection of cathode reactions. a) X-ray diffraction patterns of pristine, fully discharged, and fully charged Pd/FeO_x/3DOm carbon cathode. The cathode after 60 cycles was also fully discharged and examined with the confirmation of Li_2O_2 formation. b) XPS spectra of O 1s signal confirms the chemical composition of discharge product on the Pd/FeO_x/3DOm
carbon cathode. C) The DEMS detection of gaseous recharge product confirmed the reversible generation of O_2 with minimum CO_2 on the Pd/FeO_x/3DOm carbon cathode.

To prove that the FeO_x coating indeed improves the stability of carbon, the gaseous recharge product was examined (Figure 3-11c). Differential electrochemical mass spectroscopy was employed here to detected the evolved O_2 (mass 32) and CO_2 (mass 44). N₂ (mass 28) was used as a reference to show that all the gaseous species measured was a result of the electrochemical process rather than the cell leakage. Immediately after the recharge process started, the oxygen signal began to increase and gradually leveled off. With the termination of recharge, the oxygen signal decreased gradually to base line. This evidence strongly supports that our electrochemical process represents the decomposition of Li₂O₂ and the formation of O₂. In comparison, the signal of CO₂ remains low until the very end of recharging process where the voltage is above 4 V. The CO₂ signal could come from two sources, the carbon corrosion and electrolyte decomposition. In the current experimental setting, these two sources can't be distinguished. But the signal of CO_2 is considerably higher in the case where no FeO_x coating was applied, indicating the overall protection effect introduced by the protective coating (Figure 3-12).



Figure 3-12 DEMS result of 1st charge of bare 35nm 3DOm carbon electrode

3.3 Conclusions

The unique pore structure and functionalized surface of 3DOm carbon offer a good platform to demonstrate our approach to protect the carbon materials. The well-defined pores around 35 nm provide ample space for the growth of Li_2O_2 while physically limiting the particles size to minimize the polarization during recharge. The hydrophilic surface enables the conformal deposition of FeO_x by ALD that physically isolates carbon with the reactive oxygen species and electrolytes. Together with the catalytic activity of FeO_x in terms of Li_2O_2 decomposition, FeO_x/C can completely remove Li_2O_2 at reduced potential. When further compensating the lost ORR activity by introducing Pd catalysts, the carbon cathode lifetime can be improved to 4 times than before.

Overall, in this chapter we demonstrated a ration strategy to enhance the stability of carbon cathode that can potentially be universal. However, stability issue associated with the electrolyte itself can't be resolved. Indeed, because the decomposition of both carbon and electrolyte can give rise to the CO_2 signals, it is hard to distinguish the two. Moreover, the coverage of metal oxide coating on carbon can't be 100 % complete. These factors leave potential pathways for the corrosion and limit the long term stability of the carbon cathode. A truly carbon-free cathode is desired to offer better long term stability and provide a cleaner platform to study the intrinsic activity of the catalyst and electrolyte.

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Chapter 4. Carbon-free cathodes for Li-O₂ batteries

A stable cathode is critical to understand the true performance of Li-O₂ batteries.^[1-2] Carbon-free cathodes provide such an opportunity to study the catalysts and electrolytes without the confounding factor of carbon induced parasitic reactions.^[3-5] Titanium disilicide (TiSi₂) nanonets provide a suitable platform for this purpose.^[6] TiSi₂ has been discovered to be conductive and have high aspect ratio, which are desired as the cathode.^[7] However, TiSi₂ exhibits poor catalytic activity toward both ORR and OER. Proper catalysts have to be incorporated to enable the oxygen cathode.^[8] Noble metal catalysts are of interest for their good catalytic activity.^[9] Pd was calculated and proven as one of the best ORR catalysts,^[10] but its OER activity was not unambiguously demonstrated before.^[11] In this chapter, we will utilize none-carbon TiSi₂ nanonets as the platform to investigate the true activity of the Pd catalyst and its associated issues. We find that Pd indeed can promote both the formation and decomposition of Li₂O₂ on TiSi₂ but suffer from the issue of detachment from the substrate. A further coating of Co₃O₄ was introduced to enhance the loading of Pd on the substrate. Together, a stable cathode was constructed with much improved cycle life. This strategy has been illustrated in Figure 4-1.



Figure 4-1 Schematic design of the desired cathode. The substrate support is $TiSi_2$ nanonets. The functional layer is Co_3O_4 . The catalyst is Pd, which promotes both ORR and OER.

4.1 Methods

4.1.1 Material synthesis

TiSi₂ nanonets were grown by chemical vapor deposition (CVD). Ti meshes (Cleveland Wire Cloth) were cleaned and used as the substrate. SiH₄ (10% in He, Voltaix), TiCl₄ (98%, Sigma-Aldrich), and H₂ (industrial grade, Airgas) were introduced to the tube furnace at 675 °C. The growth lasted typically 30 to 40 min with the pressure maintained at 5 torr for desired loading. Pd and Co₃O₄ were deposited in a Savannah S100 (Ultratech) ALD system. For Pd nanoparticles the growth temperature was 200 °C, with Pd(hfac)₂ (Palladium(II) hexafluoroacetylacetonate, heated to 60 °C) and formalin (37 wt% in H₂O, contains 10-15% methanol as stabilizer to prevent polymerization, room temperature) as reaction precursors. The purge gas was N₂ with 20 sccm (standard cubic centimeter per minute) flow rate. A typical growth sequence was Pd-adsorption-purge-

formalin-adsorption-purge, and the durations were 1 s - 15 s - 20 s - 1 s - 15 s - 20 s with the stop valve mode turned on. For Co₃O₄ growth, the two precursors were Cobaltocene (98%, Strem, 85 °C) and ozone (~120 mg/L, Savannah ozone generator, with 5 psi pressure and 0.2 liter per minute flow rate). A typical growth sequence were Coadsorption-purge-ozone-reaction-purge, and the durations were 0.5 s - 15 s - 30 s - 0.15 s - 15 s - 30 s, also with the stop valve mode turned on. For the composite structure, cobalt oxide layer was grown on TiSi₂ before the Pd deposition to serve as the functional interfacial layer. The mass loading of Co₃O₄ and Pd loading were 0.05~0.1mg/cm² respectively. The loading quantity of each individual sample was measured by the mass gain after ALD growth using a microbalance (Sartorius, CPA2P, ±1µg) and also confirmed by the inductively coupled plasma optical emission spectrometry (ICP-OES) using an Agilent 5100 ICP-OES Spectrometer.

4.1.2 Material Characterization

Samples were imaged using a transmission electron microscope (TEM, JEOL 2010F) operating at an acceleration voltage of 200 kV and a field emission scanning electron microscope (FE-SEM, JEOL 6340F) operating at 10 kV. Raman spectra were obtained in a customized air-tight sample holder using Horiba XploRA micro Raman system with excitation laser of 532 nm. The surface species and oxidation states were characterized by an X-ray photoelectron spectrometer (K-alpha XPS, Thermo Scientific, Al K α =1486.7eV). X-ray diffraction was performed on PANalytical X'Pert with Cu K α radiation. UV-Vis spectra were obtained by USB4000 spectrometer from Ocean Optics.

4.1.3 Cell Assembly and Electrochemical Characterization

0.1M LiClO₄ in dimethoxyethane (DME) with water level lower than 10 ppm was used as purchased from Novolyte (BASF). LiClO₄ (99.99%, Battery grade, Sigma-Aldrich) was further baked at 130 °C under vacuum and then dissolved into ionic liquid (PYR₁₄TFSI, Solvionic) to give a 1 M solution. Customized Swagelok type cells were used as the electrochemistry study platform. Cells were assembled in the glove box (O₂ and H₂O levels < 0.1 ppm) with Li foil as the anode, 2 Celgard 2500 film sheets as the separator, 0.1 M LiClO₄ in DME as the electrolyte. After cell assembly, O₂ (Ultrahigh purity, Airgas) was purged into the cell to replace Argon, and the cell was isolated from the gas line after reaching 780 torr. Electrochemical characterizations were carried out on an electrochemical station (Biologic, VMP3).

For commercial Li_2O_2 oxidation test, Li_2O_2 (90%, Sigma-Aldrich) was dispersed in DME by ultrasonication while sealed under Argon. The slurry was drop-coated on the TiSi₂ cathode with or without Pd loading to achieve the pre-loaded cathode.

For the cycling test, $Pd/Co_3O_4/TiSi_2$ nanonets cathodes were first assembled in the cell and cycled in oxygen to remove potential ligand remains on the surface of electrode. The treated cathode was washed and transferred to a new cell for the cycling test.

For comparison in quantification of discharge product, carbon black cathode was prepared by dispersing carbon black (Vulcan XC72) and polytetrafluoroethylene (PTFE, 60wt% dispersion, Sigma-Aldrich) with weight ratio of 95:5 in isopropanol (10mg carbon/mL) then drop coated on Ti mesh with the loading density of 0.2 mg/cm². The cathode was further dried in the vacuum oven at 100°C overnight.

4.1.4 Quantification of Discharge and Recharge Products

Ferrocenium hexafluorophosphate (97%, Sigma-Aldrich) was dissolved in the DME and filtered to give 3 mM solution. Calibration curves were generated by quantitatively diluting the original solution with pure DME, and a linear relationship between absorption and molar concentration was obtained. For GC-MS tests, the cathode was first discharged in the DME based electrolyte under pure O_2 to produce Li_2O_2 -loaded electrode and transferred to an ionic liquid based cell for test. UHP grade Helium was used to purge the cell for 60 min to remove residual gases, and the helium flow rate was then fixed at 10 sccm controlled by a mass flow controller as the carrier gas. The content of the gas was sampled with a 0.500 mL gas sampling loop every 5 min automatically for GC-MS analysis (Shimadzu QP2010 Ultra, with Carboxen 1010 PLOT column at 50°C).

