ABSTRACT

XU, GUANJIE. Carbon Nanofiber Based Electrodes for Lithium-Air Batteries. (Under the direction of Prof. Xiangwu Zhang).

Driven by the pressure of greenhouse gas emissions, same as the tremendous business prospects of portable electronic devices and electric vehicles, developing new materials for electricity storage systems have been experiencing the non-stop exponential growth\(^1\-^3\). Although having essential chemical challenges and obstacle, Li-air batteries, the so-called “breathing” battery, start to draw significant attention with the attractively-high capacity, which is 5-10 times greater than that of Li-ion batteries\(^4\). The essential chemical difficulty lies in the sluggish multi-electron-transfer oxygen reduction and evolution reactions, coupling with complexity of multi-phase systems and inert chemical nature of the reaction products. Consequently, severe polarization, poor reversibility, and low cycling stability become the performance-limiting problems that must be addressed before Li-air batteries succeeding Li-ion batteries. High-surface-area and highly-conductive carbons become the desired material choice for electrodes used in Li-air batteries. Among various carbon materials, carbon nanofiber (CNF) electrodes are particularly promising for use in Li-air cathodes considering their characteristics such as low cost, high surface area, and high conductivity. Thus, this research focused on CNF-based electrodes for Li-air batteries.

In Chapter 3, non-woven porous carbon nanofiber (PCNF) electrodes were fabricated through electrospinning and carbonization of ZnCl\(_2\)/polyacrylonitrile (PAN) precursors to evaluate the paradox effect of broadening surface area on improving cell reversibility and decreasing electrode conductivity for Li-air batteries. SEM, EDS, and nitrogen adsorption-
desorption were used to evaluate the morphology and porosity of the obtained macro/micro-porous structure. The specific surface area of the PCNF electrode made from 30% ZnCl₂/PAN precursor was found to be 20 times greater than that of carbon nanofibers (CNFs) made directly from the PAN precursor. Electrochemical performance tests showed the PCNF electrodes had lower capacity but better reversibility compared with CNF electrodes. In pursuing better electrode structure and higher performance of Li-air batteries, it is not always the larger surface area the better. Adjusting the balance between conductivity and surface area to the specific applications is of significant importance to increase the battery performance efficiently.

In Chapter 4, MnOₓ/CNF composite electrodes were prepared through electrospinning and heat treatment. SEM and STEM coupled with EDS revealed the morphology and chemical structure of the composite electrodes. An X-ray photoelectron spectroscopy was deployed to analyze the oxidation state of Mn in MnOₓ/CNF composites. Compared with CNF electrode, the synthesized MnOₓ-CNF electrodes showed larger charge capacity and higher columbic efficiency in eight cycles, indicates the catalytic role of MnOₓ in oxygen evolution reactions. It was hence demonstrated that as a binder-free and free-standing catalyst/supporting carbon mat electrode, the MnOₓ-CNF nanocomposites offered a promising material electrode candidate for Li-air cathodes.

In Chapter 5, different MnO₂/CNF electrodes with MnO₂ nanofibers anchored on the CNF surface or MnO₂ nanoparticles loaded on the CNF surface were obtained through low-current and high-current electrodeposition (LCD and HCD), respectively. The morphology of CNF and deposited MnO₂/CNF was evaluated by SEM. Chemical composition and oxidation
state of Mn in MnO$_2$/CNF was analyzed by STEM/EDS and XPS. Through electrochemical analysis, both MnO$_2$/CNF electrodes possessed much higher discharge capacity, better reversibility, and more cycling stability than regular CNF electrode. Compared with the nanoparticle/nanofiber structured HCD-MnO$_2$/CNF composite, the fiber-anchored-on-fiber structured LCD-MnO$_2$/CNF composite showed even better electrochemical performance. This illustrated the importance of catalyst morphology for Li-air batteries. This binder-free fiber-anchored-on-fiber structured MnO$_2$/CNF electrode is a promising candidate for catalyst/carbon-matrix Li-air cathode.
Carbon Nanofiber Based Electrodes for Li-Air Batteries

by

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Chair of Advisory Committee

Philip Bradford  Edmond Bowden
DEDICATION

This dissertation is gratefully dedicated to my parents, Chao Xu and Fenglan Li, my sister,
Yingzhen Xu, and my girlfriend Ying Li.
BIOGRAPHY

Guanjie Xu was born in Wugang, Henan province, China in 1985. He attended Northwestern Polytechnical University in 2002 and graduated with a Bachelor degree in Material Physics & Chemistry in 2006. After that, he went to the graduate school at Peking University and studied Condense Matter Physics under the supervision of Prof. Yin Lan. After three years’ study and research, he graduated with a Master degree in Physics.

In Fall 2009, Guanjie Xu came to North Carolina State University and started the Ph. D study and research under the supervision of Prof. Xiangwu Zhang. His current research focused on evaluating the carbon nanofibers and fabrication of catalyst/carbon nano-composites as cathodes for Li-air batteries.
ACKNOWLEDGMENTS

I would like to express the deepest appreciation to my committee chair, Professor Xiangwu Zhang, who is also my advisor. He gave me a chance to devote myself to energy materials research and always support me through the six years. Thanks to his help and supervision, I can start this newly-emerged Li-air battery project and move on. I would also like to express my appreciation to my committee members: Prof. Peter Fedkiw, Prof. Philip Bradford, and Prof. Edmond Bowden.

I would like to thank Dr. Liwen Ji, Dr. Zhan Lin, Dr. Kyung-Hye Jung, Dr. Yingfang Yao, Dr. Ozan Toprakci, Dr. Bingkun Guo, Dr. Yinzheng Liang, Dr. Shu Zhang, Dr. Shuli Li, Dr. Leigang Xue, Dr. Ying Li, Dr. Kun Fun, Dr. Meltem Yanilmaz, Mr. Yao Lu, Mr. Chen Chen, Mr. Han Jiang, and Mr. Liangqu Chen, Mr. Mahmut Dirican, Ms. Yeqian Ge, Mr. Jiadeng Zhu, for their kind help and cooperation in research.
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# LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>PCNF</td>
<td>Porous carbon nanofiber</td>
</tr>
<tr>
<td>PAN</td>
<td>Polyacrylonitrile</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy-dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>CNF</td>
<td>Carbon nanofiber</td>
</tr>
<tr>
<td>GDE</td>
<td>Gas-diffusion-electrode</td>
</tr>
<tr>
<td>DMF</td>
<td>Dimethylformamide</td>
</tr>
<tr>
<td>HPCNF #15</td>
<td>Hierarchical porous carbon nanofiber made from 15% ZnCl₂/PAN</td>
</tr>
<tr>
<td>HPCNF #30</td>
<td>Hierarchical porous carbon nanofiber made from 30% ZnCl₂/PAN</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic voltammetry</td>
</tr>
<tr>
<td>LITFSI</td>
<td>Lithium bis(trifluoromethanesulfonyl)imide</td>
</tr>
<tr>
<td>TEGDME</td>
<td>Tetra (ethylene) glycol dimethyl ether</td>
</tr>
<tr>
<td>atm</td>
<td>Standard atmosphere</td>
</tr>
<tr>
<td>STEM</td>
<td>Scanning transmission electron microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>ORR</td>
<td>Oxygen reduction reaction</td>
</tr>
<tr>
<td>OER</td>
<td>Oxygen revolution reaction</td>
</tr>
<tr>
<td>PVDF</td>
<td>Polyvinylidene difluoride</td>
</tr>
<tr>
<td>LCD</td>
<td>Low-current deposition</td>
</tr>
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</table>
1 INTRODUCTION

1.1 Request for Energy Storage

Energy consumption is the foundation of both the ecosystem and human society. The currently available energy sources on our planet include solar energy, geothermal energy, nuclear energy from radioactive decay, chemical energy from carbonaceous fossil fuels (oil, gas, and coal), hydro-energy, and mechanical energy from wind and wave. These energy sources could be converted into electrical energy, magnetic energy, kinetic energy, thermal energy, and electromagnetic waves for further use. The prosperity and efficiency on energy consumption reflect the civilization level of the society. The invention and vast application of steam engine brought the first industrial revolution. As a compact system, the steam engine produces workable mechanical energy in large scale from coals, which makes it possible to replace man power with machine power. In modern society, the dominant way to use all kinds of energy sources is to convert them to electricity. The broad application of electricity started from the second industrial revolution with the invention of electric generators and electric motors. Since then, different ways of using electric power have been tremendously developed. In applications of electric power, energy transportation, storage, and conversion are important due to the nonuniform distribution of energy sources in 5D (3Ds in Euclidean space, 1D in time, and 1D in type).

Since the end of World War II, various electronic devices have been tremendously developed. Gordon E. Moore predicted in 1965 that the transistors on integrated circuits would double in about every two years, which had been proven to be astoundingly correct for the past half century. With the increasing numbers of transistors per volume, energy
consumption increases. Vast use of portable laptops, digital cameras, and cell phones is spurring the search for high-performance energy storage systems. Another example of application of energy storage limited by energy-storage-system performance is electric vehicles (EVs). In combustion engine vehicles, the tank-to-wheel efficiency for gasoline is only 12.6%\(^5\), while the total energy efficiency from fuel to the heater in a power plant is 30% and the battery-to-wheel efficiency is about 90%\(^6\). Besides, problems of air pollution and greenhouse gas emission are applying pressures on both industry and everyday life to limit the fossil fuel consumption.

1.2 **Energy Storage or Conversion Systems**

There are lots of energy storage and/or conversion systems developed, such as fuel cells, capacitors including supercapacitors, solar cells, and batteries.

1.2.1 **Fuel Cells**

Fuel cells have been developed for more than one hundred and seventy years\(^7\). They convert chemical energy directly into electrical energy by lowering the energy of electrons chemically bounded in the fuel molecules. In fuel cells vehicles, the efficiency of hydrogen-oxygen fuel cells converting chemical energy to electrical energy and then to mechanical energy could reach 50-60%, although the practical energy efficiency is lower considering the production of hydrogen\(^8\). In combustion engines, partly restricted by the Carnot efficiency, the efficiency of converting chemical energy to thermal energy and then to mechanical energy for hydrogen-air is about 25%\(^9\). It is necessary to notice that additional fuel storage systems are required in fuel-cell-powered vehicles.
Several types of fuel cells, shown in Figures 1-1 and 1-2, have been developed including alkaline fuel cells (AFCs), polymeric-electrolyte-membrane fuel cells (PEMFCs), phosphoric-acid fuel cells (PAFCs), molten-carbonate fuel cells (MCFCs), and solid-oxide fuel cells (SOFCs). Among them, AFCs, PEMFCs, and PAFCs are operated at low temperatures, requiring high purity of hydrogen. On the other hand, MCFCs and SOFCs could be operated at high temperatures, in which both hydrogen and carbon monoxide could be oxidized. Especially in SOFCs, oxygen anion $O^{2-}$ is the charge carrier, and the fuels are not restricted to hydrogen. Instead, various types of hydrocarbons, including methanol, alcohol, or even gasoline, can be used to react with oxygen to generate electrical energy smoothly in SOFCs.

In SOFC anode side, cell reactions are limited by the three-phase-boundary (TPB) problem. The oxidation of fuel molecules can only occur where the gaseous fuel is contacted with both the solid electron conductive receiver and $O^{2-}$ anion in solid electrolyte. Density of TPB, porosity and particle size are the important factors determining the polarization property of SOFC anodes.
Table 1-1. Electrochemical reactions in various fuel cells.

<table>
<thead>
<tr>
<th>Fuel Cell</th>
<th>Anode Reaction</th>
<th>Cathode Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer Electrolyte and Phosphoric Acid</td>
<td>$\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$</td>
<td>$\frac{1}{2} \text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}$</td>
</tr>
<tr>
<td>Alkaline</td>
<td>$\text{H}_2 + 2(\text{OH})^- \rightarrow 2\text{H}_2\text{O} + 2\text{e}^-$</td>
<td>$\frac{1}{2} \text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 2(\text{OH})^-$</td>
</tr>
<tr>
<td>Molten Carbonate</td>
<td>$\text{H}_2 + \text{CO}_3^= \rightarrow \text{H}_2\text{O} + \text{CO}_2 + 2\text{e}^-$</td>
<td>$\frac{1}{2} \text{O}_2 + \text{CO}_2 + 2\text{e}^- \rightarrow \text{CO}_3^=$</td>
</tr>
<tr>
<td>Solid Oxide</td>
<td>$\text{H}_2 + \text{O}^= \rightarrow \text{H}_2\text{O} + 2\text{e}^-$</td>
<td>$\frac{1}{2} \text{O}_2 + 2\text{e}^- \rightarrow \text{O}^=$</td>
</tr>
<tr>
<td></td>
<td>$\text{CO} + \text{O}^= \rightarrow \text{CO}_2 + 2\text{e}^-$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\text{CH}_4 + 4\text{O}^= \rightarrow 2\text{H}_2\text{O} + \text{CO}_2 + 8\text{e}^-$</td>
<td></td>
</tr>
</tbody>
</table>

**Figure 1-1.** Electrochemical reactions in various fuel cells.

**Figure 1-2.** Working mechanisms of different types of fuel cells, including SOFCs, MCFCs, PAFCs, PEMFCs, and AFCs.
At the cathode side, the sluggish essence of oxygen reduction reactions (ORRs) is a big challenge, which attributes about a quarter of the potential loss for the whole cell\textsuperscript{13}. The reason for the sluggish ORRs lies in the strong double bond of oxygen molecule (498 kJ/mol) and the resulted complex multi steps for the four-electron-transfer reaction from \( \text{O}_2 \) to two \( \text{O}^2^- \). In an operating fuel cell, not all the oxygen molecules are reduced to \( \text{O}^2^- \). In general, some of them (0.01\% - 2\%) are reduced to hydrogen peroxide, depending on the conditions\textsuperscript{14}. The resultant \( \text{H}_2\text{O}_2 \) is corrosive to Nafion separator and electrolyte materials and tends to unstabilize the Pt catalyst in the long run\textsuperscript{15,16}.

The four-electron-transfer ORR was found occurring on low Miller index faces of [Au(100)] surface rather than other sites at pH above 6\textsuperscript{17}. This process began at the presence of surface absorbed \( \text{OH}^- \) anion at a high pH value, inspiringly indicating the role of absorbed anions on catalyzing the four-electron reduction\textsuperscript{17}. Later, the adsorption of anions on the electrode surface was found to affect Tafel slopes\textsuperscript{18}.

Two possible mechanisms, associate or dissociate, could be in charge for oxygen reduction. In the associate mechanism, oxygen is adsorbed on electrode surface first and then reduced to superoxide with two electrons transferred per oxygen molecule. In the dissociate mechanism, oxygen molecular dissociates on the electrode surface into two atoms. Each atom obtains one electron and is reduced separately. Several experimental studies and calculations have demonstrated that the cleavage of O-O bond occurs in peroxides, indicating
the ORR favors the associate mechanism\textsuperscript{19-21}, as shown in Figure 1-3, but which one is dominating is not in consensus yet\textsuperscript{15}.

\textbf{Figure 1-3.} Schematic of oxygen reduction with multi steps\textsuperscript{22}.

\textbf{1.2.2 Capacitors and Supercapacitors}

In capacitors, energy could be storied in the form of electric field produced by the absorbed charges. Dielectric constant, electric displacement saturation, dipole density, and breakdown electric field attribute to the energy density of a capacitor. Among the capacitors, electrochemical capacitors (ECs), also called supercapacitors or ultracapacitors, are well-known for high rate of storing and delivering energy and long cycling life. ECs are divided into electrochemical double layer capacitors (EDLCs) and pseudo-capacitors (PCs) according to different charge storage mechanisms.
1.2.2.1 *Electrochemical double layer capacitors (EDLCs)*

In EDLCs, positively charged electrode and negatively charge electrode adsorb anions and cations from the electrolyte, respectively, leading to a formation of two serial capacitors (Figure 1-4). The capacitors could be kept charged as long as the voltage is lower than the potential of redox reaction of the electrolytes. Capacitance, \( C \), and Energy stored, \( E \), can be calculated by:

\[
C = \frac{\varepsilon A}{d}, \quad E = \frac{1}{2} CV^2
\]

where, \( A \) is the surface area of the electrode (typically 500 to 2000 \( m^2/g \)), \( d \) the distance between adsorbed ion and electrode (\( \sim 1 \) nm), and \( \varepsilon \) the electrolyte dielectric constant. To obtain high-performance EDLCs, efforts have been exerted to broaden the specific surface area (SSA) of electrodes, most of which are carbon.

To produce high surface area carbon electrodes, an activation process is often needed. There are many ways to prepare high-surface-area electrodes. Ryoo et al.\(^\text{23}\) summarized methods to prepare highly porous carbon materials including 1) activation to high burn-off degree; 2) catalytic activation in the presence of certain metals; 3) combination of physical and chemical activation; 4) carbonization of polymer aerogels or cryogels; 5) carbonization of polymer blends with one thermally unstable component; 6) synthesis of multiwalled nanotubes; and 7) infiltration of an appropriate template by carbon precursors, followed by carbonization and template dissolution. These methods have been investigated based on various carbonaceous materials, activation agents, and activation processes.
Using high-surface-area electrodes, the charge density in EDLC could reach one million times of the traditional electrostatic or electrolytic capacitor\textsuperscript{24}. With the macro pores (>50 nm), meso pores (2 nm ~ 50 nm), and/or micro pores (< 2 nm) created, a very interesting question is what is the minimum size of the accessible pores for solvated ions. It was believed that the size of accessible pores should be larger than the size of solvated ions in the electrolyte. However, it was challenged by Chmiola \textit{et al}\textsuperscript{25} in 2006. When the average pore size was reduced to lower than 1 nm, the trend of capacitance vs pore size was changed and the capacity increased dramatically with the further decrease in size, which was comparable to the size of (CH\textsubscript{3}CH\textsubscript{2})\textsubscript{4}N\textsuperscript{+} (0.68 nm in diam) and BF\textsubscript{4}\textsuperscript{-} (0.33 nm in diam.)\textsuperscript{25}.

