Investigation of Discharge Products in Metal Oxygen Batteries

DISSERTATION

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Abstract

Metal air (oxygen) batteries have recently attracted extensive research attentions due to their high theoretical energy density. Nevertheless, the understanding of the cell chemistries of metal oxygen batteries such as the formation mechanism, the role of each component such as the anode, cathode, and the electrolyte is far from satisfactory.

In this dissertation, I first review the discharge products in lithium oxygen batteries, where Li$_2$O$_2$ is regarded as the major product along with other by-products such as Li$_2$CO$_3$, LiOH, and lithium polycarbonates. The complexity of the discharge products indicate the complicated cell environment of lithium oxygen batteries, ascribed to the instability of the porous carbon cathode and the electrolytes. The issues that need to be considered when changing oxygen to air are also discussed in the background. Besides lithium oxygen batteries, sodium oxygen batteries also suffer low capacity and low cycle life, and the discharge products are different from group to group. In chapter two, I investigate the instability of NaO$_2$ which is regarded as one of the common products in sodium oxygen batteries, discovering that the resting of NaO$_2$ would not generate Na$_2$O$_2$·2H$_2$O but react with the carbon cathode to form Na$_2$CO$_3$. Then we use two different cell setups to control the formation of the two different products, suggesting the importance of cell design and the control of air atmosphere. In-situ XRD measurement was performed to reveal the structural evolution of the peroxide based product. This study emphasizes the significance
of the cell configuration and the contamination effect from air, and sheds light on the future
design of sodium oxygen batteries.

Compared to sodium peroxide based batteries, sodium superoxide based batteries
have much lower charging overpotentials which may offer longer cyclability and higher
energy efficiency without much electrolyte decomposition at high voltage. In chapter 3, I
discover that sodium dendrite formation is one of the major reasons for the short circuit of
sodium oxygen batteries within few cycles. By employing a sodium ion exchange Nafion
membrane in separators, largely improved cyclability of sodium oxygen batteries was
achieved by suppressing the penetration of dendrites formed during the charging process.
With Nafion membrane’s physical preventing effect, the cycle life of sodium oxygen
batteries has been largely increased. In addition, the components of SEI layer on the sodium
anode and by-product in the air electrode were identified. These results highlight the
significance of solving dendrite penetration and blocking oxygen crossover in sodium
oxygen batteries and paved the way for further improving the performance and cyclability
of batteries.

In chapter 4, the discharge product of lithium oxygen batteries with mixed salt
electrolyte is investigated. We observe that with the addition of sodium ions in the
electrolyte, the electrochemical performance of Li-O₂ cells show a remarkable decrease of
charge overpotential from over 4 V to 3.3 V and the morphology of the discharge product
has a drastic change. The product is identified to be LiOH, which could be reversibly
charged during cycles. Interestingly, no sodium-based products on the carbon surface are
detected, indicating that sodium ions serves as a catalyst facilitating the formation and
removal of LiOH. Hence, selecting an appropriate additive could improve the cell performance to achieve high efficient and high durable Li-O$_2$ cells.

To further investigate the reaction mechanism in metal air batteries, a differential electrochemical mass spectrometer instrument is built. In chapter 5, I briefly summarize the setup of the gas line of metal air batteries based on a purchased mass spectrometer. The calibration of volumes for each part of the gas line and the mass spectrometer are introduced. It was used in investigating the reaction mechanisms in lithium oxygen batteries and sodium oxygen batteries.
Dedication

To my loving husband, Rongyue Wang and my parents, Guizhi Li and Siwei Bi.
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Chapter 1: Introduction of Metal Oxygen Batteries

1.1 Introduction

Nowadays, nation’s energy largely relies on non-renewable resources such as oil and natural gas, which not only raise the issue of air pollution but also generate large amount of carbon dioxide (CO$_2$).$^{1-2}$ In order to cut the harmful emission gases, renewable sources such as the wind, solar and water power that are low-cost and environmentally benign, have been employed as the energy supplies instead of unsustainable sources. Given the fact that those renewable sources are largely limited by weather, sunlight, and geography, they can be stored in batteries and used without time and space restrictions.$^3$

