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Investigations on Reaction Chemistry of Aprotic Lithium-air Batteries

Yuyang Hou

University of Wollongong

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Investigations on Reaction Chemistry of Aprotic Lithium-air Batteries

Yuyang Hou

Supervisors:
Prof. Jun Chen
Prof. Jiazhao Wang
Prof. Huakun Liu

This thesis is presented as part of the requirement for
the conferral of the degree:
Doctor of Philosophy in Chemistry

The University of Wollongong
Intelligent Polymer Research Institute
August 2018
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ABSTRACT

The rising importance of transport electrification has promoted the increasing need for large-scale energy storage with high energy density. Compared with conventional lithium ion batteries, lithium-air (Li-air) batteries have a much higher theoretical energy density, attracting increasing attention and research effort. The calculated mass-specific energy density of Li-air batteries is 3458 Wh kg\(^{-1}\), making itself a potential power source for electrical vehicle (EV). However, for the purpose of meeting the requirements for EV application, many issues for Li-air batteries need to be considered, such as exploring stable electrolytes, designing efficient catalysts, suppressing lithium dendrite formation, as well as preventing the contamination of CO\(_2\) and H\(_2\)O in the ambient air, etc. These issues are derived from the reaction chemistry of Li-air batteries, which is different from the intercalation chemistry of Li-ion batteries. To bring Li-air batteries closer to practical reality, understanding reaction chemistry related to electrolyte, electrode and contaminant is of great importance. In this thesis, the catalytic reaction of molybdenum carbide which occur during both discharge and charge under pure CO\(_2\), pure O\(_2\), CO\(_2\)/O\(_2\) mixture, and ambient air are studied in detail. A trend is identified between the observed overpotential during charge and the decomposition of different discharge products. Additionally, plausible mechanistic pathways under both CO\(_2\) and O\(_2\) for carbon-based and non-carbon-based electrodes are proposed, along with the potential catalyst design for practical Li-air batteries.

In Chapter 3, Mo\(_2\)C/carbon nanotube (CNT) composite material was synthesized and employed as a potential catalyst for aprotic Li-CO\(_2\) batteries to study the influence of CO\(_2\) on reaction chemistry of aprotic Li-air batteries. With its three-dimensional (3D) network of uniformly dispersed Mo\(_2\)C nanoparticles as catalysis sites and CNTs as the
conductive matrix, this cathode material has reduced the charge plateau below 3.5 V and could be reversibly discharged and charged for 40 cycles. Through a series of ex-situ characterizations such as SEM, XRD and XPS, we found that the reversible formation and decomposition of the amorphous discharge product Li$_2$C$_2$O$_4$-Mo$_2$C can reduce charge overpotential and improve the round-trip efficiency of aprotic Li-CO$_2$ battery. The introduction of Mo$_2$C has set a good example for guiding new catalyst design to improve the energy efficiency of Li-CO$_2$ batteries.

In Chapter 4, Mo$_2$C/CNT was exploited as a catalyst for practical Li-air batteries with high round-trip efficiency and good cycling performance. As a bifunctional catalyst in both O$_2$ and CO$_2$ atmospheres, Mo$_2$C/CNT can efficiently stabilize both intermediate species from reduction of O$_2$ and CO$_2$ to generate amorphous (Li-O-O)$_x$-Mo$_2$C and (Li-O-C-O)$_x$-Mo$_2$C discharge product, respectively, preventing the formation of crystalline Li$_2$O$_2$ and Li$_2$CO$_3$. Correspondingly, the charge potential can be significantly reduced owing to decomposition of the amorphous discharge products, instead of the decomposition of crystalline Li$_2$O$_2$ and Li$_2$CO$_3$. Meanwhile, this promoter has the potential to pave the way towards a commercially achievable Li-air battery in an open system, not requiring a sealed oxygen tank. The critical role of metal-oxygen bonds was clearly identified in Li-gas batteries, suggesting that the low valence metal in metal compound provides a suitable environment for surface stabilization of O$_2$ and CO$_2$ reduction product. This work has a broader implication to guide rational design strategies for other promoters such as metal carbides, metal sulfides which metal centers in the unsaturated coordination state. More importantly, the understanding of cationic redox and anionic redox further inspires us to explore new battery systems with longer life and higher energy density such as anion redox metal compound/LiO$_x$ system.
In Chapter 5, the influence of interfacial chemistry on Li$_2$O$_2$ oxidation was further studied using carbon-based (Vulcan C) electrode and non-carbon-based (Mo$_2$C) electrode. The oxidation of commercial preloaded Li$_2$O$_2$ in first charge is clearly different from the oxidation of electrochemically generated Li$_2$O$_2$ in second charge, which could be explained that insulating Li$_2$CO$_3$ generated from interfacial corrosion by LiO$_2$ intermediate in discharge process. SEI modification on the surface of carbon-based electrode is proposed and verified as a feasible method to prevent carbon-based electrode from interfacial corrosion by LiO$_2$ intermediate, facilitating decomposition of Li$_2$O$_2$. Moreover, the galvanostatic tests of Li$_2$O$_2$-preloaded Mo$_2$C electrode and Li$_2$CO$_3$-preloaded Mo$_2$C electrode were carried out to further confirm the heterogeneous catalytic property of Mo$_2$C. This work offers us a comprehensive understanding toward detrimental effect of interfacial Li$_2$CO$_3$ on Li$_2$O$_2$ oxidation using carbon-based electrode and possible role of Mo$_2$C as an efficient heterogeneous catalyst, providing useful guidance for further development of modified carbon-based electrodes and non-carbon-based heterogenous catalytic electrodes for Li-air batteries.
CERTIFICATION

I, Yuyang Hou, declare that this thesis submitted in fulfilment of the requirements for the conferral of Doctor of Philosophy, from the University of Wollongong, is wholly my own work unless otherwise referenced or acknowledged. This document has not been submitted for qualifications at any other academic institution.

__________________________

Yuyang Hou

August 2018
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>3D</td>
<td>Three-dimensional</td>
</tr>
<tr>
<td>APS</td>
<td>Ammonium persulfate</td>
</tr>
<tr>
<td>Ar</td>
<td>Argon</td>
</tr>
<tr>
<td>a.u.</td>
<td>Arbitrary unit</td>
</tr>
<tr>
<td>BSEs</td>
<td>Backscattered electrons</td>
</tr>
<tr>
<td>C</td>
<td>Carbon</td>
</tr>
<tr>
<td>cm</td>
<td>Centimeter</td>
</tr>
<tr>
<td>CNTs</td>
<td>Carbon nanotubes</td>
</tr>
<tr>
<td>CO₂</td>
<td>Carbon dioxide</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic voltammetry</td>
</tr>
<tr>
<td>DEMS</td>
<td>Differential Electrochemical Mass Spectrometry</td>
</tr>
<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
</tr>
<tr>
<td>DI</td>
<td>De-ionized</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethylsulfoxide</td>
</tr>
<tr>
<td>DN</td>
<td>Donor number</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical impedance spectroscopy</td>
</tr>
<tr>
<td>EV</td>
<td>Electric vehicle</td>
</tr>
<tr>
<td>FE-SEM</td>
<td>Field emission scanning electron microscopy</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>GDL</td>
<td>Gas diffusion layer</td>
</tr>
<tr>
<td>GO</td>
<td>Graphene oxide</td>
</tr>
<tr>
<td>h</td>
<td>hour</td>
</tr>
<tr>
<td>Symbol</td>
<td>Full Form</td>
</tr>
<tr>
<td>---------</td>
<td>-----------------------------------------------</td>
</tr>
<tr>
<td>H2O</td>
<td>Water</td>
</tr>
<tr>
<td>HEV</td>
<td>Hybrid electric vehicle</td>
</tr>
<tr>
<td>HRTEM</td>
<td>High-resolution transmission electron spectroscopy</td>
</tr>
<tr>
<td>Li-air</td>
<td>Lithium air</td>
</tr>
<tr>
<td>Li2CO3</td>
<td>Lithium carbonate</td>
</tr>
<tr>
<td>Li2O2</td>
<td>Lithium peroxide</td>
</tr>
<tr>
<td>LiO2</td>
<td>Lithium superoxide</td>
</tr>
<tr>
<td>Li-O2</td>
<td>Lithium-oxygen</td>
</tr>
<tr>
<td>LiTF</td>
<td>Lithium trifluoromethanesulfonate</td>
</tr>
<tr>
<td>LiTFSI</td>
<td>Lithium bis(trifluoromethanesulfonyl)imide</td>
</tr>
<tr>
<td>M</td>
<td>Mole per litre</td>
</tr>
<tr>
<td>mA</td>
<td>Milliampere</td>
</tr>
<tr>
<td>min</td>
<td>Minute</td>
</tr>
<tr>
<td>mV</td>
<td>Millivolt</td>
</tr>
<tr>
<td>MWCNTs</td>
<td>Multil-walled carbon nanotubes</td>
</tr>
<tr>
<td>N2</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>nm</td>
<td>Nanometre</td>
</tr>
<tr>
<td>NMP</td>
<td>N-Methyl-2-pyrrolidone</td>
</tr>
<tr>
<td>O2</td>
<td>Oxygen</td>
</tr>
<tr>
<td>O2^-</td>
<td>Superoxide anion</td>
</tr>
<tr>
<td>O2^2-</td>
<td>Peroxide anion</td>
</tr>
<tr>
<td>OCV</td>
<td>Open circuit voltage</td>
</tr>
<tr>
<td>OER</td>
<td>Oxygen evolution reaction</td>
</tr>
<tr>
<td>OEMS</td>
<td>Online electrochemical mass spectroscopy</td>
</tr>
<tr>
<td>ORR</td>
<td>Oxygen reduction reaction</td>
</tr>
</tbody>
</table>

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<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>PITT</td>
<td>Potentiostatic intermittent titration technique</td>
</tr>
<tr>
<td>PTFE</td>
<td>Poly(tetrafluoroethylene)</td>
</tr>
<tr>
<td>PVDF</td>
<td>Polyvinylidene fluoride</td>
</tr>
<tr>
<td>rGO</td>
<td>Reduced graphene oxide</td>
</tr>
<tr>
<td>RDE</td>
<td>Rotating disk electrode</td>
</tr>
<tr>
<td>RRDE</td>
<td>Rotating ring disk electrode</td>
</tr>
<tr>
<td>S</td>
<td>Siemens</td>
</tr>
<tr>
<td>s</td>
<td>second</td>
</tr>
<tr>
<td>SAED</td>
<td>Selected area electron diffraction</td>
</tr>
<tr>
<td>SEs</td>
<td>Secondary electrons</td>
</tr>
<tr>
<td>SEI</td>
<td>Solid electrolyte interface</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron spectroscopy</td>
</tr>
<tr>
<td>SWCNTs</td>
<td>Single-walled carbon nanotubes</td>
</tr>
<tr>
<td>t</td>
<td>Time</td>
</tr>
<tr>
<td>TEGDME</td>
<td>Tetraethylene glycol dimethyl ether</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
</tr>
<tr>
<td>V</td>
<td>Volt</td>
</tr>
<tr>
<td>W</td>
<td>Watt</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>Ω</td>
<td>Ohm</td>
</tr>
<tr>
<td>μ</td>
<td>Micro</td>
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Chapter 1: Introduction

1.1 Overview of Li-air Batteries

Our global society is becoming more and more dependent on energy: it is estimated that our energy demand will double in next decade with the current development speed maintained.\(^1\) This increasing demand for energy will push our humans to the era of exhausting fossil fuel. Even more worrisome, gasoline, coal and natural gas have been widely used as energy source for vehicles, factories, and power plants, leading to a dramatic increase in greenhouse gases in the atmosphere.\(^2\,^3\) Although the transition from internal engine vehicles to electric vehicles were proposed and implemented in many countries, it remains a long-term goal for large-scale energy storage system to storage clean energy such as solar energy, wind energy and nuclear energy. Compared with conventional vehicles with internal engine, the driving range of electric vehicles with a full charge is estimated as a big challenge. Therefore, the enthusiasm for electrified transportation relies heavily on the development of batteries with higher energy densities to extend a long mileage.

However, the energy density of currently used conventional Li-ion batteries is limited by the capacity of cathodes and intercalation chemistry. Beyond-lithium-ion batteries including Li-air batteries and Li-S batteries, which are not on the basis of intercalation chemistry, are proposed to offer most possibility to achieve a much higher energy density.\(^1\,^3\) Li-air batteries were proposed in the 1970s as the possible power source for automotive transportation, while they began to attract worldwide-research attention in past decade.\(^1\,^5\) The received attention owes to the highest energy density of Li-air batteries compared to other large-scale energy systems, which is theoretically similar
with that of gasoline. Moreover, the open configuration of Li-air batteries uses oxygen in ambient air as the reactant, making it become a special air-breathing storage system.\textsuperscript{2,3,6-13} Compared to the low tank-to-wheels efficiency (\textasciitilde12\%) of internal engine vehicles, the high battery-to-wheels efficiency (\textasciitilde90\%) of electric vehicle could be realized combing a Li-air battery and a high-efficiency electric propulsion system.

Currently, Li-air batteries have been developed and classified into four different types based on electrolyte employed: aprotic, aqueous, hybrid aprotic/aqueous and solid-state. In terms of the configuration, Li metal is used as an anode to provide the lithium source, and an open system is required for oxygen reduction which occurs at the cathode supports. All these four types of Li-air batteries have their own distinct advantages and significant technical challenges.

1.1.1 Aprotic Li-air batteries

Aprotic Li-air batteries were first reported by Abraham and Jang in 1996.\textsuperscript{15} The aprotic Li-air battery is made up of a lithium metal anode, a gas diffusion cathode with catalysts, and an aprotic electrolyte (Figure 1.1).\textsuperscript{8,16-20} The first reported electrolyte in aprotic Li-air batteries was a gel-type polyacrylonitrile (PAN) polymer electrolyte with LiPF\textsubscript{6} dissolved in ethylene carbonate (EC) and propylene carbonate (PC). This type of electrolyte is reported to be stable in contact with lithium metal and exhibit a conductivity of \textasciitilde10^{-3} \text{ S cm}^{-1} at room temperature.\textsuperscript{15} Other aprotic electrolytes can be made of several organic solvents including carbonates, ethers and esters, which are capable of solvating lithium salts (LiPF\textsubscript{6}, LiAsF\textsubscript{6}, LiN(SO\textsubscript{2}CF\textsubscript{3})\textsubscript{2}, and LiSO\textsubscript{3}CF\textsubscript{3}). The gas diffusion cathode is usually made of a high surface area carbon material with a nanosized noble metal or transition metal oxide catalyst.\textsuperscript{4,19,21-24} The spontaneous formation of a barrier between the anode and electrolyte (much like the solid electrolyte
membrane formed between electrolyte and anodes in conventional Li-ion batteries) could protect the lithium metal from further reaction with electrolyte and oxygen. Notably, the voltage gap between galvanostatic discharge voltage plateau and charge voltage plateau is usually between 1.3-1.8 V even at very low current density of 0.01-0.5 mA cm\(^2\) on carbon electrode. Li\(_2\)O\(_2\) produced at the cathode support is generally insoluble in aprotic electrolyte, which makes cathode support prone to clogging, resulting in battery degradation.

![Figure 1.1 Schematic of aprotic Li-air batteries.\(^5\)](image)

### 1.1.2 Aqueous Li-air batteries

Aqueous Li-air batteries were first enabled relying on the invention of the protected lithium electrode (PLE) by Polyplus Battery.\(^{25}\) The aqueous Li-air battery consists of a lithium metal anode, a gas diffusion cathode with catalysts and an aqueous electrolyte (Figure 1.2).\(^{25}\) The aqueous electrolyte is made by dissolving different kinds of lithium salts in water. Because the discharge product LiOH is water soluble, this type of Li-air battery avoids the clogging issue. Compared with aprotic Li-air batteries, aqueous Li-air batteries have a higher discharge voltage plateau. However, the reaction between lithium and water makes aqueous Li-air batteries requiring a solid electrolyte interface
between lithium metal anode and aqueous electrolyte. As the most commonly used solid electrolyte interface, lithium-conducting ceramic need to overcome its low conductivity with the order of $10^{-3}$ S cm$^{-1}$ at room temperatures. Another issue with aqueous Li-air batteries is the high self-discharge rate, owing to the direct reaction between oxygen and lithium anode. It is reported that the self-discharge rate could be efficiently reduced by the use of ceramic LATP, but the stability of such lithium conducting ceramic is still questionable in alkaline electrolyte.

![Schematic of aqueous Li-air batteries](image)

**Figure 1.2** Schematic of aqueous Li-air batteries.$^5$

### 1.1.3 Hybrid aprotic/aqueous Li-air batteries

To combine the advantages of both aprotic and aqueous Li-air batteries, the hybrid Li-air batteries were designed and fabricated (Figure 1.3). The hybrid aprotic/aqueous Li-air battery is made up of three parts: aqueous part, aprotic part, and a lithium-conducting membrane. In specific, the lithium anode is placed in the aprotic side while the cathode is placed in the aqueous side. Between aprotic side and aqueous side, a lithium-conducting ceramic is employed as the membrane separating the two electrolytes.$^{26-28}$

The NASICON family (e.g., $\text{Li}_{1-x}\text{A}_x\text{M}_{2-x}(\text{PO}_4)_3$ with $A = \text{Al, Sc or Y and M = Ti or Ge}$)
has been studied as the use of solid electrolyte ceramic. Although they have a good compatibility with alkaline electrolyte and a large electrochemical window, their Li\(^+\) ion conductivity is too low to be suitable for large-scale energy storage applications. Furthermore, both Ti and Ge could be reduced by metallic Li, requiring an intermediate polymer layer between the ceramic membrane and the lithium metal anode. It is also reported that the solid polymer electrolyte could provide a higher conductivity, at the expense of a faster crossover of H\(_2\)O which is reactive toward Li metal anode.\(^{27,29}\)

![Figure 1.3 Schematic of hybrid aprotic/aqueous Li-air batteries.\(^5\)](image)

### 1.1.4 Solid-state Li-air batteries

For safety issue, the solid-state Li-air batteries were designed and fabricated. The solid-state Li-air battery consists of a lithium anode, a gas diffusion cathode with catalysts and a ceramic electrolyte membrane (Figure 1.4). The anode and the cathode are separated by polymer-ceramic composites, enhancing charge transfer at the anode and electrochemically coupling the cathode to the electrolyte.\(^{28-34}\) This polymer-ceramic composites could also significantly reduce overall impedance. The main drawback of solid-state Li-air batteries comes from the low ionic conductivity of currently used lithium ceramic conductors\(^{32}\)
In short, the exploration of the Li-air battery is in its infancy and must be extensively studied before this energy storage system can be commercialized. Apart from a better understanding of the chemical composition, several challenges for Li-air battery need to be addressed. Firstly, stable electrolytes and cathodes should be developed under two conditions, the one is that they could be resistant to decomposition at high oxidation potentials, and the other is that they could minimize reactivity with intermediates produced during discharge/charge process. Secondly, the mechanism of electrocatalysts in cathodes should be investigated on their role in reducing overpotentials in charge and increasing cycle life. Thirdly, air-breathing membranes should be developed to allow the passing of O₂, while preventing H₂O, CO₂ and other environmental contaminants which limits the lifetime of Li-air batteries. Fourthly, the Li metal anode should be protected against reaction with trace H₂O and O₂, as well as inhibited dendrite formation in charge. Over the last three systems, stringent requirements have been imposed on the separator to better protect Li anodes against water and to facilitate high Li⁺ conductivity. Moreover, the theoretical capacity of aprotic type is higher than the other three types of Li-air batteries. Based on these two reasons, aprotic Li-air batteries have been attracted

**Figure 1.4** Schematic of solid-state Li-air batteries.⁵
most research attention in last decade.

1.2 Reaction Chemistry of Aprotic Li-air Batteries

Aprotic Li-air batteries have been hindered by several critical issues in current stage, including electrolyte instability, low round-trip efficiency, lithium dendrite formation, contamination by CO$_2$ and H$_2$O in the ambient air. These issues typically occur in conjunction with the basic redox reaction, leading to poor cyclability and low energy efficiency of aprotic Li-air batteries.$^{1,2,5,14,35-37}$ To achieve significant improvement and address these issues, especially the biggest challenge of reducing large overpotential gap by design of efficient catalyst, a fundamental understanding of reaction chemistry including electrolyte, electrode materials, atmospheric contaminants, as well as intermediate/final discharge product is important and indispensable to elucidate the origin of these issues.

1.2.1 Discharge reaction chemistry

The ideal discharge reaction chemistry, based on the electrochemical generation of Li$_2$O$_2$, could be illustrated that dissolved oxygen from the ambient air reacts with lithium ions in the aprotic electrolyte to generate LiO$_2$ in the first step, and Li$_2$O$_2$ in the subsequent step.$^{1,5,38}$

$$O_2 (g) + e^- \rightarrow O_2^- (solv) \quad (1-1)$$
$$Li^+ (solv) + O_2^- \rightarrow LiO_2 \quad (1-2)$$
$$2LiO_2 \rightarrow Li_2O_2 (s) + O_2 \quad (1-3)$$
$$LiO_2^- + Li^+ + e^- \rightarrow Li_2O_2 (s) \quad (1-4)$$

Li$_2$O$_2$ is the only stable discharge product observed above cut-off voltage of 2.0 V in practice, even though Li$_2$O is the other theoretically possible discharge product of the
aprotic Li-air batteries. In a typical procedure, oxygen is reduced on the electrode at the beginning of discharge (1-1), and consecutively combines with lithium ions in the electrolyte, generating the metastable LiO₂ intermediate (1-2). LiO₂ may subsequently go through two different reaction pathways: one is the chemical disproportionation of liberated LiO₂ to generate Li₂O₂ and release O₂ (1-3); the other is a continuous electrochemical reduction of adsorbed LiO₂* with an additional lithium ion and electron to generate Li₂O₂ (1-4). Notably, the kinetics of each step as well as the stability of the intermediates are greatly influenced by the surrounding conditions, leading to different electrochemical properties, such as specific capacity, round-trip efficiency and rate capability. It seems very simple that the discharge reaction of Li-air batteries involves only two elements of Li and O. However, the mechanism is significantly affected by the formation of different reaction intermediates. Moreover, these high oxidative intermediates can also induce side-reactions with cell components, including electrode materials, electrolytes, and atmospheric contaminants, leading the degradation of electrochemical performance of aprotic Li-air batteries. Therefore, regulating the reactivity of various intermediates should be focused in future research.

1.2.2 Charge reaction chemistry

The ideal charge reaction chemistry, based on the electrochemical decomposition of Li₂O₂, should reverse the process of the discharge reactions to release oxygen.

\[
\text{Li}_2\text{O}_2 (s) \rightarrow \text{LiO}_2^+ + \text{Li}^+ + e^- \quad (1-5)
\]

\[
\text{Li}_2\text{O}_2 (s) + \text{O}_2 \rightarrow 2\text{LiO}_2 \quad (1-6)
\]

\[
\text{LiO}_2 \rightarrow \text{Li}^+ (\text{solv}) + \text{O}_2^- \quad (1-7)
\]

\[
\text{O}_2^- (\text{solv}) \rightarrow \text{O}_2 (g) + e^- \quad (1-8)
\]

However, the charge process does not follow the predicted reverse reaction in practice.
Owing to different nature of generated discharge products in discharge, side reactions generally occur with several metastable intermediate species. During the charging process, there are three possible sites where the electrochemical decomposition of Li$_2$O$_2$ occurs. The first site is the interface between the electrode and Li$_2$O$_2$ (Figure 1.5a), which was confirmed by observation of void spaces at the interface in several in-situ studies. On this site, even large Li$_2$O$_2$ particles could be decomposed, because the void could be rapidly filled by Li$_2$O$_2$ particle collapsing in charge process.