Besides the huge capacitance, the transportation of charges in EDLCs, originated from the surface-adsorption-desorption charge storage mechanism, is much easier than the charge transfer in devices based on redox reactions. Thus, discharge and charge could reach an extraordinarily high power density of $10^6$ watts per $dm^3$ that is thousand times of the power of a similar-sized battery\textsuperscript{26}, as shown in Figure 1-5. The kinetics limitation of EDLCs lies in the ionic conductivity of electrolytes. Without chemical reactions, the phase and structure changes in the electrodes of EDLCs are not severe with cycling that they can be recharged for millions of cycles, while typical batteries can only last for hundreds or thousands cycles.
Figure 1-4. Schematic of a supercapacitor\textsuperscript{27}.

Figure 1-5. Ragone plot of capacitors, supercapacitors, Pb-acid batteries, Ni-MH batteries, Li-ion batteries, and Li metal batteries\textsuperscript{28}.
1.2.2.2 Pseudo-capacitors (PCs)

PCs are like combination of capacitors and redox batteries. Different with the non-faradaic charge storage mechanism in EDLCs, in typical PCs, the main mechanism for charge storage is faradaic-like resulting from redox reactions, just like in batteries. However, this faradaic charge storage process in typical PCs occurs mainly on the surface of electrodes while it occurs both on surface and in bulk of the electrodes in batteries. The differences between PCs and batteries lie in the depth, kinetics, and degree of redox charge transfer. In general, the diffusion of ions into Van der Waals gaps of bulk material is slow, however, it could become fast if the materials display intercalation pseudo-capacitance. The charge storage in these intercalation pseudo-capacitive materials is not realized through the phase change of the structure, but a result of a faradic adsorption of hydrogen or metal atom. This process of electroadsorption occurs at a certain potential, depending on the amount of charges adsorbed, as compared with the redox potential in battery described by Nernst equation that is independent of the amount of charges transferred. In a real battery, the reaction potential is always related to depth of discharge or charge. This difference between PCs and batteries could be described as below:

\[
\frac{dq}{dv} \sim C_p
\]

in PCs,

\[
\frac{dq}{dv} \sim 0
\]

in batteries.

Some transition metal oxides, such as RuO$_2$, MO$_3$, and TiO$_2$, were found to have a pseudocapacitive nature. The energy density in a pseudocapacitor could be 10 times higher
than a EDLC because more charges could be stored through surface redox reactions and/or facile intercalation of ions, while maintaining a much higher power density compared with batteries.

In general, EDLCs and PCs are able to deliver high power density, long cycle life, but low energy density (Figure 1-6), making them useful in applications when fast charge and/or discharge is required.

Figure 1-6. Plot of specific power verse specific energy of capacitors, batteries and fuel cells. 

\textsuperscript{26}
1.2.3 Solar Cells

Solar cells are energy conversion systems converting radiation energy into electricity. Its foundation is photoelectric effect, discovered in 1839 by Edmond Becquerel\textsuperscript{32}. In a typical semiconductor solar cell (Figure 1-7), an electron captures a photon, transforms to an excited electron in the conduction band (CB), leave a hole in the valence band (VB). The exited electron in CB is reductive since it is in a higher energy state than the Fermi level, while the hole in VB is oxidative. A solar harvesting system could be built to take advantage of the electron/hole couples.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1-7.png}
\caption{Photoelectrochemical cells based on N-type semiconductors. (a) A Electricity-generating cell; (b) a fuel-generating cell\textsuperscript{33}.}
\end{figure}

1.2.3.1 Electricity-generating solar cells

Silicon, metal oxides\textsuperscript{34}, dye-sensitive materials\textsuperscript{35,36}, and conjugated polymer-based organic materials\textsuperscript{37-39} have been developed as solar cell electrodes, as shown in Figure 1-8.
Silicon is currently the most vastly used electrode material in solar cells, although its production is quite energy-consuming, expensive, and not environmentally benign. The advantage of silicon solar cells is high efficiency (> 20 %).

In 1991, a low-cost solar cell based on a dye-sensitized colloidal TiO₂ film was reported to have an overall light-to-electric energy efficiency of 12% in diffuse daylight\textsuperscript{35}. In this dye-sensitized solar cell, the dye molecule absorbed one photon, released one electron, and injected it into the conducting band of the n-type TiO₂ film. Then, the excited electron passed through load, and returned to lower state in the dye material through redox reaction(s).

\begin{table}
\centering
\begin{tabular}{|l|c|c|}
\hline
Type of cell & Efficiency (%) & Research and technology needs \\
\hline
Crystalline silicon & 24 & Higher production yields, lowering of cost and energy content \\
\hline
Multicrystalline silicon & 18 & Lower manufacturing cost and complexity \\
\hline
Amorphous silicon & 13 & Lower production costs, increase production volume and stability \\
\hline
CuInSe₂ & 19 & Replace indium (too expensive and limited supply), replace CdS window layer, scale up production \\
\hline
Dye-sensitized nanostructured materials & 10–11 & Improve efficiency and high-temperature stability, scale up production \\
\hline
Bipolar AlGaAs/GaAs photovoltaic cells & 19–20 & Reduce materials cost, scale up \\
\hline
Organic solar cells & 2–3 & Improve stability and efficiency \\
\hline
\end{tabular}
\caption{Efficiency of several electrochemical solar cells\textsuperscript{33}.}
\end{table}
Organic materials have also been studied for use as electrode materials in solar cells\textsuperscript{39}. They are cheap, easy to process, and flexible although their efficiency is low. After more than 20 years’ research, the efficiency of organic solar cells has been improved to about 5\%\textsuperscript{40}. Fullerenes are ubiquitously used as electron acceptors considering their electron affinity and superior charge-transporting ability\textsuperscript{38}. The charge transfer from excited electrons to electron acceptors is quite complicated, requiring energetic driving forces to separate the electron/hole couple\textsuperscript{38}.

\textbf{1.2.3.1 Fuel-generating solar cells}

Converting solar energy to electricity is just one approach to use sunlight. There are many other ways to harvest solar energy. The radiation energy from the Sun was also found to be a possible source to split water using n-type semiconducting TiO\textsubscript{2} electrode without any external voltage applied\textsuperscript{41}. The reactions were given by\textsuperscript{41}.

(I) Excitation of TiO\textsubscript{2} by light:

\begin{equation}
\text{TiO}_2 + 2h\nu \rightarrow 2e^- + 2p^+ \tag{1-1}
\end{equation}

(II) Half reaction at TiO\textsubscript{2} anode:

\begin{equation}
2p^+ + H_2O \rightarrow 1/2O_2 + 2H^+ \tag{1-2}
\end{equation}

(III) Half reaction at Pt cathode:

\begin{equation}
2e^- + 2H^+ \rightarrow H_2 \tag{1-3}
\end{equation}

Without use of any catalyst, water splitting occurs when there is a potential of 1.23 V applied between two electrodes. With the existence of excited electrons and the resultant
holes in semiconducting TiO$_2$ by light, the oxygen evolution reaction starts at -0.5 V vs. SCE (Saturated Calomel Electrode) in pH 4.7 environment, which is decreased by around 0.26-1.50 V below proton reduction. This huge potential decrease in oxygen evolution is remarkable although the role of TiO$_2$ is not a catalyst technically. When halogen ions are introduced, n-type ZnO and CdS$^{42}$ also work to reduce the potential oxidation reactions under irradiation. Other n-type metal oxides, such as WO$_3$ and Fe$_2$O$_3$, have also been evaluated as photoanodes in aqueous solutions.

However, all of these splitting methods concern the oxygen evolution reactions (OERs), which are very important in Li-air batteries. Similar to oxygen reduction reaction, OERs show the similar sluggish essence, $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$, originating from multiple bond rearrangement concerning two water molecules. To improve the kinetics of the OER, catalyst are used to absorb four electrons in water oxidation and transfer them to photoactive assemblies (cathode), in which the other half reaction, i.e., the reduction of protons, is realized with the consumption of solar energy$^{43}$.

An oxo-bridged Ru(III) system, $[(\text{bpy})_2(\text{H}_2\text{O})\text{RuORu(H}_2\text{O})(\text{bpy})_2]^{4+}$ (bpy=bipyridine), was reported to achieve a high rate of water oxidation$^{44}$. It was suggested that the oxidation of the Ru(III)-Ru(III) dimer to Ru(V)-Ru(V) dimer and the reduction followed were the possible catalytic mechanism of transferring 4 electrons in water oxidation$^{44}$. The bpy dimer could be replaced by the analogous phenanthroline dimer to adjust the redox potential. In 2008, a stable Ru-based catalyst was found with the core of [Ru(IV)$_4$O$_4$] tetrahedron, while the catalytic reactions were related to the several possible
intermediates\textsuperscript{45}. The new point of this type of catalyst was that it was an intermediate between soluble catalysts which of cause had the sufficient contact with water and solid insoluble catalysts which had appealing stability\textsuperscript{43}.

Mesoporous cobalt oxide with an surface area of 250 m\textsuperscript{2}/g was recently fabricated to obtain a high turnover frequency of 2.2 × 10\textsuperscript{−3} s\textsuperscript{−1} per surface Co atom in strong acidic environment\textsuperscript{46}. It was believed that the capability of Co\textsubscript{4}O\textsubscript{4} cubane to absorb 4 electrons improved the kinetics of oxygen molecular production\textsuperscript{46}.

As a renewable electricity generating system, solar electrochemical cells are promising supplemental energy conversion systems, if they can achieve high efficiency, good stability, good scaling-up ability, low cost, and satisfactory environmental benignity. The electrochemical solar cells, using solar energy to produce clean fuel, are also very attractive considering that energy density in fuels is much higher than the energy density of sunlight.

1.3 Batteries

The first electrochemical battery was invented by Volta in 1799. It was a pile (so-called Volta Pile) consisting of serially connected positive copper electrode, a layer of cloth soaked with brine as the electrolyte, and a negative zinc electrode. Between the two separated metal electrodes, an electric field was generated since Zn oxidation and proton reduction occurred at different potentials.

Half reaction at zinc anode:
\[ Zn \rightarrow Zn^{2+} + 2e^- \quad (1-4) \]

Half reaction at copper cathode:

\[ 2H^+ + 2e^- \rightarrow H_2 \quad (1-5) \]

Although the battery faced one severe problem that the hydrogen produced tended to accumulate on surface of copper retarding further charge transfer, it was the first battery fabricated with the ability to generate electricity continuously. Since then, batteries have become important necessities in human life. In nowadays, a typical household has as many as 40 to 60 batteries in average\(^{47}\). Various types of batteries have been developed and commercialized. The following reviews briefly some representative batteries.

1.3.1 Leclanche Type Battery

Leclanche type battery is named after Georges Leclanché who made his invention in 1866. As shown in Figure 1-9, a Leclanche type battery consists of a zinc rod as the anode, ammonium chloride/water solution as the electrolyte, porous pot as the separator, manganese dioxide cathode mixed with conductive carbon as the cathode, and a current collector of carbon rod. Mixing of carbon with active material MnO₂ is aimed to increase the conductivity and wetting ability. Zinc chloride cells and alkaline manganese cells or so-called alkaline cells have also been made to overcome the limitations of Leclanche cells, such as narrow working temperature window (20°C~40°C), Zn anode passivation, and electrolyte leakage followed by short shelf life. In alkaline manganese cells, anode reaction and cathode reaction can be simply written as following, respectively:
In recent years, by carefully controlling the discharge of Mn$^{4+}$ to Mn$^{3+}$, zinc/manganese dioxide primary batteries were modified to become rechargeable$^{47}$. The resultant rechargeable zinc/manganese oxide batteries showed competitive potential in market with Ni/Cd batteries.
1.3.2 Ag-Zn Button Battery

Another important battery type with the use of zinc as the anode is the Ag-Zn “button cell” or miniature cell. In the first bunch of Ag-Zn button cells with the diameters varying from 7.9 mm to 23 mm, silver oxide (Ag₂O) was used as the cathode, showing a very constant discharging voltage at both low and high current rates\(^49\). These cells have been broadly used in calculators and electronic watches.

Ag₂O is favored than AgO (or Ag₂O\(\cdot\)Ag₂O₃), because of its low reactivity with alkaline electrolytes and its flat discharge curve. Although Ag₂O is a poor semiconductor, requiring the addition of conductive carbon into the cathode, the reduction product (Ag) is fairly conductive, improving the kinetics along with discharge\(^50\).

1.3.3 Rechargeable Batteries

1.3.3.1 Lead-Acid Battery

Before the Leclanche type battery was invented, Planté made the first practical rechargeable lead-acid battery in 1859\(^51\). The typical lead-acid battery consists of lead anode, sulphuric acid electrolyte and lead dioxide cathode. Its overall cell reaction is given by

\[
PbO_2 + Pb + 2H_2SO_4 \rightleftharpoons 2PbSO_4 + 2H_2O
\]

(1-8)

The low cost, long life time, excellent electrochemical reversibility of lead-acid batteries attribute to its overwhelming share in vehicle batteries market for the past decades\(^52\).
1.3.3.2 Ni-Cd Rechargeable Battery

A Ni-Cd rechargeable battery consists of a positive nickel hydroxide electrode, aqueous potassium hydroxide electrolyte, and a negative cadmium compound electrode.

Half reaction at anode:

\[ \text{Cd} + 2\text{OH}^- \rightleftharpoons \text{Cd(OH)}_2 + 2e^- \quad \text{0.80V vs NHE} \] (1-9)

Half reaction at cathode:

\[ \text{NiOOH} + \text{H}_2\text{O} + e^- \rightleftharpoons \text{Ni(OH)}_2 + \text{OH}^- \quad \text{0.52V vs NHE} \] (1-10)

Water is consumed during discharge and is generated during charge, leading to the change of electrolyte quantity and concentration during reactions. Ni-Cd batteries have several advantages including long shelf life and long cycling life (>500 cycles), high rate durability (>10C) originating from high ionic conductivity of alkaline solution and low internal resistance, and wide operating temperature.

1.3.3.3 Nickel Metal Hydride (NiMH) Battery

Nickel metal hydride (NiMH) battery, within which H is stored in solid hydride, is also a popular battery because of its unique properties of high energy and power densities, charging rate performance, long cycle life and wide working-temperature window. Some alloy materials were found to be able to absorb H by Vanvucht et al in 1970. Hydrogen is firstly absorbed onto the surface of alloy and then desorbed into the bulk of alloy through gas-solid reaction. The reversible nature of this H adsorption-desorption process in these alloy materials makes them quite useful as storage medium for gas-phase oxidation materials.
in water anode in rechargeable nickel metal hydride batteries. These alloys generally contain Ni, Co, Al, Mn, or earth elements such as La, Ce, Pr or Nd\textsuperscript{53}. The cell reactions are given as below:

At anode:

\[
\text{MH} + \text{OH}^- \rightleftharpoons \text{M} + \text{H}_2\text{O} + \text{e}^-, \quad -0.80\text{V vs NHE} \quad (I-11)
\]

At cathode:

\[
\text{NiOOH} + \text{H}_2\text{O} + \text{e}^- \rightleftharpoons \text{Ni(OH)}_2 + \text{OH}^-, \quad 0.52\text{V vs NHE} \quad (I-12)
\]

1.3.4 Lithium-Ion Battery

Since 1990s, Li-ion batteries (LIBs) have been vastly developed and used in the emerging portable electronic devices such as laptops, cell phones, and camcorders. In LIBs, Li\textsuperscript{+} works as the charge transfer agent shuttled between two electrodes, which are both Li-hosting materials. Figure 1-10 shows several Li-hosting materials, in which Li could be reversibly intercalated and extracted out. The working potentials of several Li intercalation materials are shown in Figure 1-10.
1.3.4.1 Li Insertion materials

a) Layered Li-intercalation materials

In layered-transition-metal-oxide cathode materials (Figure 1-11), Li\(^+\) ions are inserted into the Van de Waals gaps, so-called “gallery space”, between the layers, during discharge and extracted out during charge. The covalent chemical bond between transition metal and oxygen is strong that the layered structure could be maintained stable in the insertion/extraction cycles. Layered Li\(_x\)CoO\(_2\) was found to be able to maintain its structural integrity during Li inserting/extracting as long as \(x\) was small than 0.5\(^56\). As the first generational LIB cathode material, LiCoO\(_2\) shows extraordinary cycling and rate
performance with high capacity retention of 80% after 500 cycles at 1C discharge rate\textsuperscript{57}. In LiCoO\textsubscript{2}, the high Co\textsuperscript{3+}/Co\textsuperscript{4+} potential, arising from low 2p-bond electrons of O\textsubscript{2}\textsuperscript{4−}, makes the high energy density possible\textsuperscript{58}. The strong Co-O bond maintains the stable structure for achieving a reasonable cycling life. Co-Co interaction in transition metal layer increases the electron conductivity, which is crucial for high-rate performance. However, the limit reserve of Co on Earth makes the LiCoO\textsubscript{2} battery expensive and not suitable in large-scale applications such as EV.

\textbf{Figure 1-11.} The crystal structure of layered-transition-metal-oxide-cathode materials with the stable and closely-packed layer (blue) and the redox-active layer (yellow)\textsuperscript{58}.