Secondary batteries with high volumetric and gravimetric energy density enable the storage of renewable energies without dissipation. Current commercialized battery technologies in the world are lithium-ion (Li-ion), lead acid, sodium-sulfur (Na-S), nickel-metal hydride, flow batteries, etc. Among them, lithium ion batteries are the dominant technology in the battery market, but the high cost and low energy density are major impediments for their applications in electric vehicles (EVs) or large-scale energy storage stations.$^{4-5}$ Metal air batteries have the potential to offer up to 10 times the energy density of lithium-ion batteries. The high energy density originates from the utilization of oxygen and it could be directly obtained from the air without reactants storage at the air electrode. Lithium oxygen (Li-O$_2$) batteries could reach a theoretical energy density of 3500 Wh·kg$^{-1}$.
1, on the basis of the Li₂O₂ formation; while sodium oxygen (Na-O₂) batteries have a theoretical energy density of 1100 Wh·kg⁻¹, on the basis of the formation of NaO₂.

This chapter mainly focuses on introducing discharge products of aprotic Li-O₂ and Na-O₂ batteries. In Li-O₂ batteries, the formation mechanism and the influence of properties of the discharge product on the electrochemical behaviors will be introduced. In addition, the challenges and the problems in aprotic Li-O₂ batteries will be discussed, which are the major obstacles and impede the development of Li-O₂ batteries. Furthermore, the current status of Li-air batteries will be included as well as the effects of the contaminants such as carbon dioxide (CO₂) and water (H₂O) in the air atmosphere based on the writing of a book chapter. Although Li-O₂ and Na-O₂ share similar electrochemical environment, the discharge products are different, controlled by both thermodynamics and kinetics of the cell reactions. For Na-O₂ batteries, the debate on the discharge products and the major obstacle in developing long life Na-O₂ batteries will be introduced in the latter part of the chapter.

1.2 Lithium oxygen batteries

A typical aprotic Li-O₂ battery consists of a lithium metal, a separator soaked with aprotic solvent electrolyte, and a porous carbon cathode. During discharge, lithium is oxidized at anode to form lithium ions, while the oxygen is reduced at cathode. The reduced oxygen species (superoxide or peroxide) meet lithium ions at the air electrode to form the product, lithium peroxide (Li₂O₂). Since Li₂O₂ is insoluble in the electrolyte, it deposits on the surface of the porous carbon substrate. During charge, Li₂O₂ decomposes to oxygen
and lithium ions, where the latter transport to the anode and are further reduced at the metal surface. The ideal reactions in an aprotic Li-O$_2$ battery are shown as follows.

Discharge: Anode: $2\text{Li} \rightarrow 2\text{Li}^+ + 2\text{e}^-$ 
Cathode: $\text{O}_2 + 2\text{e}^- + 2\text{Li}^+ \rightarrow \text{Li}_2\text{O}_2$ (1.1)

Charge: Anode: $2\text{Li}^+ + 2\text{e}^- \rightarrow 2\text{Li}$ (1.3)
Cathode: $\text{Li}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{e}^- + 2\text{Li}^+$ (1.4)

Overall reaction: $2\text{Li} + \text{O}_2 \leftrightarrow \text{Li}_2\text{O}_2$ $E^0 = 2.96$ V (vs. Li$^+/\text{Li}$) (1.5)