4.2 **Results and discussions**

4.2.1 Pd as bifunctional catalyst on TiSi₂

Pd was known as a good ORR catalyst in both aqueous and non-aqueous solutions,^[12-13] but its activity toward OER has not been conclusively studied on non-carbon substrate.^[11] While some reports showed that the addition of Pd to carbon (or non-carbon) cathode reduced the recharge overpotentials,^[14-15] the product of Li₂O₂ was found to assume distinct morphologies and crystallinity, upon which the recharge behaviors depend to a great extent.^[11,16-17] This inconsistancy of the starting material makes it difficult to

conclude the acitivity of Pd. So, commercial Li_2O_2 was employed as a standard to evaluate whether Pd can promote the decomposition of Li₂O₂. This can eliminate the variables induced in the discharge process.^[18] For this purpose, we mixed commerically obtained Li₂O₂ (c-Li₂O₂) with Pd-decorated TiSi₂ nanonets (Pd/TiSi₂) and assembled in to electrochemical cells. The voltage profile of the electrode at a constant current of 100 mA/g_{Pd} was recorded and compared. It is seen in Figure 4-2a that the voltage quickly rised from 2.8 V to 3.8 V, a process corresponding to the initial polarization of the electrode for Li₂O₂ decomposition. The rate at which the voltage increases slowed afterward, indicative of steady deomposition of Li₂O₂ above 3.8 V. By contrast, the voltage of the electrode without Pd nanoparticles quickly rised beyond 4.2 V without meaningful Li₂O₂ decomposition capacities. A third set of data presented in Figure 4-2a are from the control sample where Pd/TiSi₂ was used but without commerical Li₂O₂, and the purpose was to confirm that Pd as a catalyst does not decompose the electrolyte. The results as shown in **Figure 4-2a** verify this premise. Taken as a whole, we conclude that Pd nanoparticles grown on TiSi₂ nanonets indeed can catalyze Li₂O₂ decomposition. Given that the ORR activities of Pd nanoparticles in non-aqueous solutions have been previously demonstrated,^[10,15,19] Pd/TiSi₂ nanonets should serve as a reasonable cathode electrode to support both Li₂O₂ formation and decomposition.



Figure 4-2 Activities of Pd-decorated TiSi₂ nanonets. a) Direct recharge curves of $c-Li_2O_2$ mixed TiSi₂ nanonets with (black trace) and without (green) Pd nanoparticles. The data from the control sample without $c-Li_2O_2$ are shown in orange. Current density: 100 mAh/g_{Pd}. b) Cycling performance of Pd/TiSi₂ nanonets. The capacity was limited to 500 mAh/g_{Pd}. Current density: 200 mA/g_{Pd}.

Next, we examined the cycling performance of the electrode in a Swagelok cell with Li foil as the anode and 0.1 M LiClO₄ dissolved in dimethoxyethane (DME) as the electrolyte. In accordance to the practice commonly adapted in the literature, the cell capacity was limited to 500 mAh/g_{Pd}. It is seen in **Figure 4-2b** that the terminal overpotentials for both discharge and recharge, as measured by the difference between the terminal voltages and the thermodynamic equilibrium voltage of $Li_2O_2 \leftrightarrow Li + O_2$ (2.96 V), gradually increased for the first 40 cycles. Afterward, the increase became more rapid for the discharge overpotentials, and the discharge terminal voltage reached 2.0 V at the 63rd cycle, at what point we stopped the experiment. This trend can be seen more clearly in **Figure 4-3**, where the full details of voltage profile was displayed.



Figure 4-3 Voltage-capacity profile of Pd/TiSi₂, with 200 mA/g_{Pd} current density for 63 cycles

4.2.2 The instability of Pd on TiSi₂ and the improvement

The elimination of carbon was supposed to reduce the Li₂CO₃ formation and result in a much more stable cathode. But the gradual degradation of the Pd/TiSi₂ cathode indicates there certain degradation mechanism is still jeopardizing the cathode.

To understand the degradation mechanism, we examined the Pd/TiSi₂ nanonets using transmission electron microscope (TEM). While the distribution of Pd nanoparticles on TiSi₂ nanonets right after growth was uniform (**Figure 4-4a**), significant detachment and aggregation was observed after repeated discharge and recharge (**Figure 4-4b**). The detachment of catalyst particles from their support during electrochemical processes is common.^[20-21] For instance, similar phenomenon has been widely reported for commercial Pt/C catalyst for proton exchange membrane fuel cells.^[22-23] It is nevertheless

noted that Pt nanoparticles grown on TiO₂ coated TiSi₂ nanonets by ALD were found to be stable upon electrochemical cycling in aqueous electrolytes.^[8]



Figure 4-4 Transmission electron micrographs of Pd/TiSi₂ nanonets. (a) as-grown; (b) after 63 cycles of discharge/recharge.

We collaborated with Prof. De-en Jiang to understand this phenomenon from computational perspective. The difference of the stabilities can be explained by the difference in the interface energies between TiSi₂ and metal nanoparticles.^[24] Pt, Pd and Ru nanoparticles was modeled on the b plane (top and bottom surfaces of the nets) and c plane (sides of the nets) of TiSi₂ (**Figure 4-5**). The adsorption energy is defined as $E_{ad} =$ $E_{NP/TiSi2} - E_{NP} - E_{TiSi2}$, where $E_{NP/TiSi2}$, E_{NP} , and E_{TiSi2} are the energies of the adsorbed system, the isolated nanoparticle, and the clean TiSi₂ surface, respectively. A negative E_{ad} indicates a favorable interaction. The result has been summarized in **Table 4-1**. A clear trend can be observed that the b planes have higher affinity toward the nanoparticles. This affinity decrease in the order of Ru > Pt > Pd. This idicates that Pd with the lowest interface energy is most prone to detach. Since b planes are the most exposed planes of the 2D nanonets, this simulation result correlates well with the experimental observation.



Figure 4-5 : Illustration for DFT calculation of adsorption energy. Initial (a) and final (b) states of the Pt38 nanoparticle on the b-plane of the TiSi₂ C49 structure; initial (c) and final (d) states of the Pt38 nanoparticle on the c-plane of the TiSi₂ C49 structure.

Table 4-1	Summary of ada	orption energy of	different nano	particles onTiSi2
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Nanoparticles (38 atoms)	Adsorption Energy on b plane	Adsorption Energy on c plane			
	(010) of C49 TiSi ₂ (eV)	(001) of C49 $TiSi_2$ (eV)			
Pd	-48.0	-44.3			
Pt	-49.0	-40.0			
Ru	-54.0	-38.0			

Based on the adsorption energy, Pt is should possess similar property with Pd. Indeed, it has been previous observed that the deposition of Pt on $TiSi_2$ already requires a pre-deposition of TiO_2 to achieve the stable loading. The instability of Pd on $TiSi_2$ is reasonable. Another interesting comparison is the difference of adsoption energy between b plane and c plane. The large difference in the case of Pt and Ru both results in the selective deposition, which is reported in our previous work.^[8,24] The minimized difference for Pd to growth on b plane and c plane may further increase the mobility of Pd nanoparticles during the repeated battery operation.



Figure 4-6 Transmission electron micrographs of functionalized $TiSi_2$ nanonets. a) as-grown Co_3O_4 on $TiSi_2$ nanonets. b) as-grown $Pd/Co_3O_4/TiSi_2$, the dark particles are Pd while light contrasted film is Co_3O_4 .

Inspired by the prevolus work to enhance the surface bonding of Pt on TiSi₂ by TiO₂ coating and others's work to improve the deposition of Pd by Al₂O₃ coating.^[8,25] We introduced catalytic active Co₃O₄ as the interfacial layer to improve the loading of Pd nanoparticles. The deposition of Co₃O₄ on TiSi₂ was achieved by ALD to enable the uniform coverage with controllable thickenss. With the growth rate of 0.5~0.7 Å/cycles, 100 cycles growth will result in 5~7 nm coating of Co₃O₄, which can be visualized as the granular particles composed films on the outer surfaces of nanonets (**Figure 4-6a**).

Further loading of Pd (also by ALD, see methods) results in the decoration of discrete ~ 10 nm Pd nanoparticles on top of Co₃O₄ (**Figure 4-6b**).

Their identification has been obained by XRD (**Figure 4-7**). The XRD pattern confirmed the phase of Co_3O_4 and Pd metal. The relative small loading of material limited the signal of these two materials, only the major peak can be observed at 37 ° and 46 ° respectively. Reference JCPDFS numbers are as follows, Pd: 05-0681; Co_3O_4 : 042-1467; Ti: 05-0682; TiSi₂ C54: 02-1120; TiSi₂ C49: 10-0225. To be noted that the TiSi₂ nanonets have a slight shift comparing with standard C49 phase as indicated previously.^[26] Raman spectroscopy also confirmed the phase of Co_3O_4 after growth, which will be shown later.



Figure 4-7 X-ray diffraction patterns of as-grown Pd/Co₃O₄/TiSi₂ on Ti mesh.