Among other layered transition metal oxides, such as LiVO\textsubscript{2}, LiCrO\textsubscript{2}, LiNiO\textsubscript{2}, LiMnO\textsubscript{2}, LiNi\textsubscript{y}Mn\textsubscript{1-2y}O\textsubscript{2}, and LiVSe\textsubscript{2}, LiCrO\textsubscript{2} is not usable because of the difficulty to
extract Li\textsuperscript{59}. In LiVO\textsubscript{2}, vanadium tends to migrate into Li planes, making it difficult to maintain the structural stability\textsuperscript{60}. LiNiO\textsubscript{2} suffers from oxygen evolution probably because of the overlap of Ni\textsuperscript{3+/4+} bond with 2p-bond electrons in oxygen\textsuperscript{61,62}. Layered LiMnO\textsubscript{2} is less expensive but tends to go through phase transition to spinel structure, leading to poor cycling performance. LiCo\textsubscript{x}Ni\textsubscript{y}Mn\textsubscript{1-x-y}O\textsubscript{2} has reasonable electrochemical performance, and could reduce the cost by introducing comparably cheaper Ni and Mn\textsuperscript{63}.

Intercalation materials could also be used as anode materials, such as graphite. Graphite has a stacking structure of graphene layers. Both cations (Li\textsuperscript{+}, K\textsuperscript{+}, Rb\textsuperscript{+}, or Cs\textsuperscript{+}) and anions (Br\textsuperscript{−}, SO\textsubscript{4}\textsuperscript{2−}, or SbF\textsubscript{6}\textsuperscript{−}) could be inserted into the van der Waals gap between these graphene layers\textsuperscript{64}. Graphite has a low Li-insertion potential between 0 and 0.3V (vs. Li/Li\textsuperscript{+}), making it a suitable anode material. The insertion occurs in different stages due to the different energy required for insertion into different interlayers along with the increasing Li content.

\textit{b) Spinel and olivine structured Li-hosting materials}

Spinel LiMn\textsubscript{2}O\textsubscript{4} is a low-cost cathode material with a practical capacity of 140 mAh/g. Spinel structure is similar to the layered structure, but the metal oxide also presents in the redox-active layer. Olivine structured LiFePO\textsubscript{4} is of great interest in large-scale applications due to its low cost compared with LiCoO\textsubscript{2}. In LiFePO\textsubscript{4}, covalently bonded tetrahedral PO\textsubscript{4}\textsuperscript{3−} keeps it structurally and chemically stable. With a theoretical capacity of 170 mAh/g and the environmental benignity, LiFePO\textsubscript{4} has the potential to replace LiCoO\textsubscript{2}.
cathodes in future EVs. However, its poor electron and Li-ion conductivity limit the rate performance and hinder the further development.

### 1.3.4.2 Li-alloying materials

There are some materials that can form alloys with Li, including Li₅Zn (x<1.5), Li₅Cd (x<2.33), Li₅Al (x<0.9), Li₅Ga (x<1.93), Li₅In (x<2.67), Li₅Si (x<4.4), Li₅Sn (x<4.4), Li₅Pb (x<4.4), Li₅Sb (x<3), and Li₅Bi (x<2.82)\(^{64}\). These alloy materials show high Li-storage ability. Among them, silicon has the highest theoretical capacity. Lithium can form several alloys with silicon, such as Li₁₂Si₇, Li₇Si₃, Li₁₃Si₄, Li₁₅Si₄, and Li₂₁Si₄. At room temperature, the fully lithiated phase is Li₁₅Si₄ instead of Li₂₁Si₄ as reported by Obrovac and Christensen\(^{65}\). The irreversible capacity in the first cycle is mainly related to the formation of solid electrolyte interface (SEI). However, the formation of fine particles of amorphous silicon also contributes to the irreversible capacity if the silicon precursor is crystalline\(^{66}\). This amorphous Li-Si alloy could be cycled very well. When further lithium was inserted into the amorphous Li-Si alloy, to a low potential of 50 mV (vs Li/Li\(^+\)), it became crystalline again\(^{65}\). Although the Li-alloying materials show high capacity, they suffer huge volume-expansion, which limits the cycling ability significantly.

### 1.3.4.3 Replacement-reaction materials

Some metals, such as Co, Cu, Ni, or Fe don’t form alloy with Li. Their oxides cannot be used as Li-hosting materials due to absence of voids for Li intercalation\(^{67}\). However, when made into nanosize, these oxides can go through a replacement reaction with Li. The overall reaction is shown below:
Here M could be Co, Cu, Ni, Mn, Mo or Fe. Although the bulk Li$_2$O is insulator, the nanoparticles of Li$_2$O in the size of 1-5 nm was reported to show a fair electrochemical activity even after 100 cycles$^{68}$.

1.3.4.4 Electrolytes and interfaces

The typical LIB anode works at low voltage, which is below the electrochemical stable window of most liquid electrolytes. The electrolytes are reduced and form a solid-electrolyte-interface (SEI) film on anode surface. The SEI film can stabilize in a few cycles and prevent further reaction between electrolytes and the anode material. However, the formation of SEI consumes a large amount of Li, which generally comes from the cathode material. Thus, an excess mount of heavy cathode material must be added to the battery, lowering the energy density of the full cell. On the cathode side, if the its working potential is higher than the electrochemical window of electrolytes, a SEI film could also form.

1.4 Lithium-Air Battery

Since the beginning of the 21$^{\text{th}}$ century, LIBs have shown their limitations on fulfilling the demands for high-performance energy storage systems, especially with the vast development of various multifunctional and portable electronic devices. Moreover, pressure of reducing CO$_2$ emissions pushes the replacement of combustion-engine vehicles with electric vehicles (EVs). The current choices for power supply in EVs are typically LIBs with two Li-intercalation electrodes (e.g., C$_6$/LiMO$_2$, where “M” refers to Ni, Mn or Co), which
are far from ideal in terms of gravimetric energy density (100-200 Wh/kg in cell level) or volumetric energy density (250-450 Wh/L), cost, and safety\textsuperscript{6,69}. Surpassing the intercalation chemistry technology, Li-air batteries (LABs) could reach a gravimetric energy density of 1000 Wh/kg, which is 5-10 times higher than current LIBs. As shown in Figure 1-12, the practical energy density of LABs is comparable to gasoline.

![Figure 1-12. Theoretical and practical capacity of various types of batteries\textsuperscript{70}.](image)

1.4.1 Reaction Mechanisms

In aprotic LABs, the overall electrode reactions could be written as below:

\[
\frac{1}{2} \text{Li}_2\text{O} \quad \longleftrightarrow \quad \frac{1}{4} \text{O}_2 + \text{Li}^+ + e^- \quad 2.95 \text{ V vs Li/Li}^+ \quad (1-14)
\]
$$\frac{1}{2}\text{Li}_2\text{O}_2 \leftrightarrow \frac{1}{2}\text{O}_2 + \text{Li}^+ + e^- \quad 3.05 \text{ V vs Li/Li}^+$$  \hspace{1cm} (1-15)

But neither the oxygen reduction reactions (ORRs) nor oxygen evolution reactions (OERs) in LABs are simply occurring as depicted in the above equations. The possible chemical and electrochemical ORRs are shown in Figure 1-13. In protonic fuel cells, there are two types of ORRs: associates ($O_2 + 2e^- \rightarrow O_2^{2-}$) and dissociates ($O_2 + 2e^- \rightarrow O^- + O^-$), with the former favored$^{19-21}$. In LABs, similar trend of ORRs is observed with Li$_2$O$_2$ identified as dominating discharge products at voltage higher than 2 V (vs. Li/Li$^+$)$^{71-89}$. Li$_2$O present in ORR products when the cell was discharged to below 2 V or 1 V$^{90,91}$. Although both Li$_2$O$_2$ and Li$_2$O are bulk insulators, surface of Li$_2$O$_2$ was half-metallic, while Li$_2$O not, by first-principle calculation$^{92}$. It indicates that preventing fully discharge of LABs to a voltage below 2 V or 1 V could facilitate the reversibility of the discharge products.

Although the dominating ORR mechanism is associates with Li$_2$O$_2$ as the main ORR products, there are still several possible ways leading to the formation of Li$_2$O$_2$: R1+R2, R1+R3, or R4 (Figure 1-13)$^{93}$. The former two mechanisms involve with the formation of LiO$_2$ as intermediates. The highly active LiO$_2$ radicals could disproportionate into Li$_2$O$_2$ or be further reduced to Li$_2$O$_2$, which has been observed by several groups$^{94-96}$. High-level quantum chemical calculations revealed that (LiO$_2$)$_6$ cluster was thermodynamically more stable than the LiO$_2$ dimer$^{97}$. It may survive long enough to be incorporated into ORR products and be detected. Theoretically, whether the first ORR step favors R1 or R4 depends on the comparable concentration of Li$^+$ and O$_2$ on the phase boundary of Li$^+$, O$_2$, and C. It was observed that the oxygen partial pressure and electrolyte composition had effect on the
discharge products constitutions\textsuperscript{98-100}. In discharge, ORRs could become diffusion-limited along with the consumption of Li\textsuperscript{+} and O\textsubscript{2} in the electrolyte. Thus the preference may change due to the different diffusing ability of electrolytes for Li\textsuperscript{+} and O\textsubscript{2}, making the ORRs even more complicated\textsuperscript{96}. 

\begin{center}
Figure 1-13. Possible oxygen reduction reactions in LAB\textsuperscript{93}.
\end{center}

While the ORR mechanism in LABs has been addressed extensively, the mechanism of OERs remains less understood. Given that Li\textsubscript{2}O\textsubscript{2} is the bulk ORR product, its oxidation could be decisively important to reveal the true nature of OERs in LABs. By tracing the phase changes of electrochemically generated Li\textsubscript{2}O\textsubscript{2}, Swapna Ganapathy \textit{et al} found the oxidation of crystalline Li\textsubscript{2}O\textsubscript{2}, following the decay of amorphous Li\textsubscript{2}O\textsubscript{2}, went through a Li-deficient phase (Li\textsubscript{2-x}O\textsubscript{2}), shown in Figure 1-14\textsuperscript{101}. That indicates that the OERs in LABs are also sluggish multi-step reactions. The effect of Li\textsubscript{2}O\textsubscript{2} size on the electronic transport properties and its oxidation was observed\textsuperscript{102}. The presence of LiO\textsubscript{2} in the mixture of ORR products could facilitate the oxidation of Li\textsubscript{2}O\textsubscript{2} in OERs to some extent\textsuperscript{94}. The high over-
potential of LABs in charge indicates that OERs are not simply the reversal ORRs but follow different paths instead.\textsuperscript{103-105}

![Figure 1-14. Oxidation of (a) E-Li\textsubscript{2}O\textsubscript{2} and (b) C-Li\textsubscript{2}O\textsubscript{2}. Obtained from ref\textsuperscript{101}.](image)

The two-stage OERs are also found in ionic liquids (ILs).\textsuperscript{94} In the CV of glass carbon conducting in O\textsubscript{2}-satureated ILs, two broad anodic peaks appeared, as shown in Figure 1-15a. The peak III, at 3.6 V, was identified as the oxidation of Li\textsubscript{2}O\textsubscript{2}, through comparison with the direct oxidation of Li\textsubscript{2}O\textsubscript{2}, shown in Figure 1-15b. In Figure 1-15b, the mixture of glass carbon with Li\textsubscript{2}O\textsubscript{2} electrode was charged first in the O\textsubscript{2}-free electrolyte. It showed an anodic peak at the same position with the peak III. The oxygen evolved from Li\textsubscript{2}O\textsubscript{2}, and dissolved in water. It was argued that the peak II was the oxidation of amorphous Li\textsubscript{2}O\textsubscript{2}, since it could be more easily oxidized compared with crystalline Li\textsubscript{2}O\textsubscript{2} that was pre-added to the electrode.

Besides, the oxidation ability of Li\textsubscript{2}O\textsubscript{2} is also related to its size. Figure 1-16 is the schematic of a ALD-Al\textsubscript{2}O\textsubscript{3} coated Pd/C electrode. The overpotential in charge was quite low, around 0.2 V. It was attributed to the small size of the Li\textsubscript{2}O\textsubscript{2} produced. When the size of
Li₂O₂ is reduced to nanosize, its electronic conductivity could be remarkably increased. It was in accordance with the previous discussion that the surface of Li₂O₂ was half-metalic.

Figure 1-15. CVs in ionic liquids. Obtained from ref⁹⁴
1.4.2 Work Principles

A LAB combines the characteristics of a typical fuel cell and a LIB, as shown in Figure 1-15. In discharge, oxygen is fed from the outside of the battery as in fuel cells. In LABs, Li\(^+\) is shuttled between the anode and cathode and works as the charge transfer agent, as in rechargeable LIBs. Different with fuel cells, the ORR products in LABs are hardly soluble in electrolyte. In LABs, both the ORRs and OERs are multi-phase reactions including gaseous oxygen, liquid electrolyte containing Li\(^+\), solid carbon as the electron source, and solid ORR products. The solid ORR products are stored within the voids of porous cathode. With the accumulation of ORR products in cathode, charge-transfer resistance increases and the diffusion channels for Li\(^+\) and O\(_2\) on the cathode surface become blocked. This four-phase mechanism brings several challenges for LABs.
A porous structure is required for the gas-diffusion-electrode (GDE). The size of pores, porosity, and specific surface areas are the important factors to evaluate the air cathode. If the structure of the GDE is not well-designed, the occupancy of solid discharge products in some of the voids could hinder the diffusion of lithium ions and oxygen, invalidate the other pores or channels, and lower the efficiency of pores dramatically. To increase the pore efficiency, the GDE could be made into a coordinating system with macropores, mesopores, and micropores working together, as shown in Figure 1-15\textsuperscript{100}.

The four-phase problem is generally transferred to a three phase-problem with the dissolving of oxygen into the liquid electrolyte. Thus, the reaction kinetics could be highly sensitive to the solubility and diffusing ability of oxygen in the electrolyte. Generally, catalyst is required to improve the kinetics of ORRs and OERs, as discussed in previous
chapters. Incorporation of catalyst into the multi-phase GDE makes it more complicated, challenging the design of structure.

![Diagram of a coordinating GDE containing macropores, mesopores, and micropores](image)

**Figure 1-18.** The schematic diagram of a coordinating GDE containing macropores, mesopores, and micropores\(^\text{100}\).

### 1.4.3 Air Cathode

As discussed above, high surface area is needed to increase the contact between electrolyte and electrode. At the same time, high pore volume is also expected to realize the good diffusion and transportation of the electrolyte with oxygen in it and the storage of newly produced Li\(_2\)O\(_2\) or Li\(_2\)O. However, fundamentally, the increase of surface area and porosity tends to decrease the conductivity, which is critically important for any electrode in an electrochemical system. Hence, high surface area and highly-conductive carbons become the desired material choice for LABs.
Various high-performance carbon particles, including BP 2000, Calgon, Ketjen black EC600JD, Super P, Ketjen black 300 and 600, Black Pearls 2000, Denka black, Ensaco 250G, and mesoporous aerogels were evaluated for use in LABs. Typically, incorporation of 0-D carbon into the porous current collector requires addition of extra amount of binders than the amount used in LIBs due to the use of perforated current collectors in LABs. The addition of large amount of binders decreases the conductivity, pore efficiency, and energy efficiency of the electrode.

One dimensional carbon nanofibers and carbon nanotubes were also introduced to LABs as air cathode materials. These electrodes showed structure stability with considerable discharge capacities. Nitrogen doping into the carbon nanotubes was reported to have a catalytic role in oxidizing Li$_2$O$_2$. A hierarchical activated carbon microfiber (diam ~ 10 $\mu$m) woven electrode was evaluated by Aurbach et al. The high discharge capacity was achieved because of the high surface area, hierarchical microstructure, and the presence of $\alpha$-MnO$_2$. The formation of a self-standing binder-free GDE facilitates the diffusion of O$_2$ and Li$^+$, increases surface area, and improves electrochemical performance.

Two-dimensional functionalized graphene sheets showed an extremely large discharge capacity of 15,000 mAh/g. A C/O ratio of 14 was reported to perform better than the C/O ratio of 100 due to more defects and functional groups on the graphene sheet surface with higher O content. Discharge abilities of graphene nanosheets were also compared with BP 2000 and Vulcan XC-72 and showed extraordinary high capacity and rate ability but not the reversibility (Figure 1-15).
3-D mesoporous carbon foam air cathode prepared from nanocasting showed a 40% increase in capacity compared with other commercial carbon black\textsuperscript{115}. A meso-macro hierarchical porous carbon was synthesized and possessed a high discharge capacity of 10,000 mAh/g\textsuperscript{116}.

![Galvanic discharge-charge curves of BP-2000, Vulcan XC-72, and graphene nanosheets in the first cycle](image)

**Figure 1-19.** Galvanic discharge-charge curves of BP-2000, Vulcan XC-72, and graphene nanosheets in the first cycle\textsuperscript{114}.