The decomposition of Li$_2$O$_2$ also occurs at the interface of Li$_2$O$_2$ and the electrolyte (Figure 1.5b). This second site could easily release lithium ions and oxygen from the Li$_2$O$_2$ surface, in the case that the charge carrier can be transferred through the Li$_2$O$_2$ particles. It is claimed that the decomposition of Li$_2$O$_2$ mainly occurs at the second site by a recent study based on the observation of an in-situ environmental scanning electron microscope. Due to the electrically insulating nature of crystalline Li$_2$O$_2$, it is difficult to expect for a fast charge transfer to decompose large Li$_2$O$_2$ particles on this site. In addition, based on the theoretical calculation for the transition state of the crystalline Li$_2$O$_2$ decomposition, in the absence of charge transfer, the overpotential of releasing lithium ions and oxygen on the surface of Li$_2$O$_2$ is estimated to be small (<0.2 V), and the charge is much higher (> 1.5 V). These findings suggest that the problem of charge transport in Li$_2$O$_2$ is a nonnegligible factor, and the nature of electrochemically generated Li$_2$O$_2$ should be carefully considered.\textsuperscript{38}

The last reaction site of charge process is at the electrode/electrolyte interface, where the species of LiO$_2$ or Li$^+$–O$_2$\textsuperscript{2−} ion pairs could be decomposed electrochemically (Figure 1.5c). This reaction site is less dominant owing to the unfavorable dissolution energy of Li$_2$O$_2$ to produce LiO$_2$ or Li$^+$–O$_2$\textsuperscript{2−} ion pairs. It is believed that the
decomposition reactions at these three sites would occur simultaneously in charge. Accordingly, the main charge reaction is supposed to be determined by the transferring pathway of charge carriers across Li$_2$O$_2$ particles. This pathway would be significantly affected by the previous discharge reaction and the solubility of discharge product in the electrolyte.

![Diagram of possible reaction sites]

**Figure 1.5** Three possible reaction sites where electrochemical decomposition of Li$_2$O$_2$ occurs: a) electrode/Li$_2$O$_2$ interface, b) Li$_2$O$_2$/electrolyte interface, c) electrode/electrolyte interface.$^{38}$

### 1.3 The Influence of Electrolyte on Reaction Chemistry

Electrolyte in aprotic Li-air batteries plays a critical role in determining the overall electrochemical performance. A good electrolyte should hold the following qualities: good stability against O$_2^-$ attack; low viscosity; high oxygen solubility and diffusivity, stability to the reaction with metallic lithium, as well as a wide potential window to withstand high oxidation potentials.$^{1-2}$ The organic liquid electrolyte includes organic solvents and lithium salts. Understanding the influence of each part on reaction chemistry may help solve the problems related to electrolyte.
1.3.1 The influence of electrolyte solvents on discharge reaction

It is proposed in recent studies that there are two different discharge reaction pathways in different electrolyte solvents. One involves the generation of toroidal-like Li$_2$O$_2$ through chemical disproportionation of LiO$_2$ intermediate, and the other involves the formation of film-like Li$_2$O$_2$ on the surface of electrode.\textsuperscript{39-41} The two different pathways for Li$_2$O$_2$ formation can be explained by a simple physical parameter: donor number (DN) of the aprotic solvent. Johnson \textit{et al.} investigated comparatively on the reduction processes of O$_2$ in four solvents with different DN$s$ (acetonitrile (MeCN) with DN of 14, dimethoxyethane (DME) with DN of 20, dimethyl sulfoxide (DMSO) with DN of 30, 1-m thylimidazole (Me-IM) with DN of 47).\textsuperscript{41} It has been suggested that solvents with low DN such as DME and MeCN exhibit weak solvation ability; therefore, the intermediate LiO$_2^+$ cannot be released stably into the electrolyte from the surface of the electrode where it is produced. The accumulation of LiO$_2^+$ on the surface of the electrode is unstable, leading to a surface-driven growth mechanism. The reduction in second step to Li$_2$O$_2$ rapidly occurs on the electrode surface, depositing a thin-film discharge product as shown in \textbf{Figure 1.6a}. In contrast, solvents with high DN such as Me-IM and DMSO, could solvate and stabilize LiO$_2$ intermediate in the electrolytes. The sufficient solvation stabilizes the soluble LiO$_2$ in the electrolyte, which guarantee the disproportionation of LiO$_2$ stably occurs in the solution, accompanying the growth of Li$_2$O$_2$ particles. This solution-mediated growth mechanism results in continuous precipitation, generating large Li$_2$O$_2$ particles as shown in \textbf{Figure 1.6b}.

It is worth noting that different pathways induce different properties and morphologies of Li$_2$O$_2$. The surface-driven pathway in the low-DN solvents generally results in the formation of film-like Li$_2$O$_2$ on the electrode surface. On the contrary, the solution-
mediated pathway in the high-DN solvents leads to precipitation of large Li$_2$O$_2$ particles with toroidal shape.$^{40-42}$ Note that the crystallinity of film-like Li$_2$O$_2$ is inferior to that of the toroidal shape.$^{43,44}$ This finding is attributed to the metastable LiO$_2^*$ adsorbed on the electrode surface, as well as a rapid second reduction to Li$_2$O$_2$, which prevent the formation of crystalline Li$_2$O$_2$. In addition, the specific capacity of the Li-O$_2$ batteries, is determined by the different morphologies of Li$_2$O$_2$. As shown in Figure 1.6a, the specific capacity of Li-O$_2$ cell in low-DN electrolytes is generally low. Forming an insulating Li$_2$O$_2$ film on the surface could easily passivate the surface of active electrodes, and as the discharge progresses, thereby reducing the total capacity. However, the solution-mediated Li$_2$O$_2$ growth in high-DN electrolytes, which produces larger toroidal particles, results in a much higher specific capacity in Li-O$_2$ batteries as shown in Figure 1.6b. The lesser tendency to passivate the new electrode surface contributes to the sustained electrochemical reaction on the electrode. However, it should be noted that the high-DN solvents are not always a best choice for Li-O$_2$ batteries because of the fundamental trade-off between capacity and electrolyte stability.$^{45}$

![Figure 1.6](image-url) Schematic of discharge pathways in different solvents with a) high DN and b) low DN.$^{38}$

Although high-DN solvents can increase the discharge capacity by triggering solution-
mediated \( \text{Li}_2\text{O}_2 \) growth, high-DN solvents that cause solvent degradation are easily H-extracted due to the high concentration of \( \text{O}_2^- \).\textsuperscript{45,46} The stability of the solvent for the H-extraction reaction (nucleophilic attack rate) and the tendency to drive solution-mediated \( \text{Li}_2\text{O}_2 \) growth (\( \text{LiO}_2^- \) solubilization energy) were plotted in Figure 1.7.\textsuperscript{45} There is a negative correlation between the two competing effects: solvents with stronger solvating properties are relatively unstable to the H-extraction reaction (blue region), while solvents with better anti-H-extraction stability show relatively poor \( \text{LiO}_2^- \) solvating properties (green region), therefore exhibit reduced discharge capacity. Selecting a suitable electrolyte with good solvating properties and stability is still challenging, as observed in the electrolyte system known in Figure 1.7, indicating that the red region should be expected as the electrolyte system. Although a fundamental understanding of solvent effects is still under discussion and deserves further study, it is clear that the nature of the electrolyte is an important factor to consider when designing Li-O\(_2\) batteries.

**Figure 1.7** Relationship between the free energy of \( \text{LiO}_2^- \) dissolution and the rate of nucleophilic attack of \( \text{O}_2 \) for the reported solvents. The free energy of \( \text{LiO}_2^- \) dissolution represents the solvation ability of the solvent, whereas the nucleophilic attack rate represents anti-H-extraction stability.\textsuperscript{38,45}
1.3.2 The influence of electrolyte salts on discharge reaction

In addition to the electrolyte solvent affecting the discharge reaction, the type of salt dissolved in the electrolyte also affects the discharge reaction of Li-O₂ batteries. The discharge capacity of Li-O₂ batteries can be improved by changing the properties of the electrolyte with an appropriate salt anion.⁴⁷,⁴⁸ As shown in Figure 1.8, by adding LiNO₃ to the electrolyte, the specific capacity can be systematically increased. The specific capacity of Li-O₂ batteries with 0.7 M LiNO₃ increased more than four times compared to the case without LiNO₃. As shown in the SEM images in Figure 1.8, the addition of LiNO₃ also changes the morphology of the discharge product to a larger toroidal shape. It has been claimed that NO₃⁻ anions in solvents can enhance the donicity of electrolytes, leading to an increase in O₂⁻ stability in the solvent and triggering the growth mechanism of solution-mediated Li₂O₂ formation.⁴⁷ Because the reaction intermediates are coordinated in the electrolyte, the solvent molecules are surrounded by salt ions, and the reaction path is affected by its chemical properties; therefore, the choice of electrolyte should be carefully considered in Li-O₂ batteries.

![Figure 1.8](image_url) SEM images and galvanostatic discharge profiles of Li–O₂ batteries with different LiNO₃ concentrations.⁴⁸
1.4 The Influence of Electrode on Reaction Chemistry

It is well known that electrode is another important factor strongly affecting the performance of Li-air batteries. In the past few years, many types of electrode materials have been developed and investigated to catalyze the Li₂O₂ formation and decomposition, hoping to reduce the discharge/charge potential gap. These materials can be divided into two categories: one is carbon-based materials such as CNT, graphene, carbon black, etc. and the other is non-carbon-based materials including precious metal, metal oxides, metal carbides, metal sulfides, etc. Understanding the influence of different kinds of electrode on reaction chemistry could serve as guidelines for catalyst design, improving the energy efficiency in lithium-air battery.

1.4.1 Kinetics of Li₂O₂ formation on carbon electrode

Carbon materials are widely used as electrode for lithium oxygen batteries, due to their low cost, excellent electrical conductivity and large surface areas. Understanding the intrinsic discharge reaction kinetics and limitations associated with the formation of Li₂O₂ on carbon is critical to the development of O₂ electrodes. The ORR on CNTs was investigated to probe kinetics under both potentiostatic and galvanostatic discharge conditions. Under potentiostatic discharge, the average current increases from 0 to 1,000 mA/gc with decreasing voltage from 2.76 to 2.0 V (Figure 1.9a). The voltage of 2.76 V corresponds to the minimum overpotential required to observe a significant ORR current. Therefore, the voltage of 2.76 V is the maximum potential at which nucleation and growth of Li₂O₂ occurs on CNTs. The tendency is also confirmed by measuring the currents and voltages under galvanostatic discharge (Figure 1.9b), which agree well with those under potentiostatic discharge.
Figure 1.9 a) Current vs. capacity of CNT electrodes discharged potentiostatically over a range of potentials between 2.0 and 2.76 V. b) Voltage vs. capacity of CNT electrodes discharged galvanostatically between 10 and 1,000 mA/g.\textsuperscript{78}

1.4.2 **High charge overpotential of Li$_2$O$_2$ oxidation on carbon electrode**

Compared with low discharge overpotential on carbon electrode, the charge overpotential on carbon electrode is not only higher, but also increasing with charge process proceeding (Figure 1.10).\textsuperscript{18} The high charge overpotential of Li$_2$O$_2$ oxidation results in a low round-trip efficiency and increasing rate of electrolyte decomposition and other potential-driven side reactions.

Figure 1.10 Voltage profiles of Li-O$_2$ batteries employing a) either P50 carbon paper or b) XC72 bound to 316SS mesh using PTFE as cathode, and 1 M LiTFSI in DME as electrolyte.\textsuperscript{18}
The origin of high charge overpotential on carbon electrode has not been known to date. In some studies, different reaction mechanisms have been proposed to explain the observed charge overpotential on carbon electrode and its effect on charge reaction kinetics. There are roughly six mechanisms proposed, which includes different Li$_2$O$_2$ particle distribution (Figure 1.11a), high electric resistance of Li$_2$O$_2$ (Figure 1.11b), interfacial Li$_2$CO$_3$ layer generated on the electrode surface (Figure 1.11c), the core-shell structure of Li$_2$O$_2$ with a LiO$_2$-like surface (Figure 1.11d), the presence of a nonstoichiometric phase Li$_{2-x}$O$_2$ and its topotactic de-lithiation (Figure 1.11e), and the morphology of Li$_2$O$_2$ (Figure 1.11f).

![Figure 1.11 a-f) Possible charge reaction kinetics for high charge overpotentials.](image)

1.4.3 Twin problems of interfacial carbonate on carbon electrode

The stability of carbon electrode exposed to LiO$_2$ and Li$_2$O$_2$ in discharge, as well as the highly oxidation environment in charge is also problematic. Li$_2$O$_2$ is metastable on carbon because of the reactions between Li$_2$O$_2$ and carbon occurring,
\[ \text{Li}_2\text{O}_2 + \text{C} + \frac{1}{2} \text{O}_2 \rightarrow \text{Li}_2\text{CO}_3 \quad \Delta G = -542.4 \text{ kJ/mol}; \]
\[ 2 \text{Li}_2\text{O}_2 + \text{C} \rightarrow \text{Li}_2\text{O} + \text{Li}_2\text{CO}_3 \quad \Delta G = -533.6 \text{ kJ/mol} \]

where \( \Delta G \) is the change of Gibbs free energy at 300 K. As shown in Figure 1.12, during the discharging process, since \( \text{Li}_2\text{O}_2 \) must be in contact with carbon to carry out these reactions, several monolayers of \( \text{Li}_2\text{CO}_3 \) can be formed at the interface between carbon electrode and \( \text{Li}_2\text{O}_2 \) because the initially generated \( \text{Li}_2\text{CO}_3 \) prevents \( \text{Li}_2\text{O}_2 \) from entering the surface of carbon. These \( \text{Li}_2\text{CO}_3 \) monolayers abate the transmission current by two orders and abate the exchange current of all electrochemical reactions relying on charge transfer.\(^{18}\) During the charging process, the \( \text{Li}_2\text{O}_2 \) layer is partially covered by \( \text{Li}_2\text{CO}_3 \) via the electrochemical reaction between \( \text{Li}_2\text{O}_2 \) and electrolyte. The surface of any dispersed \( \text{Li}_2\text{CO}_3 \) formed in the surface is concentrated and does not oxidize under a low charging voltage plateau. As the charging process continues, the surface becomes completely covered by \( \text{Li}_2\text{CO}_3 \). Since the ratio of \( \text{Li}_2\text{O}_2 \) on the surface is getting smaller during charging, the overpotential of OER must be increased to maintain a constant galvanostatic charge rate until charging to 4 V, even if \( \text{Li}_2\text{CO}_3 \) is oxidized to produce \( \text{CO}_2 \). This rising potential caused serious problems with the electrochemical stability of the electrolyte during charging. In summary, the monolayer carbonate at the interface between carbon electrode and \( \text{Li}_2\text{O}_2 \) causes the exchange current density to decrease by about 10-100 times due to the interfacial resistance to charge transport. The monolayer of carbonate at the interface between \( \text{Li}_2\text{O}_2 \) and electrolyte results in a rising potential in charge and consequent electrolyte stability issues in high charge voltage plateau.
Figure 1.12 Panels indicate what happen in the deposit during discharging and charging cause the rising charging potential. Monolayer of Li$_2$CO$_3$ forms at the C interface during discharging, and some dispersed carbonate possibly forms because of electrolyte decomposition during charging.\textsuperscript{18}

1.4.4 Computational studies on carbon electrode

Computational studies on bulk electrode materials, surface of electrode, defects and lattice distortions, is essential to understand the reaction chemistry of Li$_2$O$_2$ growth and decomposition. The discharge reaction on carbon electrode was systematically studied by a simple graphitic carbon modeling.\textsuperscript{93} According to the DFT calculations (Figure 1.13), it was found that the graphitic basal plane does not stabilize the LiO$_2$ intermediate because of its chemical inertness. The reversible potential of the O$_2$ reduction is accordingly limited to the voltage of 1.1 V. The armchair edge and di-vacancy in basal plane of the defect sites, are found to be highly reactive and can be oxidized under ambient conditions to generate various CO$_x$ groups. Subsequently, according to the DFT results, the oxidized carbon species (CO$_x$) was reduced by Li through redox reaction at the voltage of 1.2-1.4 V. These CO$_x$ groups could also act as active sites for the catalytic reduction of O$_2$, occurring at the voltage of 1.8-2.3 V by stabilizing the LiO$_2$ intermediate.
Figure 1.13 Minimum-energy geometries in top (upper panels) and side (lower panels) views for Li-O species at the armchair edge: a) Li; b) epoxy (2C:1O); c) quinone (2C:2O); d) anhydride (2C:3O); e) carbonate (2C:4O); f) lactone (2C:5O); g) 2C:4O:4Li; h) LiO₂@2C:4O; i) LiO₂@2C:3O; j) lone carbonyl (1C:1O); k) 1C:1O:1Li. Grey, white, red, and small white spheres represent C, Li, O, and H atoms respectively.²³

1.4.5 Reaction kinetics on non-carbon electrode

As studies of carbonaceous electrodes discussed above, carbon was found to suffer from instability related to oxidation at high voltage and in the presence of the O₂-/LiO₂ and Li₂O₂. More recently, carbon-free electrodes have been under examination. In the work of Lu et al, the carbon used as a support was passivated by Al₂O₃ and the surface was decorated with Pd nanoparticles to drastically lower the overpotential on charge relative to a pure carbon electrode.⁴ Also, in the work of Peng et al., a nanoporous gold electrode was used in conjunction with a DMSO electrolyte to obtain 100 cycles with reversible capacity. Since all reactions occur at the surface of any given electrode material, an understanding of the surface reaction chemistry is required to design stable and active catalysts.¹⁷
Compared with intense studies on catalysts for oxygen evolution reaction, catalysts for oxygen reduction reaction was less studied in last decade. One of the reasons is that carbon materials have a good ORR performance with relatively low discharge polarization, compared with its poor OER performance with high charge polarization.\textsuperscript{87,95,96} The other reason is that OER catalyst is considered to be more important in reducing the charge overpotential.\textsuperscript{14,21,36,97} However, several studies have confirmed that ORR catalysts could greatly influence crystallinity and morphology of discharge product, as well as the nature of intermediate discharge products. As discussed above, Li$_2$O$_2$ preferentially exhibits a toroidal shape in a strongly solvating electrolyte as shown in Figure 1.14a. However, it has been claimed that embedding some of the crystalline catalysts in the electrode forms a film-like morphology on the electrode surface, as shown in Figure 1.14b. The reason for the different morphologies of the reaction products even in the same electrolyte is explained depending on the oxygen affinity of the catalyst. The catalyst surface can have a preferential affinity for the reactive oxygen species (O$_2$ and LiO$_2$), which will delay the release of LiO$_2$ into the electrolytes. Once captured on the surface, the discharge intermediate would combine with additional electrons to generate film-like Li$_2$O$_2$ instead of dissolving into the electrolyte.

Lu et al. suggested that the known solid LiO$_2$ intermediate could be stabilized by Ir-decorated reduced graphene oxides.\textsuperscript{98} With a similar crystal lattice with LiO$_2$, the generated intermetallic compound Ir$_3$Li is suspected to provide a favorable growth site for LiO$_2$ (Figure 1.14c). Therefore, epitaxial growth of LiO$_2$ on a (121) face of Ir$_3$Li could form a needle-stable intermediate by providing the active site for stable growth. This research provides an effective method in utilizing a metastable LiO$_2$ phase as a final discharge product, as well as proposes a novel Li-O$_2$ battery with an essentially
low overpotential. However, the proposed reaction pathway and discharge intermediate should be further verified before considering the practical feasibility.\textsuperscript{40,99}

Figure 1.14 Schematic illustration of morphologies of the discharge products with and without a catalyst. a) Toroidal-like Li$_2$O$_2$ forms in a strongly solvating electrolyte. b) Use of a catalyst can induce film-like formation. c) Epitaxial growth of the LiO$_2$ phase supported by a similar crystallographic lattice of the intermediate compound Ir$_3$Li.\textsuperscript{38}

1.4.6 Computational studies of on non-carbon electrode

Although there is a intense debate about the role of catalyst in Li-air batteries,\textsuperscript{83,100} the DFT calculation can provide some insights into the thermodynamics of catalysts in molecule-level, that either promote OER/ORR or accommodate Li$_x$O$_y$ species in their structures.\textsuperscript{92,101-106}

Dathar et al. suggested that the intrinsic activity of Li on the ORR of Au, Ag, Pt, Pd, Ir and Ru forms a volcano-like tendency (Figure 1.15), relative to the similar adsorption energy of H-ORR in hydrogen fuel cells.\textsuperscript{107} By ignoring the atomic defects, effects of
impurities, and electrolyte interfaces, Pt and Pd are predicted to be the most active metal for O₂ adsorption energy. The Au and Ag metal surfaces were found to be chemically inert with respect to other metals and have a relatively small O₂ adhesion probability. The strong oxygen-metal interactions of Ru and Ir is likely to reduce the ability of oxygen to bind to lithium. According to their calculation and conclusions, O₂ reduction involves an association mechanism that facilitates the disproportionation of LiO₂ to form Li₂O₂.

![Graph showing U_eq of the first e⁻ transfer step in the Li-ORR on the six metals plotted against the adsorption energy of atomic O relative to that on Pt, on the close-packed and step edge surfaces, respectively.](image)

**Figure 1.15** Uₐₐ of the first e⁻ transfer step in the Li-ORR on the six metals plotted against the adsorption energy of atomic O relative to that on Pt, on the close-packed and step edge surfaces, respectively.¹⁰⁷

The concept of a “dual-purpose” transition metal oxide as a lithium intercalation compound and the promotion of Li-O₂ reaction were proposed by Trahey *et al.*¹⁰⁸ Using DFT+U, they studied the insertion of Li and LiₓOᵧ into the 2×2 and 2×1 tunnels of α-MnO₂ and ramsdellite-MnO₂, respectively (**Figure 1.16a**). They found that when Li inserted into α-MnO₂ and ramsdellite-MnO₂ to form LiₓMnO₂, it occurs at 2.6-3.5 V, when x < 0.5, the voltage is higher than 3 V, and when x > 0.5, the voltage is lower than
3V. Since Li_2O_2 and Li_2O generate at an equilibrium voltage of about 3 V, Li intercalation α-MnO_2 and ramsdellite-MnO_2 reaction through Li-O_2 reactions. On the other hand, the insertion of Li_xO_y into the tunnels has an equilibrium voltage of 2.8-3.2 V, the lower limit of which is similar to the experimentally observed first discharge voltage. Therefore, the Li_xO_y species may be incorporated into the tunnel during the discharging process.