The addition of Co_3O_4 can indeed brought extra catalytic activity, especially on the OER side. But as measured in **Figure 4-8a**, the catalytic activity of Pd is dominating. Co_3O_4 mainly plays a supporting role in facilitating Li₂O₂ decomposition, reducing the recharge overpotential by a marginal 200 mV.^[18,27-28] The real benefit of Co₃O₄ became obvious when the cell was tested for extended period of time, lasting 126 cycles (**Figure 4-8b**), as opposed to 63 cycles without Co_3O_4 . The extraordinary stability of the Pd/Co₃O₄/TiSi₂ combination is understood as the immobilization effect offered by Co_3O_4 , as evidenced by TEM studies on the electrode after 60 cycles of discharge/recharge (**Figure 4-8c**), where no obvious aggregation or morphology changes of Pd nanoparticles can be observed.



Figure 4-8 Effects of Co_3O_4 functional layer. a) Voltage-capacity profiles of $TiSi_2$ (100 mA/g_{TiSi2}), $Co_3O_4/TiSi_2$ (200 mA/g_{Co3O4}), Pd/TiSi_2 (200 mA/g_{Pd}) and Pd/Co₃O₄/TiSi_2 (200 mA/g_{Pd+Co3O4}) cathodes for the first cycle. b) Voltage-time profile of Pd/Co₃O₄/TiSi_2 cathodes for 126 cycles with 500 mAh/ g_{Pd+Co3O4} capacity and 200 mA/ g_{Pd+Co3O4} current density. c) TEM image of Pd/Co₃O₄/TiSi_2 cathode after 60 cycles still exhibited good dispersion of Pd nanoparticles.

The nanostructure of the nanonets is advantageous from the perspective of forming intimate contact between the cathode and product. When carbon is used as cathode, Li_2O_2 usually forms toroid particles sitting on top of the carbon surface. This

physically increases the overpotential to decompose Li_2O_2 . As we observed in the SEM images, nanonets structures or similar nanowire structures enabled the facile electron transport pathway by penetrating into the Li_2O_2 films (or particles) to shorten the average charge transport distance. This is clearly depicted in **Figure 4-9**, in which the morphologies of the nanonets cathode at different stages of the recharge were compared. The fully discharged cathode in **Figure 4-9a** was covered by film like particles with TiSi₂ nanonets penetrating through. With the depth of charge going deeper, the film was gradually removed, regenerating the fresh porous surfaces. The branched morphology of the nets can enlarge the contact area between Li_2O_2 and the cathode, shorting the distance of charge transport. This can also lower the polarization.



Figure 4-9 Morphology evolution of cathode surface at different stage during recharge: a) 0%, b) 50%, c) 90%, d) 100% recharged. All scale bars are 2 μm.

4.2.3 Confirmation of electrochemical reactions by Raman

spectroscopy

After discharge, the test cell was disassembled in an O₂-tolarating Ar glovebox, and the cathode material was washed with anhydrous DME trice to remove remaining LiClO4 salts. The cathode was then sealed in a customized container that features a thin glass window, through which the Raman signals were collected. Because Li₂O₂ will be transformed to LiOH and Li₂CO₃ upon contact with H₂O and CO₂, this procedure ensures that the discharged cathode is not exposed to ambient air. The detected features are plotted in Figure 4-10a, where the peaks at ca. 300 cm⁻¹ are from TiSi₂ (C49 phase), the peaks between 450 to 700 cm⁻¹ correspond to Co_3O_4 , and the peak at ca. 950 cm⁻¹ is from residual LiClO₄. Of them, we emphasize the peak at ca. 810 cm⁻¹, which is close to, but does not overlap exactly with, the Raman shift mesaured on commercial Li₂O₂ (790 cm⁻¹). After considering all possible related product (Figure 4-10b), we concluded that this peak corresponds to Li₂O₂ formed during discharge. Note that direct observations of Li₂O₂ formed during discharge by Raman are not consistent in the literature,^[29-31] and many authors, us included, failed to observe the unequivocal evidence of Li₂O₂.^[32] We and others have suspected that electrochemically formed Li2O2 might differ from commerically obtained crystalline Li₂O₂.^[17,33-36] For instance, here we suggest that the peak shifts (from 790 cm⁻¹ to 810 cm⁻¹) due to its interactions with the Co_3O_4 surfaces,^[27,35] whose Raman shift is also different from that of pristine crystalline Co₃O₄ (Figure 4-10b).



Figure 4-10 Production detection. a) Raman spectra of discharged and recharged cathode made of $Pd/Co_3O_4/TiSi_2$. b) Raman spectra of potential chemical species.

To further support that the peak at 810 cm⁻¹ is indeed from Li₂O₂, we next exposed the sample to ambient air. It is expected that the peak at 810 cm⁻¹ would decrease and finally diminish, and new peaks corresponding to LiOH and Li₂CO₃ would appear. The observed results indeed confirmed the expectation. As shown in **Figure 4-10a**, the peak at 1080 cm⁻¹ corresponds to Li₂CO₃; the peaks of LiOH would be buried under those by TiSi₂ and were not examined here. Furthermore, no peaks indicative of any of the product (Li₂O₂) or by-product (Li₂CO₃) are observed on the fully recharged sample.

4.2.4 A new approach to quantify Li₂O₂ with the presence of catalyst

By now, we have emphasiszed the importance of confirming the discharge and recharge product to be desired in the qualitative fashion. A quantitative evaluation will provide better understanding and more accurate description of the system. So far the quantification of Li_2O_2 was most accurately carried out by iodometric titration introduced by B. D. Mcloskey et al.^[37] However, the conversion from Li_2O_2 to H_2O_2 in the process limits the application in the catalyst free systems. This is because H_2O_2 will be promoted to disproportionate by a wide variety of metal or metal oxide catalysts.

Here we proposed and developed a back-tritration method that can directly measure the quantity of Li₂O₂ formed on the cathode regardless of exsistance of catalyst. As a popularly studied redox pair in a wide range of electrochemical systems,^[38-40] ferrocene/ferrocenium (Fc/Fc⁺) is exploited as the reagent to react with Li₂O₂ for the quantification. Fc⁺ reacts with Li₂O₂ quantitatively following $2Fc^+ + Li_2O_2 \rightarrow Fc + 2Li^+$ + O₂. The changes in the concentration of the Fc⁺ can be tracked by the absorption in UV-Vis spectroscopy.



Figure 4-11 Titration of Li_2O_2 by Ferrocenium (Fc⁺) reduction. a) Calibration curve of Fc⁺ absorbance at λ =618 nm. b) Fc⁺ consumption vs discharge capacity plot for quantification of discharge product. For this group of data, an average yield of 72.7% was determined

For this set of experiments, a calibration curve that correlates the concentration of Fc^+ and its absorbance at λ =618 nm was first generated. The good linear relationship (r = 0.99983) provides the basis for the quantification of Li₂O₂ (**Figure 4-11a**). The discharged electrode was first removed from the test cell and sealed in a solution (1-2 mL in volume, 3 µmol/g Fc⁺) for 20 h to allow for complete reactions. The exact amount of

 Fc^+ and solvents (DME, which contained phosphorous hexafluoride, PF_6^- , as the counter anion) used for each specific experiment was recorded. The resulting solution was examined again by UV-Vis for the end concentration and, hence, the amount of remaining Fc⁺. The consumption was deduced from the difference. To eliminate single sample variations and scaling effect, a set of no fewer than 4 tests were performed, and the slope of the Fc^+ consumption rate was used for yield calculation (Figure 4-11b). When Vulcan carbon was used as a reference, an average total Faradaic efficiency of 74.0% was measured (Figure 4-12). Note that the best reported Faradaic efficiencies as quantified by titration method (e.g., iodometric titration; see Table 4-2) are in the range of 70-83% for Vulcan carbon cathode.^[37,41-42] A Faradaic efficiency of 72.7% was obtained on the Pd/Co₃O₄/TiSi₂ cathode when the discharge potential was limited to >2.0 V. The yield was increased to 74.3% when the discharge potential was set at >2.5 V. It indicates that appreciable side reactions do take place during discharge. More studies are needed to further understand the nature of these side reactions. The extent of the side reactions, however, is not out of line of relevant literature reports.^[37,41-42]



Figure 4-12 Quantification results of Vulcan carbon cathodes

Table	4-2 Literature	values of	Li ₂ O ₂ yi	ields de	termination	from	electroc	hemical	disch	narging
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Method	Cathode and electrolyte	Yield	References
Iodometric	Vulcan or Super P carbon in DME	77~90%	[37]
Iodometric	Vulcan carbon in TEGDME	82%	[41]
Iodometric	Carbon nanotube in TEGDME	70%	[42]
TEMPO UV-Vis "back titration"	Carbon nanotube in DEME-NTf ₂	>99%	[40]
Fc ⁺ /Fc UV-Vis "back titration"	Vulcan Carbon in DME Pd/Co ₃ O ₄ /TiSi ₂ in DME	74% 72.7~74.3%	Our result

4.2.5 Quantification of gas product generation

The DEMS method adopted previously can generate reliable qualitative gas analysis with high time resolution.^[19] But the quantification is cumbersome due to the nature of mixed gas entering the ionization chamber. Gas chromatography-mass spectroscopy (GC-MS) provides a better way to quantify the mixed gas content by isolating the gases with different retention time in the column. This ensures the ionization condition to be reproducible for each individual gas species. The sampling of the gas, however, has to be taken in a different way. In DEMS, nearly vacuum atmosphere condition was employed in the head space. In the GC-MS an ultra-high-purity Helium carrier gas was used to carry the generated gas to the sampling loop.