Figure 1.1 Discharge/charge profile of an aprotic Li-O$_2$ cell with a cut-off capacity of 1000 mAh·g$^{-1}$ based on a pure Li metal anode and super P carbon cathode. The electrolyte is 1 M lithium trifluoromethanesulfonate (LiCF$_3$SO$_3$) in tetraethylene glycol dimethyl ether (TEGDME) and the applied current is 100 mA·g$^{-1}$. Modified from ref 9. 2013 Nature Publishing Group.
The production of Li\textsubscript{2}O\textsubscript{2} determines the cell chemistry of the batteries not only for thermodynamics but also kinetics. The equilibrium potential for the overall reaction is 2.96 V vs. Li\textsuperscript{+}/Li, originated from the standard free energy ($\Delta_rG = -570.18$ kJ·mol\textsuperscript{-1})\textsuperscript{6} of Equation 1.5. The theoretical energy density of aprotic Li-O\textsubscript{2} batteries is calculated to be 3500 Wh·kg\textsuperscript{-1} based on the mass of Li\textsubscript{2}O\textsubscript{2}.\textsuperscript{7-8} Figure 1.1 shows a typical discharge/charge profile of a Li-O\textsubscript{2} cell with a super P carbon substrate at the air electrode.\textsuperscript{9} The electrolyte is 1 M lithium trifluoromethanesulfonate (LiCF\textsubscript{3}SO\textsubscript{3}) in tetraethylene glycol dimethyl ether (TEGDME) and the applied current is 100 mA·g\textsuperscript{-1}. With a cut-off capacity of 1000 mAh·g\textsuperscript{-1}, the discharge voltage in the Li-O\textsubscript{2} cell is around 2.5 V, corresponding to an overpotential of ~0.46 V; while the charging voltage is around 4.3 V, leading to a high overpotential of over 1.3 V. As a rechargeable product in an electrochemical cell, Li\textsubscript{2}O\textsubscript{2} should have a decent electrical conductivity to guarantee the current flow. However, Li\textsubscript{2}O\textsubscript{2} is proved to be an insulator, which passivates the cathode surface in oxygen reduction reaction (ORR) and generates high polarization during its decomposition in oxygen evolution reaction (OER). Thus, understanding the nature of Li\textsubscript{2}O\textsubscript{2} is critical to investigate the cell chemistry of aprotic Li-O\textsubscript{2} batteries.

1.2.1 Structure and morphology of Li\textsubscript{2}O\textsubscript{2}
Figure 1.2 Structure and charge transport pathways structure of Li$_2$O$_2$. (a) Crystalline structure of Li$_2$O$_2$.\textsuperscript{10} (b) The experimental x-ray diffraction (XRD) of commercial Li$_2$O$_2$ (Sigma-Aldrich) powders and the simulated XRD of the Föppl structure based on a wavelength of Cu Ka, 1.5406 nm.\textsuperscript{11} (c) Different charge transport pathways predicted in amorphous Li$_2$O$_2$ and crystalline Li$_2$O$_2$. Reprinted from ref 23. Copyright 2014, American Chemical Society.

Two main structures of Li$_2$O$_2$ were discovered back to 1950s by Föppl\textsuperscript{12} and Féher\textsuperscript{13} but they are contradicted to each other. Recently, calculation studies from different groups confirmed the Föppl’s structure.\textsuperscript{10-11, 14} Cota et al. employed density functional theory (DFT) quantum mechanical calculations on the two structures and emphasized that the Föppl’s structure was more convincing.\textsuperscript{10} The crystalline structure of Li$_2$O$_2$ is shown in Figure 1.2a. It belongs to P63/mmc space group and the cell parameters are $a = 3.1830$ Å and $c = 7.7258$ Å with $\alpha = 1.003^\circ$. As shown in Figure 1.2a, the cell consists of alternative layers of trigonal prisms and octahedra/tetrahedra, with oxygen sites lying on the vertices of the polyhedra.\textsuperscript{15} Li$^+$ atoms occupy two different sites with one in the same layer as peroxide dimer and the other residing between peroxide layers. The arrangement of Li atoms (capital letters, labeled in Figure 1.2a) and O atoms (lower letters, labeled in Figure
1.2a) can be described as AcBcAbCbA. From phonon and electronic properties analysis, the O-O bond of peroxo ions (O$_2^{2-}$) suggest that Li$_2$O$_2$ is a molecular ionic solid in nature, and its fundamental properties (structural, electronic, vibrational and dielectric properties) depend on the coupling and decoupling of the localized O$_2^{2-}$ with the rest of Li$^+$ from surroundings.$^{11}$ Based on Föppl’s structure, the simulated XRD pattern and experimental XRD of the commercial Li$_2$O$_2$ powders are shown in Figure 1.2b. Most peaks match well for both the theoretical and experimental patterns, but commercial Li$_2$O$_2$ has a poor crystallinity and thus the experimental XRD is not sufficient to reveal the structure itself.