**Figure 1.16** a) Structures of α- and ramsdellite-MnO_2 showing 2×2 and 2×1 tunnels. b) DFT + U predicted equilibrium voltages for Li and Li_xO_y insertion into αMnO_2, compared to those of Li_2O and Li_2O_2 formation. c) Charge (green) on the O_2 molecule and O–O distance (blue), as well as binding energy (red) between the O_2 molecule and αMnO_2 surface, as a function of the position of an O_2 molecule inside/outside of the tunnel. The charge and O–O distance are scaled to vary between that of a neutral O_2 molecule and a superoxide anion.\textsuperscript{108}

The proximity of the voltages of Li_xO_y insertion into the tunnels of MnO_2 to the voltages of Li_2O or Li_2O_2 formation (Figure 1.16b), could be seen that MnO_2 act as a “Li_xO_y-storage materials”, which reversibly storing lithium-oxide species during the Li-O_2
reactions. The DFT calculation of O\textsubscript{2} entering through the tunnel entrance of partially lithiated α-MnO\textsubscript{2} (Figure 1.16c) indicates that the barriers to O\textsubscript{2} entry and exit from the tunnel are low, approximately 0.5 V and 0.2 eV, respectively. In addition, as shown in Figure 1.16c, the O\textsubscript{2} molecule is reduced to a superoxide species in terms of O-O bond length and Bader charge upon entering the tunnel. Instead, O\textsubscript{2}\textsuperscript{-} in the tunnel can be easily removed from the tunnel into neutral O\textsubscript{2} molecules. This indicates that the tunnel entrance of partially lithiated α-MnO\textsubscript{2} can effectively guide the ORR and OER.

1.5 The Influence of Atmospheric Contaminants on Reaction Chemistry

To achieve improvement from Li-O\textsubscript{2} batteries in an oxygen tank to practical Li-air batteries in ambient air, it is essential to investigate the possible influence of atmospheric contaminants on reaction chemistry. However, most researches to date on aprotic Li-air batteries used pure O\textsubscript{2} rather than air, for the purpose of avoiding unwanted parasitic reactions with air contaminants (H\textsubscript{2}O, CO\textsubscript{2}, etc.). Only a few studies focused on the influence of H\textsubscript{2}O and CO\textsubscript{2} on reaction chemistry for electrochemical performance. Through DEMS and FTIR, both H\textsubscript{2}O and CO\textsubscript{2} were found to increase the capacity of Li-O\textsubscript{2} batteries, change the reaction pathway for discharge/charge, as well as influence the electrochemical performance of batteries.

1.5.1 The influence of H\textsubscript{2}O on discharge/charge reaction

The influence of H\textsubscript{2}O on discharge reaction is nonnegligible that even a trace amount of water dissolved in aprotic electrolyte can have a significant effect on discharge reaction. One of the significant effects is that the addition of water in the electrolyte could increase the discharge capacity of lithium-air batteries.\textsuperscript{109-112}
Meini et al. investigated and discussed the influence of H$_2$O on discharge reaction of aprotic Li-air batteries. Small amounts of water were added into a DME/LiTFSI electrolyte before the cell was assembled. The introduction of even a small amount of H$_2$O (500 ppm) leads to a large increase in cell capacity (Figure 1.17a). However, the ratio of electron and oxygen (e$^-$/$O_2$) was observed as $\sim 2.05$, which is nearly identical to the ratio in pure DME/LiTFSI, regardless of the amount of water added to the electrolyte. The similar ratio of electron and oxygen indicates that Li$_2$O$_2$ formation is still the dominant discharge reaction, even in the presence of trace H$_2$O. Furthermore, cathodes were extracted after discharge and observed using FTIR, showing that the amount of Li$_2$O$_2$ on the cathode surface decreases with H$_2$O concentration increasing (Figure 1.17c). Therefore, it is confirmed that Li$_2$O$_2$ reacts with H$_2$O to generate soluble products such as H$_2$O$_2$ and LiOH. Since the discharge capacity is determined by electrical passivation of insulating Li$_2$O$_2$ on the surface of electrode, the capacity could obtain an increase after the removal of Li$_2$O$_2$. The influence of H$_2$O on charge reaction was also investigated in this study. Isotopic O$_2$ evolution was monitored after a discharge under $^{18}$O$_2$ and using H$_2^{16}$O as the contaminant (Figure 1.17b). Only $^{18}$O$_2$ evolution could be observed, which indicates that O$_2$ evolution only occurs from Li$_2$O$_2$ which was generated in discharge, yet from other species generated by the reaction of H$_2$O with Li$_2$O$_2$. Furthermore, the influence of H$_2$O on reaction chemistry is also reflected that O$_2$ evolution rate decreases at high concentration of H$_2$O, as well as H$_2$ evolution because of the H$_2$O reaction with the lithium metal anode. Above all, the H$_2$O contamination significantly influences reaction chemistry of aprotic Li-air batteries and reduces the rechargability of aprotic Li-air batteries.
Figure 1.17  

a) Galvanostatic discharge-charge curves for cells with 12, 500 and 5000 ppm H₂O contamination in the electrolyte (XC 72 carbon based cathode, 1M LiTFSI in DME electrolyte, i = 0.47 mA/cm², discharge under \(^{18}\)O₂, charge under Ar);  
b) \(^{18}\)O₂ evolution for cells studies in a) \(^{18}\)O₂ was the only O₂ isotope evolved);  
c) FTIR of extracted P50 cathodes discharged for 5 mAh in the H₂O-contaminated electrolytes.¹¹¹  

To explain the increasing capacity by introduction of H₂O, another mechanism was proposed that the addition of water in the electrolyte aids in the dissolution of LiO₂⁺ from the electrode surface and the formation of large crystalline Li₂O₂ (Figure 1.18a).³⁹  

Specifically, H₂O as a strong electron acceptor, could stabilize O₂⁻ in electrolyte and promote the dissolution of LiO₂⁺ into the electrolyte, which sequentially allows the disproportionation reaction to generate Li₂O₂ and O₂. This induced solution mechanism leading to the precipitation of large toroidal Li₂O₂, could explain the substantially enhanced discharge capacity by increasing the content of H₂O in the electrolyte.  
(Figure 1.18b), as well as the gradually noticeable toroidal particles schematically illustrated (Figure 1.18c). Another explanation is proposed by Kwabi et al. that H₂O
decreases the nucleation rate of Li$_2$O$_2$ at the electrode surface, leading to large Li$_2$O$_2$ growth through solution-mediated growth.$^{110}$

![Image](image.png)

**Figure 1.18** Influence of H$_2$O on reaction chemistry of aprotic Li–air batteries.$^{38}$ a) XRD patterns of the discharged electrodes 1 M LiTFSI in DME with different H$_2$O contents.$^{39}$ b) Relation between discharge capacities and increasing H$_2$O contents.$^{39}$ c) Schematic illustration of different morphologies of Li$_2$O$_2$ in aprotic electrolyte with different H$_2$O contents.$^{113}$

The other significant effect of H$_2$O is that the addition of water could change discharge product in aprotic Li-air batteries. Discharge products generated in the electrolyte with H$_2$O is in disk shape, instead of typical toroidal shape in the electrolyte without H$_2$O. Zhou *et al.* suggested that excessive amount of H$_2$O would react with Li$_2$O$_2$ in discharge, producing LiOH and H$_2$O$_2$ by the reaction of Li$_2$O$_2$(s) + 2H$_2$O(l) = 2LiOH(s) + H$_2$O$_2$(l). The H$_2$O$_2$ is then decomposed into H$_2$O and O$_2$ with the aid of electrolytic manganese oxide by the reaction of H$_2$O$_2$(l) = H$_2$O(l) + 1/2O$_2$(g). The use of electrolytic manganese
oxide triggers continuous generation of LiOH with discharge processing.\textsuperscript{113-116} Large toroidal particles of Li\textsubscript{2}O\textsubscript{2} react with H\textsubscript{2}O, forming large sheets of the LiOH in the electrode. Moreover, Liu et al. revealed that LiI could also induce the growth of large LiOH crystals.\textsuperscript{117} The reversible deposition and decomposition of large LiOH crystals with the help of LiI could lead to an extremely low charge overpotential and a high specific capacity. A series of studies above have confirmed that the H\textsubscript{2}O content in the electrolyte has significant influence on reaction chemistry by tuning the nature of discharge products. Therefore, the H\textsubscript{2}O contamination should be carefully controlled in aprotic Li-air batteries.

1.5.2 The influence of CO\textsubscript{2} on discharge/charge reaction

CO\textsubscript{2} is known to react with Li\textsubscript{2}O\textsubscript{2} to generate Li\textsubscript{2}CO\textsubscript{3} and O\textsubscript{2} via the reaction of CO\textsubscript{2} + Li\textsubscript{2}O\textsubscript{2} = Li\textsubscript{2}CO\textsubscript{3} + 1/2 O\textsubscript{2}.\textsuperscript{118} Hence, the formation of Li\textsubscript{2}CO\textsubscript{3} from CO\textsubscript{2} contamination could also influence the battery performance, as similar as the effects of Li\textsubscript{2}CO\textsubscript{3} derived from instability of electrolyte or Li\textsubscript{2}CO\textsubscript{3} produced owing to C cathode instability.

Gowda et al. investigated the influence of CO\textsubscript{2} on Li-air batteries by discharging cells under different atmosphere: pure CO\textsubscript{2}, pure O\textsubscript{2}, and CO\textsubscript{2}/O\textsubscript{2} mixture with the ratio of 10/90 (\textbf{Figure 1.19a}).\textsuperscript{119} Under a mixture of CO\textsubscript{2}/O\textsubscript{2}, the cell has a similar discharge voltage plateau (~2.6 V) as that of the cell under pure O\textsubscript{2}, although delivering a larger discharge capacity. The ratio of (e\textsuperscript{−}/O\textsubscript{2})\textsubscript{dis} is ~2.0 at the discharge voltage plateau of 2.6 V, regardless of CO\textsubscript{2} contamination occurring. This indicates that the dominant reaction product in discharge is still Li\textsubscript{2}O\textsubscript{2} even if CO\textsubscript{2} with ratio of 10 % involved. However, FTIR of discharged electrodes indicates that significant Li\textsubscript{2}CO\textsubscript{3} deposited in discharge under CO\textsubscript{2}/O\textsubscript{2} atmosphere. As shown in \textbf{Figure 1.19b}, FTIR spectra of electrodes discharged under a pure O\textsubscript{2} and a CO\textsubscript{2}/O\textsubscript{2} was compared. In each case, a large Li\textsubscript{2}O\textsubscript{2}
absorbance could be observed, with smaller amounts of HCO$_2$Li, Li$_2$CO$_3$, and LiTFSI presented. For the discharged electrode under CO$_2$/O$_2$, Li$_2$CO$_3$ and HCO$_2$Li absorbance are significantly higher than that under pure O$_2$. These results confirm that some Li$_2$O$_2$ formed through spontaneous chemical reaction with CO$_2$ to generate Li$_2$CO$_3$, instead of electrochemical reaction in discharge.

**Figure 1.19** a) Galvanostatic discharge profiles (0.47 mA/cm$^2$) of Li cells discharged under three atmospheres: pure CO$_2$, pure O$_2$, and a 10:90 CO$_2$/O$_2$ mixture. XC27-based cathodes were used. b) FTIR of cathodes extracted from cells discharged (0.9 mA/cm$^2$, 4.7 mAh/cm$^2$) under pure O$_2$ and a 10:90 CO$_2$/O$_2$ mixture. In the pure O$_2$ spectra, peaks at 1064, 1138, 1202, and 1340 cm$^{-1}$ can all be attributed to the electrolyte salt (LiTFSI). P50 carbon paper was used as the cathode.$^{119}$

It is worth noting that batteries discharged under CO$_2$/O$_2$ exhibit higher capacity than batteries discharged under pure O$_2$. The exact mechanism for increasing the discharge capacity is unclear, but consistent with another study showed that CO$_2$/O$_2$ mixtures exhibited higher capacity than under pure O$_2$.\textsuperscript{120} It is probably that the increase in capacity is related to morphological changes. The spontaneous reaction between CO$_2$ and Li$_2$O$_2$ also affects the charging behavior of the Li-air batteries. The first galvanostatic discharge and charge cycle of cells discharged under pure O$_2$ and CO$_2$/O$_2$
are compared in Figure 1.20. The more rapid rise in charging potential with charge capacity for the CO₂/O₂ cell is likely due to increased concentrations of Li₂CO₃ at the Li₂O₂-electrolyte interface. O₂ evolution at the onset of charge (3-3.5 V) for both cells is ~2.1-2.2 V (e⁻/O₂)chg. Both cells also exhibit a decrease in O₂ generation as the charge proceeds, although the decrease is significantly faster in the CO₂/O₂ cell. CO₂ is also evolved in both cells at U>4.2 V, with significantly more CO₂ evolved from the CO₂/O₂ cell. More CO₂ evolution and faster reduction in the rate of oxygen evolution also indicate the presence of higher Li₂CO₃ concentration compared to Li₂O₂, in the CO₂/O₂ cell cathode than the pure O₂ cell cathode.

Figure 1.20 Galvanostatic discharge and charge (0.47 mA/cm²) of cells discharged under a1–c1) a pure ^18O₂ headspace and a2–c2) a 10:90 C¹⁸O₂/¹⁶O₂ mixture. a) discharge and charge profiles under different atmosphere. b) O₂ evolution rate (m’O₂) during cell charge. c) isotopic CO₂ evolution rate (m’) during cell charge. Cells were charged under an Ar headspace.¹¹⁹
In the cell discharged under CO\(_2\)/O\(_2\), carbonate deposits are present not only from cathode and electrolyte decomposition but also from the thermal reaction between atmospheric CO\(_2\) and Li\(_2\)O\(_2\). By artificially creating a higher Li\(_2\)CO\(_3\) concentration in the bulk electrodeposit via the reaction between Li\(_2\)O\(_2\) and CO\(_2\), the observed charge overpotential increase as shown in Figure 1.20-a1) and Figure 1.20-a2). These results have indicated that Li\(_2\)CO\(_3\) or other insoluble species deposited on the surface of electrode, resulting from atmospheric contaminants, will have a detrimental influence on round-trip efficiency.

As discussed above, it is clear that H\(_2\)O and CO\(_2\) will be detrimental to reaction chemistry of Li-air batteries and must be removed from feeding air for Li-air batteries. The “oxygen-diffusion” membrane was proposed and designed that selectively permeates O\(_2\) and retains other gaseous species.\(^{121}\) However, the biggest problem of such a membrane is that the critical parameters are unknown at this pioneering stage. Although this membrane is technically feasible to eliminate CO\(_2\) and H\(_2\)O in ambient air, it is still unclear whether this membrane could be employed in practical application as other technical issues are addressed. As H\(_2\)O is polar molecules, it is much easier to be separated compared to CO\(_2\). If H\(_2\)O could be separated successfully, to develop a catalyst decomposing both Li\(_2\)CO\(_3\) and Li\(_2\)O\(_2\) at low charge voltage plateau would be another possible approach.

**1.6 Scope of this Thesis**

Chapter 1 is a general introduction of pertinent research that has been undertaken in past few years on the aprotic Li-air batteries. Chapter 2 is an overview of the research methods and techniques that were used in this thesis. Chapter 3 contains the results of a study on the influence of molybdenum carbide in a Li-CO\(_2\) battery. The work has
on molybdenum carbide under oxygen, and the extension of this type of catalyst into 
practical Li-air batteries. The work has been published elsewhere: Hou, Y., Liu, Y., 
the intermediate species towards practical Li-air batteries” Electrochim. Acta (2018), 
259, 313-320; Copyright 2018: Elsevier. Chapter 5 contains a fundamental study on 
Li₂O₂ and Li₂CO₃-preloaded carbon-based electrode (Vulcan C) and non-carbon-based 
electrode (molybdenum carbide) under O₂ and CO₂, as well as the electrochemical test 
of commercial molybdenum and SEI modified carbon. The work has been summarized 
and in preparation for submission. Chapter 6 concludes and summarizes this entire 
thesis, and additionally proposes some perspective of carbon-based and non-carbon-
based catalyst design for Li-air batteries.

1.7 References

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Chapter 2: Experimental Methods and Theory

2.1 Chemicals and Materials

The chemicals and materials used in this doctoral work are summarized in Table 2.1.

Table 2.1 Chemicals and materials used in this work:

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<th>Chemicals / Materials</th>
<th>Purity</th>
<th>Supplier</th>
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<td>1-methyl-2-pyrrolidinone</td>
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<td>Sigma-Aldrich</td>
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<td>Ammonium molybdate tetrahydrate</td>
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<td>Ammonium peroxydisulfate</td>
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<td>Timcal</td>
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<tr>
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<td>Carbon paper</td>
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<td>Sigma-Aldrich</td>
</tr>
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<td>Cabot Corp.</td>
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</table>
2.2 Preparation Techniques

2.2.1 Ball mill

Ball milling is a grinding method that grinds materials such as ores, chemicals, ceramics into fine powders. With its development, the high energy ball-milling method has been used extensively to produce alloys from powders, as well as been widely used in the preparation of materials for energy storage system.\textsuperscript{1,2} The ball mill typically consists of a hollow cylindrical shell rotating around its axis. The axis of the shell may be either horizontal or with a small horizontal angle. It is generally filled with the milling balls, which made of tough materials such as stainless steel, ceramic, or zirconia. The inner surface of the cylindrical shell is usually made up of abrasion-resistant materials such as rubber or manganese steel. In this doctoral work, a QM-1SP2 Planetary ball mill (Figure 2.1) was used to mix precursors for and electrode materials.

\textbf{Figure 2.1} Photograph of QM-1SP2 Planetary ball mill
2.2.2 Tube furnace

A tube furnace is an electric heating device used in inorganic compounds synthesis generally and in organic synthesis occasionally. The tube furnace consists of a cylindrical cavity surrounded by heating coils. Some advanced tube furnaces have two or three heating zones for transforming experiments, in that temperature can be precisely controlled by the thermocouple. Some temperature controllers could be digitally permitted to using program segments such as ramping, soaking, or sintering. Materials offered in certain models, such as molybdenum di-silicide, could produce working temperatures up to 1800 °C. The commonly used materials for the reaction tubes include alumina and fused quartz. Samples are placed inside the tube in ceramic or quartz boas using a long push rod. In this doctoral work, Carbolite TZF-12 tube furnace was used for thermal treatment of our materials under argon atmosphere (Figure 2.2).

Figure 2.2 Photograph of Carbolite TZF-12 tube furnace.
2.3 Electrochemical Methods

2.3.1 Electrode fabrication

2.3.1.1 Gas diffusion electrodes

In Chapter 3, 4 and 5, the gas diffusion electrodes were prepared by casting active (catalyst materials + binder) layer on Toray carbon paper. Active materials, NMP and PVDF were well mechanically mixed for 10 minutes. Films of this mixture were cast onto the Toray carbon paper ($1.5 \text{ cm}^2$). These electrodes were dried at 120 °C in vacuum oven for 24 hours. Details about electrode especially the ratio of catalyst materials, binder and conductive carbon (not in all electrode) are noted in each chapter.

2.3.1.2 Preloaded electrodes

In Chapter 5, the $\text{Li}_2\text{O}_2$-preloaded Vulcan C cathodes were made by combining Vulcan XC carbon (Cabot Corp.), $\text{Li}_2\text{O}_2$ (Sigma-Aldrich, 90%) and PVDF power with a weight ratio of 4:1:1 in NMP and casting the mixture on Toray carbon paper. The $\text{Li}_2\text{CO}_3$-preloaed Vulcan C cathodes were made by combining Vulcan XC carbon (Cabot Corp.), $\text{Li}_2\text{CO}_3$ (Sigma-Aldrich, 99%) and PVDF power with a weight ratio of 4:1:1 in NMP and casting the mixture on Toray carbon paper. The $\text{Li}_2\text{O}_2$-preloaded $\text{Mo}_2\text{C}$ cathodes were made by combining commercial $\text{Mo}_2\text{C}$ (Sigma-Aldrich, 99.5%), $\text{Li}_2\text{O}_2$ (Sigma-Aldrich, 90%) and PVDF power with a weight ratio of 8:1:1 in NMP and casting the mixture on Toray carbon paper. The $\text{Li}_2\text{CO}_3$-preloaed $\text{Mo}_2\text{C}$ cathodes were made by combining $\text{Mo}_2\text{C}$ (Sigma-Aldrich, 99.5%), $\text{Li}_2\text{CO}_3$ (Sigma-Aldrich, 99%) and PVDF power with a weight ratio of 8:1:1 in NMP and casting the mixture on Toray carbon paper. The preparation of electrode was carried out in an argon filled glove box ($\text{H}_2\text{O}$ and $\text{O}_2$ content < 1ppm). These preloaded electrodes were dried at 80 °C in glove box.
to remove NMP. The fresh bottles of lithium peroxide and lithium carbonate were used as received.

2.3.2 Electrochemical cell assembly

Non-aqueous Li-O₂ cells were assembled using a modified coin cell design (Figure 2.3)⁴. 1M LiCF₃SO₃ in dry, distilled TEGDME electrolyte was used in all studies. A typical cell was assembled in an argon filled glovebox with a cathode case, a gasket, a gas diffusion electrode coated with catalyst, a porous separator, a lithium metal anode, a spacer, a spring and an anode case in sequence. 100 μl of electrolyte was added to the separator during cell assembly.

![Stacking components of a modified CR2032 coin cell](image)

**Figure 2.3** Stacking components of a modified CR2032 coin cell⁴.

2.3.3 Cyclic voltammetry

As a type of potentiodynamic electrochemical measurement, cyclic voltammetry (CV) is widely used to probe the kinetics and thermodynamics of the electron transfer in the reaction of an electrochemical cell.⁵ In a cyclic voltammetry experiment, the working electrode potential is ramped linearly versus time (Figure 2.4a). After the set potential
is reached, the working electrode’s potential is ramped in the opposite direction to return to the initial potential. A pair of distinct peaks could be observed at both forward and reverse scans, if a redox reaction is present in the electrochemical reaction. In this doctoral work, the CV was performed using a CHI 720C electrochemical work station (Figure 2.4b), and the applied scan rates varied from 0.1 mV s\(^{-1}\) to 1 mV s\(^{-1}\).

![Example of the applied signal for cyclic voltammetry](image)

**Figure 2.4** a) Example of the applied signal for cyclic voltammetry; b) Photograph of CHI 720C electrochemical workstation.

### 2.3.4 Galvanostatic cycling

The galvanostatic cycling is a technique commonly used to investigate the capacity and cycling performance of the materials for batteries.\(^{6-8}\) With this technique, a constant current is applied to the testing cell until a predetermined cut-off voltage or capacity is reached and the current is reversed. When a negative current is applied, the battery is being discharged; and when a positive current is applied, the battery is being charged. The discharge or charge capacity \((Q)\) can be plotted simply as electrical charge and calculated as the applied current \((I)\) multiplied by the time \((t)\): \(Q = I \times t\), or also normalized to the surface area or mass of the electrode. The testing cells underwent galvanostatic discharge/charge using various current densities to either cutoff voltage or cutoff capacity. In this doctoral work, the cells were equilibrated at open circuit for
4 h before testing and were controlled with a Land CT 2001 battery testing system (Land®, Wuhan, China) (Figure 2.5) in different atmosphere (pure O₂, pure CO₂, mixed O₂/CO₂, and ambient air) at room temperature.