The Pd/Co₃O₄/TiSi₂ cathode was first discharged in a DME-based electrolyte. The electrolyte was then replaced by one with significantly reduced vapor pressures, Nbutyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl) imide (PYR₁₄TFSI; 1 M LiClO₄ was dissolved for enhanced ionic conductivities; see Methods). The switch of electrolyte was necessary as the high vapor pressure of DME makes it impractical to conduct online detection by GC-MS. Constant current was applied for recharge, and the gaseous products were sampled every 5 min automatically. O₂ (m/Z = 32, retention time 4.9 min) and CO₂ (m/Z = 44, retention time 30 min) counts were recorded (**Figure 4-13**). A rapid rise of O₂ was observed at the beginning of recharge, which tapered off and continued after the recharge was stopped due to the retention of gases by the container. The amount of detected O₂ accounts for 78.4% of the total charges extracted and 93.5% of the total detectable gases (**Figure 4-13**). CO₂ was only observed toward the end of recharge at high applied potentials (>4.0 V), presumably as a result of electrolyte decomposition. No other gaseous product was observed during the whole process. The measured yield is considered relatively high and in line with other reports of 2.45~3.58 e/O₂ during recharge or 74~77% OER/ORR yields.^[37,41,43] Factors that contribute to the loss include capacitive behaviors of the electrochemical setup, limited yield of Li_2O_2 from discharge, and parasitic reactions of electrolyte decompositions.



Figure 4-13 Gas chromatography–mass spectrometry result. (a) Recharge products detected with 50μ A constant current from 60^{th} to 120^{th} min. The corresponding voltage profile (blue dotted line) is superimposed to the graph. (b) The overall gas detected and its comparison to the charge passed.

The GC-MS gives compositional information of the gas generation. The utilization of ionic liquid or TEGDME instead of DME is a good mimic but not identical to the operation condition in DME electrolyte. Thus an in-situ measurement of the gas consumption and generation is important to evaluate the system. In a closed system like our electrochemical cell, the consumption and generation of O_2 will result in the change of pressure at the head space. This generally following the ideal gas law: PV=nRT, where P represents the pressure of the head space, V represents the volume of the head space, n represents the moles of the gas, R present the gas constant and T stands for the

temperature. With the volume and temperature being constant, the change of P (in torr) can be directly converted in to the change of n (in μ mol), which can further by compared with the electrons passed to the system. For our setup, the head space volume was 8 mL which was filled with pure O₂ and the testing temperature was maintained at 29 °C. The pressure change during the discharge and charge was recorded electronically by a pressure sensor (MKS 902B, ±0.1 torr).



Figure 4-14 Gas consumption and generation of Pd/Co3O4/TiSi2 cathode calculated from the pressure change of the cell head space during the discharge and recharge process.

The change of O_2 in the discharge process traces the 2-e process of oxygen reduction almost perfectly (black trace in **Figure 4-14**). The recharge curve deviates from the 2-e process of oxygen generation. Less gas was generated indicating the involvement of 4-e or higher processes. This correlates well with yield measured in the titration and the gas measured in the GC-MS results. Indicating that the oxygen indeed was reduced in a 2-e fashion, but the discharge product was not 100% Li₂O₂. Parasitic reactions

consumed the reduced oxygen species leading to lease decomposable Li_2O_2 in the recharge process. The instability of liquid electrolytes was assumed as the culprit.

4.3 Conclusions

In conclusion, we demonstrated that ALD-grown Pd nanoparticles can serve as bifunctional catalysts to enable TiSi2 nanonets as a cathode for Li-O2 batteries. Although successful in promoting both ORR and OER reactions, Pd nanoparticles exhibited severe detachment and aggregation, leading to cell failures after 63 cycles of discharge/recharge. The problem could be addressed by adding a layer of Co_3O_4 , also grown by ALD, doubling the cycling lifetime to 126 cycles. The Co₃O₄ not only improved the attachment of Pd nanoparticles, it also helped promote OER for reduced recharge overpotentials. The main discharge products were confirmed as Li₂O₂ by Raman spectroscopy, XPS, and Ferrocenium titration. The main recharge products of O₂ were verified by GC-MS and quantified by pressure change measurements. The results further validate TiSi₂ as a cathode support for Li-O₂ battery applications. While the design does not solve problems connected to electrolyte decomposition, it helps to isolate these issues by eliminating synergistic decompositions between carbon cathode and the electrolyte. The results are expected to contribute to the goal of better understanding and controlling of parasitic chemistries involved in Li-O2 batteries, which must be resolved before the realization of the Li-O₂ batteries as a practical energy storage technology.

The improved loading of Pd on Co_3O_4 functionalized $TiSi_2$ is still not good enough. The involvement of Co_3O_4 in the cathode reactions implicate that prolonged cycling may still result in the reconstruction of the surfaces. An inherently good connection between the catalyst and substrate is still desirable. As indicated by the computational work, Ru might be such a good candidate, which will be studied in the next chapter.

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Chapter 5. A truly stable cathode for Li-O₂ batteries

Ru as a good catalyst for both ORR and OER, is only 1/20 in price compared with other noble metal including Au, Pt or Pd.^[1] More importantly, it does not promote the decomposition of electrolyte like Pt and has better adhesion on TiSi₂ than Pd.^[2] Also, even if the surfaces of Ru were oxidized during the initial operation in Li-O₂ batteries, the resulting RuO₂ is still a good catalyst for the ORR and OER.^[3-4] These advantageous features promote the investigation of Ru as the catalyst for Li-O₂ batteries.^[5]



Figure 5-1 Illustration of the Ru/TiSi₂ carbon free cathode and the design of the full battery.

In this chapter, we employed the ALD and achieved the selective deposition of Ru on $TiSi_2$ directly. The elimination of interfacial layers simplifies the cathode structure and provides the best performance in our exploration for stable cathode materials. The resulting Ru/TiSi₂ cathode enabled the continuous operation of Li-O₂

battery over 100 cycles without major degradation. The discharge and recharge product was also confirmed by microscopic and spectroscopic evidence.

5.1 Methods

5.1.1 Material synthesis

TiSi₂ nanonets were prepared by a chemical vapor deposition (CVD) method. A Ti mesh (Cleveland Wire Cloth) was placed in the reaction chamber and heated to 675 °C. SiH₄ (10% in He, Voltaix; at 50 standard cubic centimetres per minute, or sccm), TiCl₄ (98%, Sigma-Aldrich; 2 sccm), and H₂ (industrial grade, Airgas; 60 sccm) were introduced to the chamber concurrently. The growth lasted typically 10 to 120 min with the pressure maintained at 5 Torr.

Ru nanoparticles were deposited on as-grown TiSi₂ nanonets in an Arradiance (Gemstar) ALD system. The growth temperature was 290 °C, with bis(ethylcyclopentadienyl) ruthenium(II) (Ru(EtCp)₂, heated to 110 °C) and compressed air (room temperature) as reaction precursors. Each cycle consisted of 4 repeated pulse/purge sub-cycles of Ru(EtCp)₂ for sufficient surface adsorption and 1 pulse/purge of O₂ to decompose Ru(EtCp)₂. The purge gas was N₂, and its flow rate was 90 sccm. The loading of Ru was quantified using inductively coupled plasma optical emission spectrometry (ICP-OES) at the MIT Center for Materials Science and Engineering (CMSE) using an ACTIVA S (Horiba) ICP-OES Spectrometer. Samples were imaged using a transmission electron microscope (JEOL 2010F) operating at an acceleration voltage of 200 kV.

5.1.2 Electrochemical Characterizations

0.1M LiClO₄ in dimethoxyethane (DME) with water level lower than 10 ppm was used as purchased from Novolyte (BASF). Tetra ethylene glycol dimethyl ether (TEGDME, \geq 99%, Sigma-Aldrich) was first stored over freshly activated 4 Å molecular sieves and then distilled. The distilled TEGDME was stored over molecular sieves before usage. LiClO₄ (99.99%, Battery grade, Sigma-Aldrich) was further baked at 130 °C under vacuum in the heatable tray of a glove box (MBraun) and then dissolved into TEGDME to give a 1M solution. Customized Swagelok type cells were used as the electrochemistry study platform. Cells were assembled in the glove box (O_2 and H_2O levels < 0.1 ppm) with Li foil as the anode, 2 Celgard 2500 film sheets as the separator, 0.1 M LiClO₄ in DME or 1 M LiClO₄ in TEGDME as the electrolyte. Ru-decorated TiSi₂ nanonets on Ti mesh (1 cm²) were used as the cathode directly without further treatment. No binder or carbon was added in our system. After assembly, oxygen (ultrahigh purity, Airgas) was filled into the cell to replace Argon and the cell was then isolated from the gas line after reaching 780 tor. The mass loading of TiSi₂ on Ti mesh is 0.1mg/cm² and Ru loading on each cathode is around 0.1mg/cm^2 as well. The total weight ratio of Ru:TiSi₂ = 1:1. The loading quantity of each individual sample was carefully measured by the weight gain after ALD growth using a microbalance and also confirmed by the ICP-OES. Electrochemistry tests were performed on an electrochemical station (Biologic, VMP3).

5.1.3 DFT calculation

The Vienna ab initio simulation package (VASP) [6-7] was used to perform periodic density functional theory calculations with planewave bases. The projector augmented wave (PAW) method was used to describe the interaction between electrons and the nuclei,^[8] standard VASP-PAW potentials were used for Ti, Si, Pt, and Ru with a recommended kinetic energy cutoff of 245 eV. The Perdew-Burke-Ernzerhof form of the generalized gradient approximation was used for electron exchange and correlation.^[9] Due to the large unit cell of the simulated systems, only Γ-point only was used for the k-point sampling for structural optimization with a force convergence criterion of 0.025 eV/Å. The DFT optimized lattice parameters of the TiSi₂ C49 structure (a=3.54 Å, b=13.54 Å, c=3.58 Å) are in excellent agreement with the experiment (a=3.56 Å, b=13.61 Å, c=3.56 Å).^[10] The metal nanoparticle was modeled as a 38-atom cluster. Both the TiSi₂ b plane [the (010) surface] and the c plane [the (010) surface] were modeled as a six-layer slab. The nanoparticle was placed on top of the surface; the bottom three layers of the surface were fixed at their bulk positions. The adsorption energy, E_{ad} , is defined as $E_{ad} = E_{NP/TiSi2} - E_{NP} - E_{TiSi2}$, where E_{NP/TiSi2}, E_{NP}, and E_{TiSi2} are the energies of the adsorbed system, the isolated nanoparticle, and the clean TiSi2 surface, respectively. So a negative Ead indicates a favorable interaction.