All the above research about carbon with different morphology shows the importance of high surface area and porous structure. A practical design about the air cathode structure could be the key for high pore efficiency. The effect of depth of discharge on reversibility of a carbon electrode without any catalyst was evaluated by Laoire et al in 2011\textsuperscript{91}. As shown in Figure 1-17, with full depth of discharge, the battery faded in two cycles. In contrast, the battery worked in 8 cycles with the discharge cut-off capacity set as 800 mAh/g.
Figure 1-20. (a) Galvanic discharge-charge curves of the carbon electrode cycled between 1.5 V and 4.5 V with full depth of discharge. (b) The galvanic discharge and charges curves of the same electrode with controlled depth of discharge and (c) its cycling performance plot.\textsuperscript{91}

Recently, the stability of carbon in LABs was examined.\textsuperscript{117} It was found that, in the presence of Li\textsubscript{2}O\textsubscript{2}, small amount of carbon tended to be oxidized to Li\textsubscript{2}CO\textsubscript{3} when charged to above 3.5 V (vs Li/Li\textsuperscript{+}).\textsuperscript{117} Moreover, carbon also catalytically increased the decomposition
of electrolytes (carbonates, dimethyl sulfoxide (DMSO), and tetraglyme electrolytes). Although more research to evaluate the feasibility of carbon in various electrolytes is needed, carbon is among the top choices for the air cathode materials because of its abundance, high malleability, and extraordinary conductivity.

Besides carbon, nano-porous gold was also tested as the supporting electrode\textsuperscript{118}. After 100 cycles, the electrode was still stable in LiClO\textsubscript{4}/DMSO electrolyte with the proportion of Li\textsubscript{2}O\textsubscript{2} exceeding 99\% (less than 1\% Li\textsubscript{2}CO\textsubscript{3} or HCO\textsubscript{2}Li in discharge products). However, the comparably low capacity and extremely high cost make it impracticable for commercial use.

\textbf{1.4.4 Catalysts}

In LABs, catalysts are required to reduce the polarization and improve the rate performance due to the sluggish ORRs and OERs. Bruce \textit{et al} found that that the electrolytic manganese dioxide (EMD) was a potential catalyst for LABs in 2006, as shown in Figure 1-18\textsuperscript{103}. The discharging potential of the EMD/carbon air cathode was at 2.5 - 2.7 V with the recharging occurring at 4.2 - 4.4 V. When increasing the current rate from 70 to 100 mA/g, discharge capacity decreased more than 30\%. At the rate of 70 mA/g, capacity retention was 60\% after 50 cycles. Through comparing the charging of prepared EMD/Li\textsubscript{2}O\textsubscript{2}/carbon and Li\textsubscript{2}O\textsubscript{2}/carbon, Bruce \textit{et al} found the existence of EMD decreased the charging potential by 0.25V, which clearly exhibited the important role of EMD on oxygen evolution reaction\textsuperscript{103}. They demonstrated that the main charging reaction was \[\text{Li}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{Li}^+ + 2\text{e}^-\] through in situ mass spectrometry, while small amount of carbon dioxide was released. That meant
the charging of the cell involved the electrolyte. The electrode reaction mechanism with the participating of the electrolyte is still not clear.

Figure 1-21. (a) Galvanic discharge-charge curves and (b) cycling performance of EMD/Super S electrode\textsuperscript{103}.

Figure 1-22. Cycling performance of several types of MnO\textsubscript{2} catalyst\textsuperscript{119}.
Several types of transition metal oxides and several types of manganese dioxide with different crystalline structures were tested, as shown in Figure 1-19\textsuperscript{120,119}. Among them, $\alpha$-MnO$_2$ worked the best both on ORRs and OERs. Manganese dioxide (MnO$_2$) was also evaluated as a catalyst by Zhang et al\textsuperscript{108} as shown in Figure 1-20. The MnO$_2$ material was prepared through hydrothermal reaction from KMnO$_4$. At the fourth cycle, the discharge capacity fades to less than 1/10 of the first discharge capacity.

![Figure 1-23. Galvanic discharge-charge curves of electrode with MnO$_2$\textsuperscript{108}.](image)

Lei Jin \textit{et al} prepared titanium containing $\alpha$-MnO$_2$ octahedral molecular sieves with a hollow sphere structure and used them as the catalyst for LABs\textsuperscript{121}. With the existence of $\alpha$-MnO$_2$, the capacity reached 2.3 Ah/g. However the catalytic role of titanium is not obvious. One group in Japan made Pd/MnO$_2$ electrode without carbon\textsuperscript{122}. The battery showed low capacity because of the low surface area and low porosity of the electrode without high-
performance carbon. However, the resultant LAB didn’t fade obviously for 20 cycles and the energy efficiency was increased from 60% to 89% by decreasing the charging potential to around 3.6V. MnO₂ nanoflakes coated on multi-wall carbon nanotubes were used as the catalyst for LABs by Liu and Xing et al¹²³. The MnO₂ was grown on the surface of carbon nanotubes by reducing KMnO₄. The battery prepared showed good capacity retention for the first cycle and then faded in a few cycles. The charging potential was close to 3.8V.

Besides MnO₂, some fuel cell catalysts were investigated in LABs. Lee et al¹²⁴ made a silver-polymer-carbon composite electrode to improve the discharging capacity. Shao-Horn Yang’s group in MIT found that the Au/C nanoparticle could improve the ORRs and increase the discharging potential, while the Pt/C nanoparticle could improve the ORR and decrease the charging potential¹²⁵. Thus, they prepared Au/Pt nanoparticle alloy and used it as the catalyst to reduce the polarization of the electrode. The discharge potential was increased to ~2.75 V and the charging potential was decreased to ~3.6V. The Au/Pt nanoparticle alloy showed very active catalytic characteristic by decreasing the uplimit of the electrochemical stable window to 4.0 V. The first cycle of the battery showed larger charging capacity than discharging capacity, indicating the side reaction with electrolyte.

Ren et al studied on the ORR catalysts and argued that the discharging may follow the process below¹²⁶:
In this mechanism they proposed, the catalyst-sites in LABs play the role of promoting the formation of LiO₂ and disproportionation of LiO₂ dimers. However, there is still controversy about the working mechanism of electrocatalysts in OER. By using differential electrochemical mass spectrometry (DEMS), McCloskey et al. found that Au, Pt, and MnO₂ had no catalytic activity on oxygen evolution in dimethoxyethane (DME) since they had no effect on oxygen evolution potential (3.15-3.2V) observed through tracing oxygen amount. The catalyst lowered the potential for CO₂ evolution during electrolytes decomposition instead.

Although the mechanism of catalyzing the ORRs and OERs in LABs is not clear or in consensus, the requirement for catalysts in LABs is true. Designing a catalyst/supporting material composite electrode with an effective structure that could guarantee the sufficient contact between reactants and catalyst along with the accumulation of ORR products is of great interest in the development of LAB cathode.
1.4.5 Electrolytes

Till now, four possible configurations of electrolyte systems were investigated in LABs, including non-aqueous (aprotic organic solvents, ionic liquids), aqueous, mixed aprotic-aqueous, and fully solid systems. Non-aqueous systems have been widely researched since 1996. In early work, J Read characterized the effects of organic electrolytes including propylene carbonate (PC), ethylene carbonate (EC), 1,2-dimethoxyethane (DME), diethyl carbonate (DEC), dimethyl carbonate (DMC), $\gamma$-butyrolactone ($\gamma$-BL), tetrahydrofuran (THF), and tetrahydropyran (THP) on the rate capability, discharge capacity and rechargability. They found that the electrochemical performance varied remarkably with the changing of electrolyte by analyzing the oxygen concentration in electrolyte. Among the various electrolytes tested, the PC:DEC:LiPF$_6$ electrolyte has the highest discharge capacity based on weight of electrode or amount of oxygen in electrolyte with various types of carbon electrode including Super P, SAB, or BP2000:SAB.

However, it was found that carbonates were not stable to attack of superoxide radicals. For example, PC undergoes ring-open reactions that produces various organic lithium salts, includes $C_3H_6(OCO_2Li)_2$, Li$_2$CO$_3$, HCO$_2$Li, and CH$_3$CO$_2$Li, as shown in Figure 1-21. These Li salts could be partially oxidized during charge with the byproducts of CO$_2$, and H$_2$O. The different reaction mechanism in discharge and recharge results in large polarization. In the meantime, accumulation of these salts with the decompletion of electrolytes leads to the capacity fading and battery failure. Besides, ethers and dimethylformamide (DMF) were also evaluated as electrolytes for LABs but showed
instability\textsuperscript{105,130}. Tetraethylene glycol dimethyl ether (TEGDME) is relatively stable to superoxide attack\textsuperscript{131}. Salts in the electrolyte such as lithium bis(oxalato)borate is not stable either to superoxide attack\textsuperscript{132}.

Figure 1-24. (a) FTIR after first discharge of super P/α-MnO\textsubscript{2}/Kynar electrode in 1 M LiPF\textsubscript{6} in propylene carbonate. (b) Cycling performance of the same electrode. (c) FTIR of the electrode at different cycles.

1.4.6 Li-Anode

Li metal anode has been studied for use in LIBs for many years. It has the low potential and light weight, which makes it attractive as an anode material. However, Li
chemically reacts with polar aprotic solvents and anions. The products form a SEI film on the Li electrode surface through complicated reactions to prevent further corrosion. However, this SEI is not sufficient to protect Li electrode especially in high rate.

Partially because of the insufficient SEI, Li deposition would occur easier and faster on some favored spots in the absence of nucleation barrier. When the battery is continually cycled, these spots could become more favored for Li plating because of their shortened diffusion length for Li. This type of self-amplification behavior would lead to the growth of Li dendrite and hence increase the risk of short circuit of the battery, which could increase the temperature sharply and result in explosion because of thermal instability of Li/organic solvents system.

Introduction of additives to improve the chemical and electrochemical stability and physical uniformity of SEI is another choice to prevent Li dendrite growth. To prevent Li dendrite growth during Li deposition, an additive of CsPF$_6$ or RbPF$_6$ was introduced into the electrolyte. The Cs$^+$ and Rb$^+$ cations have reduction potentials lower than Li/Li$. Thus they could be attracted by negative Li electrode and tend to accumulate on the surface in the charge process when the Li deposition occurs on the anode. When a small Li dendrite is formed, the accumulation of Cs$^+$ or Rb$^+$ on this rigid spot is enhanced to prevent further gathering of Li$^+$ and inhibits the growth of Li dendrite.

Efforts have been taken to reduce the activity of Li by using Li$_3$N with Li or making Li-Al alloys. It was reported that deterioration of Li anode was an important factor that lead to capacity fading and failure of LABs. Lithiated silicon was studied as the anode to
make metal-free LABs or Li$_2$Si-O$_2$ battery$^{136}$. However, problems originating from buffering volume change and preventing pulverization must be overcome before the practical use of lithiated silicon anode.

Based on the discussion above, research is needed to improve the structure and performance of both electrode supports and catalysts. Table 1 shows the state-of-the-art supports and catalysts of Li-air batteries, and they can be used for comparison in Li-air battery research.
Table 1-1. State-of-the-art supports and catalysts of Li-air batteries

<table>
<thead>
<tr>
<th>Year Published</th>
<th>Electrode Support</th>
<th>Catalyst</th>
<th>Electrolytes</th>
<th>1st Discharge Capacity (Current Density)</th>
<th>1st Charge Capacity (Current Density)</th>
<th>Cycling</th>
</tr>
</thead>
<tbody>
<tr>
<td>1996&lt;sup&gt;98&lt;/sup&gt;</td>
<td>black carbon</td>
<td>-</td>
<td>LiPF&lt;sub&gt;6&lt;/sub&gt; in EC/PC</td>
<td>1410 mAh/g (0.1 mA/cm&lt;sup&gt;2&lt;/sup&gt;)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Carbon/polymer electrolyte</td>
<td>cobalt</td>
<td></td>
<td>100 mAh/g (0.1 mA/cm&lt;sup&gt;2&lt;/sup&gt;)</td>
<td>112 mAh/g (0.1 mA/cm&lt;sup&gt;2&lt;/sup&gt;)</td>
<td>105 mAh/g in 3&lt;sup&gt;rd&lt;/sup&gt; charge</td>
</tr>
<tr>
<td>2006&lt;sup&gt;103&lt;/sup&gt;</td>
<td>Super S carbon</td>
<td>EMD</td>
<td>1 M LiPF&lt;sub&gt;6&lt;/sub&gt; in PC</td>
<td>~1000 mAh/g (70 mA/g)</td>
<td>~800 mAh/g (50 mA/g)</td>
<td>~600 mAh/g in 50&lt;sup&gt;th&lt;/sup&gt; discharge</td>
</tr>
<tr>
<td>2010&lt;sup&gt;137&lt;/sup&gt;</td>
<td>Vulcan XC-72 carbon</td>
<td>Pt/Au</td>
<td>1 M LiClO&lt;sub&gt;4&lt;/sub&gt; in PC/DME</td>
<td>~2100 mAh/g (50 mA/g)</td>
<td>&gt;2500 mAh/g (50 mA/g)</td>
<td>~1300 mAh/g in 3&lt;sup&gt;rd&lt;/sup&gt; discharge;</td>
</tr>
<tr>
<td>2010&lt;sup&gt;108&lt;/sup&gt;</td>
<td>Super P carbon</td>
<td>α-MnO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1 M LiPF&lt;sub&gt;6&lt;/sub&gt; in EC/DMC</td>
<td>1068 mAh/g (0.15 mA/cm&lt;sup&gt;2&lt;/sup&gt;)</td>
<td>≥1068 mAh/g (0.15 mA/cm&lt;sup&gt;2&lt;/sup&gt;)</td>
<td>75 mAh/g in 4&lt;sup&gt;th&lt;/sup&gt; discharge</td>
</tr>
<tr>
<td>2011&lt;sup&gt;110&lt;/sup&gt;</td>
<td>Nitrogen-doped carbon nanotubes</td>
<td>-</td>
<td>1 M LiPF&lt;sub&gt;6&lt;/sub&gt; in EC and PC (1:1 w/w)</td>
<td>866 mAh/g (75 mA/g)</td>
<td>~200 mAh/g (75 mA/g)</td>
<td>&lt;150 mAh/g in 3&lt;sup&gt;rd&lt;/sup&gt; discharge</td>
</tr>
</tbody>
</table>
1.5 Other Air Batteries

Zinc-Air Battery

Primary zinc air battery has also received a lot of research attention\(^{138}\). Since 1980s, it has been widely used in hearing-aids and some watches, which are all low-rate equipment. The zinc-air button cell has a gravimetric energy density of 370 Wh/kg and a volumetric energy density of 1300 Wh/L, but low power output\(^{50}\). Primary zinc-air cell has cell reactions as following:

(i) Anode reaction

\[
\text{Zn} + 2\text{OH}^- \rightarrow \text{ZnO} + \text{H}_2\text{O} + 2e^- \quad (1-16)
\]

(ii) Cathode reaction

\[
\frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2e^- \rightarrow 2\text{OH}^- \quad (1-17)
\]

ZnO is not soluble in water, but it can react with OH\(^-\) and form soluble zincates (Zn(OH)\(_2\))\(^{2-}\). Since the active oxidant comes from the atmosphere, the main part of a Zn/air cell is a zinc anode as shown in Figure 1-14. The development of Zn-air battery is enhanced with the invention of hydrophobic polymers made from fluorocarbons, which makes it possible to produce an air diffusing, but water proof cathode.
The rate limiting chemistry lies in the reduction of oxygen in the alkaline environment, which is a multi-step reaction with the mediate product of $O_2H^-$. The second step concerning the decomposition of $O_2H^-$ is a slow process

\[
O_2 + H_2O + 2e^- \rightarrow OH^- + O_2H^- \\
O_2H^- \rightarrow OH^- + \frac{1}{2}O_2 \tag{1-18}
\]

To catalyze the decomposition of $O_2H^-$, metal compounds or oxides are used in air cathodes, such as CoO, noble metals, rare earth metal compounds, or MnO$_2$\textsuperscript{141,142}. The anode also has problems. For example, some impurities in zinc anode, such as Cu, Fe, and Sn, could lead to self-discharge, Zn corrosion, evolution of hydrogen, safety issues, and short shelf life\textsuperscript{50}. According to Chakkaravarthy and Udupa’ research in 1983, the addition of no less than 0.5% of mercury was necessary to minimize self-discharge\textsuperscript{143}. Zinc was also made into alloy
with other metals, such as aluminum, to work as the anode for Zn-air battery\textsuperscript{144}. It was found that the Al-rich phase in Zn/Al alloy could increase the reaction rate with KOH, create pores on surface, and hence decrease the passivation of anode\textsuperscript{144}.

The use of expensive catalysts increased the cost of primary zinc-air battery. To reduce the cost, zinc-air batteries could be made into “mechanically rechargeable” zinc air fuel cells (ZAFC) by feeding new Zn and electrolytes and removing discharge products\textsuperscript{145}.

Different with “mechanically rechargeable” zinc-air fuel cells, electrically rechargeable zinc-air batteries require noble metal catalysts as discussed. However, these catalysts do not work so well in the charge process, resulting from the hydrogen evolution and accumulation on the surface\textsuperscript{146}. To overcome this limitation, electrically rechargeable zinc-air batteries are made into three-electrode-batteries in commercialized products, with two air cathodes parallel and one zinc anode, while one of the cathode works in discharge, the other for charge.

On the anode side, zinc-air rechargeable battery has the dendrite problem arising with the redeposition and relocation of zinc, similar to the anode problem in lithium batteries.

**Sodium-Air Battery**

Sodium is known as an abundant element on Earth. Sodium-air battery is hence considered as a low-cost battery, which is favored in large scale use. However, quite few research has been done on sodium-air battery. There are three typical reactions between sodium and oxygen, as follows:
Liquid sodium-air battery running at above 100 mA/cm² was built by Peled et al.\textsuperscript{147}. The melting sodium anode was believed to have the potential ability to improve kinetics and prevent dendrites formation for practical use\textsuperscript{147}. However, at high temperatures, the SEI formed on melting anode was not able to remain stable, leading to fatal problems during electrochemical cycles.