**Figure 2.5** Photograph of Land CT 2001 battery testing system

### 2.3.5 Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) is an important experimental measurement technique to test the inner resistance of a Li-air battery.⁹ EIS could be determined by the electrochemical processes including charge transfer, ion diffusion, mass transport and chemical reactions, and the interpretation of the resulting spectra is aided by analogy to equivalent circuits. In a typical EIS impedance spectrum, a high frequency semicircle included corresponds to the kinetic process, and a low frequency linear tail included relates to the diffusion of ions into electrode materials. In this doctoral work, EIS data were collected to investigate the on a Princeton 2273 workstation (Princeton Applied Research), and the frequency range was from 100 kHz to 0.01 Hz.
2.4 Characterization Techniques

2.5.1 Scanning electron microscopy

The scanning electron microscopy (SEM) is an imaging tool that provides information about the morphology and topography of the specimen at nanoscale. In principle, the electron gun produces high-energy electrons that are focused into a beam, scanning across the surface of the sample. The elastic and inelastic interaction of the beam electrons with the sample atoms produces a wide variety of radiation products, such as secondary electrons, backscattered electrons, absorbed electrons, etc. When the primary electron beam strikes the sample, it is determined that an electron beam interaction process occurs, and then secondary electrons (SEs) and backscattered electrons (BSEs) are generated. A particular type of detector can detect the SEs and BSEs, and the detector signal can be used to create an image and provide information about the nature of the sample.

Figure 2.6 Photograph of JEOL-7500FA field-emission scanning electron microscope (FE-SEM) with a Bruker X-Flash 4010 SDD energy-dispersive X-ray detector.
In this doctoral work, materials and electrodes were observed with a field-emission scanning electron microscopy (FE-SEM, JEOL JSM-7500FA, 15kV, shown in Figure 2.6).

2.5.2 X-Ray diffraction

X-ray diffraction (XRD) is a basic and robust technique to identify an unknown crystallographic structure, the crystalline size (grain size), and the preferred orientation in polycrystalline or powdered solid samples. The principle of XRD is illustrated in Figure 2.7a. In XRD, X-rays strike a powder sample at a certain incident angle and since the powder is composed of small crystals, a portion of these crystals will be oriented with their crystallographic planes at the Bragg angle \( \theta \). Since every crystal features a set of unique \( d \)-spacings, the XRD pattern has a functional relationship with the crystal structure, which is described by Bragg’s law: \( n\lambda = 2d \sin \theta \), where \( n \) is an integer, \( \lambda \) is the wavelength of the incident X-ray beam, \( d \) is the lattice spacing of the given crystal, and \( \theta \) is the incidence angle. In this doctoral work, all the XRD measurement were performed using a GBC MMA X-ray generator and diffractometer with Cu K\( \alpha \) radiation (\( \lambda = 1.5406 \) Å) (Figure 2.7b).

![Figure 2.7](image.png)

**Figure 2.7** a) Schematic illustration of Bragg’s Law as the principle of XRD; b) Photograph of GBC MMA XRD machine used for XRD experiments.
2.5.3 Raman spectroscopy

Raman spectroscopy is a powerful characterization method to investigate the structure of a material.\textsuperscript{12} It can provide the vibrational, rotational, and other low frequency modes of a structure. In Raman spectroscopy, laser light from a monochromatic light source is employed to irradiate the sample, leading to both elastic scattering (Rayleigh scattering) and inelastic scattering (Stokes and anti-Stokes Raman scattering). Energy shifts from the incident radiation occur in Stokes and anti-Stokes Raman scattering, which are called the Raman effects. These energy shifts reflect the frequency or wavelength of a specific chemical composition and structure. By comparing the obtained spectra, materials with specific molecular features can be identified. Raman spectroscopy therefore is employer as a complementary measurement technique to XRD. In this doctoral work, the Raman spectroscopy was performed using a JOBIN YVON HR 800 Horiba Raman spectrometer (Figure 2.8) with the laser wavelength at 623.8 nm. A neutral density filter was applied to adjust the laser intensity in the measurement.

\textbf{Figure 2.8} Photograph of JOBIN YVON HR 800 Horiba Raman spectrometer.
2.5.4 **Fourier transform infrared spectroscopy**

Fourier transform infrared spectroscopy (FTIR) is a commonly used means of analysis of absorption spectroscopy.\textsuperscript{13} The absorption, emission, photoconductivity, or Raman scattering in the infrared spectrum of a material can be collected. In the testing process, IR radiation interacts with the material through which the infrared radiation is transmitted or absorbed. After that, the chemical bonds in the molecules of the sample material can be detected from the spectral pattern of molecular absorption and transmission. In this doctoral work, FTIR spectra were collected on a Shimazu IR Presting-21 model Fourier transform infrared spectrometer (**Figure 2.9**). For measurement, the sample materials were mixed with potassium bromide (KBr) powder, which acts as the background, and pressed in a die with a barrel.

**Figure 2.9** Photograph of Shimazu IR Presting-21 model Fourier transform infrared spectrometer.
2.5.5 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is a surface-sensitive quantitative spectroscopic method to analyze the surface chemistry of a material.\textsuperscript{14} It can provide information on the elemental composition, empirical formula, chemical state, and electronic state of the elements within a material. When a beam of X-rays is employed to interact with the sample material, the kinetic energy and number of electrons that escape from the top surface of the material (0-10 nm) are simultaneously monitored, from which the XPS spectra are obtained. Based on the characteristic binding energies associated with electrons in their orbitals, the valence states and the ratios of the valence states of elements could be determined. In this doctoral work, XPS analysis was conducted on a VG Scientific ESCALAB 2201XL system using Al K\textsubscript{α} X-ray radiation and fixed analyzer transmission mode (Figure 2.10). A commercial XPS 2.3.15 software package was used to analyze the XPS data.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2_10.jpg}
\caption{Photograph of VG Scientific ESCALAB 2201XL system.}
\end{figure}
2.5.6 Thermo-gravimetric analysis

Thermo-gravimetric analysis (TGA) is a widely utilized weight analysis technique. It shows the weight changes with the increasing temperature, revealing information on the physical and chemical properties of materials. A typical thermo-gravimetric analyzer consists of a sample pan located inside the furnace, a precision balance, and a programmable temperature controlling system. The temperature is generally increased at constant rate to incur a thermal reaction, so this analysis could show some of the material characteristics reflected by the precise weight changes caused by oxidation, decomposition, or loss of volatiles. In this doctoral work, TGA was conducted using Q500 (TA Instruments) (shown in Figure 2.11) in air, with the Q Series software V.2.5.0.255 for data analysis. The testing temperature range is generally from room temperature to 950 °C at a rising rate of 10 °C min⁻¹.

Figure 2.11 Photograph of TGA Q500 system.
2.5.7 Transmission electron microscopy

Transmission electron microscopy (TEM) is a microscopy technique based on the principle that a beam of electrons transmits through a sample to form an image.\textsuperscript{16} After the electron transmission and interaction with the specimen, the image is magnified and focused on the imaging device. It is used to characterize morphology, electronic structure, lattice spacing, crystal orientation, sample-induced electron phase shifts of sample materials.\textsuperscript{17} Additionally, selected area electron diffraction (SAED), as a crystallographic experimental technique coupled with TEM, is used to identify crystal phases and their orientations.

In this doctoral work, the TEM observations were carried out on a JEOL 2011 TEM (200 keV) (\textbf{Figure 2.12a}) and a JEOL ARM-200F TEM (200 keV) (\textbf{Figure 2.12b}). After ultrasonic dispersion in ethanol, the sample dispersion was dropped and dried on a copper grid with holey carbon support film. The grid was then loaded onto a sample holder, which was attached to the specimen stage.

\textbf{Figure 2.12} Photographs of \textbf{a) JEOL 2011 TEM and b) JEOL ARM-200F TEM}

2.5.8 Energy dispersive X-ray spectroscopy

Energy-dispersive X-ray spectroscopy (EDS) is an analytical technique used for the
elemental analysis or chemical characterization of a sample. The characterization of EDS is based on the fundamental principle that each element has a unique atomic structure allowing a unique set of peaks on its electromagnetic emission spectrum. To stimulate the emission of characteristic X-rays from the sample, a high-energy beam of charged particles such as protons, electrons or a beam of X-rays, is focused into the sample. The number and energy of the X-rays emitted from the sample can be measured by an energy-dispersive spectrometer. As the energies of the X-rays are characteristic of the difference in energy between the two shells and of the atomic structure of the emitting element, EDS allows the elemental composition of the specimen to be measured. In this doctoral work, EDS results in the SEM observations were collected by a Bruker X-Flash 4010 SDD energy-dispersive X-ray detector (10 mm², 127 eV), and EDS results in the TEM observations were collected by a JEOL Centurio SDD detector (100 mm²).

2.5 Basic Concepts of Electrochemical Properties

Some basic concepts of electrochemical properties are illustrated in order to properly describe the electrochemical properties and evaluate the cell performance.

2.5.1 Potential

Each electrochemical reaction relates to a standard electrode potential ($E^o$). It could be calculated from the Gibbs free energy ($\Delta G^o$) from Equation (2-1):

$$\Delta G^o = W = -nF E^o$$  \hspace{1cm} (2-1)

If all Gibbs free energy was completely transformed to electrical energy, the electrode potential ($E^e$) could be calculated from Equation (2-2) as follows:
\[ E' = -\Delta G^o / nF \quad (2-2) \]

Where \( \Delta G^o \) is the Gibbs free energy, \( F \) is the Faraday constant \((96485 \text{ C mol}^{-1})\), \( n \) is the number of electrons involved in a stochiometric reaction, and \( E^o \) is the electrode potential.

### 2.5.2 Overpotential

In electrochemistry, overpotential refers the potential difference between the experimental observed potential in a redox reaction and its thermodynamically determined potential. In batteries, the existence of overpotential implies the cell requires more energy than thermodynamically expected to drive a reaction.

### 2.5.3 Capacity

Capacity of batteries refers the total charge that the cathode or anode delivers in the redox reaction during the charge/discharge process. It can be calculated by Equation (2-3):

\[ Q = \int I(t)dt = nzF \quad (2-3) \]

Where \( I(t) \) is the current, \( t \) is the time, \( n \) is the number of the ions, \( z \) is the valence of the ions, and \( F \) is the Faraday constant \((96485 \text{ C mol}^{-1})\).

### 2.5.4 Round-trip Efficiency

Round-trip efficiency is defined as the ratio of the energy recovered from the energy storage device and the energy put into the device. The round-trip efficiency can never be equal to 100 % because there will be energy losses e.g. heat loss inside the energy storage device.
2.6 References


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Chapter 3: Mo2C/CNT as an Efficient Catalyst for Rechargeable Li-CO2 Batteries

3.1 Introduction

Due to the increasingly serious greenhouse effect on the global climate, the increasing CO2 content in the atmosphere has received significant attention in recent years. As a result, several technologies including CO2 capture, CO2 conversion, as well as CO2 electrochemical reduction, have been developed to control the concentration of CO2 in the atmosphere.1-4 To find a method to utilize CO2, the strategy of enhancing the discharge capacity of the Li-air battery by combining CO2 with oxygen was proposed.5 The formation of Li2CO3 during the discharge process can be seen as a novel method to capture and utilize CO2, but the difficult electrochemical decomposition of Li2CO3 has limited its use as a secondary battery. In the light of this, a primary Li-CO2 battery was reported as a novel method for CO2 capture and utilization, which showed a tremendous enhancement at 100 °C compared with its performance at low temperature.6 Recently, Lim et al. found that the electrochemical activation of CO2 within the high dielectric medium of dimethyl sulfoxide (DMSO) led to Li2CO3 as a side product of Li-O2 batteries, which was formed and decomposed reversibly.7 On the basis of this reversible reaction of Li2CO3, a rechargeable Li-CO2 battery was first proposed as a novel battery and CO2 conversion device.8 The utilization of this greenhouse gas in electrochemical energy storage systems provides a promising environmental friendly strategy for reducing fossil fuel energy consumption and slowing global warming.9-11 Moreover, this kind of metal-CO2 battery has the potential to become the energy source for scientific exploration and future immigration to Mars in the long run, since the atmosphere of Mars is composed mostly of carbon dioxide. In addition, with the
presence of CO₂ in ambient air, it is still a challenge to develop Li-air batteries, since Li₂CO₃ is formed upon discharge as the side product. Only through a better understanding of the mechanism of the Li-CO₂ battery can we hope realize expansion of the application of the Li-O₂ battery to the Li-air battery.¹²

Carbon materials have been extensively utilized as the cathode materials in the rechargeable Li-CO₂ batteries investigated so far, mainly because of their adequate electrical conductivity and large surface area.⁸,⁹,¹³,¹⁴ According to previous experimental results, rechargeable Li-CO₂ batteries were realized based on the reversible reaction: 4Li + 3CO₂ ↔ 2Li₂CO₃ + C.⁶,⁸ This electrochemical reaction shows that lithium ions combine with electrons and CO₂ to form Li₂CO₃ and carbon during discharge in the forward reaction, and Li₂CO₃ combines with carbon to release lithium ions, electrons and CO₂ during charge in the backward reaction. It was also calculated that the theoretical potential is about 2.8 V, based on the formula \( E = -\Delta G/\eta F \), in which \( \Delta G \) represents the change in Gibbs free energy, \( \eta \) is the electron transfer number, and \( F \) is the Faraday constant.⁶ Unfortunately, Li₂CO₃ is a wide band-gap insulator and insoluble in this aprotic system. As a result, Li₂CO₃ is deposited on the cathode and accumulates upon discharge, leading to an increase in the impedance up to a “sudden death”, similar to the case of Li₂O₂ deposits during discharge in the aprotic Li-O₂ battery, which causes a high overpotential for Li₂O₂ decomposition during charge process. Therefore, it is essential to develop new cathode materials to reduce this high charge potential plateau and to improve the round-trip efficiency.

Molybdenum carbide (Mo₂C) has been widely studied due to its excellent catalytic behavior, similar to that of metals in group VIII, and has attracted extensive attention for methane reforming,¹⁵ the water gas shift reaction,¹⁶ the hydrogen evolution reaction
(HER),\textsuperscript{17,18} and the CO\textsubscript{2} reduction reaction.\textsuperscript{19} Compared with Mo, the high activity of Mo\textsubscript{2}C originates from the electronic properties introduced by the carbon, which affects the Mo–C binding energy and the reactivity of adsorbates. Most recently, as the catalyst for Li-O\textsubscript{2} batteries, Mo\textsubscript{2}C showed high electrical efficiency and reversibility due to its partially oxidized surface.\textsuperscript{20}

In this work, we employed Mo\textsubscript{2}C/carbon nanotube (CNT) as the cathode for rechargeable Li-CO\textsubscript{2} batteries. With its three-dimensional (3D) network of uniformly dispersed Mo\textsubscript{2}C nanoparticles as catalysis sites and CNTs as the conductive matrix, this cathode material has reduced the charge plateau below 3.5 V and could be reversibly discharged and charged for 40 cycles. Through a series of ex-situ characterizations, we found that the reversible formation and decomposition of the amorphous discharge product Li\textsubscript{2}C\textsubscript{2}O\textsubscript{4}-Mo\textsubscript{2}C can reduce charge overpotential and improve the round-trip efficiency of the rechargeable Li-CO\textsubscript{2} battery. The introduction of Mo\textsubscript{2}C has set a good example for guiding new catalyst design to improve the energy efficiency of Li-CO\textsubscript{2} batteries. Moreover, this work provides a feasible method to resolve the problem of atmospheric CO\textsubscript{2} in Li-O\textsubscript{2} batteries.

3.2 Experimental Details

3.2.1 Synthesis of Mo\textsubscript{2}C/CNT materials

Molybdenum carbide (Mo\textsubscript{2}C)/carbon nanotube (CNT) composite material was prepared via carbothermic reduction of a mixture of molybdenum trioxide (MoO\textsubscript{3}) and CNTs. In a typical procedure, the starting materials (MoO\textsubscript{3} and CNTs) were accurately weighed according to the stoichiometric amounts for the equation of 2MoO\textsubscript{3} + 7C = Mo\textsubscript{2}C + 6CO and mixed by ball milling for 24 hour. The rotation speed and ball-to-
powder weight ratio were 300 rpm and 20:1, respectively. To protect the materials from oxidation, the milling operation was carried out under high purity Ar atmosphere. After that, the mixture was heated to 950 °C at the heating rate of 10 °C min⁻¹, and maintained for 1 hour.

3.2.2 Preparation of Li-CO₂ batteries

Mo₂C/CNT (or pure CNT) materials were mixed in N-methyl-2-pyrrolidone (NMP) liquid with a polyvinylidene fluoride binder (PVDF), with a weight ratio of active materials to PVDF of 8:2. The slurry was pasted onto carbon paper disks (diameter of 14 mm) and dried for 12 hours at 120 °C under vacuum to remove the residual solvent. The loading of electrodes was ~4 mg. Electrochemical tests were carried out using coin cells containing the active material working electrode, a lithium metal anode, and electrolyte (1 M LiCF₃SO₃ in tetraethylene glycol dimethyl ether (TEGDME) impregnated into a glass fiber separator (Whatman GF/D microfiber filter paper, 2.7 μm pore size). All cell assembly procedures were conducted in an argon-filled glovebox (oxygen and water contents less than 0.1 ppm). Tests were carried out in a CO₂-filled chamber, and before testing, the cells were placed in this CO₂-filled chamber to allow stabilization for 3 hours.

3.2.3 Physical characterizations

Powder X-ray diffraction (XRD) was performed on a GBC MMA XRD (λ = 1.54 Å), with the voltage and current kept at −40 kV and 25 mA, respectively. Scanning electron microscopy (SEM) images were obtained from a JEOL JSM-7500FA field emission SEM, in which the accelerating voltage was set at 5.0 kV and the emission current was 10 mA. Transmission electron microscopy (TEM) investigations were performed using a 200 kV JEOL ARM-200F instrument. Raman spectroscopy was carried out on a
Jobin-Yvon Horiba 800 with a 10 mW helium/neon laser at 632.81 nm excitation. Thermogravimetric analysis (TGA) was carried out in air using a Q500 (TA Instruments), with data analysis carried out using the Q Series software V. 2.5.0.255. The temperature range studied was between room temperature and 1000 °C, with heating at the rate of 10 °C min⁻¹. X-ray photoelectron spectroscopy (XPS) measurements were performed on a VG Scientific ESCALAB 2201XL instrument configured with Al Kα X-ray radiation. All spectra were fitted with Gaussian-Lorentzian functions and a Shirley-type background using CasaXPS software. For the analysis of Mo 3d spectra, constraints were used on the fitting for component pairs: peak area ratio of 2:3 for 3d5/2:3d3/2 and a maximum 0.2 eV difference in the full width half maximum (FWHM). The binding energy values were calibrated using the adventitious C 1s peak at 284.6 eV.

3.3 Results and Discussion

3.3.1 Structure and morphology

Molybdenum carbide/carbon nanotube (Mo₂C/CNT) was prepared by the carbothermal reduction of a ball-milled mixture of molybdenum trioxide (MoO₃) and CNT. The ball-milled mixture consists of commercial bulky MoO₃ with particle size in the range of of 200-500 nm and CNTs with a diameter of 10-20 nm (Figure 3.1a). During the carbothermal reduction, MoO₃ was reduced by the CNT to form Mo₂C. The as-prepared Mo₂C/CNT features a 3D network with uniformly dispersed 50 nm Mo₂C nanoparticles in a CNT framework (Figure 3.1b), where the Mo₂C particles could serve as catalysis active sites and the CNT matrix could improve the electrical conductivity of the composite electrode.
The crystalline phase compositions of the products were examined by X-ray diffraction (XRD) (Figure 3.2a). The characteristic peaks of Mo$_2$C at 34.4, 38.0, 39.4, 52.1, 61.5, 69.6, and 74.6 ° are attributed to the diffractions of the (002), (020), (211), (221), (203), (231), and (223) lattice planes, respectively, which confirms the conversion of MoO$_3$ into Mo$_2$C during the carbothermal reduction. The carbon peak is substantially diminished when the carbon is consumed. This transition process was also proved by the Raman spectra, which are consistent with the XRD results: the characteristic peaks of Mo$_2$C/MoO$_3$ increased while the carbon D-band and G-band peaks were reduced in the Raman spectra (Figure 3.2b), indicating that CNT was continuously consumed during the carbothermal reduction.

High-resolution transmission electron microscopy (HRTEM) images reveal that prepared Mo$_2$C/CNT holds high crystallinity and well-defined atomic planes (Figure 3.3). The planar d (0.149 nm and 0.227 nm) of product is consistent with the (110) and (101) planes of β-Mo$_2$C, respectively. The EDS with HRTEM in a highly resolved small area of Mo$_2$C/CNT shows the morphology and shape of as prepared Mo$_2$C/CNT, and
this mapping analysis also shows uniformity of Mo and C elements.

![Figure 3.2](image1)

**Figure 3.2** a) XRD patterns of the precursor mixture of MoO$_3$ and CNT, pure CNT, and as-prepared Mo$_2$C/CNT; b) Raman spectra of the precursor mixture of MoO$_3$ and CNT, pure CNT, and as-prepared Mo$_2$C/CNT.

![Figure 3.3](image2)

**Figure 3.3** a) The HRTEM image of nanoparticle of as-prepared Mo$_2$C/CNT composite material; b-e) EDS with HRTEM in a highly resolved small area of Mo$_2$C/CNT (yellow: C, red: Mo).

The CNT and Mo$_2$C contents of the as-prepared Mo$_2$C/CNT were further investigated using thermogravimetric analysis (TGA) (**Figure 3.4**). In the TGA curve of Mo$_2$C/CNT,
the initial weight gain from 300 °C to 500 °C is attributed to the gradual oxidation of Mo₂C to MoO₃, followed by a slight weight loss caused by the combustion of CNTs. When Mo₂C/CNT is heated to 700 °C, it is completely transformed into MoO₃. According to these results, the Mo₂C content is estimated to be 94.8 wt.% in Mo₂C/CNT, based on the following equation: \[ m \text{ (Mo}_2\text{C)} = 133.8 \text{ wt.\%} \times \frac{\text{M(Mo}_2\text{C)}}{2\text{M(MoO}_3)} = 94.8 \text{ wt.\%} \], and the CNT content is calculated to be 5.2 wt.%. Although the molecular ratio of the precursors before carbothermal reduction was strictly adjusted according to the chemical reaction, CNTs still resided in the Mo₂C/CNT, since the efficiency of reduction cannot be 100%. This very low CNT content is not expected to contribute capacity and reactivity with CO₂ at any significant level, although it is still important in suppressing the growth in size of Mo₂C nanoparticles and supplying sufficient electrical conductivity.

**Figure 3.4** TGA curves of CNT and Mo₂C/CNT, indicating that Mo₂C was completely transformed into MoO₃ while the CNT was transformed into CO₂.

### 3.3.2 Electrochemical Studies with Mo₂C/CNT

Cyclic voltammetry and galvanostatic cycling were conducted to evaluate battery
performance and CO₂ electrode reversibility. The test cells were assembled as described in the Supporting Information (Experimental). Cyclic voltammetry tests were carried out between 2.5 V and 4.2 V (vs. Li/Li⁺) at a scan rate of 0.1 mV s⁻¹. As revealed in Figure 3.5, Mo₂C/CNT shows a cathodic peak starting from 2.8 V and an anodic peak appearing between 3.4-3.5 V under CO₂.

![Cyclic voltammograms (CV) of Mo₂C/CNT electrodes under N₂ and CO₂, and CNT electrode under CO₂. Counter and reference electrodes: Li metal. Scan rate: 0.1 mV s⁻¹. Voltage window: 2.5 V - 4.2 V vs. Li/Li⁺.](image_url)

To exclude the background current from the reaction of Mo₂C/CNT in this voltage range, the corresponding test was also conducted under N₂. We found that no additional Faradic current could be observed, indicating that this pair of peaks observed under CO₂ corresponds to the CO₂ reduction reaction and the CO₂ evolution reaction, respectively. CNT electrode was tested as a comparison, and it shows a cathodic peak and an anodic peak under CO₂ starting from 2.8 V and 4.0 V, respectively, which is a typical response for carbon based electrodes. It is worth noting that the current began to tail off as the potential went above 3.7-3.8 V when Mo₂C/CNT was used as cathode.
under either N₂ or CO₂, which may be ascribed to the reaction of Mo₂C at such a high voltage.