5.1.4 Detection of gas product

For the Differential Electrochemical Mass Spec (DEMS) characterization, the cell was first discharged under 780 torr pure O₂. Cell was then evacuated for 3 hours to

remove all O_2 in the chamber prior to DEMS characterization. The gas content was analyzed by a customized mass spec with quadrupole rods mass analyzer (Microvision 2, MKS).

The cell was further studied in two ways – in-situ and accumulation methods. For the in-situ analysis, the cell was connected to the Mass Spectrometer under vacuum with a dry rotary pump (nXDS 10i, Edwards) as the primary pump and a turbo pump to power the Mass Spec. The cell was also connected with a potentiostat (609D, CH Instruments) to perform recharging. For a typical in-situ test, a constant current (500 mA/g_{Ru}) was applied to the cell and the gas generated was analyzed simultaneously to get the profile of gas content at the different stages of recharging. Every Mass Spec scan was collected from 28 to 44 amu within 2s to give both the desired time resolution and accuracy.

For the Faradic efficiency test, the cell was treated in the same way to generate an evacuated discharged cell. The cell was then sealed and recharged (200 mA/g_{Ru}, 1000 mAh/g_{Ru}) to the capacity harvested from the discharging step. At the end of charging, all the gas generated was introduced to the mass spec test at once with the same set up mentioned above and Oxygen (m/Z=32) signal was acquired and integrated to get the peak area. Calibration curve was done by introducing a certain amount of oxygen into the cell and carrying out the same procedure of data acquiring and processing without recharging current pass through the cell. A linear relationship between the peak area and amount of Oxygen in the cell was obtained. Background was also deducted by carrying out the same procedure of recharging and data acquisition without any recharging current pass through the cell. The final faradic efficiency was obtained by dividing the amount of O₂ detected in the Mass Spectrometer by the theoretical value calculated from the charged provided to the cell.

5.1.5 Details of Raman characterization

Raman spectra were acquired using a micro-Raman system (XploRA, Horiba) with a 532 nm laser as excitation. Discharged/charged cell was first disassembled in an O_2 tolerated Argon filled glove box (dew point -100°C) and washed by anhydrous pure DME (Signal-Aldrich) for three times. Then the cathode was assembled into a custom-made air-tight sample holder with a thin glass window. The discharged cathode was first examined within the sample holder and no obvious peak for Li₂O₂ or Li₂CO₃ was detected. When the same sample was exposed to ambient air for several hours, we were able to detect significant amount of Li₂CO₃ on the same piece of sample. This is because the electrodeposited Li₂O₂ on our cathode was amorphous thus the phonon behavior was less well defined than commercial crystalized Li₂O₂. But after absorbing H₂O and CO₂ from ambient air, it was transformed to more crystalized Li₂CO₃ which is easier to be detected.

5.1.6 Analysis of XPS data

Surface analysis was carried out using a K-Alpha XPS (Thermo Scientific) with Al Kalpha micro-focused monochromator at a spot size of 400 μ m. The sample was also washed by DME with the same procedure mentioned above and mounted on the sample stage with minimal exposure to the ambient air before entering the load lock. The chamber was pumped down to 8×10^{-8} mbar prior to tests. Data was fitted by CasaXPS after the correction by referring C 1s to 248.8eV. Li 1s peak of Li₂O₂ peak was assign to be around 55.1 eV, LiOH was assigned to be around 54.3 eV and Li₂CO₃ was assigned to be around 55.7 eV.
5.2 **Results and discussions**

5.2.1 The deposition of Ru on TiSi₂

The unique advantages offered by $TiSi_2$ nanonets, such as the high aspect ratio (100:1), good conductivity (10^5 S/cm) and good stability (toward reactive oxygen species).^[11-13] We have discovered is that bare $TiSi_2$ does not offer ORR or OER activity.^[14] This seemly disadvantageous property is actually beneficial for the stability and control of the discharge product.^[15] The inertness of $TiSi_2$ implies its resistance toward the participation of oxygen chemistries. This passivation significantly improves the stability compared with carbon cathodes.^[16] The lack of catalytic activity can promote the formation of Li_2O_2 to be limited to be around the catalyst sites, making bi-functional catalyst more meaningful.^[17]

To introduce an effective bi-functional catalyst, Ru nanoparticles were selected. As we discussed in **Chapter 4**, the high adsorption energy of Ru nanoparticle on TiSi₂ could result in robust adhesion (**Figure 5-2a, 2b**). Atomic layered deposition provides such as way that can achieve this thermodynamically stable deposition. 100 cycles growth of Ru result in the average particle diameter around 6 nm. This is statistically shown in the inset of **Figure 5-2c**. The crystal structure of Ru metal was also confirmed by the high resolution transmission electron microscopy (HRTEM) in **Figure 5-2d**.



Figure 5-2 Site-selective growth of Ru nanoparticles on $TiSi_2$ nanonets. DFT calculations show that Ru clusters prefer the b planes (A) over the c planes of C49 $TiSi_2$ (B). The prediction is consistent with experimental observations by TEM from the top (C), where b planes are parallel to the viewing direction. Inset: size distribution of Ru nanoparticles by a 100-cycle ALD growth. When viewed from the side (D), where b planes are perpendicular to the viewing direction, no Ru nanoparticles are seen on the c or a planes. Inset: high-resolution TEM confirming the crystalline nature of the Ru nanoparticles.

5.2.2 Catalytic activity of Ru on TiSi₂

Next, the electrochemical performance of Ru was examined. Direct evidence was provided by the cyclic voltammetry in 0.1M LiClO₄/DME electrolyte (**Figure 5-3a**). By comparing the CV of Ru/TiSi₂ in O₂, Ru/TiSi₂ in Ar, TiSi₂ in O₂ and TiSi₂ in Ar, we can find only the sample of Ru/TiSi₂ in O₂ exhibits prominent reduction and oxidation behavior in the potential window of 2.0 V- 4.2V. This confirmed the good catalytic activity of Ru toward O₂ and the inertness of TiSi₂ itself. Further, the Galvanostatic discharge and recharge was employed in with the constant current density of 100 mA/g_{Ru} for Ru/TiSi₂ and the same value for TiSi₂. For bare TiSi₂ sample, no discharge plateau could be found. Instead, the voltage decreased nearly

linearly, indicating the capacitive nature of the electrode. Once decorated by the Ru catalyst, the discharge voltage plateaus around 2.5 V, indicating continuous electrochemical reaction is taking place (**Figure 5-3b**).



Figure 5-3 Cyclic voltammetry (a) and Galvanostatic discharge and recharge data in oxygen (b) for the confirmation of the catalytic activity of Ru and inertness of TiSi₂.

5.2.3 Battery performance of Ru/TiSi₂ cathode in Li-O₂ batteries

After assembling into a full battery with Li metal as the anode and 0.1 M LiClO₄/DME as the electrolyte, cycling performance was measured with the current density of 200 mA/g_{Ru} and the cut off capacity of 1000 mAh/g_{Ru}. As can be observed in **Figure 5-4**, the discharge voltage plateaued at around 2.65 V, generating only 310 mV overpotential at such high current density. The recharge curves were featured by the gradually sloping, which is typical in the Li-O₂ batteries. The terminal recharge voltages were always below 4.0 V, lower than the decomposition potential of the electrolyte in this system (>4.2 V as measured in **Figure 5-3a**). This low recharge voltage ensures the relative stability of electrolyte within the limited cycles. The average recharge voltage was calculated to be around 3.6 V, giving the overall round trip efficiency over 70 %. This value is stable over 100 cycles and represents one of the highest in comparable literatures. Moreover, the Ru/TiSi₂ is so robust that even

after the cell failure the cathode can be easily regenerated by using mild acid wash. The acid (0.1 M HCl) mainly removes the inevitable decomposition products of electrolyte (carbonates) on the surface of the catalysts. The regenerated cathode performs as new in a newly assembled cell.



Figure 5-4 Electrochemical characterization of the $Ru/TiSi_2$ cathode. (a) Potential vs. Capacity profile over 100 cycles. The dotted horizontal line marks the thermodynamic equilibrium potential. (b) Average discharge (solid circle), recharge (hollow circle), and round-trip efficiencies over 100 cycles.

5.2.4 Product detection

DEMS measurement was performed again to confirm the composition of generated gas to be O_2 . The recharge was carried out in the similar setting as in **Chapter 3**. The gas generated during the recharge was identified dominantly as the O_2 . Interestingly, the gas generation undergoes a two-step process (**Figure 5-5a**). The first oxygen evolution process immediately takes place when the voltage is above the equilibrium potential of Li₂O₂ decomposition. This low overpotential region may be related with the Li₂O₂ that are directly in contact with the catalyst. The consumption of these easily decomposed Li₂O₂ leaves only the particles that are located far from the catalytic activity sites available for the latter half of the recharge process. Once the

recharge voltage is high enough, the polarization induced by the electrode is great enough to reach these less accessible particles, leading to the second wave of oxygen generation. In contrast, the CO_2 signal was nearly invisible in the test even after integration (**Figure 5-5b**), indicating the lower reactivity induced by the Ru toward the decomposition of electrolyte. Also, the carbon-free nature of our electrode also significantly reduced the chance of Li₂CO₃ formation.