Room-temperature sodium-air battery was also constructed with a high capacity of 3600 mAh/g at low current rate (1/60C)\textsuperscript{148}. The capacity was calculated based on carbon electrode. The electrolyte used was carbonate-based, which was considered not stable in Li-air batteries\textsuperscript{104}. The discharge products were determined to be Na₂O₂ and sodium carbonates, which were both oxidized in charge\textsuperscript{148}. These inert reduction products could be the possible reason for the overpotential in recharge, which was higher than 1 V.

More recently, a reversible sodium-air battery was reported\textsuperscript{149} with main discharge product of crystalline NaO₂, as shown in Figure 1-15. The over potential between charge and discharge was decreased to 200 mV, compare with the typical value of 1.3 V in lithium-air batteries. This extraordinary low polarization was attributed to the formation of super sodium oxide, which was kinetically favored than sodium oxide, although it was thermodynamically

\[
\begin{align*}
\text{Na} & + \text{O}_2 \rightarrow \text{NaO}_2 & (E^0 = 2.27 \text{ V}) \\
2\text{Na} & + \text{O}_2 \rightarrow \text{Na}_2\text{O}_2 & (E^0 = 2.33 \text{ V}) \\
2\text{Na} & + \frac{1}{2}\text{O}_2 \rightarrow \text{Na}_2\text{O} & (E^0 = 1.95 \text{ V})
\end{align*}
\]
less favored. However, the charge/discharge reversibility was still restricted to less than 10 cycles, while the mechanism for this capacity fading was not specified\textsuperscript{149}.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{image.png}
\caption{A SEM image of the discharged cathode on the oxygen side\textsuperscript{149}.}
\end{figure}

**Aluminum-Air Battery**

Considering its high oxidized state and light weight, Al-air battery can achieve a very high gravimetric energy density, which is close to that of Li-air batteries and much higher than that of Zn-air batteries. One mole of electrons transferred only consumes 9 grams of Al in Al-air batteries, while the value is 7 grams in Li-air batteries or 38 grams in Zn-air batteries. Moreover, the Al-air battery also has the potential to reach a very high power density in aqueous alkaline environment, which is necessary to dissolve the insulating oxygen reduction product ($\text{Al}_2\text{O}_3$). High gravimetric energy density and high power density,
combining with low cost, make the Al-air battery a very promising candidate for large-scale use, etc. in vehicles.

It has cell reactions as follows:

(i) Anode reaction

\[ \text{Al} + \text{KOH} + 3\text{OH}^- \rightarrow \text{KAl(OH)}_4 + 3e^- \]  \hspace{1cm} (1-20)

(ii) Cathode reaction

\[ \frac{3}{4}\text{O}_2 + \frac{3}{2}\text{H}_2\text{O} + 3e^- \rightarrow 3\text{OH}^- \]  \hspace{1cm} (1-21)

(iii) Corrosion reaction

\[ \text{Al} + \text{KOH} + 3\text{H}_2\text{O} \rightarrow \text{KAl(OH)}_4 + \frac{3}{2}\text{H}_2\uparrow \]  \hspace{1cm} (1-22)

(iv) Crystallization reaction

\[ \text{KAl(OH)}_4 \rightarrow \text{KOH} + \text{Al(OH)}_3\downarrow \]  \hspace{1cm} (1-23)

The alkaline electrolyte is consumed during the discharge, hence decreasing the ionic conductivity. However, through crystallization of aluminum trihydroxide, the electrolyte could be replenished. The cell can reach a stead state when these two reactions are in equilibrium. The oxidized Al cannot be reduced to Al in aqueous environment. One possible way to make the Al-air battery be used again is to make it into a fuel cell through refueling it
with new Al anode and electrolyte, like the case in Zn-air fuel cells. All these require good electrolyte composition and battery design\textsuperscript{150}.

However, the Al-air battery suffers a fatal problem coming from the corrosion of aluminum with small impurity in alkaline solution. For example, the presence of iron, a typical impurity in aluminum, could increase the corrosion rate remarkably\textsuperscript{151}. Thus, high-purity aluminum, no less than 5N (99.999\%) for Al-air batteries, is required, which costs 10 to 20 times more than normal aluminum\textsuperscript{152}.

Citroen has built a model car using both rechargeable lithium-ion battery (LIB) and primary Al-air battery, employing the extended-range electric vehicle (EREV) technique. Using the LIB alone, the battery should be charged every 100 miles. However, using the Al-air battery, it can keep running for 1000 miles before refuel aluminum, although the electrolyte should be replenished by refilling distilled water every 200 miles\textsuperscript{153}.

Compared with mechanically recharging the battery, electrochemically recharging is difficult because the potential of Al/Al\textsuperscript{3+} (-1.676 V vs NHE) is lower than that of H/H\textsuperscript{+}.

1.2.6.1 Iron-air battery

Iron-air battery is low-cost. The cell reactions are

\[ \text{O}_2 + 2\text{H}_2\text{O} + 2\text{Fe} \rightleftharpoons 2\text{Fe(OH)}_2 \]
\[ 3\text{Fe(OH)}_2 + 1/2\text{O}_2 \rightleftharpoons \text{Fe}_3\text{O}_4 + 3\text{H}_2\text{O} \]

(1-24)
Although two steps appear during iron oxidation, there is no relocation of Fe in discharge/charge cycles, since the Fe(OH)$_2$ is not soluble in water. Thus, dendrite are not formed in Fe-air batteries, making them competitive compared with Zn-air or Li-air batteries. Active iron anode will expand in discharge and be covered by a layer of Fe$_3$O$_4$. To make good use of ion anode requires a design of porous structure$^{154}$. The oxygen reduction in Fe-Air batteries is also a multi-step reaction with H$_2$O$_2$ as the intermediate.

\[
\begin{align*}
O_2 + 2H_2O + 2e^- & \rightarrow 2OH^- + H_2O_2 \\
H_2O_2 + 2e^- & \rightarrow 2OH^-
\end{align*}
\]

(1-25)

The presence of fairly active H$_2$O$_2$ affects the battery performance greatly. H$_2$O$_2$ molecules tend to attack the substrates, catalysts, separator, even the water-proofing film. Comparing with Al-air battery, electrochemically charging Fe/air battery is easier. Combining with the non-relocation of Fe during charge/discharge cycles, the enhanced potential ability of electrochemical recharge makes Fe/air a possible candidate for large scale use in electric vehicles, although the output potential of Fe/air is low, decreasing the energy density.
2 RESEARCH OBJECTIVES

Along with the development of various types of new multifunctional electronic devices and electrical vehicles, Li-ion batteries have shown their limitations on fulfilling the increasing energy storage demands. The Li-air batteries have the potential of bidding for the next-generational energy storage system to power the electric vehicles and portable electronic devices, providing 5-10 times the gravimetric energy density of conventional Li-ion batteries. The essential chemical difficulty lies in the sluggish multi-electron-transfer oxygen reduction and evolution reactions (ORR and OER), coupling with complexity of multi-phase systems and inert chemical nature of the reaction products. Consequently, severe polarization, poor reversibility, and low cycling stability become the performance-limiting problems that must be addressed before Li-air batteries succeeding Li-ion batteries.

As discussed in the previous chapter, high-surface-area and highly-conductive carbons become the desired material choice for LABs. Carbon nanofiber (CNF) electrodes are good material candidate for LAB air cathodes considering their characteristics such as low cost, high surface area, and high conductivity. Thus, this research focused on synthesizing and evaluating CNF-based electrodes for LABs.

In the fourth chapter, non-woven porous carbon nanofiber (PCNF) electrodes were fabricated through electrospinning and carbonization of ZnCl₂/polyacrylonitrile (PAN) precursors to evaluate the paradox effect of broadening surface area on improving cell reversibility and decreasing electrode conductivity for Li-air batteries. SEM, EDS, and nitrogen adsorption-desorption were used to evaluate the morphology and porosity of the
obtained macro/micro-porous structure. The specific surface area of the PCNF electrode made from 30% ZnCl₂/PAN precursor was found to be 20 times greater than that of carbon nanofibers (CNFs) made directly from the PAN precursor. Electrochemical performance tests showed the PCNF electrodes had lower capacity but better reversibility compared with CNF electrodes. The results indicate that the paradox effect of broadening surface area decreased the electronic conductivity of carbon electrode and increased the reversibility of deposited Li₂O₂ or Li₂O on electrode surface.

In the fifth chapter, MnOₓ/carbon nanofiber (CNF) composite electrodes were prepared through electrospinning and heat treatment. Scanning electron microscopy (SEM) and scanning transmittion electron microscopy (STEM) coupled with energy dispersive X-ray spectroscopy (EDS) revealed the morphology and chemical structure of the composite electrodes. An X-ray photoelectron spectrooscope (XPS) was deployed to analysis the oxidation state of Mn in MnOₓ/CNF composites. These binder-free and self-standing MnOₓ/CNF composite electrodes exhibited better cycling performance and reversibility compared with carbon nanofiber electrode. It is, therefore, demonstrated that the electrospinning technique offered a unique and promising way to prepare gas-diffusion catalyst/carbon nanocomposite air cathodes for Li-air batteries.

In the sixth chapter, different MnO₂/CNF electrodes with MnO₂ nanofibers anchored on the CNF surface or MnO₂ nanoparticles loaded on the CNF surface were obtained through low-current and high-current electrodepositions (LCD and HCD), respectively. The morphology of CNFs and deposited MnO₂/CNFs was evaluated by SEM. Chemical
composition and oxidation state of Mn in MnO$_2$/CNFs was analyzed by STEM/EDS and XPS. Through electrochemical analysis, both MnO$_2$/CNF electrodes possessed much higher discharge capacity, better reversibility, and more cycling stability than regular CNF electrode. Compared with the nanoparticle/nanofiber structured HCD-MnO$_2$/CNF composite, the fiber-anchored-on-fiber structured LCD-MnO$_2$/CNF composite showed even better electrochemical performance. This illustrated that the importance of catalyst morphology for lithium-air batteries. This binder-free fiber-anchored-on-fiber structured MnO$_2$/CNF electrode is a promising candidate for catalyst/carbon-matrix lithium air cathode.
3 MACROPOROUS/MICROPOROUS CARBON NANOFIBER ELECTRODES
FOR LITHIUM-AIR BATTERIES

3.1 Abstract

Non-woven porous carbon nanofiber (PCNF) electrodes were fabricated through electrospinning and carbonization of ZnCl₂/polyacrylonitrile (PAN) precursors to evaluate the paradox effect of broadening surface area on improving cell reversibility and decreasing electrode conductivity for Li-air batteries. SEM, EDS, and nitrogen adsorption-desorption were used to evaluate the morphology and porosity of the obtained macro/micro-porous structure. The specific surface area of the PCNF electrode made from 30% ZnCl₂/PAN precursor was found to be 20 times greater than that of carbon nanofibers (CNFs) made directly from the PAN precursor. Electrochemical performance tests showed the PCNF electrodes had lower capacity but better reversibility compared with CNF electrodes. In pursuing better electrode structure and higher performance of Li-air batteries, it is not always the larger SSA the better. Adjusting the balance between conductivity and surface area to the specific applications is of significant importance to increase the battery performance efficiently.

3.2 Background

The Li-air batteries have the potential of bidding for the next-generational energy storage system to power the electric vehicles and portable electronic devices, providing 5-10 times the gravimetric energy density of conventional Li-ion batteries. However, the commercialization of Li-air batteries stays far before the several critical challenges being overcome. The discharge products, which are not soluble in typical aprotic electrolytes, have
inert electrochemical properties, poor electronic and ionic conductivities. The accumulation of discharge products on the air cathode could cut off the contact of oxygen, lithium-ion electrolyte with the cathode, prevent further mass transfer, and passivate the cathode. When the thickness of Li$_2$O$_2$ was increased to 5-10 nm, the “sudden death” of the battery could occur due to the retarded charge transport\textsuperscript{155}.

One way to solve the problem of passivation is to replace aprotic electrolyte with protonic electrolyte to dissolve oxygen reduction products, which can also facilitate the oxygen revolution in charge\textsuperscript{156}. However, highly corrosive H$^+$ reacts with Li and brings significant safety issues and/or cost, thus hinders its widespread application. Another way is to develop the high-surface-area and high-porosity electrodes that the sufficient contact between the electrolyte, oxygen and electrode could buffer the passivation of oxygen reduction products. Great efforts have been made on both developing materials and designing structure for air cathodes. Various carbon materials including graphite powders\textsuperscript{98}, carbon blacks\textsuperscript{90,91,103,157-159}, carbon nanotubes\textsuperscript{110,111}, carbon foam\textsuperscript{115} and graphene\textsuperscript{113,114,160-162} have been studied as high-surface-area supporting materials for air cathodes. Typically, the use of high-performance carbon for the air cathode requires higher amount of binder than that used in Li-ion batteries because of the porous current collector, which will lower the conductivity, pore efficiency and specific energy density of the cathode. Application of the binder-free and self-standing gas-diffusion-electrode (GDE) is of great interest considering the problem of binder\textsuperscript{100}. In the binder-free GDE, macropores work as conduits for the passage of both O$_2$ and Li$^+$, boosting especially the high-rate performance\textsuperscript{161}. 
However, in the binder-free GDE, less oxygen reduction product was observed on the separator side than those observed on the air side at fully discharged state, indicating that comprehensive designs of the GDE are essential for structure efficiency\textsuperscript{111}. The non-woven fibrous and macroporous carbon naonofiber membranes have been demonstrated to be a feasible platform for designing a functional GDE for Li-air batteries\textsuperscript{109,111,112,163,164}. On one hand, sufficient diffusing ability of Li\textsuperscript{+} and O\textsubscript{2} could be boosted by countless inter-connected macropores between fibers. On the other hand, self-standing winded-together fibers form conductive network, broaden the surface area, and increase the contact between reactants. Efforts have been made to activate the carbon fibers to further enlarge the surface area, and enhance the positive effects\textsuperscript{165}. However, introducing pores into GDE will inevitably decrease the electronic conductivity and slow the charge transfer kinetics dramatically along with the accumulation of inert discharge products at high current. In the designing of binder-free GDE, it is of great importance to address this two-blade effect of broadening the surface area.

In this work, based on the non-woven fibrous and macroporous membrane, micro pores (≤ 2 nm) were created on the fiber surface to build a hierarchical porous structure. The paradox effect of porous structures on the electrochemical performance of Li-air batteries was investigated on this unique hierarchical porous GDE.
3.3 Experimental

Polymer Fiber Fabrication

A solution of 8 wt% PAN (PAN, Pfaltz & Bauer Inc., $M_w = 150,000$) in dimethylformamide (DMF) was prepared and then stirred at 60 °C for 24 hours. Anhydrous ZnCl$_2$ (Sigma Aldrich, >99.995%) was dried at 80 °C in oven for 24 hours and then dried at 120 °C in vacuum oven for another 24 hours. Dried ZnCl$_2$ was added to the PAN/DMF solution with a ZnCl$_2$/PAN weight ratio of 15:100 or 30:100, while PAN/DMF solution was used to prepare the control sample. The concentration of ZnCl$_2$ was controlled because of the low saturation concentration of ZnCl$_2$ in DMF and the increased difficulty of electrospinning along with the increased ZnCl$_2$ concentration in the solution.

A high voltage of 15 kV was applied between the precursor solution and Al collector to initiate the electrospinning process. The feeding rate of precursor solution was controlled by a pump at 0.7 ml/h while the needle-to-collector-distance was set as 15 cm. The humidity was lowered to below 30% to enhance the evaporation of solvent in the jet fiber during spinning. The polymer nanofiber mat was obtained after three-hour electrospinning and then peeled off from the Al collector for the following thermal treatment.

Thermal Treatment and Acid Etching

Electrospun PAN and ZnCl$_2$/PAN nanofiber mats were heated in furnace (Model 7AM-C12, LUCIFER) in air environment to 280 °C with a heating rate of 5 °C/min and hold for 5.5 h. Then the air-stabilized nanofiber mats were heated to 700 °C in argon with a heating rate of 2 °C/min and hold for 2 h to undergo carbonization. The carbonized nanofiber
mats obtained from ZnCl₂/PAN were etched in a 5% HCl solution for 12 h at 70 °C to remove the Zn and Cl compounds. Etched samples were washed in deionized water to remove the residual HCl and then dried at 100 °C overnight. The etched nanofiber samples made from 15% ZnCl₂/PAN and 30% ZnCl₂/PAN were labeled as PCNF #15 and PCNF #30, with CNF as the control sample.

**Structure Characterization**

The morphology of CNFs and PCNFs was examined by FE-SEM (Zeiss Merlin and Verio 460 L). Element distribution maps were obtained by analyzing the energy-dispersive X-ray spectra (EDS).

**Cell Assembly and Electrochemical Analysis**

Cyclic voltammetry (CV) was conducted in a Swagelok cell by sandwiching the electrode with two stainless steel plates for conductivity measurement. The voltage was increased from -0.10 V to 0.10 V with the scanning rate of 0.01 V/s.

For electrochemical tests, Swagelok Li-air batteries were prepared consisting of prepared CNF or PCNF cathode, lithium ribbon anode, glass fiber (Whatman, GF/D) separator, 1M lithium bis(trifluoromethanesulfonyl)imide (LITFSI) in tetra(ethylene)glycol dimethyl ether (TEGDME) as electrolyte, and Al-mesh (Dexmet Corporation, 2Al 4-050) current collector. Before use, LiTFSI was dried at 80 °C for 6 hours and then kept in vacuum oven for 12 hours while the water content in TEGDME was removed by LiH. Cell-assembling was performed in an argon-filled glove box with controlled water and oxygen.
contents less than 0.1 ppm. Cells were purged 10 times with oxygen and tested while keeping
the pressure of supplied oxygen at ~7 atm.