Figure 3.6 Galvanostatic discharge-charge profiles of Mo₂C/CNT electrodes under N₂ and CO₂, and CNT electrode under CO₂ with the current at 20 μA.

The galvanostatic discharge and charge of Mo₂C/CNT was tested at the current of 20 μA, in a potential window of 2.0 V-3.8 V under CO₂. It delivered a reversible capacity of 1150 μAh during discharge and charge, showing that this discharge product can be decomposed below 3.8 V. On the contrary, Mo₂C delivers only 41 μAh under N₂, which indicates that the capacity delivered under CO₂ is related to the reversible CO₂ reduction and evolution process. CNT delivered the capacity of ~2850 μAh during discharge under CO₂, but no capacity was observed under charge process even above 4.0 V, implying that this discharge product cannot be decomposed below 4.0 V (Figure 3.6).

The first cycle galvanostatic discharge-charge curves of CNT electrode and Mo₂C/CNT electrode with a fixed capacity of 100 μAh at the current of 20 μA are presented in Figure 3.7, and the round-trip efficiency could be obtained to be 77% when Mo₂C/CNT was used as cathode in Li-CO₂ cells, compared with 60% for the pure CNT electrode.
Figure 3.7 Galvanostatic discharge-charge profiles of CNT and Mo$_2$C/CNT electrodes under CO$_2$ at the current of 20 μA, up to the capacity of 100 μAh.

Moreover, the Mo$_2$C/CNT showed good cycling performance, which lasted for 40 cycles, when it was galvanostatically discharged and charged to cut-off capacity of 100 μAh at the current of 20 μA (Figure 3.8).

Figure 3.8 Cycling performance of Mo$_2$C/CNT electrode for selected cycles under CO$_2$ at the current of 20 μA, up to the capacity of 100 μAh.
It was reported that Mo$_2$C is unstable in Li-O$_2$ batteries, as it reacts to form a surface layer of MoO$_2$ on discharge, which appears to result in low charge overpotential, but, in fact, it forms soluble Li$_x$MoO$_3$ and leads to electrode degradation$^{21}$ By detecting the colour change in the separator, we attempted to verify the relation between the discharge/charge process and the stability of Mo$_2$C in Li-CO$_2$ batteries (Figure 3.9).

![Graph](image)

**Figure 3.9** Galvanostatic discharge and charge profile (left) of the Mo$_2$C/CNT cathode in a Li-CO$_2$ cell, and corresponding images of separators taken out of the battery at the indicated stages (right).

Typically, a Li-CO$_2$ battery with Mo$_2$C/CNT as cathode was discharged to 2.0 V, as shown in step A, at which point the separator was clean, indicating that the battery is stable during discharge; it was then charged to 3.65 V at step B, at which the separator was still clean, indicating that the decomposition of discharge product is stable; the battery was then charged to the capacity delivered upon discharge at step C, at which the separator was slightly blue, indicating full decomposition of the discharge product,
although the electrode started to decompose at this voltage; the battery was finally charged to 3100 μAh at step D, at which the separator was dark blue, indicating that the Mo₂C had become unstable and was starting to dissolve in electrolyte above 3.8 V, as also proved by the stable voltage plateau.

This finding implies that the soluble species arise from the dissolution of Mo₂C at high voltage, not from the decomposition of the discharge product. By limiting the charge cut-off voltage to 3.65 V, Mo₂C/CNT was fully discharged and charged for three cycles, which showed stable and low charge potential and good reversibility (Figure 3.10).

**Figure 3.10** Galvanostatic cycling for the first 3 cycles of the Mo₂C/CNT cathode in a Li-CO₂ cell at the current of 20 μA in a 2.0 V – 3.65 V (vs. Li/Li⁺) voltage window. 20 μA of current was applied for both discharge and charge. Although there is still degradation during cycling, this might have come from insufficient decomposition of the discharge product.
3.3.3 Ex-situ studies of Mo$_2$C/CNT electrodes

To understand the different performances of CNT and Mo$_2$C/CNT in CV and galvanostatic discharge/charge, CNT and Mo$_2$C/CNT electrodes in different discharge/charge stages were investigated via ex-situ characterizations. It is important to analyse the discharge product and its charging behaviour, which can provide essential insight into the mechanism of rechargeable Li-CO$_2$ batteries. To obtain the CNT and Mo$_2$C/CNT materials after discharge, Li-CO$_2$ cells were discharged to 2.0 V at the current of 20 μA. Typically the cathode was extracted from coin cells in an Ar-filled glove box and rinsed with TEGDME solvent to remove residual LiCF$_3$SO$_3$ salt. The electrode was then sealed in Kapton tape for protection against air contamination. Based on XRD, SEM, and Raman spectroscopy, it is concluded that the CNT cathode is passivated by crystalline Li$_2$CO$_3$ during discharge, which is consistent with previous reports.$^{6,8,13,14}$

![XRD pattern of CNT electrodes at different stages](image)

**Figure 3.11** XRD pattern of CNT electrodes at different stages (pristine CNT: black line; and discharged CNT: red line), with the inset showing an enlargement of the indicated range.
As shown in Figure 3.11, the carbon paper exhibited the typical graphite structure, with a sharp (002) XRD graphite peak at $2\theta \approx 26.55^\circ$ and a small (004) XRD graphite peak at $2\theta \approx 54.75^\circ$. After discharge, some characteristic peaks appeared, which correspond to the formation of Li$_2$CO$_3$, according to XRD card PDF#22-1141. As shown in SEM images (Figure 3.12), The pristine CNT features a homogeneous crosslinked structure, with the diameters of the nanotubes in the range of 10-20 nm. After discharge to 2.0 V at the current of 20 μA, the crosslinked structure was filled with some plate-like product.

**Figure 3.12** SEM images of CNT electrode at different stages: a) pristine CNT; b) discharged CNT.
The D band and G band of pristine CNT and discharge CNT electrodes are clearly shown in the Raman spectra (Figure 3.13), which should be ascribed to the CNT. Compared with the pristine CNT, there is a new peak at 1089 cm$^{-1}$, corresponding to the formation of Li$_2$CO$_3$.

**Figure 3.13** Raman spectra of CNT electrodes at different stages (pristine CNT: black line; discharged CNT: red line).

Compared with clear evidence of crystalline Li$_2$CO$_3$ in discharged CNT electrode which confirmed by a series of physical characterizations including XRD, SEM and Raman, the XRD patterns of pristine Mo$_2$C/CNT and discharged Mo$_2$C/CNT electrode shows that there are no additional new peaks observed after discharging (Figure 3.14). This indicates that some amorphous product generated on the surface of Mo$_2$C/CNT, but not crystalline Li$_2$CO$_3$. 
Figure 3.14 XRD patterns of Mo$_2$C/CNT electrodes at different stages (pristine Mo$_2$C/CNT: black line; discharged Mo$_2$C/CNT: red line), with the inset showing an enlargement of the indicated range.

To probe this amorphous discharge product, ex-situ analyses of the surfaces of electrodes at different stages (pristine, discharged, and charged) via SEM, Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS) were carried out. As shown in Figure 3.15a, the pristine Mo$_2$C/CNT electrode shows a porous structure, which has the same morphology of Mo$_2$C/CNT powders. After discharge to 2.0 V, the cathode pores were filled with some film-like material, indicating the formation of an amorphous discharge product on the surface of the Mo$_2$C/CNT electrode. This film-like product disappeared after the cell was fully charged, indicating the decomposition of this amorphous discharge product. The amorphous morphology and low charge potential may well be linked to a similar phenomenon in the Li-O$_2$ battery. It was reported that amorphous peroxide is more ionically conductive than the crystalline phase, and some superoxide-rich surface could reduce the charge potential.\textsuperscript{22,23}
Figure 3.15 a) SEM images of Mo$_2$C/CNT electrode at different stages: pristine (top), discharged (middle), charged (bottom); b) Raman spectra of Mo$_2$C/CNT electrode at different stages: pristine (top), discharged (middle), charged (bottom); c) X-ray photoelectron spectra (XPS) of Mo 3d for Mo$_2$C/CNT electrode at different stages: pristine (top), discharged (middle), charged (bottom); d) X-ray photoelectron spectra (XPS) of C 1s for Mo$_2$C/CNT electrode at different stages: pristine (top), discharged (middle), charged (bottom).

To verify the reversible formation and decomposition of the amorphous product, Raman spectroscopy was carried out to elucidate the electrode compositions and the chemical bonds that are formed and broken (Figure 3.15b). Two bands of pristine Mo$_2$C/CNT electrode at 1325 cm$^{-1}$ and 1575 cm$^{-1}$ are respectively assigned to the disorder band (D band) and the graphitic band (G band) of carbon,$^{24}$ where the D band and the G band represent the sp$^3$ C–C single bond and the sp$^2$ C=C double bond, respectively. After discharge, there is a new peak that appears at 897 cm$^{-1}$, indicating
the formation of a new Mo−O sp³ hybridization bond. This stretching peak disappears after charge, indicating the breaking of the Mo−O bond. This would suggest that oxygen in CO₂ may combine with molybdenum in Mo₂C to form the amorphous product upon discharge, and this amorphous product releases CO₂ when the Mo−O bond breaks upon charge step. It seems that this strong coupling and the resulting electron delocalisation in the special pair plays a pivotal role in stabilizing such reduced compounds, which can be seen as the Mo−O coupling intermediate.

XPS analysis was further carried out to analyse the oxidation states and composition of the surface of Mo₂C/CNT electrodes in different discharge/charge stages, which was intensively applied to explore the catalysis mechanism, especially for β-Mo₂C. The Mo 3d spectra are fitted into 3d5/2 and 3d3/2 peaks because of the spin-orbital coupling feature, and the fitting parameters of XPS are shown in Table 3.1. As shown in Figure 3.15c, the peak fitting suggests that there are four oxidation states for Mo (Mo²⁺, Mo³⁺, Mo⁵⁺, Mo⁶⁺) on the surface of pristine Mo₂C/CNT electrode. Mo−C bonds in Mo₂C can explain the Mo²⁺ and low oxidation states of Mo³⁺. Previous studies indicated that the surface of Mo₂C would be contaminated with MoO₂ and MoO₃ when it is exposed to air, which can explain the existence of Mo⁵⁺ and Mo⁶⁺. After discharge, the shares of the Mo²⁺, Mo³⁺, and Mo⁵⁺ states were steeply decreased, while that of the Mo⁶⁺ state rapidly increased, indicating the oxidation of Mo in the low valence state to the high valence state. Consistent with the Raman spectra, the oxidation of Mo in the low valence state to Mo in the high valence state means that Mo acts as an electron donator. The outer electrons of Mo have been transferred to strong electron accepting materials, a role which should be ascribed to the O atoms in some CO₂ reduction product. Upon charge, the proportions of Mo²⁺, Mo³⁺, Mo⁵⁺, and Mo⁶⁺ returned to the initial stage, indicating that the delocalized electrons return to Mo during this reversible charge
process. The C 1s spectra (shown in Figure 3.15d) also show that the C−O peak at 286.6 eV increases after discharge and is reduced after charge, indicating CO$_2$ capture and release during the discharge/charge process. It is worth noting that no peak related to O−C=O could be observed, indicating that no carbonate radicals are formed during discharge.

**Table 3.1** Fitting parameters (peak position, full width at half maximum (FWHM), and species percentage) for both Mo 3d$_{3/2}$ and Mo 3d$_{5/2}$ spectra collected from Mo$_2$C/CNT electrode in different stages (pristine, discharged, charged).

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<tr>
<th>Electrode</th>
<th>Species</th>
<th>Peak position for Mo 3d$<em>{5/2}$ (former); Mo 3d$</em>{3/2}$ (latter) / eV</th>
<th>FWHM for Mo 3d$<em>{5/2}$ (former); Mo 3d$</em>{3/2}$ (latter) / eV</th>
<th>Species percentage / %</th>
</tr>
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<tr>
<td>Pristine</td>
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<tr>
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<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Mo$_2$C/CNT</td>
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<td>-</td>
<td>-</td>
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</table>
3.3.4 Mechanism of stabilizing the intermediate product by Mo$_2$C

Compared with the intensive research on the rechargeable Li-O$_2$ battery, research on the rechargeable Li-CO$_2$ battery is still an ongoing task. Therefore, some results reported for the Li-O$_2$ battery may shed light on exploring the mechanism of this new system. It is generally accepted that the reduction in an aprotic Li-O$_2$ battery proceeds through the general steps shown in Table 3.2.$^{26,27}$ Equations (1-4) show one-electron reduction of O$_2$ to form O$_2^-$ at the beginning stage, and then a lithium ion combines with O$_2^-$ to form LiO$_2$, followed by the chemical disproportionation reaction in which LiO$_2$ disproportionates to Li$_2$O$_2$ and O$_2$, or LiO$_2$ combines with a lithium ion and an electron to form Li$_2$O$_2$. The decomposition of Li$_2$O$_2$ will induce high overpotential in the charge process, since it is typically insoluble and electronically insulating. Similarly, in the Li-CO$_2$ battery, when carbon materials are used as cathode for Li-CO$_2$ batteries, the discharge product is proved to be Li$_2$CO$_3$, and the total reaction can be proposed as: $^{6,13,14}$

$$4\text{Li}^+ + 4\text{e}^- + 3\text{CO}_2 \rightarrow 2\text{Li}_2\text{CO}_3 + \text{C}.$$ 

Although the pathway is still unclear, based on lithium carbonate and carbon as the discharge product, as well as the proved disproportionation of LiO$_2$ in the Li-O$_2$ battery, it would be plausibly assumed that some disproportionation reaction takes place in the Li-CO$_2$ battery, as shown in Table 3.2.

Table 3.2 Pathway of discharge process in the Li-O$_2$ battery and possible pathway of discharge process in the Li-CO$_2$ battery.

<table>
<thead>
<tr>
<th>Li-O$_2$ battery</th>
<th>Li-CO$_2$ battery</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$_2$ + e$^-$ \rightarrow O$_2^-$ (1)</td>
<td>2CO$_2$ + 2e$^-$ \rightarrow C$_2$O$_4^{2-}$ (5)</td>
</tr>
<tr>
<td>Li$^+$ + O$_2$ \rightarrow LiO$_2$ (2)</td>
<td>C$_2$O$_4^{2-}$ \rightarrow CO$_2^{2-}$ + CO$_2$ (6)</td>
</tr>
</tbody>
</table>
Equation (3-5) shows the one-electron reduction of CO$_2$ to C$_2$O$_4^{2-}$ on the surface of carbon materials, for which the open circuit voltage could be calculated to be 3.0 V.$^{28}$ It is probable that unstable C$_2$O$_4^{2-}$ disproportionate through two steps to CO$_3^{2-}$ and C, as shown in Equations (6) and (7). Once crystalline Li$_2$CO$_3$ has formed in Equation (8), it is difficult to decompose below 4.0 V.

In the Li-O$_2$ battery, to reduce charge overpotential, metals in Group VIII such as Ru and Ir were utilized in Li-O$_2$ battery electrodes.$^{29-31}$ It was confirmed that the partial oxidation of the ruthenium facilitates stabilizing the highly unstable peroxide/superoxide ions in the Li$_{2-x}$O$_2$ phase, and thus reduces the overpotential for Li extraction from the Li$_2$O$_2$.$^{29}$ Also, the use of Ir-based electrode could absorb and stabilize LiO$_2$ to form the product of the reaction rather than an intermediate, which dramatically reduces the charge overpotential down to 3.2 V.$^{30}$ As it is known to have similar catalytic effects to these metals in Group VIII, Mo$_2$C probably stabilizes the intermediate product C$_2$O$_4^{2-}$ on discharge to form an amorphous product, which can be decomposed at low charge potential in the Li-CO$_2$ battery. Based on experimental results and the similar phenomenon in the Li-O$_2$ battery, the sequence of proposed possible reaction steps of Mo$_2$C for rechargeable Li-CO$_2$ battery are summarized in the following two equations:

\[
2\text{CO}_2 + 2e^- \rightarrow \text{C}_2\text{O}_4^{2-} \quad (5)
\]

\[
\text{C}_2\text{O}_4^{2-} + 2\text{Li}^+ + \text{Mo}_2\text{C} \rightarrow \text{Li}_2\text{C}_2\text{O}_4\cdot\text{Mo}_2\text{C} \quad (9)
\]

Equation (5) represents the one-electron reduction of CO$_2$ to C$_2$O$_4^{2-}$, and the open circuit voltage is calculated to be 3.0 V.$^{28}$ In the presence of Mo$_2$C, some metal-oxygen
coupling between Mo in Mo$_2$C and O in C$_2$O$_4$ stabilizes this unstable C$_2$O$_4^{2-}$ through coordinative electron transfer.\textsuperscript{32} This can prevent the formation of insulating Li$_2$CO$_3$ and thus easily release CO$_2$ and Li$^+$ through uncoupling of the Mo-O chemical bond during charge, which can reduce the charge potential below 3.5 V. These reactions can be summarized by the schematic illustration shown in Figure 3.16. The characteristics that make Mo$_2$C suitable for this stabilizing function are due to the low valence of molybdenum in Mo$_2$C, which can promote the transfer of outer electrons to oxygen in the Li$_2$C$_2$O$_4$ intermediate product and prevent its disproportionation to Li$_2$CO$_3$. It is confirmed that only amorphous Li$_2$C$_2$O$_4$-Mo$_2$C could release lithium ions and CO$_2$ at a lower charge voltage plateau below 3.5 V. Once crystalline Li$_2$CO$_3$ formed, the charge voltage plateau will increase to 4.0 V or more. Therefore, Mo$_2$C is assumed to play an important role in stabilizing the C$_2$O$_4^{2-}$ as intermediate product, to prevent its further disproportionation reaction.

**Figure 3.16** Schematic illustration of reactions during discharge and charge of Mo$_2$C/CNT in the Li-CO$_2$ battery. CO$_2$ is reduced at the Mo$_2$C/CNT electrode surface on discharge, forming Li$_2$C$_2$O$_4$, and then this intermediate product is stabilized by
Mo$_2$C, forming an amorphous discharge product that can be easily decomposed on charge.

Moreover, most reported Li-air batteries are operated under a pure O$_2$ atmosphere, while CO$_2$ and moisture in ambient air can significantly affect the cycling performance when this kind of battery applied in real utilization. As Mo$_2$C/CNT has been reported as catalyst in Li-O$_2$ battery,$^{20}$ and confirmed as a potential catalyst with high round-trip efficiency in Li-CO$_2$ battery in this work. Moreover, it is likely that this material could reduce the deleterious impact of CO$_2$ contamination from air on the cell processes. Even though a membrane is still needed to prevent moisture invasion for such an open system, Mo$_2$C/CNT may hold promise for utilization of Li-air battery under ambient air.

### 3.4 Conclusions

In summary, Mo$_2$C/CNT was prepared via a carbothermal reduction process and employed as the catalyst for Li-CO$_2$ batteries. This composite material shows a high round-trip efficiency of 77%, as well as a good cycling performance. Through a series of characterizations of pure CNT and the as-prepared Mo$_2$C/CNT, it is clearly shown that CO$_2$ reduction in the presence of Mo$_2$C follows a different route that avoids the formation of insulating Li$_2$CO$_3$, so to reduce potential plateau on charge and improve round-trip efficiency of rechargeable Li-CO$_2$ battery. Raman and XPS analysis revealed that the amorphous discharge intermediate product, Li$_2$C$_2$O$_4$-Mo$_2$C, is deposited and decomposed during discharge/charge when Mo$_2$C/CNT is used as cathode for Li-CO$_2$ batteries, and it could be well decomposed below 3.5 V. Although further studies using in-situ characterizations are still needed to provide direct evidence for understanding the mechanism behind this reversible reaction, we expect that such an effective catalyst can represent a good example to solve the problems of low electrical efficiency and
poor cyclability in Li-CO$_2$ batteries.

### 3.5 References


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Angamuthu, R.; Byers, P.; Lutz, M.; Spek, A. L.; Bouwman, E. Electrocatalytic
CO$_2$ conversion to oxalate by a copper complex. *Science* 2010, 327, 313
Chapter 4: Metal-oxygen Bonds: Stabilizing the Intermediate Species towards Practical Li-air Batteries

4.1 Introduction

The Li-air battery, as one of the most promising power sources for electric vehicles, has attracted increasing attention over the last decade, owing to its specific energy density, which is 3-5 times as high as that of the state-of-the-art lithium ion batteries.\textsuperscript{1,2} Certain factors, however, such as sluggish reaction kinetics, chemical instability of the electrolyte, and moisture susceptibility, act as the major obstacles to realizing practical Li-air batteries. One major challenge for the realization of the Li-air batteries is reducing large voltage hysteresis and thus improving low round-trip efficiency through a clear understanding of the reaction mechanism of the catalyst. Although numerous catalysts have been recently developed to reduce the large charge-discharge voltage gap to increase the energy efficiency,\textsuperscript{3-7} a better understanding of the detailed mechanisms of the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER) still requires further systematic investigation. Given the mechanism of discharge product growth and decomposition, it is somewhat hard to envision how electrocatalysis could actually occur. As is well known, electrocatalysis occurs when an active catalytic site lowers the barrier of the kinetic limiting step in the mechanism, but the catalytic site itself is not changed during the reaction. It is difficult to see, however, how Li$_2$O$_2$ and LiO$_2$ could have enough mobility for true catalysis to occur, owing to their insolubility in the electrolyte. There is no true electrocatalysis in the same way as is observed for aqueous ORR/OER, where soluble products are formed, but added nanoparticles could have some beneficial effects on the morphology and charge transport at higher currents and capacities.\textsuperscript{8} If there were such particles, however, such as platinum on the surface
of carbon, they would rapidly be covered up by solid Li$_2$O$_2$ or LiO$_2$, and the dominant electrochemistry then becomes simply the Li-O$_2$ ORR on Li$_2$O$_2$ or LiO$_2$. The material design which has been already successfully applied in aqueous ORR/OER needs to be changed, because the intermediate product is soluble in aqueous electrolyte, which could not affect the catalytic sites of nanocatalyst particles.

Noble metal and transitions metal oxides have been extensively investigated as catalysts for Li-O$_2$ batteries, and several catalytic mechanisms have been proposed. Yao et al. proposed that enhancement of Li$_2$O$_2$ oxidation is mediated by chemical conversion of Li$_2$O$_2$ with slow oxidation kinetics to a lithium oxide.$^5$ Wang et al. proposed that partial oxidation of ruthenium catalyst can stabilize the highly unstable peroxide/superoxide that is caused by the lithium-deficient Li$_2$O$_2$ (or Li$_{2-x}$O$_2$), forming Li$_{2-x}$O$_2$(solid)-Ru at the interface.$^9$ Recently, a one-electron charge process in lithium oxygen batteries was observed, and it was reported to be responsible for low overpotential during the charge process. Lu et al. demonstrated that the LiO$_2$ formed in the Li-O$_2$ battery is stable enough so that the battery could be repeatedly charged and discharged with a very low charge potential, and they proposed that the intermetallic compound Ir$_3$Li and LiO$_2$ both have a similar orthorhombic lattice, so it may act as a template for the growth of crystalline LiO$_2$.\textsuperscript{10} Meanwhile, Trahey et al. proposed that MnO$_2$ can act as a “Li$_x$O$_{2-x}$-storage material”, reversibly storing lithium-oxide species during the Li-O$_2$ reactions, based on density functional theory (DFT) computations, and in this case, the transition metal oxides in Li-air batteries do not act as “catalyst” in the traditional sense of facilitating a chemical reaction while remaining unchanged, but actually undergo chemical and structural changes themselves as well.$^{11}$ All the above shows the synergetic effect between the catalyst and the intermediate discharge product Li$_x$O$_2$, which possibly can account for the reduced charge overpotential due to the solid state
reaction in the discharge process. Even though extensive studies have been conducted to elucidate the role of conventional solid catalysts, the operating mechanism remains elusive and controversial in Li-O₂ batteries.