Figure 5-5 Detection of recharge products. (A) Real time mass spectrometry detection of gases generated at a fast 500 mA/gRu charging rate. (B) Accumulated counts of CO_2 and O_2 . Data collected in 1.0 M LiClO₄ in TEGDME.

5.3 Summary and outlook

With higher adsorption energy, Ru bonds strongly with TiSi₂ selectively on the b plane. Together with the adequate ORR and OER activity of Ru metal in non-aqueous system, we demonstrate a truly stable cathode system that can be operated over 100 cycles with little performance degradation. With a stable cathode, the only limitation for the long terms stability is the organic liquid electrolytes. The decomposition product of the electrolyte by the reactive oxygen species will build up on the surface of the cathode. An added benefit for the Ru/TiSi₂ system is the stability against acid

that can be used to regenerate the clean cathode surfaces. These merits of the $Ru/TiSi_2$ cathode promise a good platform for the comparative study of electrolyte stability and the further materialization of Li-O₂ batteries.

Resolving the stability of the cathode leaves the major task to be the stability of anode and electrolyte for future studies. Exciting researches surrounding these two areas are emerging and encouraging. For the electrolyte, ionic liquids, molten salts and solid electrolytes are promising to bring better stability.^[18-20] For the anode, the protection of Li metal by artificial SEI layers and high-porosity current collectors are also trending.^[21] Besides the stability, improving the efficiency and lowering the overpotential of the cathode are also of interest.^[22] Brief exploration along these angles has also been pursuit during the preparation of this thesis. But the discussion on these efforts will not be expanded here.^[23-24] One effort to explore the new battery systems beyond Li metal batteries, however, will be discussed in the next chapter to provide insight to the future development of energy storage devices.

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Chapter 6. Beyond Li metal: A demonstration of Mg-Br₂ battery

The notorious dendritic growth of Li metal remains unresolved and is prohibiting the use of Li metal in the rechargeable batteries.^[1] Mg metal, on the contrary, is featured by its dendritic free deposition in the electro plating process thus preferable.^[2] As the fifth most abundant element on the crust of Earth, Mg features advantages over Li by the low cost and abundancy.^[3] In addition, the divalent nature of Mg enables high volumetric capacity (3833 mAh/cm³ for Mg vs. 2046 mAh/cm³ for Li), which is recognized as an extra benefit.^[4] These unique properties motivate researchers to enable Mg as the anode.^[2]

For instance, researchers have examined cathode materials that would enable facile Mg^{2+} intercalation for high cyclability.^[5] The divalent nature of Mg^{2+} nevertheless presents a critical challenge for such efforts, and only limited success has been reported.^[2] Parallel efforts have also been focused on conversion chemistries between Mg and O₂.^[6] The low discharge potential and difficulty to recharge due to the spontaneous formation of MgO represent major roadblocks that must be overcome for future development toward that direction.^[7-8] Alternatively, the conversion between Mg and S is yet another possibility that has been explored.^[9] The low voltages (typically 0.9 – 1.5 V), however, significantly compromise the promises held by Mg-S batteries.^[2,9-10] Up to date, the advantages held by Mg as an energy storage material remains untapped.^[11]



Figure 6-1 The design principle of Mg-Br₂ batteries. Top: Schematic illustration of the Mg-Br₂ battery design, where Mg metal serves as the anode, and Br₂ with carbon paper current collector serve as the cathode. The catholyte consists of $PYR_{14}TFSI$ and the anolyte is made of DME and diglyme (1:1 ratio by volume). Bottom: Cyclic voltammetry of the anode (gray trace, left) and the cathode (orange trace, right). The current densities are normalized for illustration purposes.

In response to these challenges, here we propose to enable rechargeable Mgbatteries with conversion chemistry between Mg and Br₂ species (**Figure 6-1**). Halogens have been previously explored for energy storage applications in Al-Cl₂, Zn-Br₂, Li-I₂ and Li-Br₂ systems.^[12-16] Compared with other halogens, Br₂ offers the unique balance between energy density and chemical stability (335 mAh/g_{Br2}; Br₂/Br⁻= + 1.07 vs SHE) and has received the most research attention. As the reactivity of Br₂ would prohibit longterm utilization of aprotic electrolyte such as DMSO (dimethyl sulfoxide), THF (tetrahydrofuran) or organic carbonates,^[17-19] previous studies on Br₂ batteries were mostly carried out in aqueous solutions.^[20-22] The necessity for H₂O as a catholyte greatly limits the anode choices. For instance, aqueous catholyte would prevent the utilization of Li metal as an anode unless a ceramic Li ion conductor is present, which unfortunately introduces issues such as cost, high resistivity and safety concerns due to possible leakages of the electrolyte to react with Li.^[23-24] Moreover, the hybrid design adopted in the Li-Br₂ studies that utilize ceramic solid electrode to compartmentalize the cell components is not applicable for the Mg battery due to the lack of room-temperature Mg^{2+} conductive solid electrolyte, to the best of our knowledge.^[2,25]

Inspired by these previous efforts,^[26-27] we propose a new strategy to address the challenges associated with Mg batteries. As is shown in **Figure 6-1**, our strategy employs separate electrolytes for the anode and cathode. To solve issues connected to the reactivity of Br_2 , we introduce catholyte based on ionic liquid and Br^- as stablizing agent; to enable reversible striping and plating of Mg, we use a mixed non-aqueous anolyte. Together, this strategy permits the measurement of high cell voltage (3.0 V) and good cyclability (>20 cycles) using Mg metal as the anode and MgBr₂ as the starting materials (with carbon paper as the cathode current collector).

6.1 Methods

6.1.1 Chemicals and materials

MgBr₂, DME, Diglyme and liquid bromine (all anhydrous grades) were purchased from Sigma-Aldrich. The solvents were further dried with 4Å molecular sieves prior to use and MgBr₂ were further dried in vacuum at 150 °C. Mg metal (Ribbon, \geq 99% trace metals basis, Sigma-Aldrich) was scraped by a blade to remove the surface passivation layer before usage. $Mg(TFSI)_2$ and $PYR_{14}TFSI$ were purchased from Solvionic and further dried under vacuum at 240 °C and 150 °C overnight, respectively. Carbon paper (Toray 120) as cathode current collector was purchased from the Fuel Cell Store and cleaned sequentially by acetone, methanol and isopropanol, then dried under vacuum at 120 °C before use.

6.1.2 Electrochemical tests

0.1 M Mg(TFSI)₂ was dissolved in the mixture of DME/Diglime=1:1 (vol) to be used as anolyte and in the PYR₁₄TFSI (1-butyl-1-methylpyrrolidinium the pure bis(trifluoromethanesulfonyl)imide) as the catholyte. A custom-made cell with two glass chamber connected by a glass frit (fine grade, thickness: 2 mm, diameter: 1 cm, pore diameter: 4 µm) was used for testing. Two scraped Mg metal strips were inserted into the anolyte to serve as the counter and reference electrode, respectively. Carbon paper was immersed in the catholyte as the working electrode for the bromine chemistry. Stirring was achieved with a magnetic stirring bar. The immersed area varied between $0.5 \sim 1 \text{ cm}^2$ for samples measured for this study. The volume of the anolyte and catholyte were both 2 mL. Varying amount of MgBr₂ was added to the catholyte as electroactive material (the specific amount is noted for each test throughout the Chapter). Liquid Br₂ was used to generate various high concentration of Br_3^- in the catholyte for the overpotential measurements and Raman characterization. All electrochemical tests were performed in an Argon glovebox (Mbraun, O_2 and $H_2O < 0.1$ ppm) at room temperature.

6.1.3 Coulombic efficiency measurements

0.05 M MgBr₂ was dissolved in PYR₁₄TFSI solution with 0.1 M Mg(TFSI)₂ as the supporting electrolyte. The full cell was assembled in a configuration as described above. Constant current of 0.4 mA/cm² was applied to charge the cell for 2 h and discharged to the cut off voltage of 1.5 V vs Mg metal reference electrode. The discharge capacity dived by charge capacity gives the Coulombic efficiency. Then the cell was continuously cycled using the same parameters for 20 cycles. The average voltages were calculated by averaging the discharge or recharge voltage over time.

6.1.4 Faradic efficiency measurements

30 mM Ferrocene (Fc^{0}) in DME solution was prepared and stored in a glovebox. For each test, 1.6 mL of Fc^{0} in DME solution was used as the reagent. 0.2 mL sample (ionic liquid with active bromine species) was added to the Fc^{0} solution. The UV-Vis spectra of the resulting solution were then collected using an Ocean Optic USB4000 spectrometer and the peak intensity at 618 nm was used as a quantification standard. Ferrocenium (Fc^{+}) hexaflouraphosphate was used as the standard to generate the calibration curve and pure 1.6 mL DME + 0.2 mL ionic liquid solution was used as the blank background.

6.1.5 Raman Characterizations

Raman spectra were obtained using an XploRA micro-Raman system (Horiba) with an excitation laser of 532 nm. A liquid sample was dropped onto a thin glass plate and the

laser was focused on the top surface of the droplet. Pure ionic liquid was used as received. Ionic liquid with Br₂ sample was prepared by pre-mixing the liquid Br₂ with ionic liquid and the reddish solution on the top was extracted for test. (*Cautions:* Liquid Br₂ is volatile and corrosive to inhale systems and skins, adequate ventilation or encapsulation of the sample stage is needed.) The discharged samples at different stages were obtained by extracting the catholyte after the discharge operation from Br₂, without pre-addition of any MgBr₂.