Galvanostatic discharge-charge experiments were carried out with cut-off voltages as
2.0 V and 4.3 V, respectively, while keeping the discharge current density at 500 mA/g and
charge current density at 125 mA/g. The cut-off capacity for discharge and charge was set as
100 mAh/g. CV studies were conducted between 1.5 V and 4.5 V (vs. Li/Li+) with a scanning
rate of 0.1 mV/s.

3.4 Results and Discussion

SEM images of the electrospun polymer nanofibers and CNFs are shown in Figure
3-1. PAN nanofibers exhibit smooth surfaces without the presence of bead-on-fiber
formation. Undergoing pyrolysis at high temperatures, PAN nanofibers shrunk and formed a
free-standing non-woven CNF membrane. When the membrane electrode is wetted by the
electrolyte, inter-connected macrospores between individual fibers form micro-sized
channels functioning as diffusion pathways of O₂ and Li⁺. Figures 3-2 and 3-3 present SEM
images of electrospun 15% and 30% ZnCl₂/PAN nanofibers, corresponding carbonized
nanofibers, and etched porous CNFs (PCNFs) #15 and #30, respectively. All nanofibers
possess the similar morphology with CNFs, except the more heterogeneous fiber diameter
distribution. The changes in morphology reflect the effect of dissolved and ionized ZnCl₂ on
electrospinning, which works at high voltage (15 kV).
Figure 3-1. SEM images of (a) electrospun PAN nanofibers, and (b) carbonized nanofibers.

Figure 3-2. SEM images of (a) electropsun 15% ZnCl₂/PAN composite nanofibers, (b) carbonized nanofibers, and (c) etched carbonized nanofibers.
Figure 3-3. SEM images of (a) electropsun 30% ZnCl$_2$/PAN composite nanofibers, (b) carbonized nanofibers, and (c) etched carbonized nanofibers.

Figure 3-4 shows SEM/EDS images, EDS spectrums, and EDS maps showing carbon, zinc and chlorine atomic profiles of un-etched PCNF #15 and etched PCNF #15. Comparing Figures 3-4b, d, and e with g, i, and f, the Zn and Cl contents decrease remarkably after etching. Table 3-1 shows the quantitative results of C, Zn, and Cl, obtained by analyzing the EDS spectrums (Figures 3-4b and g). It is seen that residual Zn content is reduced from 4.58% to 0.18% after etching. The atom ratio between zinc and carbon is decreased from 1:16 to 1:392. In PCNF #30, residual Zn atoms are reduced from 3.31% to 0.05%, while the atom
ratio between zinc and carbon is decreased from 1:23 to 1:1599. Although it is difficult to calibrate the EDS measurements because of the lack of standards, significant decrease of the residual Zn and Cl after HCl etching is obvious, which is important to allow for evaluating their effect on electrode morphology and hence cell performance without interference. Meanwhile, it is worth noticing that in un-etched samples, the atom ratios of Cl and Zn are 1:13.74 and 1:10 for #15 and #30, respectively, while it was 1:0.5 in precursor solution. The drops of Cl:Zn ratio after carbonization indicate that Cl plays the role of dehydrating agent\textsuperscript{166}. 
Figure 3-4. SEM/EDS analysis of (a-e) un-etched PCNF #15 and (f-j) etched PCNF #15; (a, f) SEM images; (b, g) EDS spectrums; (c-e, h-j) EDS maps showing carbon, zinc and chlorine atomic profiles.
Table 3-1. SEM/EDS Analysis Results on Un-etched and Etched PCNF #15.

<table>
<thead>
<tr>
<th>Element</th>
<th>C un-etched Atom.[at.%]</th>
<th>C etched Atom.[at.%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>73.74</td>
<td>70.60</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>15.76</td>
<td>16.39</td>
</tr>
<tr>
<td>Oxygen</td>
<td>5.59</td>
<td>12.77</td>
</tr>
<tr>
<td>Chlorine</td>
<td>0.33</td>
<td>0.06</td>
</tr>
<tr>
<td>Zinc</td>
<td>4.58</td>
<td>0.18</td>
</tr>
</tbody>
</table>

Figure 3-5. SEM/EDS maps showing carbon, zinc and chlorine atomic profiles in (a-c) un-etched PCNF #30 and (d-f) etched PCNF #30.
Table 3-2. SEM/EDS Analysis Results on Un-etched and Etched PCNF #30.

<table>
<thead>
<tr>
<th>Element</th>
<th>C (un-etched) Atom.[at.%]</th>
<th>C (etched) Atom.[at.%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>76.14</td>
<td>79.93</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>13.18</td>
<td>11.86</td>
</tr>
<tr>
<td>Oxygen</td>
<td>7.08</td>
<td>7.9</td>
</tr>
<tr>
<td>Chlorine</td>
<td>0.3</td>
<td>0.27</td>
</tr>
<tr>
<td>Zinc</td>
<td>3.31</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Isotherms of CNFs and PCNFs (Figure 3-6) can be used to investigate the effect of ZnCl₂ loading. The PCNF #30 has an adsorption curve which consists of an initial jump and an almost horizontal plateau, indicating that the isotherm is type I and most of pores are micropores (< 2 nm), in agreement with other works⁶⁶,⁶⁷. These micropores are too small to be observed in SEM images. The specific BET surface areas could be obtained from

\[ S_{BET} = \frac{v_m N s}{a V} \]

where \( v_m \) is the monolayer absorbed gas quantity obtained from the linear BET plot of \( 1/v(\frac{p_0}{p} - 1) \) with \( p/p_0 \), \( N \) is Abogadro’ number, \( s \) is the adsorption cross section of the adsorbing species, \( V \) is the molar volume of the adsorbate gas, and \( a \) is the mass of the sample. PCNFs #15 and #30 possess a specific surface area (SSA) of 36.2 m²/g and 221 m²/g, respectively, while the SSA of CNFs is 7.9 m²/g (Figure 3-6d), since ZnCl₂ decreases the amount of tars produced during carbonization⁶⁷. During carbonization, ZnCl₂ played the
role of a dehydration agent to enhance the cross-linking of polymers and increase the char yield and hence the surface area\textsuperscript{168}. The removal of trapped ZnCl\textsubscript{2} or ZnO in HCl also benefits the creation of micropores\textsuperscript{166}.

![Figure 3-6. Nitrogen adsorption/desorption isotherms of (a) CNFs, (b) PCNF #15, and (c) PCNF #30; (d) effect of ZnCl\textsubscript{2} loading amount on specific surface areas.](image)
Figure 3-7 presents the electrical conductivity measurements of CNF and PCNF electrodes. Conductivity $\sigma$ was obtained from: $\sigma = \frac{1}{\rho} = \frac{l}{RA}$, where $\rho$ is the resistivity, $l$ is the thickness, $R$ is the electrical resistance, and $A$ is the cross-sectional area of the electrode. The electronic conductivity of CNFs is $\sim 2.59 \, S/m$, while the conductivities of PCNF #15 and #30 are $\sim 1.33 \, S/m$ and $\sim 0.32 \, S/m$, respectively. The loss of conductivity is consistent with the broadening of surface area and creation of micropores in carbon nanofibers, since the creation of pores leads to the formation of less ideal graphitic phase$^{165}$. 
Cyclic voltammograms (CVs) of CNF and PCNF electrodes in Li-air batteries were collected and present in Figure 3-8. A well-defined cathodic peak occurs at ~2.3 V in the CNF electrode with a small shoulder to the right of the main peak at ~2.4 V. The main cathodic peaks in PCNFs are below 1.5 V. There are shoulders to the right of these main peaks at ~2.0 V and ~1.9 V in PCNF #15 and #30, respectively. As discussed in previous chapters, the oxygen reduction reactions (ORRs) in Li-air batteries are multistep reactions with 2-4 electrons transferred\textsuperscript{93}. The split of oxygen reduction peaks, which is also observed
by Yang et al\textsuperscript{165}, is in accordance with the complicated mechanism of ORRs. The shift of the main cathodic peak from 2.3 V to lower than 1.5 V indicates the slowing-down of kinetics resulting from the activation of the CNF electrode. No anodic peak presents in CNF electrode. In PCNF #15, two broad anodic peaks appear at \(~3.3\) V and \(~4.0\) V, while two anodic peaks are observed at \(~3.4\) V and \(~4.1\) V in PCNF #30. Since the PCNF electrode had higher surface area than CNFs, the thickness of deposited reduction products could be decreased, facilitating the oxidation of these reduction products. The splitting of broad anodic peaks in both PCNF #15 and #30 illustrates the complex composition of ORR products.
Figure 3-8. Cyclic Voltammetry profiles of (a) CNF, (b) PCNF #15, and (c) PCNF #30 electrodes. The cyclic voltammetry studies were conducted with a scanning rate of 0.1 mV/s from 1.5 V to 4.5 V (vs. Li/Li⁺).

Electrochemical performance of the CNF and PCNF electrodes, shown in Figure 3-9, was evaluated between 2.0 V and 4.3 V with the cut-off capacity of 100 mAh/g. Discharge current density used was 500 mA/g, while charge current density was 125 mA/g. The discharge current density used in this research is 3-6 times higher than other works\textsuperscript{103,127,169}, considering that the purpose of elaborating the paradox effect of roughing surface of the electrode to increase surface area and porosity. A lower current density in charge than in
discharge was used considering that the electrode resistance tended to increase during discharge due to the accumulating of oxygen reduction products on electrode surface and hence passivation of electrode. Discharge curves of the CNF electrodes are more stable than those of PCNF electrodes (Figures 3-9a, c, and e). This is because the CNF electrode has higher conductivity, which plays a significant role in achieving the electrochemical equilibrium of cell reactions. The discharge capacity doesn’t fade in 100 cycles with a cumbic efficiency of ~85% in most cycles (Figure 3-9b).

Low conductivity of PCNFs leads to slope-like discharging curves demonstrating the rate-limited or kinetics-limited nature, as shown in Figures 3-9c and e. Although PCNF #15 and PCNF #30 have low discharge capacities of 45.8 mAh/g and 43.7 mAh/g at the 20th cycle, its cumbic efficiency in each cycle is close to 100% in most cycles (Figures 3-9d and f). As discussed in previous chapter, the thickness of deposited discharge products could be smaller if its capacity is not larger than CNF, since the PCNF electrode has higher surface area. Thinner layer of oxygen reduction products facilitates oxidation in charge. When comparing PCNF #15 with #30, it has slightly higher capacity and higher charge curves benefitting from the higher conductivity (Figures 3-9c, d, e, and f). However, the cumbic efficiency of PCNF #30 is greater testifying the role of broadening surface on reversibility of oxygen reduction products.
Figure 3-9. Galvanic charge-discharge profiles and cycling-performance plot of (a, b) CNF, (c, d) PCNF #15, and (e, f) PCNF #30 electrodes.
3.5 Summary

PCNF electrodes were fabricated and offered a feasible platform to evaluate the paradox effect of increasing surface area and decreasing electrode conductivity on the electrochemical performance of Li-air batteries. With increase in surface area, thinner Li$_2$O$_2$ deposition on electrode surface could be realized in constant discharge capacity, leading to better electrochemical properties and better reversibility. However, this was accomplished with the sacrifice of electronic conductivity which would worsen the kinetics and decrease the capacity especially at high current densities. Therefore, in pursuing better electrode structure for Li-air batteries, it is not always the larger SSA the better. Adjusting the balance between conductivity and surface area to the specific applications is of significant importance to increase the battery performance efficiently.
4 A NEW TYPE OF BINDER-FREE NON-WOVEN MnOx/CNF NANOCOMPOSITE CATHODE FOR LITHIUM-AIR BATTERIES

4.1 Abstract

MnOx/carbon nanofiber (CNF) composite electrodes were prepared through electrospinning and heat treatment. Scanning electron microscopy (SEM) and scanning transmission electron microscopy (STEM) coupled with energy dispersive X-ray spectroscopy (EDS) revealed the morphology and chemical structure of the composite electrodes. An X-ray photoelectron spectroscopy (XPS) was deployed to analyze the oxidation state of Mn in MnOx/CNF composites. Compared with CNF electrode, the synthesized MnOx-CNF electrodes showed larger charge capacity and higher columbic efficiency in eight cycles, indicates the catalytic role of MnOx in oxygen evolution reactions. It was hence demonstrated that as a binder-free and free-standing catalyst/supporting carbon mat electrode, the MnOx-CNF nanocomposites offered a promising material electrode candidate for Li-air cathodes.

4.2 Background

Driven by the pressure of greenhouse gas emissions, same as the tremendous business prospects of portable electronic devices and electric vehicles, developing new materials for electricity storage systems have been experiencing the non-stop exponential growth\textsuperscript{1-3}. Although having essential chemical challenges and obstacle, Li-air batteries, the so-called “breathing” battery, start to draw significant attention with the attractively-high capacity, which is 5-10 times greater than that of Li-ion batteries\textsuperscript{4}. The essential chemical difficulty lies in the sluggish multi-electron-transfer oxygen reduction and evolution reactions (ORR
and OER), coupling with complexity of multi-phase systems and inert chemical nature of the reaction products. Consequently, severe polarization, poor reversibility, and low cycling stability become the performance-limiting problems that must be addressed before Li-air batteries succeeding Li-ion batteries.

Nano-structured MnO₂, Co₃O₄, or noble metal are introduced into the air cathode as catalysts with the purpose of improving kinetics of ORR and OER. Abundance of Mn in Earth shell makes the MnO₂ less costly compared with Co₃O₄ or noble metal and favored in large scale applications such as in electric vehicles. Meantime, highly porous and conductive carbon is used as the supporting material to buffer the passivation of accumulated chemically and electrochemically inter Li₂O and offering diffusing channels for electrolyte and oxygen to keep the battery “breath”. Typically, incorporation of catalysts into the porous carbon electrode requires addition of binders, the amount of which is higher than the amount used in Li-ion batteries due to the use of perforated current collectors in Li-air batteries. Therefore, pore efficiency and energy efficiency decrease, along with the decreasing conductivity. To design a binder-free porous electrode is of great interest to address the above problem.

Electrospinning combined with heat treatment was a versatile and convenient way to produce particle/carbon fiber composite. In this paper, electrospinning was employed to obtain a binder-free non-woven catalyst-on-fiber nanocomposite electrode.
4.3  Experimental

Synthesis

An electrospinning solution of 8 wt % polyacrylonitrile (PAN) (Pfaltz and Bauer) in
dimethylformamide (DMF) (Sigma Aldrich, anhydrous) was prepared and stirred for 24
hours at the temperature of 60 °C. Mn(OAc)₂ was added to the PAN/DMF solution with a Mn(OAc)₂:PAN weight ratio of 30:100 or 50:100 and stirred for another 24 hours at room
temperature. Electrospinning was conducted under 15 kV at the feeding rate of 0.7 ml/hour
with the needle-to-collector distance of 15 cm. Electrospun nanofibers were obtained with an
area-density of 1-5 mg/cm².

Heat treatment was applied to the electrospun fiber mats in two steps. Firstly,
electrospun nanofiber mats were stabilized at 280 °C for 5.5 hours in air. Secondly, stabilized
nanofiber mats were carbonized at 700 °C for 2 hours in argon. Obtained MnOₓ/carbon
composite nanofiber mats were directly punched into chips in diameter of 7/16" (~1.11cm)
and dried at 110 °C for 24 hours for use. The samples made from 30% Mn(OAc)₂/PAN and
50% Mn(OAc)₂/PAN were labeled as MnOₓ-CNF #30 and MnOₓ-CNF #50, respectively.

SEM, STEM, and STEM-EDS Characterization

SEM (JOEL 6400F FESEM) was used to evaluate the morphology of the nanofiber
mat. FEI Titan probe aberration-corrected scanning transmission electron microscopy
(STEM) with monochromator was employed to take the images of samples on carbon grids
operated at 200 keV. Samples were briefly sonicated in methanol for TEM sample
preparation. Energy-dispersive X-ray spectroscopy (EDS) in STEM mode was employed for
distribution of MnOₓ catalysts. The distribution of Mn, C, and O was obtained by identification of their peaks observed in the EDS spectrum during three-minute mapping. X-ray photoelectron spectroscopy of synthesized MnOₓ/CNF composites was collected in PHOIBOS 150 analyzer (<1 eV resolution) with a beam of Mg Kα radiation (1500 eV; 400 W) to determine the mean state of Mn.

**Cell Assembly and Electrochemical Measurements**

Swagelok Li-air batteries were prepared consisting of CNF electrode, lithium ribbon anode, glass fiber (Whatman, GF/D) separator, electrolyte of 1M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in tetra(ethylene)glycol dimethyl ether (TEGDME), and Al-mesh (Dexmet Corporation, 2Al 4-050) as current collector. LiTFSI was dried at 80 °C for 6 hours and then kept in vacuum oven for 12 hours before use. TEGDME was dried by adding LiH. Assembling was done in an argon-filled glove box with water and oxygen contents smaller than 0.1 ppm. Cells were purged 10 times with pure oxygen before testing. During testing, the pressure of supplying oxygen was kept at ~7 atm.