The other major challenge to realize practical Li-air batteries is how to eliminate the influence of CO₂ and H₂O when operate in ambient air. Supposing that H₂O, which is known to fatally degrade electrolyte and lithium anode, is removed by an air dehydration membrane¹², CO₂ should have the most influence on the chemistry of Li-air batteries among various constituents of air. Despite its low concentration in air, the high solubility of CO₂ gas in organic electrolytes results in the huge possibility of CO₂ being incorporated into battery reactions.¹³ It is critical to understand the reactions involving CO₂ and the chemistry of the discharge products. To exclusively investigate and understand the operating mechanism of CO₂, a rechargeable Li-CO₂ battery was proposed and extensively studied based on the reversible reaction of 4Li + 3CO₂ = 2Li₂CO₃ + C.¹⁴⁻¹⁹ As a wide band-gap insulator and insoluble discharge product, Li₂CO₃ causes a high overpotential (> 4.0 V vs. Li/Li⁺) to decompose in charge.

The work in Chapter 3 has shown that Mo₂C/carbon nanotube (CNT) could stabilize CO₂ reduction intermediate to generate amorphous discharge product in discharge, avoiding ultimate formation of Li₂CO₃. The stabilized discharge product could decompose at low potentials (~ 3.5 V vs. Li/Li⁺) in charge, efficiently reducing charge overpotential and CO₂ evolution barrier in Li-CO₂ batteries.²⁰ Somewhat differently, it is still under debate whether Mo₂C can have any effect on charge and how Mo₂C improve oxygen evolution in Li-O₂ batteries. Kwak et al. demonstrated that Mo₂C could increase the electrical efficiency and improve the cycling performance of Li-O₂ batteries, owing to the formation of metallic non-crystalline MoO₃-like layers on the
Mo$_2$C nanoparticle. However, Kundu et al. observed white glass fiber separator changes to dark blue after several discharge-charge cycles, so they concluded the low charge potential of Mo$_2$C comes from the oxidation of Li$_x$MoO$_3$. In this chapter, we demonstrate the improved electrochemical performance of the Li-O$_2$ battery using Mo$_2$C/CNT as promoter, and carried out essential electrochemical techniques, with analytical techniques such as X-ray powder diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and energy dispersive X-ray spectroscopy (EDS) to investigate the reaction mechanism of Mo$_2$C/CNT. Based on the presented data and as an extension for our previous Li-CO$_2$ battery studies, we proposed the mechanism that Mo$_2$C/CNT could efficiently stabilizes the highly reactive LiO$_2$ to generate amorphous (Li-O-O)$_x$-Mo$_2$C as discharge product, thus preventing the formation of crystalline Li$_2$O$_2$, which is difficult to decompose and induces high overpotential during charge in Li-O$_2$ battery. We found that the stabilization of Mo-O bonds could prevent the formation of both crystalline Li$_2$O$_2$ and Li$_2$CO$_3$, so to maintain good cycling performance and high round-trip efficiency of Li-air batteries and Li-CO$_2$/O$_2$ batteries. These studies may offer insight and guidance of solid promoter design, as well as provide a feasible method for addressing major technical barriers to practical Li-air batteries.

4.2 Experimental Details

4.2.1 Synthesis of Mo$_2$C/CNT composite materials

200 mg of MoO$_3$ and 700 mg of CNTs were weighed as precursors based on the equation $2\text{MoO}_3 + 7\text{C} = \text{Mo}_2\text{C} + 6\text{CO}$. The precursors were mixed and ball-milled at rotation speed of 300 rpm. The milling time was 24 h and the ball-to-powder weight ratio was 20:1. The milling jar was assembled and sealed in glovebox under high purity
Ar atmosphere, for the purpose to protect precursors from oxidation. The well-mixed precursors were transferred into quartz crucible for thermal carboreduction at 950 °C for 1 h under argon, with a heating rate of 10 °C min⁻¹.

4.2.2 Preparation of batteries in different atmospheres

The prepared materials (Mo₂C/CNT) (or commercial CNTs) were mixed with a polyvinylidene fluoride binder (PVDF) at a weight ratio of 8:2 in the N-methyl-2-pyrrolidone (NMP) liquid. After mixing uniformly, the slurry was pasted onto carbon paper disks (diameter of 14 mm). To remove the residual solvent, these carbon disks were dried for 12 hours at 120 °C under vacuum. The loading of materials on carbon paper disks was ~4 mg. For next-step battery test, coin cells were assembled with composition of a carbon paper with loading materials as cathode, a lithium metal disk as anode, and a separator (Whatman GF/D microfiber filter paper, 2.7 μm pore size) with impregnated electrolyte. The electrolyte was prepared with 1M LiCF₃SO₃ in tetraethylene glycol dimethyl ether (TEGDME). All cell assembly procedures were carried out in an argon-filled glove box (oxygen and water contents less than 0.1 ppm). Different types of battery were carried out in chamber with different gas atmosphere: Li-O₂ battery tests were carried out in an O₂-filled chamber. Li-air battery tests were carried out in an air-filled chamber with molecular sieves to reduce the moisture of ambient air. Li-CO₂/O₂ battery tests were carried out in an O₂/CO₂-filled chamber with ratio of 1:1. Before battery testing, coin cells were left for 3 hours in chamber for stabilization after filling with different gas.

4.2.3 Physical characterizations

Powder X-ray diffraction (XRD) was performed on a GBC MMA XRD (λ = 1.54 Å) with the voltage at 40 kV and the current at 25 mA. Raman spectroscopy was carried
out on a Jobin-Yvon Horiba 800 with a 10-mW helium/neon laser at 632.81 nm excitation. Scanning electron microscopy (SEM) images were obtained from a JEOL JSM-7500FA field emission SEM with the accelerating voltage at 5.0 kV and the emission current at 10 mA. Transmission electron microscopy (TEM) investigations were performed using a 200 kV JEOL ARM-200F instrument. Thermogravimetric analysis (TGA) was carried out in air using a Q500 (TA Instruments), with the temperature range from room temperature to 1000 °C at raising rate of 10 °C min\(^{-1}\). TGA data analysis was carried out using the Q Series software V. 2.5.0.255. XPS measurements were performed on a VG Scientific ESCALAB 2201XL instrument configured with Al Kα X-ray radiation. CasaXPS software was used to fit all spectra with Gaussian-Lorentzian functions and a Shirley-type background. Constraints were used on the fitting for component pairs of Mo 3d: peak area ratio of 2:3 for 3d\(_{5/2}\):3d\(_{3/2}\) and a maximum 0.2 eV difference in full width at half maximum (FWHM). The adventitious C 1s peak at 284.6 eV was used to calibrate the binding energy values.

4.3 Results and Discussion

4.3.1 Structure and morphology

A schematic diagram depicting the preparation of Mo\(_2\)C/CNT composites is shown in Figure 4.1a, and the synthesis procedure at each step was also confirmed by SEM images (Figure 4.1b). Bulk MoO\(_3\) and CNTs were mixed via ball milling and calcinated. After calcination, the mixture of MoO\(_3\) and CNT turned into uniformly distributed Mo\(_2\)C/CNT. MoO\(_3\) was reduced by CNT, and bulk MoO\(_3\) was transformed into Mo\(_2\)C nanoparticles, but unreacted CNT still existed and acted as the conductive skeleton for the composites.
Figure 4.1 a) Schematic illustrations depicting the synthesis procedure for Mo$_2$C/CNT composite materials; b) SEM images of the synthesis procedure at each step.

The final product was investigated by XRD (as shown in Figure 4.2), in which several typical diffraction peaks at 34.4, 38.0, 39.4, 52.1, 61.5, 69.6, and 74.6° were respectively assigned to the (002), (020), (211), (221), (203), (231), and (223) planes of β-Mo$_2$C (PDF-# 35-0787), confirming that MoO$_3$ was reduced to Mo$_2$C after thermal treatment.

Figure 4.2 XRD pattern of Mo$_2$C/CNT composites.
To investigate the content of Mo$_2$C and CNT in the composite, Thermo-gravimetric analysis (TGA) of CNT and Mo$_2$C/CNT was carried out between room temperature and 900 °C at increasing temperature of 10 °C min$^{-1}$ in air (Figure 4.3).

![TGA curves of CNT (blue) and Mo$_2$C/CNT (red)](image)

Figure 4.3 TGA curves of CNT (blue) and Mo$_2$C/CNT (red)

The initial weight gain from 150 °C to 490 °C is attributed to the gradual oxidation of Mo$_2$C to MoO$_3$, followed by a slight weight loss caused by the combustion of CNTs. When Mo$_2$C/CNT is heated to 650 °C, the composite material totally transformed to MoO$_3$, followed by the thermolysis of MoO$_3$ above 700 °C. According to these results, the Mo$_2$C content is estimated to be 94.8 wt.% in Mo$_2$C/CNT based on the following equation: $m$ (Mo$_2$C) = 133.8 wt.% * $M$(Mo$_2$C)/2$M$(MoO$_3$) = 94.8 wt.%, where $m$ is the wt.% and $M$ is the number of moles, and the CNT content is calculated to be 5.2 wt.%.

The high-resolution TEM (HRTEM) image indicates that the particles possess a typical crystalline texture, and the selected area electron diffraction (SAED) pattern of the as-
prepared Mo$_2$C/CNT shows (002), (100) rings of CNT and (002), (100) rings of Mo$_2$C, confirming the presence of carbon nanotubes and crystalline Mo$_2$C, which is in accordance with the XRD data (Figure 4.4a). TEM images in a highly resolved small area of Mo$_2$C/CNT show uniform distributions of Mo$_2$C and carbon nanotubes in both bright field and dark field, and energy dispersive spectroscopy (EDS) elemental mapping images in the same area show uniform distributions of Mo and C elements (Figure 4.4b). With all the above data, it was confirmed that uniformly dispersed Mo$_2$C/CNT was successfully synthesized.

Figure 4.4 a) transmission electron microscope (TEM) image with SAED pattern of the as-prepared Mo$_2$C/CNT; b) The corresponding bright field (BF) image, dark field (DF) image, and element mapping of Mo$_2$C/CNT composite (green for C, and yellow for Mo).

4.3.2 Electrochemical characterization

The electrochemical testing was carried out using coin cells composed of a lithium metal anode, a glass fiber separator impregnated with electrolyte (1 M lithium triflate
(LiCF$_3$SO$_3$) in tetraethylene glycol dimethyl ether (TEGDME)), and a cathode (loaded with CNT or Mo$_2$C/CNT on carbon paper). The reaction kinetics of Mo$_2$C/CNT was examined by cyclic voltammetry (CV) under oxygen and nitrogen between 2.0-4.2 V (vs. Li/Li$^+$) at the scan rate of 0.1 mV s$^{-1}$. As shown in Figure 4.5a, the cathodic peak of Mo$_2$C/CNT starts from 2.7 V (vs. Li/Li$^+$), where the oxygen reduction reaction takes place in the cell, while half of the anodic peak starts from 3.3 V (vs. Li/Li$^+$) where the deposited product starts to decompose. For comparison, there is no obvious peak under nitrogen, showing that the reaction is derived from the reduction of oxygen.

**Figure 4.5** Electrochemical tests: **a)** Cyclic voltammograms of Mo$_2$C/CNT in oxygen and nitrogen; **b)** Galvanostatic discharge-charge voltage profiles of Mo$_2$C/CNT in oxygen for selected cycles; **c)** Cyclic voltammograms of Mo$_2$C/CNT and CNT in oxygen; **d)** Voltage profiles of the CNT and Mo$_2$C/CNT cathodes.
The reversibility of Mo$_2$C/CNT under oxygen was tested at a cut-off capacity of 100 μAh at the current rate of 20 μA, and the results showed that Mo$_2$C/CNT exhibits a remarkably low charging potential of 3.35 V, after 40 discharge-charge cycles (Figure 4.5b). On the contrary, the current contributed by CNTs to the cathodic peak is relatively high, indicating that CNT has larger surface area and more active sites for oxygen reduction; but the current contributed by CNT to the anodic peak is low, indicating that the decomposition of discharge products cannot proceed well in this voltage range (Figure 4.5c). In full discharge-charge tests, the potential gap for CNTs between discharge and charge is 1.67 V, but for Mo$_2$C/CNT, it is only 0.76 V, showing that the introduction of Mo$_2$C/CNT can significantly reduce charge overpotentials (Figure 4.5d).

4.3.3 Investigations on low charge potential

To investigate the cause of low charge voltage plateau, continuous galvanostatic discharge-charge in switched N$_2$/O$_2$ atmosphere was carried out (Figure 4.6).

![Figure 4.6](image.png)

**Figure 4.6** Discharge and charge voltage curves under different atmospheres.
This test was intended to exclude the de-intercalation of lithium ions in the charge process, and the cell was tested as follows: 1) purge with oxygen for 3 hours, then discharge and charge for 20 hours separately; 2) purge with nitrogen, then discharge to 2.35 V; 3) purge with oxygen, then discharge and charge for 20 hours separately for the second time. There are corresponding plateaus in oxygen at steps 1) and 3), while there is no plateau, but only rapid fading to 2.35 V in nitrogen at step 2), suggesting that lithium ion de-intercalation and intercalation of the discharge product be excluded. This study initially confirmed that the low charge voltage plateau is related to oxygen, not related to de-intercalation of lithium compound in same voltage range.\(^{22}\)

**Figure 4.7** a) Voltage profiles (left) and photographs (right) of glass fiber separators corresponding to different galvanostatic discharge and charge stages using Mo\(_2\)C/CNT as cathode under N\(_2\). b) Voltage profiles (left) and photographs (right) of glass fiber
separators corresponding to different galvanostatic discharge and charge stages using Mo$_2$C/CNT as cathode under O$_2$.

Meanwhile, galvanostatic discharge-charge of the cell using Mo$_2$C/CNT as electrode in nitrogen was carried out, and we detected that white glassfibers separator change to dark blue when the cell was overcharged under nitrogen (Figure 4.7). Only overcharging the Mo$_2$C/CNT electrode made the glass fiber turn dark blue, which shows that the blue color was not due to dissolution of the discharge product or lithium extraction from the discharge product, but due to Mo$_2$C self-decomposition at a high voltage. Based on this, we attribute the blue color of the glassfibers to the reaction of Mo$_2$C at high voltage, not to the de-intercalation and dissolution of Li$_x$MoO$_3$ formed in discharge as previously reported.

To obtain insight into the structural origins of the observed low charge potential and improved cycling performance, we prepared electrodes at different stages and characterized these electrodes by several methods. In a typical procedure, we assembled two Li-O$_2$ cells with Mo$_2$C/CNT as cathode, one was discharged to 2.0 V at the current rate of 20 μA, and after disassembly, we obtained the discharged electrode; the other was discharged to 2.0 V first, then charged to 3.8 V at the current rate of 20 μA, and after disassembly, we obtained the charged electrode. The pristine electrode is a freshly prepared Mo$_2$C/CNT electrode without any previous electrochemical testing. The voltage profile for electrode preparation is shown in Figure 4.8a, and the pristine electrode, discharged electrode, and charged electrode were positioned at points A, B, and C in the voltage profile. We first used XRD to determine the structural changes of Mo$_2$C/CNT electrode during discharge-charge process. As shown in Figure 4.8b, the XRD patterns show peaks corresponding to Mo$_2$C and graphite from carbon paper in
the pristine, discharged, and recharged Mo$_2$C/CNT cathodes, but there is no peak showing the presence of crystalline Li$_2$O$_2$ in the discharged Mo$_2$C/CNT electrode, indicating that an amorphous discharge product was formed during the discharge process.

SEM was then used to confirm the existence of the amorphous discharge product, as shown in Figure 4.8c-e. Uniformly dispersed Mo$_2$C and CNT were observed in the pristine Mo$_2$C/CNT electrode before discharge; after discharge, there is a thin film on the surface of the Mo$_2$C/CNT electrode, and then this thin film disappears after the electrode is fully charged.

**Figure 4.8** a) Full discharge and charge cycle of Mo$_2$C/CNT in a Li-O$_2$ battery (pristine electrode at position A, fully discharged electrode at position B, and fully recharged electrode at position C). b) XRD images of Mo$_2$C/CNT electrode at different stages (pristine, discharged, recharged). c-e) SEM images of Mo$_2$C/CNT of Mo$_2$C/CNT electrode at different stages (pristine, discharged, recharged).
To investigate this amorphous thin film on the surface of the Mo$_2$C/CNT electrode, X-ray photoelectron spectroscopy (XPS) of Mo 3d was carried out and fitted with the contributions of Mo$^{2+}$, Mo$^{3+}$, Mo$^{5+}$, or Mo$^{6+}$ on the surfaces of the Mo$_2$C/CNT electrodes (fitting details shown in Table 4.1).

Table 4.1 Fitting parameters (peak position, full width at half maximum (FWHM), and species percentages) for both Mo 3d$_{3/2}$ and Mo 3d$_{5/2}$ spectra collected from Mo$_2$C/CNT electrodes at different stages (pristine, discharged, charged).

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Species</th>
<th>Peak position for Mo 3d$<em>{3/2}$ (former); Mo 3d$</em>{3/2}$ (latter) / eV</th>
<th>FWHM for Mo 3d$<em>{3/2}$ (former); Mo 3d$</em>{3/2}$ (latter) / eV</th>
<th>Species percentage / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine Mo$_2$C/CNT</td>
<td>Mo$^{2+}$</td>
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<td>18.4</td>
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<tr>
<td></td>
<td>Mo$^{3+}$</td>
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<td>1.60; 1.57</td>
<td>13.2</td>
</tr>
<tr>
<td></td>
<td>Mo$^{5+}$</td>
<td>231.33; 234.89</td>
<td>1.69; 1.72</td>
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</tr>
<tr>
<td></td>
<td>Mo$^{6+}$</td>
<td>233.05; 236.09</td>
<td>1.81; 1.96</td>
<td>53.4</td>
</tr>
<tr>
<td>Discharged Mo$_2$C/CNT</td>
<td>Mo$^{2+}$</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Mo$^{3+}$</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Mo$^{5+}$</td>
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<td>1.47; 1.49</td>
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<tr>
<td></td>
<td>Mo$^{6+}$</td>
<td>233.26; 236.48</td>
<td>1.72; 1.75</td>
<td>82.6</td>
</tr>
<tr>
<td>Charged Mo$_2$C/CNT</td>
<td>Mo$^{2+}$</td>
<td>228.28; 231.79</td>
<td>1.35; 1.38</td>
<td>16.1</td>
</tr>
<tr>
<td></td>
<td>Mo$^{3+}$</td>
<td>229.58; 232.81</td>
<td>1.35; 1.37</td>
<td>12.0</td>
</tr>
<tr>
<td></td>
<td>Mo$^{5+}$</td>
<td>231.17; 234.68</td>
<td>1.31; 1.33</td>
<td>15.0</td>
</tr>
<tr>
<td></td>
<td>Mo$^{6+}$</td>
<td>233.09; 236.13</td>
<td>1.83; 1.90</td>
<td>56.9</td>
</tr>
</tbody>
</table>

For the pristine Mo$_2$C/CNT electrode, the low oxidation states of Mo$^{2+}$ and Mo$^{3+}$ can be explained for the existence of both Mo-Mo and Mo-C bonds, and the high oxidation
states of Mo$^{5+}$ and Mo$^{6+}$ can be explained for the contaminated surface of molybdenum oxides such as MoO$_2$ and MoO$_3$ when the Mo$_2$C/CNT was exposed in air (Figure 4.9a). After discharge in oxygen, peaks for Mo$^{2+}$ and Mo$^{3+}$ disappeared while peaks for Mo$^{5+}$ and Mo$^{6+}$ increased, indicating the oxidation of Mo$_2$C surface with the formation of Mo-O bonds (Figure 4.9b). After recharge in oxygen, peaks for Mo$^{2+}$, Mo$^{3+}$ recovered while peaks for Mo$^{5+}$ and Mo$^{6+}$ decreased to pristine state, indicating the reduction of oxidized Mo$_2$C surface with the cleavage of Mo-O bonds (Figure 4.9c). Based on these results, the reversible formation and cleavage of Mo-O bonds may be responsible for the low charge overpotentials and high cyclability.

**Figure 4.9** XPS spectra showing Mo 3d peaks of Mo$_2$C/CNT electrode at different stages a) pristine, b) discharged and c) recharged.

To corroborate the reversible formation and decomposition of the oxygen reduction product, we simultaneously characterized these different stages of Mo$_2$C/CNT electrodes by survey spectra of XPS (Figure 4.10) and EDS (Figure 4.11). The survey spectra of XPS clearly shows the change of oxygen peaks, indicating deposition of oxygen species in discharge and releasing of oxygen species in charge.
**Figure 4.10** XPS survey spectra of pristine, discharged, and recharged Mo$_2$C/CNT electrode. The survey spectra clearly show the intensity change of O1s and C1s peaks, indicating deposition of oxygen reduction species in discharge, and releasing oxygen reduction species in charge.

In agreement with the XPS results, we found uniformly dispersed oxygen element in oxygen mapping of discharged electrode, suggesting that a large amount of oxygen was reduced and stabilized on the surface of the Mo$_2$C/CNT during discharge. Surprisingly, the disappearance of oxygen element in oxygen mapping of the charged electrode shows that oxygen was released during charge.
Figure 4.11 Energy dispersive spectroscopy (EDS) of pristine (top row), discharged (middle row), and charged (bottom row) Mo$_2$C/CNT electrodes. The element mapping clearly shows that oxygen reduction species are deposited on the surface of the Mo$_2$C/CNT electrode during the discharge process and released from the surface of the Mo$_2$C/CNT electrode during the charge process.

Moreover, when these electrodes were exposed to air for several days, crystalline Li$_2$MoO$_4$ was detected only in the discharged Mo$_2$C/CNT electrode, not in the exposed pristine and charged Mo$_2$C/CNT (Figure 4.12). This finding reflects that the exposure under moisture promotes the transformation of the amorphous discharged product into products that have similar chemical properties of mixed LiOH•H$_2$O and MoO$_3$, suggesting the rise of molybdenum valence state after discharge.
Figure 4.12 a) Raman spectra, and b) XRD patterns of Mo$_2$C/CNT electrodes at different stages after exposure in ambient air for several days; c) SEM image of discharged Mo$_2$C/CNT electrode, and d) SEM image of charged Mo$_2$C/CNT electrode, both were characterized after exposure in ambient air for several days.