The electronic band structure of Li$_2$O$_2$ was predicted by theoretical calculation studies. The bulk Li$_2$O$_2$ had a band gap as large as over 4.0 eV based on G$_0$W$_0$ calculation.$^{16-18}$ The dominate charge carriers in Li$_2$O$_2$ were ascribed to lithium vacancies (the missing Li$^+$ in the lattice) and hole polarons.$^{15, 19}$ The migration of the lithium vacancies contributes to the ionic conductivity, which is calculated to be $\sim 4 \times 10^{-19}$ S·cm$^{-1}$. On the other hand, the hopping of the holes contributes to the electronic conductivity, which is calculated to be $\sim 5 \times 10^{-20}$ S·cm$^{-1}$. However, compared to a commonly used positive electrode material in Li-ion batteries, LiFePO$_4$, which has an electronic conductivity of $\sim 10^{-9}$ S·cm$^{-1}$, the conductivities of Li$_2$O$_2$ is still far from satisfactory and thus they are considered to be a major limiting factor for the performance of Li-O$_2$ batteries. Being an insulator, the charge transport through the bulk Li$_2$O$_2$ is very unlikely during the electrochemical processes.

Although theoretical calculation studies predicted that bulk Li$_2$O$_2$ had both low ionic conductivity and low electronic conductivity, the conductivities of the discharge
product in Li-O2 cells seemed much higher than expected. One possibility is that the bulk crystalline Li2O2 is not the only species that contributes to the charge transport. The understanding of the discharge mechanism and the composition of the discharge product has not been well established yet, but recent studies suggest that multiple factors could affect the band gap of Li2O2 including charge state of Li, O and O2 vacancies and grain boundaries. During the discharge process, as well as the crystalline Li2O2, amorphous Li2O2 was formed, which shared similar band gap and equilibrium electrochemical potentials to crystalline Li2O2. Amorphous Li2O2 was predicted to have much improved conductivities, illustrated in Figure 1.2c. According to the DFT calculation study from Feng et al., the ionic conductivity of amorphous Li2O2 was 2×10^{-7} S·cm^{-1}, 12 orders of magnitude larger than that of crystalline Li2O2. The electronic conductivity was calculated to be 2×10^{-16} S·cm^{-1}, which was 4 orders of magnitude higher than that of crystalline Li2O2. The ionic and electronic conductivities were also measured experimentally by AC impedance and DC polarization. From the experiments, the ionic conductivity was measured to be 7.1×10^{-8} S·cm^{-1} and the electronic conductivity was 5.0×10^{-9} S·cm^{-1}, respectively. The latter showed larger discrepancy to the theoretical value and it was probably because the structure and composition of Li2O2 were much more complicated than the theoretical study. It was proved that amorphous Li2O2 possesses higher Li^+ mobility and higher density of O2^- defects than crystalline Li2O2. Further evidence was supported by in-situ transmission electron spectroscopy (TEM). Yang’s group conducted in-situ TEM in a solid-state Li-O2 cell and applied a constant potential to decompose the pre-formed Li2O2 particle on a carbon nanotube. The result shows that Li2O2 first
decomposes at the interface between \( \text{Li}_2\text{O}_2 \) and carbon nanotube instead of the interface between \( \text{Li}_2\text{O}_2 \) and the solid electrolyte. It suggests that \( \text{Li}^+ \) moves faster than the electrons and thus electronic conductivity is a limiting factor in the OER process. Kushima et al. then used \( \text{O}_2 \) saturated liquid electrolyte to study the formation/decomposition of \( \text{Li}_2\text{O}_2 \) on a three-phase interface and obtained similar results.\(^{26}\)

**Figure 1.3** Scanning electron microscopy (SEM) images of morphology of \( \text{Li}_2\text{O}_2 \) formed in the ketjen black (KB) carbon cathodes at different discharge capacities. (a) pristine cathode, (b) 250 mAh·g\(^{-1}\), (c) 1300 mAh·g\(^{-1}\), (d) 4000 mAh·g\(^{-1}\), (e) 5200 mAh·g\(^{-1}\), (f) 7500 mAh·g\(^{-1}\). The electrolyte is 0.5 M \( \text{LiC}_2\text{F}_3\text{SO}_3 \) in diethylene glycol dimethyl ether (DEGDME). The applied current is 0.1 mA·cm\(^{-2}\). Reprinted from ref 27. Copyright 2014, American Chemical Society.