6.1.6 SEM characterizations

SEM images were taken using a JEOL 6340F microscope operating at 10 KV and 20 KV. Energy-dispersive X-ray spectroscopy was taken by the TEAM system (EDAX) attached to the SEM. All samples were soaked and washed by DME 3 times to remove remaining salts and further dried under vacuum to remove DME before loading into the SEM chamber.

6.2 **Results and Discussions**

6.2.1 The reactions on the electrodes and the electrolyte choices

The first and foremost thing to develop a new battery is to identify the cathode and anode chemistries. The full operation of this battery system can be described as follows.

During discharge, the Mg anode was electrochemically oxidized to Mg²⁺, and Br₂ was reduced on the carbon paper surface to Br. During recharge, Br was oxidized back to Br_2 at the cathode and Mg^{2+} was platted onto the Mg anode. As will be discussed later in this chapter, Br₂ was found to readily bind with excess Br⁻ to form polybromide complexes (Br_n, n=3, 5, 7...), this helps to stabilize the free Br_2 and the polybromides/bromide redox pair determines the equilibrium voltage.^[28-31] For our study, we try to eliminate the complex composition of polybromide by using excess amount of Br, which makes the dominating polybromide specie to be Br₃. The voltage reported in aqueous solution for Br_3^{-}/Br^{-} is nearly identical with that for $Br_2/Br^{-}, [^{31-32}]$ but the value in aprotic solution varies depending on the solvent (0.6~0.7V vs SHE).^[18-19,28,33] Our primary goal for the present work is to utilize the conversion between Br₃ and Br $(Br_3 \leftrightarrow Br)$ for a new electrochemical energy storage system. The cyclic voltammograms (CV) of the anode and the cathode are presented in Figure 6-2, where the equilibrium potentials of 0 V and 3 V (vs. Mg²⁺/Mg; all voltages presented in this Chapter are relative to Mg^{2+}/Mg) for the anode and the cathode, respectively, are clearly seen.



Figure 6-2 Original data of CV scans of the anode and cathode tested separately. a) Mg anode chemistry with the scan rate of 20 mV/s. Testing electrolyte: 0.1 M Mg(TFSI)₂ in DME/diglyme (1:1 vol) solution. The reference electrode and the working electrode were both Mg metal strips. b) MgBr₂ on Pt electrode with the scan rate of 100 mV/s. Testing electrolyte: 10 mM MgBr₂ and

 $0.1 \text{ M Mg}(\text{TFSI})_2$ in PYR₁₄TFSI solution. The counter and the reference electrode were Mg metal strips, whereas the working electrode was a Pt wire.

Proper chemical can only takes place in proper electrolytes. For the cathode reaction, ionic liquid was employed as the catholyte. PYR₁₄TFSI features relatively high anodic stability,^[34] sufficient solubility of MgBr₂,^[35] relatively low viscosity and the lack of unsaturated bonds.^[36] These properties are desired for the Bromine based cathode reactions. Especially, the anodic stability of PYR₁₄TFSI is above 3.7 V, which promises the full operation of Bromine cathode (**Figure 6-3**). But the high overpotential for the plating of Mg prohibits the utilization of this ionic liquid as the anolyte (**Figure 6-4**).



Figure 6-3 The stability of the electrolytes characterized by linear scan voltammogram for 0.1 M $Mg(TFSI)_2$ in ionic liquid (red trace) and in DME+diglyme solution (blue trace). Pt wire served as the working electrode and two Mg strips served as the counter and reference electrode, respectively. Stability of pure PYR₁₄TFSI catholyte (>3.7 V) would be suitable for the Br₂ chemistry. The ether-based mixed electrolyte starts to decompose at or above 3.2 V.



Figure 6-4 Comparison of Mg anode chemistry in ether-based electrolyte (black trace) and ionic liquid (blue trace). The working electrode, the reference electrode and the counter electrode were all Mg strips. Scan rate: 20 mV. The overpotential in ILs for both plating and stripping are significantly higher than that in ether based electrolytes.

For the anolyte, we adopted 0.1 M Mg(TFSI)₂ in a mixed glyme/diglyme solvent (1:1 in volume). This electrolyte choice we have here represents an optimized compromise between considerations of stability and performance.^[37-38] To be noted, the electrolyte that can both enable fully reversible Mg anode and possess high anodic stability is still under investigation and currently unavailable. These two electrolytes were connected by a fine porous glass frit (4 μ m nominal pore size) which can slow down the crossover of bromine species but allows for exchange of Mg²⁺ to balance the charge.

6.2.2 Battery performance

Our next task is to examine the full charge/discharge characteristics. To ensure the full consumption of the starting material, we adopted two configurations for the charge/discharge but plotted in one figure (Figure 6-5a) for comparison purposes. For

the charging process, we added an exact amount of $MgBr_2$ (15 µmol, 7.5 mM; 0.8 mAh, 4 Ah/L) to the catholyte. This cell was then charged with a constant current (0.4 mA/cm², normalized to the projected area of the carbon paper current collector). A relatively high initial voltage (ca. 3.4 V) was observed (Figure 6-5a). Several reasons may be responsible for the observation of a high initial voltage. They include poor initial catalytic activity of the carbon paper, poor initial diffusion of Br to the pores in the carbon paper and reactions dominated by Br₂/Br⁻ at the beginning of recharge. For reasons to be discussed later, we are inclined to attribute the phenomenon to poor initial diffusion of Br. It is nevertheless important to note that the feature as seen in Figure **6-5a** is highly reproducible and was observed in all 5 measurements conducted for this portion of the study. The voltage quickly dropped to a plateau at ca. 3.1 V, which likely corresponds to the continuous oxidation of Br. Toward the end of the charging process, when Br in the solution was being depleted, the potential gradually increased and reached the cut-off voltage of 3.7 V. To study the discharge behaviour, we first preoxidized 0.05 M MgBr₂ to the equivalent of 0.8 mAh (4 Ah/L, 15% of Br⁻ utilization) to get a known amount of Br_3^- in the solution and then carried out Br_3^- reduction reactions. The characteristic voltage-capacity trace is also shown in Fig. 2a. It is seen that the system quickly reached a discharge plateau of ca. 2.4 V, which then gradually decreased to 2.0 V before a rapid decrease was observed at 275 mAh/ g_{MgBr2} (theoretical value: 290 mAh/g_{MgBr2}). The sudden decrease of the discharge potential corresponds to the depletion of Br₃. As will be shown later, the measured charges are indeed connected to the conversion chemistry between Br and Br₃ (3Br - 2e \leftrightarrow Br₃) with a Faradaic efficiency of ca. 95%.



Figure 6-5 Electrochemical performance. a) The voltage profile during discharge (orange trace) and charge (blue trace) with limited Br_3^- or MgBr₂ respectively. Capacity normalized to the active MgBr₂. Current density: 0.4 mA/cm². The cutoff voltage is 3.7 V for the charging and 1.5 V for discharging process. b) Coulombic efficiency, average discharge/charge voltage measured over 20 cycles with 0.05 M MgBr₂ in the starting catholyte. Absolute current: 0.2 mA, charging time: 2 h, 7.5 % utilization of total Br⁻.

For the cycling test, we started with 0.05 M MgBr₂ in the catholyte. The cell was first charged for 2 h at 0.4 mA/cm² (7.5% of total Br⁻ utilized) and then was discharged until the voltage dropped to the cut-off of 1.5 V. Coulombic efficiencies were calculated as the ratios between the discharge and charge capacities ($C_{discharge}/C_{charge}$), which was consistently ca. 96% (**Figure 6-5b**). Also shown in Fig. 2b are the average charge and discharge potentials (ca. 3.1 V and ca. 2.2 V, respectively) for each cycle. An average round trip efficiency of 70% was obtained. It is noted that at the end of the 20th cycle, no obvious sign of degradation was observed within the limited cycles. The experiment was terminated artificially. As such, the 20-cycle performance should represent a lower bound of the cyclability for full discharge operations. To prove this point, a prolonged cycling test with deeper cycling depth was also performed (15 % utilization of Br⁻, Figure 6-6).



Figure 6-6 Extended battery lifetime test. With limited amount of $MgBr_2$ (0.05M) in the solution, the charge/fully discharge depth was doubled (0.8 mAh) for accelerated degradation test. Coulombic efficiency was recorded as Fig S3a and representative voltage-capacity

6.2.3 Rate performance and cathode kinetics

The conversion chemistry of Br^{-}/Br_{3}^{-} was known for its fast kinetics as a result of high reactant solubility and facile electron transfer. But in our current experimental setup, a relatively high overpotential is observed when the current density is high. Possible reasons for the overpotential are the low concentration of the active species, high internal resistance of the electrolyte and membrane, high viscosity of the ionic liquid and the possible surface passivation of the electrodes.

In our case, the major overpotential comes from the internal resistance of the electrolyte. This can be demonstrated by varying the current density and study the V-I relationship. We employed a high concentration of Br_3^- to ensure the sufficient supply of reactants. The applied current density was varied from 0.04 mA/cm² to 2 mA/cm². For each current step, equilibrium voltage was obtained after 0.5 h of discharge or charge after the voltage plateaus were established. If we plot the overpotential vs the current density, a linear relationship was observed indicating internal resistance as the major

contributor for the overpotential (**Figure 6-7**). If the electrode reaction was attributed as the reason for the overpotential, an exponential change will be expected following the Tafel equation.