The electrochemical window of the electrolyte was tested by charging the prepared cell directly without the first discharge process in argon and air, respectively. Galvanostatic discharge-charge experiments were done using Arbin 2000 at different current densities between 2.0 V and 4.5 V. The cyclic voltammetry studies were conducted with a scanning rate of 0.1 mV/s from 1.5 V to 4.5 V (vs. Li/Li⁺).
4.4 Results and Discussion

Figure 4-1 shows SEM images of electrospun PAN nanofibers, carbon nanofibers (CNFs), Mn(OAc)$_2$/PAN nanofibers, and MnO$_x$/C composite carbon nanofibers (MnO$_x$-CNF #30 and #50). The surfaces of MnO$_x$-CNFs and CNFs are smooth showing no bead-on-fiber structure demonstrating the good homogeneity of the electrospinning process. The diameters of the polymer nanofibers shrinked clearly during carbonization due to the pyrolysis of PAN and Mn(OAc)$_2$. Both CNFs and MnO$_x$-CNFs form free-standing nonwoven mats, which can not only hold the integrity of the binder-free electrodes but also serve as electronic conductive networks. Moreover, the channels between fibers in CNF and MnO$_x$-CNF mats offer diffusion pathways for Li$^+$ and O$_2$, when wetted by the electrolyte. With enhanced electronic conductivity, improved Li$^+$ conductivity, effective O$_2$ diffusion, and embedded catalysts, the MnO$_x$-CNFs can offer a reasonable catalyst-carbon-nanocomposite air cathode.
Figure 4-1. SEM images of electrospun nanofibers, and carbon nanofibers with different Mn(OAc)$_2$ concentrations: (a, b) 0% Mn(OAc)$_2$, (c, d) 30% Mn(OAc)$_2$/PAN, and (e, f) 50% Mn(OAc)$_2$/PAN.

To better describe the effect of introducing Mn(OAc)$_2$ on the chemical composition of CNFs, scanning transmission electron microscopy (STEM) coupled with energy dispersive
X-ray spectroscopy (EDS) was employed. Figure 4-2 shows STEM images of MnO$_x$-CNF #30 and MnO$_x$-CNF #50 and the STEM/EDS maps of manganese, carbon, and oxygen atomic profiles. It is seen that MnO$_x$-CNF #30 (Figures 4-2a and b) possesses nanoparticles in the size of $\sim 5 \text{ nm}$. The STEM/EDS maps (Figures 4-2c-e) localized around these nanoparticles reveal that more manganese and oxygen accumulate in these particles than other areas. Larger-size nanoparticles ($\sim 50 \text{ nm}$) are formed in MnO$_x$-CNF #50 (Figure 4-2f). The STEM/EDS maps (Figures 4-2g-i) show significant accumulation of Mn and O in these nanoparticles. The distribution of Mn, O, and nanoparticles match each other very well, except that the background density of O is relatively high resulting from the O content in CNF. When the Mn(OAc)$_2$ concentration increases from 30% to 50%, the size of nanoparticles increases from $5 \text{ nm}$ to $50 \text{ nm}$. These nanoparticles are either embedded in the fiber or dispersed on the fiber surface. Without any binder, MnO$_x$-CNF electrode possesses a good contact between MnO$_x$ catalysts and carbon matrix. These catalysts could become the active sites for oxygen reduction and/or oxygen evolution given good contact with electron source, Li$^+$, and O$_2$. 

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Figure 4-2. STEM/EDS analysis of (a-c) MnO_x-CNF #30 and (f-i) MnO_x-CNF #50 showing (a, b, f) STEM images, EDS maps of (c, g) Mn, (d, h) C, and (e, i) O atomic profiles.
XPS spectra of CNF, MnO$_x$-CNF #30 and #50 are present in Figure 4-3. O 1s, N 1s, and C 1s peaks were observed in wide scan showing the main composition of CNFs (Figure 4-3a). With the introduction of MnO$_x$, O 1s peak gets stronger while N 1s and C 1s get weaker. In narrow scan (Figures 4-3d and h), O 1s shows multiple peak-splitting in MnO$_x$-CNF #30 (530.20-531.29 eV) and #50 (530.16-531.23 eV), which is in accordance with Mn-O-H at 530.5-531.5 eV and slightly higher than Mn-O-Mn at 529.3-530.0 eV$^{174}$. The multiple peak-splitting of O 1s illustrates the addition of complex MnO$_x$ mixture. A typical peak-splitting of Mn 2p can be observed with an energy separation of 11.64 eV and 11.68 eV between Mn 2p$_{1/2}$ and 2p$_{3/2}$ for MnO$_x$-CNF #30 and #50, respectively (Figures 4-3e and i). To further examine the oxidation state of Mn in MnO$_x$-CNF compound, a narrow scan of Mn 3s of MnO$_x$-CNF #30 and #50 were obtained (Figures 4-3f and j). The splitting of Mn 3s peak with energy separation of 5.21 eV and 5.30 eV, respectively, occurs for MnO$_x$-CNF #30 and #50, resulting from the spin coupling of 3s electron with 3d electron during the photoelectron ejection$^{174,175}$. This energy separation has a linear relationship with the mean state of Mn in MnO$_x$, plotted in Figure 4-4$^{176}$. Thus, the oxidation state of Mn in MnO$_x$-CNF #30 and #50 could be determined to be 3.23 and 3.05, respectively, illustrating that higher concentration of MnO$_x$ precursor leads to lower oxidation state of Mn in MnO$_x$. 
Figure 4-3. XPS analysis of (a, b) CNFs, (c-f) MnO$_x$-CNF #30, and (g-j) MnO$_x$-CNF #50 showing (a, c, g) wide-scan spectra and narrow scan spectra of (b, d, h) O 1s, (e, i) Mn 2p, and (f, j) Mn 3s. Raw data are presented in solid line while the fitted data are presented in dash line.
Figure 4-4. Plot of energy separation of Mn 3s versus mean oxidation state of Mn in MnO\textsubscript{x}. Sample data (square dots) were obtained from ref\textsuperscript{175}, from which the linear relationship between $\Delta E$ and mean oxidation of Mn was fitted in dash line.

Cyclic voltametry curves of CNFs and MnO\textsubscript{x}-CNFs are shown in Figure 4-5. CNF electrode has a clear cathodic peak at 2.25 V with a shoulder at 2.45 V, but no anodic peak. MnO\textsubscript{1.6}-CNF #30 has a cathode peak at 1.85 V with an indistinct shoulder at 2.53 V, and an anodic peak at 3.28 V followed by a plateau (Figure 4-5b). MnO\textsubscript{1.5}-CNF #50 has two cathodic peaks at 2.55 V and 1.80 V and two anodic peaks at 2.80 V and 3.29 V (Figure 4-5c). The first anodic peak of MnO\textsubscript{1.5}-CNF #50, which is at a potential lower than 2.91 V (Li/Li\textsubscript{2}O\textsubscript{2}), could be ascribed to side reactions related to the oxidation of low-oxidation-state Mn\textsuperscript{3+}. Compared with the CNF electrode, the MnO\textsubscript{x}-CNF electrodes have higher anodic current and clearer peaks, demonstrating the catalytic role of MnO\textsubscript{x} in oxygen evolution reactions (OERs), while the breadth of the anodic peak indicates the multi-step nature of OERs in Li-air batteries.
Figure 4-5. Cyclic Voltammetry profiles of (a) CNF, (b) MnO$_{1.6}$-CNF #30, and (c) MnO$_{1.5}$-CNF #50. The cyclic voltammetry studies were conducted with a scanning rate of 0.1 mV/s from 1.5 V to 4.5 V (vs. Li/Li$^+$).

The electrochemical performance of the CNF mat is shown in Figure 4-6. In the first cycle, as shown in Figure 4-6a, the CNF electrode starts to discharge at 2.5 V and charge at 3.9 V with a charge-discharge overpotential of 1.4 V. In the fifth cycle, the overpotential increases to 1.9 V. Discharge capacity increases in the second cycle to above 2000 mAh/g and starts to decrease thereafter, as shown in Figure 4-6b. The capacity increase in the second cycle could result from the limited penetration of liquid electrolyte into the electrode and
limited dissolving and diffusing of oxygen in the electrolyte. The charge capacity drops gradually to less than 200 mAh/g in 8th cycle. The low capacity retention in each cycle indicates that certain amount of oxygen reduction products are not oxidized during charge and accumulate in the pores of electrodes, which decreases the capacity and increases the polarization.

Figures 4-7a and b show the charge-discharge curves and cycling performance of the MnO1.6-CNF #30 electrode. The discharge starts at 2.5 V while the charge starts at 4 V. Similar to the CNF electrode, MnO1.6-CNF #30 shows an increase in capacity in the first three cycles due to the same reason related to the limited diffusion of liquid electrolyte and especially oxygen. Compared with the CNF electrode, MnO1.6-CNF #30 shows higher charge and discharge capacities and slower capacity fading, indicating the catalytic role of manganese oxide. Figures 5-8c and d show the electrochemical performance of the MnO1.5-CNF #50 electrode. The first discharge starts at 2.6 V, which is slightly higher than that of MnO1.6-CNF #30. The first charge curve starts at 3.7 V and has a clear three-stage (slope-platform-slope) shape, which is in accordance with Lu and Yang’s work177. The over potential is around 1.4 V, which is similar to those of CNF and the MnO1.6-CNF #30 electrodes. The charge capacity of MnO1.5-CNF #50 keeps stable in eight cycles at 402 mAh/g, compared with 180 mAh/g of the CNF electrode or 280 mAh/g of the MnO1.6-CNF #30 electrode. Both the MnO1.6-CNF #30 and MnO1.5-CNFs #50 show the catalytic role of manganese oxide when comparing their capacities at the 8th cycle with that of the CNF electrode. Typically, the mean oxidation state of Mn in MnO_x-CNF (1 ≤ x ≤ 2) is proportional to its catalytic ability178. The higher capacity of MnO_x-CNF is mainly resulted from the high MnO_x content.
However, the size of the catalyst particles is also important. When the size of the nanoparticles increased from 5 nm to 50 nm, the capacity increased. The reason for this increase could be that larger catalyst particles have better chances to be exposed outside of the CNF and be contacted with the electrolyte and oxygen. As shown in the STEM images, the nanoparticles could be exposed to the surface when their size increased to 1/3 or 1/4 of the fiber diameter. Therefore, the results illustrated that the higher MnO$_x$ catalyst content and more exposed manganese oxide created more active site for the oxygen reduction and oxygen evolution reactions thus increased the capacity.

**Figure 4-6.** (a) Galvanic charge-discharging curves, and (b) cycling performance of the CNF electrode.
Figure 4-7. Galvanic discharge and charge curves and cycling performance of (a, b) MnO_{1.6}-CNF #30 and (c, d) MnO_{1.5}-CNF #50 electrodes.

4.5 Summary

MnO_{x}-CNF nanocomposites were successfully fabricated and applied in Li-air batteries through electrospinning and heat treatment. With different Mn salt concentration in precursors, synthesized MnO_{x}-CNF nanocomposites had different morphology of MnO_{x}. Mean oxidation states of Mn in MnO_{x}-CNF composites prepared from 30% and 50% precursors were determined to be 3.23 and 3.05, respectively. Compared with CNF electrode,
MnO$_x$-CNF showed larger charge capacity and higher cumbic efficiency in eight cycles, indicates the catalytic role of MnO$_x$ in oxygen evolution reactions. It was hence demonstrated that as a binder-free and free-standing catalyst/supporting carbon mat electrode, the MnO$_x$-CNF nanocomposites offered a promising material electrode candidate for Li-air cathodes.
5 MnO₂/CNF COMPOSITE AS LITHIUM-AIR CATHODE VIA ELECTROSPINNING AND ANODIC ELECTRODEPOSITION

5.1 Abstract

Different MnO₂/CNF electrodes with MnO₂ nanofibers anchored on the CNF surface or MnO₂ nanoparticles loaded on the CNF surface were obtained through low-current and high-current electrodeposition (LCD and HCD), respectively. The morphology of CNF and deposited MnO₂/CNF was evaluated by SEM. Chemical composition and oxidation state of Mn in MnO₂/CNF was analyzed by STEM/EDS and XPS. Through electrochemical analysis, both MnO₂/CNF electrodes possessed much higher discharge capacity, better reversibility, and more cycling stability than regular CNF electrode. Compared with the nanoparticle/nanofiber structured HCD-MnO₂/CNF composite, the fiber-anchored-on-fiber structured LCD-MnO₂/CNF composite showed even better electrochemical performance. This illustrated the importance of catalyst morphology for Li-air batteries. This binder-free fiber-anchored-on-fiber structured MnO₂/CNF electrode is a promising candidate for catalyst/carbon-matrix lithium-air cathode.

5.2 Background

Growing demand for mobile energy is spurring the search for high-performance energy storage systems. Pressure of reducing CO₂ emissions pushes the switch from fossil fuels to renewable energy, such as sunlight, wind, rain, tides, waves and geothermal heat, or nuclear as energy sources, following which electrical vehicles (EVs) are being developed and commercialized to replace combust engine vehicles. The current choice for power supply in EVs, Li-ion batteries with two intercalation electrodes (e.g., C₆/LiMO₂, where “M” refers to
Ni, Mn or Co), are far from ideal in terms of gravimetric energy density (100-200 Wh/kg in cell level) or volumetric energy density (250-450 Wh/L), cost, or safety\textsuperscript{6,69}. Surpassing the intercalation chemistry technology, Li-air batteries could reach a gravimetric energy density of 1000 Wh/kg, which is 5-10 times higher than current Li-ion batteries.

This intercalation chemistry nature in Li-air batteries requires the engineering of electrode microstructure to offer rooms for the discharge products (Li$_2$O or Li$_2$O$_2$) because neither Li$_2$O nor Li$_2$O$_2$ is soluble in the currently used electrolytes. The mostly-used porous carbon electrodes suffer from the pore-clogging and passivation by these insoluble and insulating lithium oxides\textsuperscript{113}. This results in hindered charge transfer on the surface of cathode and poor oxygen diffusion rate, which is vitally important in both discharge (oxygen reduction) and charge process (oxygen evolution). At the same time, the oxygen feeding of this breathing battery comes from the environment, while it will lead to the well-known three-phase boundary in cathode\textsuperscript{90,100}. Thus, to build a successful Li-air battery, a functional three-phase gas-diffusion-electrode is the first essential step.

Another obstacle facing the development of high-performance Li-air batteries is the hysteresis phenomenon in charge and discharge. The high charging voltage of oxygen reduction products leads to the oxidative decomposition of organic electrolytes, safety issues and battery failure. Catalysts are often employed to reduce the polarization and improve the reversibility and cycling life of Li-air batteries. So far, manganese dioxide and noble metal are the most studied catalysts\textsuperscript{6,103,118,119,137,179,180}. Noble metals have been used widely in fuel cells for oxygen reduction reactions as reviewed in the first chapter. However, the high cost
of noble metal prevents their practical use in large scale applications. In contrast, manganese oxides attract more attention due to their high catalytic efficiency, abundance and affordability.

To make a catalyst/porous carbon composite electrode, a binder, e.g., polyvinylidene difluoride (PVDF), is often used and its content is typically higher than 10% and sometimes higher than 30 wt%\textsuperscript{104,105,108}, in order to maintain the integrity of the electrode. The addition of insulating polymer binder lowers the conductivity of the electrode, worsens the clogging and passivation problems, lowers the kinetics, and decreases the energy density of the whole cell. Moreover, it has been found that PVDF is dehydrofluorinated by superoxide $\text{O}_2^-$ anions and reacts with catalysts, thus defunctionalizes the catalysts and breaks the integrity of the electrode\textsuperscript{131}.

Hence, to build a binder-free gas-diffusion catalyst/carbon electrode is of great interest. One-dimentional carbon nanofibers (CNFs) are believed to be a promising structure for use as supporting electrodes in Li-air batteries\textsuperscript{109}. CNFs have high surface area and good conductivity, which are important requirements for Li-air cathode to overcome the multi-phase problem. At the same time, CNFs are cheap compared with carbon nanotubes. In the previous chapter, manganese oxide-embeded CNFs was constructed. Theoretically, it could be much more efficiency if all the manganese oxide particles are loaded on the surface so that they can have good contact with oxygen and electrolyte. In the work discussed in this paper, manganese oxides particles were loaded onto the surface of carbon fibers through electrodeposition. By combing electrospinning and electrodeposition, nano-catalyst/carbon
nanofiber composite membranes were designed and evaluated as air cathode for Li-air batteries.

5.3 Experimental

Electrospinning and Heat treatment

An electrospinning solution of 8 wt% polyacrylonitrile (PAN) in dimethylformamide (DMF) was prepared and then stirred at 60 °C for 24 hours. Electrospinning was conducted under 15 kV with a feeding rate of 0.7 ml/h and a needle-to-collector-distance of 15 cm. The electrospun PAN mats were heated in air to 280 °C with a heating rate of 5 °C/min and kept at that temperature for 5.5 hour. The air stabilized mats were heated to 700 °C in argon with a heating rate of 2 °C/min and kept for 2 hour for carbonization. After the carbonization process, CNF mats were obtained.

Electrodeposition

CNF mats were washed several times in deionized water before the electrodeposition of MnO₂. A solution of 0.1 M manganese(II) acetate (Sigma Aldrich, 98%) and 0.1 M sodium sulfate (Sigma Aldrich≥99.0%) was used for electrodeposition. Platinum wires (Alfa Aesar, 99.95%, 0.5 mm in diam.) were used as the counter electrode while the Calomel as the reference electrode. The anodic current was applied with the current density of ~0.25 mA/cm² for low-current-deposition (LCD) and 0.5 mA/cm² for high-current-deposition (HCD). The electrodeposition time was kept as 10 minutes. During the deposition, the solution was kept stirring at 200 r/minutes. After electrodeposition, the mats were washed with deionized water and dried in air for 10 h at 110 °C for further use. The electrodeposited
samples were labeled as LCD-MnO$_2$/CNFs and HCD-MnO$_2$/CNFs respectively, while CNF was the control sample.