As Raman spectra (Figure 4.12a), XRD (Figure 4.12b) and SEM (Figure 4.12c-d) shown, only discharge Mo$_2$C/CNT electrode could generate crystalline Li$_2$MoO$_4$, indicating amorphous discharge product may react with moisture in ambient air to generate Li$_2$MoO$_4$. According to this, we confirmed the formation of Mo-O bonds in discharge and proposed a possible reaction mechanism of the formation of Li$_2$MoO$_4$ as flowing equations showed. (4-1, 4-2, 4-3)

$$\text{Li}_x\text{O} + \text{H}_2\text{O} \rightarrow \text{LiOH} \quad (4-1)$$

$$\text{Mo}_x\text{O}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{MoO}_4 \quad (4-2)$$

$$\text{H}_2\text{MoO}_4 + \text{LiOH} \rightarrow \text{Li}_2\text{MoO}_4 + \text{H}_2\text{O} \quad (4-3)$$
4.3.4 Proposed mechanism of Mo$_2$C in O$_2$ and CO$_2$

As mentioned above, Mo$_2$C does not operate as an electrocatalyst like Pt/C in the aqueous oxygen reduction reaction. Neither does it operate as an OER catalyst, decomposing crystalline Li$_2$O$_2$, which can normally be characterized by diffraction methods. Instead, it operates by a different mechanism that changes the pathway of O$_2$ reduction to insulating Li$_2$O$_2$, but stabilizes the reactive LiO$_2$ intermediate to form an amorphous product through solid-state reaction. In the absence of Mo$_2$C, reduction of O$_2$ to Li$_2$O$_2$ proceeds via the LiO$_2$ intermediate on the surface of CNT electrode during discharge.\(^{24}\) Equation (4-4) shows the oxygen undergoes one-electron reduction to form O$_2^-$, then combines with a Li$^+$ ion to form LiO$_2$ in solution or surface adsorbed LiO$_2$ intermediate. Equation (4-5) and (4-6) show LiO$_2$ as a transient intermediate is not stable at room temperature and quickly converts to Li$_2$O$_2$ via a disproportionation reaction or an additional Li$^+$-induced charge transfer. As a wide band-gap insulator and insoluble species, bulk Li$_2$O$_2$ is difficult to decompose below 4.0 V. Moreover, this highly oxidized LiO$_2$ intermediate could also induce the oxidization of the carbon surface to Li$_2$CO$_3$, and even one monolayer of Li$_2$CO$_3$ at the C-Li$_2$O$_2$ interface can cause a \(~10\-100\)-fold decrease in the exchange current density due to interfacial resistance to charge transport.\(^{25}\) Unlike NaO$_2$ in Na-O$_2$ batteries, which generates and stably exists in the discharge stage and decomposes at low voltage plateau in the charge stage, the LiO$_2$ converts to Li$_2$O$_2$, which decomposes at high voltage above 4.0 V in the charge stage.

\[
\begin{align*}
O_2 + Li^+ + e^- & \rightarrow LiO_2 & (4-4) \\
2LiO_2 & \rightarrow Li_2O_2 + O_2 & (4-5) \\
LiO_2 + Li^+ + e^- & \rightarrow Li_2O_2 & (4-6)
\end{align*}
\]
To capture and stabilize LiO₂ species could prevent them from surface-mediated disproportionation and further reduction to Li₂O₂. It is reported that Glassy carbon with surface defects, oxidized carbon and Ir-based catalyst were proved to stabilize LiₓO₂/LiO₂ species in discharge and faciley decompose in the subsequent charge.¹⁰⁻²⁸ Unsaturated coordination of Mo states on the Mo₂C surface is thought to be responsible for its high catalytic activity towards dehydrogenation and electrochemical hydrogen evolution. Meanwhile, this metal center was expected to have a strong affinity for oxygen, thus favoring a surface mediated ORR process or CO₂ reduction process.²⁰ Moreover, the active surface is expected to be highly electrically conductive, owing to the well-known metallic properties of the underlying Mo₂C. Therefore, we speculate that Mo₂C could stabilize the active LiO₂ intermediate to generate amorphous (Li-O-O)ₓ-Mo₂C via the formation of Mo-O bonds, preventing further reduction and disproportionation of LiO₂ intermediate to crystalline Li₂O₂ in Equation (4-7). The facile decomposition of amorphous (Li-O-O)ₓ-Mo₂C in Equation (4-8), instead of difficult decomposition of crystalline Li₂O₂ may be responsible for the reduced charging overpotentials observed in our results.

\[ x\text{LiO}_2 + \text{Mo}_2\text{C} \rightarrow (\text{Li-O-O})_x\text{-Mo}_2\text{C} \quad (4-7) \]

\[ (\text{Li-O-O})_x\text{-Mo}_2\text{C} \rightarrow \text{Mo}_2\text{C} + x\text{O}_2 + x\text{Li}^+ + xe^- \quad (4-8) \]

This is also confirmed by the electrochemical behavior of Mo₂C/CNT in both O₂ and CO₂ in full discharge-charge testing (Figure 4.13a). Different discharge voltage plateaus showed different reduction voltages based on the different electrochemical reduction of O₂ or CO₂. When the Mo in Mo₂C completes the coordination with O, regardless of whether the unsaturated Mo bonds with O from O₂ or CO₂, the Mo-O bond dissociation energy is the same, so the charge voltage plateau remains the same.
in both O₂ and CO₂ atmospheres. We also compared CNT and Mo₂C/CNT in cut-off capacity discharge-charge, and the Mo₂C/CNT prominently reduced the charge overpotential and improved the round-trip efficiency in both O₂ and CO₂ (Figure 4.13b). At this point, we speculate that the formation of Mo-O bonds could stabilize the reduction intermediate with oxygen-containing groups. As shown in Figure 4.13c, the reversible formation and decomposition of the amorphous discharge product in both O₂ and CO₂ by the formation and cleavage of Mo-O bonds in the Li-O₂ batteries and the Li-CO₂ batteries, make Mo₂C/CNT a potential efficient promoter in practical Li-air batteries.

**Figure 4.13 a)** Voltage profiles of Mo₂C/CNT as cathode in full discharge-charge for the Li-O₂ battery and the Li-CO₂ battery. **b)** Voltage profiles of Mo₂C/CNT as cathode in cut-off capacity discharge-charge for the Li-O₂ battery and the Li-CO₂ battery. **c)** Schematic illustration of the stabilization mechanism of Mo₂C/CNT in the Li-O₂ battery and the Li-CO₂ battery, showing the formation and cleavage of Mo-O bonds between Mo₂C and intermediate species from reduction of O₂ and CO₂ on discharge and charge.

4.3.5 **Electrochemical performance in ambient air and O₂/CO₂**
To demonstrate the practical applicability of the Mo₂C/CNT, we conducted galvanostatic full discharge-charge testing under ambient air with a dehydration device. The voltage profile of Mo₂C/CNT shows a remarkably lower overpotential and correspondingly higher energy efficiency of 80%. After 5 cycles between 2.0 V and 3.8 V, it can still maintain more than 80% of the capacity of the first discharge (Figure 4.14a). Other side-reactions from the electrolyte still exist, however, which might account for the fading during full discharge-charge cycling. Testing of CNT for comparison shows fast capacity fading to 40% over 5 cycles, and the huge charge overpotential makes the charge voltage extend to 4.6 V (Figure 4.14b). We also carried out cut-off capacity discharge-charge testing, and it was found that the Mo₂C/CNT can reversibly discharge and charge for 40 cycles (Figure 4.14c) with high round-trip efficiency, showing good cycling performance even in presence of a trivial amount of CO₂.

To investigate the influence of CO₂, we increased the ratio of CO₂ by filling a mixture of CO₂ and O₂ which contained 50% CO₂ instead of ambient air into the chamber. The cell using Mo₂C/CNT can still reversibly discharge and charge for 40 cycles with high round-trip efficiency (Figure 4.14d). Based on the low charge voltage plateau of ~3.4 V in both Li-air battery and Li-CO₂/O₂ battery, we exclude the formation of crystal Li₂O₂ and Li₂CO₃, which do not decompose until high voltage (>4V vs. Li/Li⁺). Our proposed mechanism was confirmed that the intermediate reduction species of O₂ and CO₂ could be appropriately stabilized by Mo₂C/CNT promoter via the formation of Mo-O bonds. Since amorphous (Li-O-O)ₓ-Mo₂C and (Li-O-C-O)ₓ-Mo₂C generate instead of crystalline Li₂O₂ and Li₂CO₃ during discharge process, the subsequent decomposition could remain low charge voltage in line with the charging performance of NaO₂ in Na-O₂ battery.
Figure 4.14 a) Voltage profiles of Mo$_2$C/CNT in air for the first 5 cycles, with full discharge and recharge between 2.0 V and 3.8 V, at the current rate of 20 μA. b) Voltage profiles of CNT in air for the first 5 cycles, with full discharge and recharge between 2.0 V and 4.6 V, at the current rate of 20 μA. c) Voltage profiles for selected cycles of Mo$_2$C/CNT in air, with a cut-off capacity of 100 μAh, at the current rate of 20 μA. d) Voltage profiles for selected cycles of Mo$_2$C/CNT in CO$_2$/O$_2$ (1:1), with a cutoff capacity of 100 μAh, at the current rate of 20 μA.

4.4 Conclusions

In summary, we have exploited Mo$_2$C/CNT as a promoter for practical Li-air batteries with high round-trip efficiency and good cycling performance. As a bifunctional promoter in both O$_2$ and CO$_2$ atmospheres, Mo$_2$C/CNT can efficiently stabilize both reduction intermediate species of O$_2$ and CO$_2$ to generate amorphous (Li-O-O)-Mo$_2$C and (Li-O-C-O)-Mo$_2$C discharge product, respectively, preventing the formation of
crystalline Li$_2$O$_2$ and Li$_2$CO$_3$. Correspondingly, the charge potential can be significantly reduced owing to decomposition of the amorphous discharge products, instead of the decomposition of crystalline Li$_2$O$_2$ and Li$_2$CO$_3$. Meanwhile, we predict that this promoter has the potential to pave the way towards a commercially achievable Li-air battery in an open system, not requiring a sealed oxygen tank. Our findings clearly identify the critical role of metal-oxygen bonds in Li-gas batteries, suggesting that the low valence metal in metal compound provides a suitable environment for surface stabilization of O$_2$ and CO$_2$ reduction product. This has broader implications that can be applied to guide rational design strategies for other promoters such as metal carbides, metal sulfide which metal centers in the unsaturated coordination state. More importantly, the understanding of cationic redox and anionic redox further inspires us to explore new battery systems with longer life and higher energy density such as anion redox metal compound/LiO$_x$ system.

### 4.5 References


(13) Lim, H. K.; Lim, H. D.; Park, K. Y.; Seo, D. H.; Gwon, H.; Hong, J.; Goddard,


Chapter 5: The Influence of Interfacial Chemistry on Li$_2$O$_2$

Oxidation for Li-air Battery

5.1 Introduction

The research of Li-air batteries is facing many challenges in pursuit of attaining a substantial fraction of battery’s large theoretical energy density\(^1\). Even though intensive researches were conducted in last decade, many open questions remain, including the instability of electrolyte, side reactions in high voltage, slow oxygen reaction kinetics, as well as asymmetric discharge/charge curves\(^2,3\). It is found that when carbon materials used as cathode, the charge overpotential is not only higher than the discharge overpotential but also continuously rises upon progressing state of charge\(^1,4\). This results in a low round-trip efficiency and can increase the rate of potential-driven side reactions. Hence, reducing the charge overpotential by heterogenous electrocatalysis in Li-O$_2$ cells became a hot topic at its infancy stage\(^5-7\). However, noting that Li$_2$O$_2$ forms as a solid, insoluble crystal, it is difficult to envision how Li$_2$O$_2$ deposited away from active catalytic sites would be able to diffuse back to catalytic sites in typical electrolyte compositions.\(^1,8\) Furthermore, the inherent oxidation overpotential of peroxide has been calculated and shown experimentally to be quite low, raising questions about the real role of OER electrocatalysis in charge\(^9\).

Numerous researches focused on developing new electrode materials, aiming to reduce charge overpotential of Li-air batteries.\(^10-18\) However, further efforts are still required to understand the charge mechanism of heterogeneous electrocatalysis, especially the interfacial chemistry between electrode materials and discharge product.\(^19-23\) Recently, a theoretical charge-transport model suggested that the carbonate layer at the C-Li$_2$O$_2$
interface forms interfacial resistance and causes a 10-100-fold decrease in the exchange current density. As reported, this insulating monolayer causes rising potential in charge and consequent electrolyte stability problems\textsuperscript{24}. Meanwhile, it was proposed that even nanometric passivating films (TiO\textsubscript{2}/TiOC) on non-carbon material (TiC), could also completely inhibit the charge reaction of Li-O\textsubscript{2} batteries\textsuperscript{25}. Altogether, these studies clearly demonstrate the importance of interfacial chemistry (Figure 5.1), which is critical in determining the efficiency of electron transfer during the charge reaction.

**Figure 5.1** Schematic view to show a) interfacial passivating films (Li\textsubscript{2}CO\textsubscript{3}) on carbon-based electrode and b) interfacial passivating films (TiO\textsubscript{2}/TiOC) on non-carbon-based (TiC) electrode block the decomposition of Li\textsubscript{2}O\textsubscript{2}.

In this chapter, the influence of interfacial chemistry on Li\textsubscript{2}O\textsubscript{2} oxidation was studied using carbon-based (Vulcan C) electrode and non-carbon-based (Mo\textsubscript{2}C) electrode. To elucidate the mechanism of the oxidation evolution reaction on carbon-based electrode, the galvanostatic tests of Li\textsubscript{2}O\textsubscript{2}-preloaded Vulcan C electrode and Li\textsubscript{2}CO\textsubscript{3}-preloaded Vulcan C electrode were carried out. A clear difference is observed between the oxidation of commercial preloaded Li\textsubscript{2}O\textsubscript{2} in first charge and electrochemically generated Li\textsubscript{2}O\textsubscript{2} in second charge, which could be explained that insulating Li\textsubscript{2}CO\textsubscript{3} generated from interfacial corrosion by LiO\textsubscript{2} intermediate in discharge process. SEI modification on the surface of carbon-based electrode is proposed and verified as a feasible method to prevent carbon-based electrode from interfacial corrosion by LiO\textsubscript{2} intermediate, facilitating decomposition of Li\textsubscript{2}O\textsubscript{2}. To understand the mechanism of the
oxidation evolution reaction on non-carbon-based electrode, cyclic voltammetry test and galvanostatic discharge-charge test of commercial Mo$_2$C electrode were carried out. The morphology and structure of electrodes at different stage in galvanostatic test were studied by SEM and XRD. Moreover, the galvanostatic tests of Li$_2$O$_2$-preloaded Mo$_2$C electrode and Li$_2$CO$_3$-preloaded Mo$_2$C electrode were carried out to further confirm the heterogenous catalytic property of Mo$_2$C. This work offers us a comprehensive understanding toward detrimental effect of interfacial Li$_2$CO$_3$ on Li$_2$O$_2$ oxidation using carbon-based electrode and possible role of Mo$_2$C as an efficient heterogeneous catalyst, providing useful guidance for further development of modified carbon-based electrode and heterogenous catalytic non-carbon-based electrode for Li-air batteries.

5.2 Experimental Details

5.2.1 Preparation of gas diffusion electrodes

Typical gas diffusion electrodes were prepared by casting an active layer on carbon papers. Briefly, 80 wt.% Vulcan C was mixed with 20 wt.% PVDF in NMP and films were cast onto carbon paper disk substrate (1.5 cm$^2$). Similarly, 98 wt.% commercial Mo$_2$C was mixed with 1 wt.% carbon black and 1 wt.% PVDF in NMP and films were cast onto carbon paper disk substrate (1.5 cm$^2$). A small amount of additive carbon black is for the purpose of conductivity improvement. These electrodes were dried at 120 ºC under vacuum for 12 hours.

5.2.2 Preparation of Li$_2$O$_2$/Li$_2$CO$_3$ loaded electrode

Lithium peroxide (90%, Sigma-Aldrich) and lithium carbonate (99%, Sigma-Aldrich) were used as received. In an argon-filled glovebox, the Li$_2$O$_2$ (or Li$_2$CO$_3$) powder was mixed with Vulcan XC72 (or commercial Mo$_2$C), and PVDF as binder. The mass ratio
of Vulcan C: Li$_2$O$_2$ (or Li$_2$CO$_3$): PVDF was 4:1:1, and the mass ration of Mo$_2$C: Li$_2$O$_2$
(or Li$_2$CO$_3$): PVDF was 8:1:1 in all cases. The resulting paste was spread onto carbon
paper disk substrates (1.5 cm$^2$). These prepared electrodes were finally dried at 80 °C
in Ar-filled glovebox overnight.

5.2.3 **Electrochemical tests**

Electrochemical tests were carried out using coin cells containing the active material
working electrode, a lithium metal anode, and electrolyte (1 M LiCF$_3$SO$_3$ in TEGDME
impregnated into a glass fiber separator (Whatman GF/D microfiber filter paper, 2.7
µm pore size)). All cell assembly procedures were conducted in an argon-filled glove
box (oxygen and water contents less than 0.1 ppm). The cells were conducted
electrochemical tests in an O$_2$-filled or CO$_2$-filled chamber with a 4-hour stabilization
prior to testing.

5.2.4 **Characterization**

The structural characterization was analyzed by GBC MMA X-ray power diffraction
(XRD) equipped with Cu Kα radiation ($\lambda = 1.54$ Å) with the voltage and current kept
at 40 kV and 25 mA, respectively. The morphology of samples and electrodes were
examined using JEOL JSM-7500 field emission scanning electron microscope
(FESEM), in which the accelerating voltage was set at 5.0 kV and the emission current
was 10 mA.

5.3 **Results and Discussion**

5.3.1 **Li$_2$O$_2$/Li$_2$CO$_3$ oxidation on Vulcan C electrode**

To study the Li$_2$O$_2$ oxidation on carbon-based electrode, Li$_2$O$_2$-preloaded Vulcan C
The electrode was prepared in an Ar-filled glove box. Aside from the broad peaks at 26° and 44°, corresponding to (002) and (100) crystalline planes of carbon, other peaks of Li$_2$O$_2$-preloaded Vulcan C electrode associated with commercial Li$_2$O$_2$, confirming the Li$_2$O$_2$-preloaded Vulcan C electrode was well prepared without deterioration of Li$_2$O$_2$ during the electrode preparation process (Figure 5.2a). Scanning electron microscopy (SEM) image of Li$_2$O$_2$-preloaded Vulcan C electrode reveals uniform mixture of Vulcan C and Li$_2$O$_2$ (Figure 5.2b).

**Figure 5.2** a) XRD patterns of commercial Li$_2$O$_2$ and Li$_2$O$_2$ preloaded Vulcan C electrode. b) SEM image of Li$_2$O$_2$ preloaded Vulcan C electrode. c) XRD patterns of commercial Li$_2$CO$_3$ and Li$_2$CO$_3$-preloaded Vulcan C electrode. d) SEM image of Li$_2$CO$_3$-preloaded Vulcan C electrode.

Due to general “interfacial carbonate problem” of carbon-based material, Li$_2$CO$_3$-
preloaded Vulcan C electrode was also prepared in the Ar-filled glove box, aiming to elucidate the Li$_2$CO$_3$ oxidation on carbon-based electrode. The Li$_2$CO$_3$-preloaded Vulcan C electrode was confirmed to be well prepared, based on the same characteristic diffraction peaks of Li$_2$CO$_3$ powder and Li$_2$CO$_3$-preloaded Vulcan C electrode (Figure 5.2c). The uniform mixture of Vulcan C and Li$_2$CO$_3$ is revealed by SEM image of Li$_2$CO$_3$-preloaded Vulcan C electrode (Figure 5.2d).

The designed galvanostatic charge-discharge-charge test of Li$_2$O$_2$-preloaded Vulcan C, was conducted at the current rate of 0.05 mA cm$^{-2}$. The Li-O$_2$ cell with Li$_2$O$_2$-preloaded Vulcan C electrode was charged to 4.25 V as its first charge. As shown in Figure 5.3a, the voltage profile shows a rise and drop at the beginning, which could be explained as the reaction between carbon and Li$_2$O$_2$ at their interface and is referred to as the “activation process”. The first charge voltage plateau is ~3.75 V, which clearly shows the decomposition of preloaded commercial Li$_2$O$_2$ could occur under 4.0 V. It is shown that the subsequent discharge voltage plateau is ~2.7 V, corresponding to the electrochemical generation of Li$_2$O$_2$ in oxygen reduction reaction. After that, the Li-O$_2$ cell was charged to 4.5 V, corresponding to the decomposition of electrochemically generated Li$_2$O$_2$. Differ from the decomposition of commercial Li$_2$O$_2$ in first charge, it shows a drastic increased charge voltage plateau of above 4.0 V in second charge. Itkis et al. has proposed the mechanism for Li$_2$CO$_3$ formation involving the carbon electrode on discharge. The mechanism goes through three steps: 1) superoxide radicals are firstly formed; 2) the nucleophilic addition and/or electron transfer reactions promoted by superoxide radicals form epoxy-groups on the carbon electrode; 3) the epoxy-groups are then converted into carbonates. Since the inherent oxidation overpotential of peroxide has been calculated and shown experimentally to be quite low, it is possible that Li$_2$CO$_3$, which generated from the surface reaction between Vulcan C and...
intermediate LiO₂, contributed to the higher charging potential.

To confirm the detrimental effect of interfacial Li₂CO₃ on Li₂O₂ oxidation, the galvanostatic charge-discharge-charge test of Li₂CO₃-preloaded Vulcan C electrode was conducted under CO₂. As shown in Figure 5.3b, the first and the second charge voltage plateau are above 4.2 V, indicating that both preloaded commercial Li₂CO₃ and electrochemically deposited Li₂CO₃ are difficult to be decomposed by carbon materials under 4.0 V, which is consistent with previous reported results. This result indicates that Li-CO₂ cell with insulating Li₂CO₃ has a higher charge voltage plateau than Li-O₂ cell with commercial Li₂O₂ but has a similar charge voltage plateau of Li-O₂ cell with electrochemically generated Li₂O₂. According to this, we deduced that change of interfacial chemistry on carbon electrode may contribute to the different charge voltage plateau. The interfacial generation of Li₂CO₃ deteriorated the kinetic of Li₂O₂ decomposition, which probably caused by the reaction between carbon and oxidative LiO₂ intermediate.

Figure 5.3 a) Voltage profile of charge-discharge-charge with a Li₂CO₃-preloaded Vulcan C electrode at a current rate of 50 µA cm⁻² in 1 M LiCF₃SO₃/TEGDME. b) Voltage profile of charge-discharge-charge with a Li₂O₂-preloaded Vulcan C electrode at a current rate of 50 µA cm⁻² in 1 M LiCF₃SO₃/TEGDME.
5.3.2 Comparison of Li$_2$O$_2$ oxidation on Vulcan C electrode with SEI and Vulcan C electrode without SEI

As the study on Li$_2$O$_2$/Li$_2$CO$_3$ preloaded Vulcan C electrode shown, the interfacial Li$_2$CO$_3$ on carbon-based electrode is hugely influential on the charge overpotential for Li-air batteries. When carbon-based electrode is employed for Li-air battery, it is essential to protect carbon electrode from the corrosion by LiO$_2$ intermediate in discharge. For this purpose, a method that utilizing solid electrolyte interface (SEI) to modify carbon surface was proposed and tested. Detailed design and test procedures are listed in Table 5.1:

Table 5.1 Battery design and test procedures of Li$_2$O$_2$-preloaded Vulcan C electrode.