Figure 6-7 Rate performance and cyclability. a) Rate performance of the cathode in catholyte with 4 M Br₂ stabilized by Br⁻. The current density was ramped from 0.04 mA/cm² to 2 mA/cm² stepwise for 0.5 h for each discharge/charge segment b) the relationship between the overpotential and the current density.

Another factor that will influence the overpotential is the mass tranport. High concentration of active materials minimizes polarization in the solution due to the limitations of diffusion and thus minimizes overpotentials. At the same current density of 0.4 mA/cm^2 , when the concentration of the active material was increased from 7.5 mM to 2 M to 4 M, lower discharge overpotential was observed from ~ 0.8 V to ~ 0.56 V to ~ 0.5 V. The recharge overpotential (0.18 V) was also decreased. This was also reflected by other researchers' observation that the diffusion of bromine species is a major limiting factor in defining the performance of Li-Br₂ batteries.^[23] Future research is needed to improve the diffusion of bromine species and further reduce the overpotential.

6.2.4 Quantitative and qualitative detection of products

Next, we carried out product detection to corroborate the measured electrochemical characteristics with the purported Br_2 redox chemistry. The recharge product was quantified by adding the resulting catholyte to a DME solution with excess amount of ferrocene (Fc). Br_3^- (or Br_2) would quantitatively oxidize Fc to Fc^+ , which was then quantified by its distinct absorption peak at 618 nm.^[39] The quantity of Br_3^- (or Br_2) was calculated by these measurements. Note that here our measurements quantify the number of electrons passed during recharge. There is no difference whether the electrons are from $2Br^- \rightarrow Br_2$ or from $3Br^- \rightarrow Br_3^-$ (2-e⁻ process). As such, we do not distinguish Br_2 from Br_3^- for this set of experiments. The data are plotted in **Figure 6-8a** and compared with the expected values as calculated from the capacities. A Faradic efficiency of 95% was obtained. The efficiency coincides with the Coulombic efficiencies as presented in **Figure 6-5b**. We suspect that Br_2 diffusion through the glass frit during recharge was the main cause for the unaccounted 5% Faradaic efficiency loss.



Figure 6-8 Product detection. a) Faradic efficiency of Br_2 generation during recharge. Black squares: amount of Br_2 or Br_3^- as calculated from charges passed; orange circles: measured Br_2 or

 Br_3^- amount. b) Raman spectra qualitatively confirmed the reduction from Br_2 to Br_3^- to $MgBr_2$ could be complete, measurement performed at 0, 50 %, 100% depth of discharge, respectively.

To detect the discharge product of Br⁻, we started with a catholyte containing only Br₂ at the beginning. We electrochemically reduced Br₂ in the catholyte and used Raman spectroscopy to detect the Br₃⁻ signal (160cm⁻¹, Σ_g^+ band, symmetric stretch) at different stages of reduction (**Figure 6-8b**).^[30-31,35] The reduction of Br₂ produces Br⁻ which will bind with excess Br₂ to form polybromides, Br_n⁻. At 50% depth of discharge the majority of the species in the solution is Br₃⁻ (Br₂:Br⁻=1:2 in the solution). After further discharge, the yellowish colour faded resulting in a transparent solution. The Raman signal of Br₃⁻ also diminished. The species in the solution became MgBr₂ which exhibits no detectable Raman features in the ionic liquid.^[35] While the detection is qualitative in nature, the disappearance of Br₃⁻ at the final stage shows the electrochemical reduction process from Br₃⁻ \rightarrow Br⁻ could be complete.

6.2.5 The crossover of Bromine species and the necessity for glass frit

The same glass testing cell with two chambers connected by the glass frit was tested. 2 mL of 1 M Br₂ in PYR₁₄TFSI was put in one chamber and used as the diffusion source. 2 mL pure PYR₁₄TFSI was put in the other chamber as the receiving solution to be analysed. The receiving solution was constantly stirred to make sure the solution is homogenous for sampling. Samples were taken out at 5min, 10min, 1h, 4h, 8h, 24h, 72h and 100h and the bromine concentrations were quantified by the Ferrocene method similar as described in **Figure 6-8a**. Over 100 h, 0.03 M bromine species was detected in the previously clean chamber (**Figure 6-9**). To be noted that the test here is just to

normalize the crossover rate of the bromine species, so relative high concentration, symmetric solution choice and vigorous stirring of the receiving chamber were performed. The real test cell experienced fewer crossovers than the test here due to the lower concentration, asymmetric electrolyte usages and the absence of stirring in the anolyte side.



Figure 6-9 Characterization of the Br₂ species crossover rate through the glass frit.

To prove the necessity of separating the anolyte and catholyte, a control experiment was performed (**Figure 6-10**). The testing configuration is the same with the ones used before: the anode and reference electrode are both Mg strips and the cathode is the carbon paper, the electrolyte are the 1:1 mixed anolyte and catholyte with 0.05 M $MgBr_2$ as active species. The absolute current was also 0.2 mA under continuous stirring of the electrolyte. The only difference is the lack of porous glass frit to separate the anolyte and catholyte. Almost instantly, these two electrolytes merged and became one homogenous phase.



Figure 6-10 The cycling voltage profile of the cell without the porous glass frit to separate the two electrolytes.

The cell was first charged to 0.4 mAh and then discharged. No capacity could be delivered at all in this configuration. Comparing with **Figure 6-5**, the low dischargeable capacity might originate from the direct consumption of bromine species by the Mg anode or the reaction between the anolyte (ether) with the bromine species. The recharge voltage relative to reference electrode has also been shifted downward, presumably as a result of reference shift (upward) due to the competition of two redox pairs (Mg²⁺/Mg and Br₃⁻/Br⁻) in the solution.

6.2.6 The anode reactions

After proving that the cathode can reversibly produce and consume Br_3^- species as expected, we next examined how the anode changed due to Mg platting and stripping. Scanning electron microscopy (SEM) was employed for this portion of the study. The fresh Mg metal surface was smooth and featureless, as shown in **Figure 6-11a**. After charging, aggregated Mg particles were observed on the smooth surface, with no signs of dendritic growth (**Figure 6-11b**). For the anode after discharge, the etching of Mg surface is evident by holes created due to dissolution of Mg^{2+} (Figure 6-11c). After 60 cycles from the test performed in Fig. 3b, the anode surface was covered by a relatively compact layer of coating (Figure 6-11d) that was not observed after the initial recharge. This feature may help explain the increasing overpotential over time, as shown in Figure 6-12.^[37,40]



Figure 6-11 SEM images of the anode and cathode after different operations. a) pristine Mg anode; b) plated Mg anode after initial charge; c) stripped Mg anode after discharge; d) Mg anode after prolonged cycles; e) pristine carbon paper electrode; f) carbon paper electrode after cycling test in Figure S3; Scale bars: 10µm.



Figure 6-12 Average overpotentials of Mg anode during cycling. The Mg reference electrode was assumed as the equilibrium potential. The stripping/plating potential during the half cycle was averaged to generate the average operating potential. The difference between the average operating potential and the equilibrium was defined as the overpotential here. The overpotential for the stripping is high than plating in the initial cycling but levels off beyond 35 cycles. The overpotential for the plating remains low in before 20th cycle then started to grow afterward. The late take off of the plating overpotential and steady of stripping may implicate that the bromine crossover may have more effect on the plating process of Mg.

To further show that the morphology change of Mg surface was due to the repeated plating/stripping of Mg rather than the etching from bromine species, the surface of counter electrode and reference electrode from the same chamber after prolonged cycling tests were compared (**Figure 6-13**). The surface of the reference electrode remained smooth and the strips from the initial polishing of oxidation layer prior to cycling were still visible. The data further support that the roughening of the surface is due to striping and plating of Mg.



Figure 6-13 SEM images of (a) reference and (b) anode Mg after the cycling operation.

By comparison, the morphology of the carbon paper cathode remained unchanged during the cycling performance except for some residual salts and swelling of the carbon fibers (**Figure 6-11e,f**). Presumably because the operating condition was far less than the saturation condition of MgBr₂, no bulky insoluble product or by-product was observed. No obvious corrosion of the carbon paper was seen, either. Such a feature could be a major advantage of Mg-Br₂ battery over oxygen batteries, as the reactivity between carbon and reactive oxygen species has been identified as a major issue.^[41]

6.3 Summary and outlook

At the end of this thesis, an exploratory study to enable rechargeable Mg metal batteries was demonstrated. Bromine cathode with good solubility, kinetic and reversibility was demonstrated to be superior than the intercalation cathodes of Mg^{2+} .^[5,11] Efforts were devoted to the identification of proper redox reaction and the screening for suitable electrolytes. A full battery with Mg metal as anode, carbon paper and Mg(Br₃)₂ as

cathode, $PYR_{14}TFSI$ ionic liquid as the catholyte and $Mg(TFSI)_2$ in mixed glyme/diglyme as anolyte was successfully demonstrated. The challenges of this battery, including the crossover of bromine species, the stability of electrolytes and the overpotential on the anode, were identified and studied. Possible solutions resolving these challenges have been proposed and are on-going.

Overall, the high solubility of both the discharge product (MgBr₂) and recharge product (Mg(Br₃)₂) ensures the facile access of these reactants by the electrode. This is a major difference from the oxygen based chemistry (Li-O₂ or Mg-O₂) in which the discharge products are solids.^[42] It is acknowledged that solid discharge product can provide higher energy density but poor kinetics; the soluble discharge product has better kinetics but the energy density is limited by the solubility. We envision a new operation mode that combines the solid discharge product and highly soluble intermediate to be favorable both in kinetics and capacity.

6.4 Reference

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