**Characterizations**

The morphology of CNFs and electrodeposited MnO$_2$/CNFs were examined by FE-SEM (Zeiss Merlin). FEI Titan probe aberration-corrected scanning transmission electron microscopy (STEM) with monochromator was employed to take the images of samples on carbon grids operated at 200 keV. Samples were briefly sonicated in methanol for TEM sample preparation. Energy Dispersive Spectrometry (EDS) in STEM mode was employed for distribution of MnO$_2$ catalysts. The distribution of Mn, C, N, and O was obtained by identification of their peaks observed in the EDS spectrum during three-minute mapping. X-ray photoelectron spectra were obtained by irradiating the samples with a beam of Mg K$_\alpha$ radiation (1500 eV; 400 W) in PHOIBOS 150 analyzer (<1 eV resolution).

**Cell Assembly and Electrochemical Analysis**

Swagelok Li-air cells were prepared consisting of CNF or MnO$_2$/CNF cathodes, Li ribbon anode, glass fiber (Whatman, GF/D) separator, electrolyte of 1M Li bis(trifluoromethanesulfonyl)imide (LITFSI) in tetra(ethylene)glycoldimethyl ether (TEGDME), and Al-mesh (Dexmet Corporation, 2Al 4-050) as the current collector. Assembling was done in an argon-filled glove box. Cells were purged 10 times with pure oxygen before testing to remove the argon. During testing, the pressure of supplying oxygen was kept at around 7 atm.
Cycling voltammetry (CV) measurements were performed on a Gamry Reference 600 potentialstat at the scan rate of 0.1 mV/s from 1.5 V to 4.5 V with Li/Li\(^+\) as the reference and counter electrode. Galvanostatic charge-discharge experiments were carried out using Arbin 2000 at different current densities from 2 V to 4.4 V.

5.4 Results and Discussion

As shown in Figure 5-1a, in the process of low-current-deposition (LCD), the oxidization of Mn\(^{2+}\) started at \(~0.2\) V (vs. SCE) and reached a stead state above 0.3 V, which was in consistence with other researchers’ work\(^{181,182,184}\). High-current-deposition (HCD) presented the similar potential change.

Figure 5-1. Plot of potential versus time in electrodeposition of (a) LCD and (b) HCD MnO\(_2\)/CNFs.

Figure 5-2 shows the SEM images of electrospun PAN nanofibers, CNFs, and electrodeposited MnO\(_2\)/CNFs. As shown in Figure 5-2a, electronspun PAN nanofibers have
smooth surface and homogenous distribution of fiber diameters (~ 250 nm) and no beads observed. The formed free-standing CNF mat (Figure 5-2b) possesses macropores in size of microns between fibers, facilitating the diffusion of O₂ and Li⁺ when wetted by the electrolyte. LCD-MnO₂ with a fibrous morphology (diameter ~10 nm) uniformly winds on larger CNFs and form a unique fiber-anchored-on-fiber structure (Figures 5-2c and d). In contrast, Figures 5-2e and f present a homogenous particulate morphology of HCD-MnO₂ on the CNF surface. The remarkable difference in the morphology of LCD- and HCD-MnO₂ illustrates that the growth of MnO₂ crystal is sensitive to the current used during anodic electrodeposition. In both LCD- and HCD-MnO₂/CNFs, catalysts are loaded on the CNF without use of any binder, enhancing the contact of carbon, oxygen, Li⁺, and catalyst and producing active sites for the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER).
Figure 5-2. SEM images of (a) electrospun PAN nanofibers, (b) CNFs, (c, d) LCD-MnOx/CNFs, and (e, f) HCD-MnO$_2$/CNFs.

To demonstrate the nanofibers and particles formed on CNF surfaces are MnO$_2$, scanning transmission electron microscopy (STEM) coupled with energy dispersive X-ray spectroscopy (EDS) was employed. Figures 6-3a and e are the typical STEM images of
LCD-MnO$_2$/CNF with fiber-anchored-on-fiber structure and HCD-MnO$_2$/CNF with particle-fiber structure respectively. Through the analysis of collected EDS spectra of these samples, maps of Mn, C, and O were obtained, and are presented in Figures 5-3b-h. Above the carbon background in large CNF area, Mn has a much more dense distribution within the loaded nanofibers or particles than the other area (Figure 5-3b). Consistently, oxygen distribution in the loaded nanofibers or particles areas is more dense than in the other CNF areas, indicating that the formed nanofibers and nanoparticles anchored on CNF are manganese oxides (Figures 5-3d and h).
Figure 5-3. STEM/EDS analysis of (a-d) LCD- and (e-h) HCD-MnO$_2$/CNFs showing (a, e) STEM images, and EDS maps of (b, f) Mn, (c, g) C, and (d, h) O atomic profiles.
To analyze the oxidative state of manganese in its oxides, X-ray photoelectron spectroscopy (XPS) spectra of CNFs, LCD- and HCD-MnO₂/CNFs were obtained, shown in Figure 6-4. Gaussian function was used for non-linear least-square curve fitting procedure. When comparing the wide survey of CNFs with LCD- or HCD-MnO₂/CNFs, the ratio of O 1s and C 1s peaks increases remarkably due to the introduction of O during electrodeposition. The O 1s spectra of LCD-MnO₂/CNFs could be deconvoluted into two peaks at 531.33 eV and 530.06 eV (Figure 5-4d), respectively, while the O 1s spectrum of HCD-MnO₂/CNF has the similar peak splitting (531.60 eV and 530.01 eV) (Figure 5-4h). The lower-energy peaks of LCD- and HCD-MnO₂/CNFs are in agreement with Mn-O-Mn bond at 529.3-530.0 eV¹⁷⁴, while the higher energy peaks could be attributed to the O content in CNFs. Mn 2p₁/₂ and 2p₃/₂ peaks are observed at 653.99 eV and 642.44 eV for LCD-MnO₂/CNFs (Figure 5-4e) and 654.00 and 642.48 eV for HCD-MnO₂/CNF (Figure 5-4i), respectively. The binding energy separations of Mn 2p is the same for both samples, indicating that the current density used in electrodeposition is not affecting the oxidation state of Mn. Mn 3s peak splitting was obtained with a binding energy separation of 4.7 eV for both LCD- and HCD-MnO₂/CNFs, which is related to the oxidation state of Mn due to the spin coupling of the 3s e⁻ with the 3d e⁻ during the photoelectron ejection¹⁷⁴. This value is in agreement with MnO₂, and is lower than 5.41 eV, 5.50 eV, or 5.79 eV for Mn₂O₃, Mn₃O₄, and MnO, respectively¹⁷⁴.
Figure 5-4. XPS analysis of (a, b) CNFs, (c-f) LCD-MnO$_2$/CNF #30, and (g-j) HCD-MnO$_2$/CNF #50 showing (a, c, g) wide-scan spectra and narrow-scan spectra of (b, d, h) O 1s, (e, i) Mn 2p, and (f, j) Mn 3s. Raw data are presented in solid line while the fitted data are presented in dash line.
Figure 5-5 shows the cyclic voltammetry of the CNF, LCD-MnO₂/CNF, and HCD-MnO₂/CNF electrodes at a scanning rate of 0.1 mV/s with Li/Li⁺ as the reference and counter electrode. As shown in Figure 5-5a, a cathodic peak in the first cycle for the CNF electrode appeared at 2.25V and increased slightly at the second cycle, which was in accordance with the cycling performance (Figure 5-7b) and indicated that a better equilibrium was reached in the second cycle. No anodic peak was observed. As shown in Figure 6-5b, a cathodic peak appeared at ~2 V in the first cycle for the LCD-MnO₂/CNF electrode showing the oxygen reduction reaction. The position of this cathodic peak shifted to higher potential in the second cycle indicating that a better equilibrium was reached. In addition, although no anodic peak was observed, an anodic bump appeared which showed an improved kinetics for oxidizing the Li₂O₂. Compared with LCD-MnO₂/CNFs, the HCD-MnO₂/CNF electrode had a similar reduction curve (Figure 5-7c). However, no anodic peak or bump was observed indicating the improved catalytic role of LCD-MnO₂/CNFs with the fiber-anchored-on-fiber structure, as compared to that of the HCD-MnO₂/CNFs with the particle/fiber structure.
Figure 5-5. CV curves of (a) CNF, (b) LCD-MnO$_2$/CNF, and (c) HCD-MnO$_2$/CNF electrodes.

Figure 5-6 shows the electrochemical performance of a CNF electrode. In the first cycle, as shown in Figure 5-6a, the CNF electrode started to discharge at 2.5 V and charge at 3.9 V with a charge-discharge overpotential of 1.4 V. In the fifth cycle, the overpotential increased to 1.9 V. Discharge capacity increased in the second cycle to above 2000 mAh/g and started to decrease thereafter, as shown in Figure 5-6b. This capacity increase could be attributed to comparably small penetration of liquid electrolyte into the electrode and limited dissolving and diffusing of oxygen in the electrolyte. The charge capacity dropped gradually
to less than 200 mAh/g in the 8th cycle. The low columbic efficiency during cycling indicated that a certain amount of oxygen reduction products were not oxidized during charge and accumulated in the pores of electrodes with cycling, which would decrease the capacity and increase the polarization.

The charge-discharge curves of LCD and HCD MnO$_2$/CNFs are shown in Figure 5-7. The first discharge capacity of the LCD-MnO$_2$/CNF electrode was around 5000 mAh/g, while it increased to around 8000 mAh/g in the second discharge. The increase in capacity could be attributed to the penetrating of liquid electrolyte into the electrode and the dissolving and diffusing of oxygen into the electrolyte. The charge capacity for the first and second cycles was around 3000 mAh/g and faded gradually in the following cycles. The charge capacity at the 6th cycle was 879 mAh/g while the discharge capacity was 882 mAh/g. Compared with the CNF electrode, the LCD-MnO$_2$/CNF electrode showed better reversibility and cycling ability, which demonstrated the catalytic role of deposited MnO$_2$ nanofibers. The HCD-MnO$_2$/CNF electrode possessed a similar discharge capacity in the first cycle at around 5000 mAh/g, then faded gradually to 458 mAh/g at the 6th cycle, while the charge capacity in the 6th cycle was 532 mAh/g. Comparing with HCD-MnO$_2$/CNF, the LCD-MnO$_2$/CNF electrode had higher discharge and charge capacities and better cycling properties. This further demonstrated that the fiber-anchored-on-fiber structure showed better catalytic role than the particle/fiber structure.
Figure 5-6. (a) Galvanic charge-discharge curves; (b) cycling performance of CNF electrode.
Figure 5-7. Galvanic electrochemical performance and cycling performance of (a, b) LCD- and (c, d) HCD- MnO₂/CNF electrodes.

5.5 Summary

Different MnO₂/CNF electrodes with MnO₂ nanofibers anchored on the CNF surface or MnO₂ nanoparticles loaded on the CNF surface were obtained through low-current and high-current electrodeposition, respectively. Through electrochemical analysis, both MnO₂/CNF electrodes possessed much higher discharge capacity, better reversibility, and more cycling stability than regular CNF electrode. Compared with the nanoparticle/nanofiber structured HCD-MnO₂/CNF composite, the fiber-anchored-on-fiber structured LCD-MnO₂/CNF composite showed even better electrochemical performance. This illustrated that
the importance of catalyst morphology for Li-air batteries. Although high-current deposited MnO$_2$/CNF electrodes have higher content of MnO$_2$, low-current deposited MnO$_2$/CNF electrodes have fibrous structure facilitating the contact between catalyst, carbon, and electrolyte. This binder-free fiber-anchored-on-fiber structured MnO$_2$/CNF electrode is a promising candidate for catalyst/carbon-matrix lithium air cathode.
6 CONCLUSIONS

PCNF electrodes were fabricated and offered a feasible platform to evaluate the paradox effect of increasing surface area and decreasing electrode conductivity on the electrochemical performance of Li-air batteries. With increase in surface area, thinner Li$_2$O$_2$ deposition on electrode surface could be realized in constant discharge capacity, leading to better electrochemical properties and better reversibility. However, this was accomplished with the sacrifice of electronic conductivity which would worsen the kinetics and decrease the capacity especially at high current density. Therefore, in pursuing better electrode structure for LABs, it is not always the larger SSA the better. Tuning the balance between conductivity and surface area based on various applications is of great importance to increase the performance efficiently in the Li-air batteries.

MnO$_x$-CNF nanocomposites were successfully fabricated and applied for Li-air battery through electrospinning and heat treatment. With different Mn salt concentration increasing from 30% to 50% in precursors, synthesized MnO$_x$-CNF nanocomposites had 10-times increase in MnO$_x$ size. Mean oxidation states of Mn in MnO$_x$-CNF composites prepared from 30% and 50% precursors were determined to be 3.23 and 3.05, respectively. Compared with CNF electrode, MnO$_x$-CNF showed larger charge capacity and higher columbic efficiency in eight cycles, indicating the catalytic role of MnO$_x$ in oxygen revolution reactions. It was hence demonstrated that as a binder-free and free-standing catalyst/supporting carbon mat electrode, the MnO$_x$-CNF nanocomposites offered a promising material electrode candidate for Li-air cathodes.
Different MnO₂/CNF electrodes with MnO₂ nanofibers anchored on the CNF surface or MnO₂ nanoparticles loaded on the CNF surface were obtained through low-current and high-current electrodepositions, respectively. Through electrochemical analysis, both MnO₂/CNF electrodes possessed much higher discharge capacity, better reversibility, and more cycling stability than regular CNF electrode. Compared with the nanoparticle/nanofiber structured HCD-MnO₂/CNF composite, the fiber-anchored-on-fiber structured LCD-MnO₂/CNF composite showed even better electrochemical performance. This illustrated the importance of catalyst morphology for Li-air batteries, and demonstrated that the binder-free fiber-anchored-on-fiber structured MnO₂/CNF electrode is a promising candidate for catalyst/carbon-matrix lithium air cathode.

In conclusion, CNFs by electrospinning offer a great platform for air cathode resulting from the morphology, low-cost, and easy-molding. Catalyst could be incorporated or loaded into the CNF electrode conveniently. Loading catalysts on the surface is much more efficient than incorporating the catalyst in the fiber that the sufficient contact between reactants and catalyst could facilitate the ORR and OER. The morphology of the loaded MnO₂ has significant effect on its catalytic performance. Although high-current deposited MnO₂/CNF electrodes have higher content of MnO₂, low-current deposited MnO₂/CNF electrodes have fibrous structure facilitating the contact between catalyst, carbon, and electrolyte. The performance of Li-air batteries is highly sensitive to the surface treatment of the electrodes. The balance between high-surface area and high conductivity is essential to the electrochemical performance especially in high-rate condition.
7 RECOMMENDED FUTURE WORK

The recommended future work includes but is not limited to:

(1) Evaluating and analyzing the effect of carbonization temperature on the manganese oxidation states in MnOx/CNF nanocomposites and their catalytic performance in Li-air batteries.

MnO₂ materials with different crystalline structures have been evaluated, showing α-MnO₂ with the best catalytic performance among electrolytic MnO₂, α-MnO₂, β-MnO₂, and γ-MnO₂\(^\text{119}\). In Chapter 6, the effect of MnO₂ morphology on the catalytic performance was demonstrated that the fibrous fiber-anchor-on-fiber electrode possessed better electrochemical performance than the particle-on-fiber electrode. The relationship between the oxidation state of Mn and its catalytic performance in Li-air cathode is not clear yet. In Chapter 5, the prepared MnOₓ/CNFs showed different catalytic performance with different manganese oxidation states and concentrations. It is of great interest to control the concentration of manganese acetate in the precursors as the same and vary the carbonization temperature to obtain MnOₓ/CNF in different Mn oxidation states and evaluate their roles in catalyzing oxygen reduction and oxygen evolution reactions in Li-air batteries.

The proposed experimental methods are similar to the method used in Chapter 5. Carbonization temperature can be varied as 700°C, 800°C, and 900°C. The oxidation state of Mn can be determined from its XPS spectra. The crystalline structure of MnOₓ and carbon can be characterized by X-ray diffraction measurements and Raman spectra. CV and electrochemical performance can be collected and analyzed. It is expected that the role of Mn
oxidation state on the catalytic performance can be illustrated clearly. It will be helpful to understand the catalyzing mechanism of MnOx in the oxygen reduction and oxygen evolution reactions in Li-air batteries.

(2) Evaluating the effect of ALD-Al2O3 coating on the electrodeposited MnO2/CNFs.

Lithium-air cathodes suffer from the problems of high polarization, low energy efficiency, and side reactions with electrolyte. Surface coating with Al2O3 by atomic layer deposition (ALD) could prevent these side reactions especially on the carbon defects sites102,185. Moreover, the ALD-Al2O3 coated Pd/C composite electrode showed a small charge overpotential as ~0.2 V during control discharge-charge cycling102.

In the proposed work, MnO2/CNFs can be obtained by electrospinning and electrodeposition, similar to the methods used in Chapter 6. The current density can be controlled at a low level to produce the fiber-anchor-on-fiber MnO2/CNF. Then Al2O3 can be deposited on the MnO2/CNF membrane by 1, 3, and 10 cycles, respectively through ALD. The obtained ALD-Al2O3 coated MnO2/CNF can be used directly as the air cathode for further electrochemical performance analysis. It is anticipated that this ALD-Al2O3/MnO2/CNF electrode with proper thickness of Al2O3 will have the advantage of low charge overpotential, high stability and better cycling performance.
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