<table>
<thead>
<tr>
<th>Cell 1# (Vulcan C without SEI)</th>
<th>Cell 2# (Vulcan C with SEI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Charge to 4.0 V under O$_2$</td>
<td>1 Charge to 4.0 V under O$_2$</td>
</tr>
<tr>
<td>1-1 -</td>
<td>1-1 Discharge to 0.01 V in Li-ion cell</td>
</tr>
<tr>
<td>1-2 -</td>
<td>1-2 Charge to 2.0 V in Li-ion cell</td>
</tr>
<tr>
<td>2 Discharge to 2.0V under O$_2$</td>
<td>2 Discharge to 2.0V under O$_2$</td>
</tr>
<tr>
<td>3 Charge to 4.5 V under O$_2$</td>
<td>3 Charge to 4.5 V under O$_2$</td>
</tr>
</tbody>
</table>

As shown in Figure 5.4a, cell 1# and cell 2# with Li$_2$O$_2$-preloaded Vulcan C electrode was charged to 4.0 V under O$_2$ in step 1), showing same charge voltage plateau of the oxidation(decomposition) of commercial Li$_2$O$_2$. After that, cell 2# was disassembled to obtain the charged electrode in glove box. This electrode was then employed as anode for a Li-ion battery assembly. After discharge to 0.01 V in step 1-1) and charge to 2.0 V in step 1-2) (Figure 5.4b), the solid electrolyte interface was generated on the surface of Vulcan C electrode. In following step, cell 2# was disassemble again to obtain the SEI modified electrode in glove box. This electrode was then employed as cathode for
Li-O₂ battery assembly. Compared with cell 2#, cell 1# did not go through step 1-1) and 1-2). In step 2) and step 3), both cell 1# and cell 2# were discharged to 2.0 V, then charged to 4.5 V under O₂. These two steps are related to the deposition and decomposition of electrochemically generated Li₂O₂ respectively. The difference was observed that the decomposition of electrochemically generated Li₂O₂ could be decomposed at a lower charge voltage plateau in cell 2#, compared with a much high charge voltage plateau in cell 1#.

Figure 5.4 a) Voltage profile of charge-discharge-charge with Li₂O₂-preloaded Vulcan C electrode with and without SEI in Li-O₂ battery. b) Voltage profile corresponding to SEI modification of Vulcan C electrode in Li-ion battery. c) Schematic view to show corrosion of carbon in discharge without SEI. d) Schematic view to show protection of carbon in discharge with SEI.

Based on this, we assumed the reason of different voltage plateau is that SEI protects the carbon material from oxidization by LiO₂ intermediate to generate insulating Li₂CO₃ (Figure 5.4c-d). It is shown that the cell using carbon materials could also
obtain low charge voltage plateau if carbon surface is protected to avoid the generation of interfacial \( \text{Li}_2\text{CO}_3 \).

5.3.3 Discharge/charge behavior of Mo\(_2\)C electrode

Based on the study on \( \text{Li}_2\text{O}_2 \) and \( \text{Li}_2\text{CO}_3 \) preloaded carbon-based materials, it is shown that interfacial \( \text{Li}_2\text{CO}_3 \) on carbon-based materials increased the charge voltage plateau. The reason that some non-carbon-based materials exhibited low charge polarity could possibly ascribed to resistance of \( \text{LiO}_2 \) intermediate to generate \( \text{Li}_2\text{CO}_3 \). In Chapter 3 and Chapter 4, Mo\(_2\)C/CNT composite materials were prepared via ball-milling and employed as catalyst. However, it is difficult to observe the morphology change of nanostructured materials. Therefore, electrode of commercial molybdenum carbide was employed for better observation of morphology change during discharge-charge processes. Cyclic voltammetry tests of three different batteries were conducted and shown in Figure 5.5.

![Cyclic voltammograms](image)

**Figure 5.5** Cyclic voltammograms of Mo\(_2\)C in Li-ion battery, Mo\(_2\)C and Vulcan C in Li-O\(_2\) battery at a scan rate of 0.1 mV s\(^{-1}\).
It is shown that there is no cathodic peak of Li-ion battery with Mo$_2$C, confirming that there is no reaction occur without oxygen; however, there is an anodic peak with on-set potential of 3.8 V, indicating the instability of Mo$_2$C above 3.8 V (red curve). Under oxygen, the oxygen reduction and evolution reaction occur in the range of 2.0 - 4.5 V, with the cathodic and anodic peaks observed at 2.3 V and 3.7 V (black curve). Compared with Li-ion battery and Li-O$_2$ battery with Mo$_2$C, the Li-O$_2$ battery with Vulcan C only shows a clear cathodic peak, indicating the reduction of O$_2$ with the generation of Li$_2$O$_2$ (green curve).

To probe the oxygen reduction and evolution mechanism on commercial Mo$_2$C, the galvanostatic discharge-charge of Li-O$_2$ cell with commercial Mo$_2$C electrode was conducted with different stages (Figure 5.6).

![Figure 5.6 Voltage profile of discharge/charge cycle with a commercial Mo$_2$C electrode at a current rate of 50 µA cm$^{-2}$ in 1 M LiCF$_3$SO$_3$/TEGDME.](image)

The electrodes and glassfibers at different stages were disassembled and analyzed. For discharging process, pristine Mo$_2$C was discharged to 1/3 capacity as step i, 2/3 discharge capacity as step ii, and whole capacity to 2.0 V as step iii. For charge process,
fully discharged Mo$_2$C was charged to 1/3 capacity as step iv, 2/3 capacity as step v, whole capacity as vi, and around 2.5-fold capacity as step vii. XRD patterns of commercial Mo$_2$C electrode at different stages shows there is no crystalline Li$_2$O$_2$ observed (Figure 5.7), indicating that amorphous discharge product might be generated and responsible for the low charge overpotential.

![XRD patterns of commercial Mo$_2$C electrode at different steps of discharge-charge of Li-O$_2$ battery.](image)

**Figure 5.7** XRD patterns of commercial Mo$_2$C electrode at different steps of discharge-charge of Li-O$_2$ battery.

The presence and disappearance of the amorphous product can be visibly confirmed from the FESEM observations at different stages. The growth of discharge product on the surface of Mo$_2$C was observed (Figure 5.8), although it is still unclear to explain as amorphous Li$_2$O$_2$ or stabilization species. As shown in Figure 5.9, the thin film of discharge product was gradually decomposed and disappeared after charging to the same capacity delivered in discharge. It is also observed that the bulk Mo$_2$C started to dissolve and collapse when the cell is overcharged. The dissolution of Mo$_2$C was also
confirmed by the photos of glassfiber at different stages (Figure 5.10). It is shown that only glassfiber in overcharged cell turns into blue colour, indicating the instability of Mo$_2$C above 3.8 V. Due to this, the voltage of 3.8 V should be a cutoff voltage for the protection of Mo$_2$C electrode.

![SEM images of pristine Mo$_2$C electrode and discharged Mo$_2$C electrode at different stages (i, ii, iii).](image)

**Figure 5.8** SEM images of pristine Mo$_2$C electrode and discharged Mo$_2$C electrode at different stages (i, ii, iii).

![SEM images of charged Mo$_2$C electrode at different stages (iv, v, vi, vii).](image)

**Figure 5.9** SEM images of charged Mo$_2$C electrode at different stages (iv, v, vi, vii).
The reversibility of Li-O₂ cell with commercial Mo₂C was confirmed by galvanostatic discharge-charge. Even in full discharge-charge between 2.0 V and 3.75 V, the Li-O₂ cell could reversibly discharge and charge for ten cycles (Figure 5.11).

![Figure 5.10 Photos of glassfiber at different steps for Li-O₂ cell using Mo₂C as cathode.](image)

![Figure 5.11 Galvanostatic discharge and charge of Li-O₂ cell with commercial Mo₂C.](image)

5.3.4 Li₂O₂/Li₂CO₃ oxidation on Mo₂C electrode

To study the charging process of Li-air batteries on Mo₂C, we prepared Li₂O₂ preloaded
Mo$_2$C electrode and carried out galvanostatic charge-discharge test under oxygen. Differ from the Li-O$_2$ cell using Li$_2$O$_2$-preloaded Vulcan C electrode, the Li-O$_2$ cell using Li$_2$O$_2$-preloaded Mo$_2$C electrode showed same voltage plateau of 3.35 V at first and second charging in same electrochemical test procedure (Figure 5.12), indicating the decomposition of both preloaded commercial Li$_2$O$_2$ and electrochemically generated Li$_2$O$_2$ on Mo$_2$C occurs at the same charge voltage plateau.

![Figure 5.12](image.png)

**Figure 5.12** Voltage profile of charge/discharge/charge cycle with a Li$_2$O$_2$-preloaded Vulcan C electrode at a current rate of 50 $\mu$A cm$^{-2}$ in 1 M LiCF$_3$SO$_3$/TEGDME.

The decomposition of preloaded commercial Li$_2$O$_2$ (in step 1) and electrochemically generated Li$_2$O$_2$ (in step 2) were confirmed by the SEM images of Li$_2$O$_2$-preloaded Mo$_2$C electrode at different discharge-charge stage (Figure 5.13). Although the morphologies of commercial preloaded Li$_2$O$_2$ and electrochemically generated Li$_2$O$_2$ are different, they could be decomposed at low voltage plateau on Mo$_2$C electrode.
Moreover, the decomposition of Li$_2$CO$_3$ on Mo$_2$C is further confirmed by galvanostatic charge and discharge of Li-CO$_2$ cell with Li$_2$CO$_3$-preloaded Mo$_2$C electrode (Figure 5.14). Mo$_2$C promoted the decomposition of Li$_2$CO$_3$ with a stable charge voltage plateau at 3.7 V for the first charging. Moreover, the deposited product after first discharging could be decomposed with a lower charge voltage plateau at 3.5 V for the second charging. Different charge voltage plateau may ascribe to the decomposition of different compounds with Mo$_2$C electrode. The charge voltage plateau at 3.7 V (in step 1) could ascribe to the decomposition of crystalline Li$_2$CO$_3$, while the charge voltage plateau at 3.5 V (in step 2) is probably derive from the decomposition of some amorphous discharge product.
Figure 5.14 Voltage profile of charge/discharge/charge cycle with a Li$_2$CO$_3$-preloaded Vulcan C electrode at a current rate of 50 $\mu$A cm$^{-2}$ in 1 M LiCF$_3$SO$_3$/TEGDME.

5.3.5 Correlation of electrode material interface to Li$_2$O$_2$ oxidation

As discussed above, the capability of carbon-based electrode material (Vulcan C) and non-carbon-based electrode material (Mo$_2$C) to decompose Li$_2$CO$_3$ and Li$_2$O$_2$ was examined. It was found that both Li$_2$O$_2$ and Li$_2$CO$_3$ could be decomposed on Mo$_2$C electrode below 4.0 V, but only preloaded commercial Li$_2$O$_2$ could be decomposed on carbon electrode below 4.0 V (as displayed in the schematic diagram in Figure 5.15). This indicates that interfacial Li$_2$CO$_3$ on carbon materials require higher voltage plateau to decompose in charge. However, Mo$_2$C could still maintain charge voltage of no more than 4.0 V even Li$_2$CO$_3$ generated, owing to its capability to decompose Li$_2$CO$_3$ at lower voltage below 4.0 V, as well as its resistance to contamination by LiO$_2$ intermediate.
Figure 5.15 Schematic diagram of the capability to decompose Li$_2$CO$_3$ and Li$_2$O$_2$ using Vulcan C and Mo$_2$C for Li-air batteries.

5.4 Conclusions

In conclusion, different oxidation processes of preloaded commercial Li$_2$O$_2$ and electrochemically generated Li$_2$O$_2$ on carbon were observed in galvanostatic discharge-charge test of the Li-O$_2$ cell with Li$_2$O$_2$-preloaded Vulcan C electrode. The charge voltage plateau for the decomposition of preloaded commercial Li$_2$O$_2$ (~3.75 V), which is much lower than the charge voltage plateau for the decomposition of electrochemically generated Li$_2$O$_2$ (above 4.2 V). Based on the following galvanostatic discharge-charge test of the Li-CO$_2$ cell with Li$_2$CO$_3$-preloaded Vulcan C electrode, which shows the high charge voltage plateau (above 4.2 V) for the decomposition of both preloaded Li$_2$CO$_3$ and electrochemically generated Li$_2$CO$_3$, we have confirmed that insulating Li$_2$CO$_3$ caused a high overpotential on charge. Although bulk conductivity plays an important role in electron transfer to promote the decomposition
of Li$_2$O$_2$ on cathode supports for the Li-O$_2$ battery, the interfacial Li$_2$CO$_3$ of these supports is most critical in determining the efficiency of electron transfer to Li$_2$O$_2$ during charge reaction.

Additionally, it is found that commercial Mo$_2$C could facilitate the decomposition of both preloaded commercial Li$_2$O$_2$ and electrochemically generated Li$_2$O$_2$ at low charge voltage plateau. Amorphous discharge product was confirmed by XRD patterns of electrode at different discharge-charge steps. SEM images clearly shows the deposition and decomposition of the thin film-like discharge product. The subsequent investigation on Li-O$_2$ cell (and Li-CO$_2$ cell) with Li$_2$O$_2$-preloaded Mo$_2$C electrode (and Li$_2$CO$_3$-preloaded Mo$_2$C electrode) shows that both preloaded commercial Li$_2$O$_2$ (and Li$_2$CO$_3$) and electrochemically generated discharge product could be decomposed at low charge voltage plateau on Mo$_2$C electrode.

The comprehensive study on Li-O$_2$ cell with carbon-based and non-carbon-based electrode provide two main criteria for catalyst design in Li-air battery. One is high conductive materials to facilitate the electron transport, and the other is high resistance to oxidation of intermediate product such as LiO$_2$ and Li$_2$O$_2$. Based on these two criteria, the potential catalysts are listed as follows:

1) Mo-based materials such as Mo$_2$C, MoS$_2$, etc.
2) Other transition metal carbide with high electrical conductivity such as VC, Fe$_3$C, Co$_2$C;
3) Carbon-based materials with modification such as Al$_2$O$_3$, TiO$_2$, SEI, etc.
4) Carbon-based matrix with non-carbon-based catalyst surface such as the composite material of CNT matrix with Mo$_2$C surface.
5.5 References


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(14) Luo, W. B.; Pham, T. V.; Guo, H. P.; Liu, H. K.; Dou, S. X. Three-dimensional array of TiN@Pt$_3$Cu nanowires as an efficient porous electrode for the lithium-oxygen battery. *ACS Nano* **2017**, *11*, 1747.


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Chapter 6: Conclusions and Perspectives

6.1 General conclusions

Designing catalysts by understanding reaction chemistry, is one of the most important topics to reduce overpotential gap for aprotic Li-air battery.\textsuperscript{1-5} Although a large number of carbon-based and non-carbon-based catalysts have been synthesized and claimed to have good catalytic properties, many of them are actually ineffective.\textsuperscript{5-11} The observed reduction of overpotential is due to the addition of carbon material to reduce internal resistance, or side reactions take place at a lower potential compared with Li\textsubscript{2}O\textsubscript{2} oxidation. Therefore, this thesis aimed at understanding the reaction chemistry of aprotic Li-air battery, including three parts as illustrated in Figure 6.1: 1) Reaction chemistry of contaminant CO\textsubscript{2}; 2) Reaction chemistry of O\textsubscript{2} in the presence of CO\textsubscript{2}; 3) Reaction chemistry of interfacial Li\textsubscript{2}CO\textsubscript{3}.

![Project Diagram](image_url)

\textbf{Figure 6.1} Illustration of thesis project outline.

In Chapter 3, Li-CO\textsubscript{2} battery is utilized to investigate the reaction chemistry of CO\textsubscript{2} and potential impact of CO\textsubscript{2} contamination on Li-air battery. Mo\textsubscript{2}C/CNT is prepared via a
carbothermal reduction process and employed as the catalyst for Li-CO$_2$ batteries. As an efficient catalyst for Li-CO$_2$ battery, Mo$_2$C/CNT shows a low charge voltage plateau at ~3.5 V, a high round-trip efficiency of 77%, as well as a good cycling performance. The different pathways of discharge reaction between CNT and Mo$_2$C/CNT is proposed according to a series of characterizations (XPS, SEM, XRD, Raman) of CNT electrodes and Mo$_2$C/CNT electrodes at different stages of Li-CO$_2$ batteries. In the absence of Mo$_2$C, insulating Li$_2$CO$_3$ was generated on CNT electrode in discharge, causing the high charge voltage plateau when it was decomposed in charge. On the contrary, it is clearly shown that CO$_2$ reduction follows a different route that avoids the formation of insulating Li$_2$CO$_3$ in the presence of Mo$_2$C. This amorphous discharge product could be easily decomposed in charge, reducing charge voltage plateau to ~3.5 V for Li-CO$_2$ battery. Although electrochemical test of Mo$_2$C/CNT has confirmed its catalytic ability to facilitate the decomposition of discharge product in Li-CO$_2$ battery, further studies using \textit{in-situ} characterizations are still needed to provide direct evidence for understanding the mechanism.

In Chapter 4, Mo$_2$C/CNT was exploited as a catalyst for practical Li-air batteries to investigate reaction chemistry of O$_2$ in the presence of CO$_2$. According to our investigation, Mo$_2$C/CNT as a bifunctional catalyst in both O$_2$ and CO$_2$ atmospheres, could efficiently stabilize both reduction intermediate species of O$_2$ and CO$_2$ to generate amorphous (Li-O-O)$_x$-Mo$_2$C and (Li-O-C-O)$_x$-Mo$_2$C discharge product, respectively, preventing the formation of crystalline Li$_2$O$_2$ and Li$_2$CO$_3$. Correspondingly, the charge potential could be significantly reduced owing to decomposition of the amorphous discharge products, instead of the decomposition of crystalline Li$_2$O$_2$ and Li$_2$CO$_3$. Meanwhile, we predicted that such bifunctional catalysts have the potential to pave the way towards a commercially achievable Li-air battery in an open system with a
waterproof membrane, not requiring a sealed oxygen tank. Our findings clearly identify the critical role of metal-oxygen bonds in Li-gas batteries, suggesting that the low valence metal in metal compound provides a suitable environment for surface stabilization of \( \text{O}_2 \) and \( \text{CO}_2 \) reduction product. This has broader implications that can be applied to guide rational design strategies for other promoters such as metal carbides, metal sulfide which metal centers in the unsaturated coordination state. Moreover, the understanding of cationic redox and anionic redox inspires us to explore new battery systems with longer life and higher energy density such as anion redox metal compound/LiO\(_x\) system.

In Chapter 5, reaction chemistry of interfacial Li\(_2\)CO\(_3\), as well as the role of solid-state catalysts were further investigated utilizing \( \text{Li}_2\text{O}_2/\text{Li}_2\text{CO}_3 \)-preloaded Vulcan C electrodes and \( \text{Li}_2\text{O}_2/\text{Li}_2\text{CO}_3 \)-preloaded Mo\(_2\)C electrodes. Different oxidation processes of preloaded commercial Li\(_2\)O\(_2\) and electrochemically generated Li\(_2\)O\(_2\) on carbon were observed in galvanostatic charge-discharge test of the Li-O\(_2\) cell with Li\(_2\)O\(_2\)-preloaded Vulcan C electrode. The charge voltage plateau for the decomposition of preloaded commercial Li\(_2\)O\(_2\) is \(~3.75\) V, is much lower than the charge voltage plateau for the decomposition of electrochemically generated Li\(_2\)O\(_2\) (above 4.2 V). Based on the following galvanostatic charge-discharge test of the Li-CO\(_2\) cell with Li\(_2\)CO\(_3\)-preloaded Vulcan C electrode, which shows the high charge voltage plateau (above 4.2 V) for the decomposition of both preloaded Li\(_2\)CO\(_3\) and electrochemically generated Li\(_2\)CO\(_3\), we have confirmed that insulating Li\(_2\)CO\(_3\) caused a high charge overpotential for Li-air battery. The interfacial Li\(_2\)CO\(_3\) of carbon-based electrode is most critical in determining the efficiency of electron transfer to Li\(_2\)O\(_2\) during charge reaction. This chapter also shows that commercial Mo\(_2\)C could facilitate the decomposition of both preloaded commercial Li\(_2\)O\(_2\) and electrochemically generated Li\(_2\)O\(_2\) at low charge voltage plateau.
Amorphous discharge product was confirmed by XRD patterns of electrode at different discharge-charge steps. SEM images clearly shows the deposition and decomposition of the thin film-like discharge product. The subsequent investigation on Li-O₂ cell (Li-CO₂ cell) with Li₂O₂-preloaded Mo₂C electrode (Li₂CO₃-preloaded Mo₂C electrode) demonstrates that both preloaded commercial Li₂O₂ (Li₂CO₃) and electrochemically generated discharge product could be decomposed on Mo₂C electrode.

6.2 Perspectives

As discussed above, controlling reaction chemistry of Li-air batteries is critical and indispensable in achieving practical application of Li-air batteries. Meanwhile, future work must always entail the examination of stability of all components of Li-air batteries. A practical battery will not be achievable if any of the battery components are subject to corrosion by the oxidant (LiO₂, O₂⁻, Li₂O₂ and O₂²⁻). In terms of electrode materials, the stability should be carefully considered when designing electrode for Li-air battery.

For carbon-based electrode, to find a method protecting carbon from corrosion by the oxidant (LiO₂, O₂⁻, Li₂O₂ and O₂²⁻) is essential in future work. Since the inherent oxidation overpotential of Li₂O₂ has been calculated and shown experimentally to be quite low in some researches, the use of carbon electrode without catalyst is possible after suitable modification. In this doctoral work, we have confirmed the detrimental influence of Li₂CO₃ on the Li₂O₂ oxidation. Only if interfacial Li₂CO₃ is avoided, carbon-based electrode could be employed as a suitable electrode for Li-air batteries. Conductive solid electrolyte interface modification in this doctoral work is a potential feasible method for carbon protection, and more detailed investigation will be carried out in our future work (Figure 6.2).
Figure 6.2 Schematic for the SEI protection of carbon electrode.

For non-carbon-based electrode, to untangle the elusive and controversial operation mechanisms is the most important direction in future work. A fundamental understanding of operation mechanism is essential before the development of new solid catalysts. In this doctoral work, we have confirmed illustrated that non-carbon-based catalyst affects the nature of the discharge products, thus affecting the charge reaction chemistry of Li-air battery. According to our research, several non-carbon-based materials were predicted to be possible catalyst for Li-air battery. As shown in Figure 6.3, possible transition metal-centered catalysts including metal carbides, sulfides and nitrides are marked red for solid catalyst design. Among them, some catalysts such as TiC and Fe₃C have been proved to work efficiently as catalysts for Li-air batteries,¹²-¹³ other relevant catalysts are still required for further investigation on their electrical conductivity and resistance to LiO₂ intermediate, as well as catalytic property for Li-air battery.

Figure 6.3 Possible transition metal for solid catalyst design.
6.3 References


(9) Luo, W. B.; Pham, T. V.; Guo, H. P.; Liu, H. K.; Dou, S. X. Three-dimensional array of TiN@Pt₃Cu nanowires as an efficient porous electrode for the lithium-


APPENDICES

APPENDIX 1: LIST OF PUBLICATIONS


APPENDIX 2: AWARDS RECEIVED

1. International Postgraduate Tuition Award (IPTA), 2014-2018, University of Wollongong


3. Student Travel Grant to Attend International Conference, 2016, University of Wollongong