In a typical aprotic Li-O\(_2\) cell, the scanning electron microscopy (SEM) images of the morphology evolution of \( \text{Li}_2\text{O}_2 \) at discharge are shown in Figure 1.3.\(^{27}\) SEM was
performed on Li$_2$O$_2$ formed on the Ketjen Black 600JD carbon (KB carbon) electrodes at different DOD. The pristine KB carbon has a high porosity composed of particles of ~30 nm, shown in Figure 1.3a. At the early stage of discharge, small disks with a diameter of less than 50 nm were formed on the electrode surface (Figure 1.3b). With the increase of DOD, Li$_2$O$_2$ continuously grows and the morphology evolves from tiny disk-like nanoparticles (Figure 1.3b-c) to a toroidal-shaped structure (Figure 1.3d-f). Toroids appear to be the typical morphology of Li$_2$O$_2$ formed in ether-based electrolytes with or without using ORR catalysts.\textsuperscript{27-32}
Figure 1.4 Morphology and SAED of Li$_2$O$_2$. (a-b) TEM images of the particles discharged at 50 mA·g$^{-1}$ with a cut-off capacity of 1000 mAh·g$^{-1}$, and 90 mA·g$^{-1}$ with a cut-off capacity of 13,000 mAh·g$^{-1}$, respectively. (c) Schematic diagram of the structural evolution of toroidal Li$_2$O$_2$. (d) Electron diffraction of Li$_2$O$_2$ with simulated zone axis (red
and blue dots). (e) Side-view and top-view schematics of a stack of crystalline plates, which compose the disc and toroid particles. The electrolyte is 0.1 M LiClO$_4$ in dimethoxyethane (DME) in this work. Reprinted from ref 32. Copyright 2013, American Chemical Society.

Although the bulk Li$_2$O$_2$ was predicted to have a hexagonal structure, the product in Li-O$_2$ cells shows a toroidal shape which is very different from expectation. The mechanism of morphological development on Li$_2$O$_2$ was investigated by Yang’s group.\textsuperscript{32} They conducted SEM and TEM on the air electrodes discharged at different capacities and discovered a similar trend that with the increase of capacity: Li$_2$O$_2$ grows from a disk-like structure to toroids. As can be seen in TEM images in Figure 1.4a and b, the disk and toroid particles consist of Li$_2$O$_2$ plates highlighted by the yellow dashed lines. The plates grow parallel to each other in the center and split apart through the center to the outer surface. Additional plates then grow in the space between the splayed plates, resulting in expanding the height of the toroid (h in Figure 1.4c). Despite the structure of Li$_2$O$_2$ displays a toroid-like, signals of single crystals are observed by the measurement of selected area electron diffraction (SAED) on a local particle. Figure 1.4d shows dotted patterns with a series of broad arcs in SAED, which could be explained by the “slightly rotational misalignment” along the c axis of the stacked plate crystallites. The diagram of the rotation of the plate is shown in Figure 1.4e and the c axis is along with the [001] direction. Experimental diffractions for the toroids formed under a variety of electrochemical conditions were discovered to match the [001] zone axis of Li$_2$O$_2$. This [001] phase is calculated to have a low surface energy for Li$_2$O$_2$\textsuperscript{33-34}

1.2.2 Reaction mechanism and the co-existence of Li$_2$O$_2$ and LiO$_2$
Figure 1.5 SEM images of Li$_2$O$_2$ obtained in different solvents. (a) DMSO at high potentials (low overpotentials), (b) DMSO at low potentials (high overpotentials), (c) CH$_3$CN at high potentials (low overpotentials), and (d) CH$_3$CN at low potentials (high overpotentials) of 100 mM LiClO$_4$. The applied current is 60 µA·cm$^{-2}$. Modified from ref 35. Copyright 2014, Nature Publishing Group.

Understanding the composition and properties of the discharge product in Li-O$_2$ batteries are helpful for probing the cell chemistry and reaction mechanism. The kinetics on formation and decomposition of Li$_2$O$_2$ determines the rechargeability of the cell and
reflect on the electrochemical performance. The reaction pathways are described as follows:

$$\text{O}_2 + e^- \rightarrow \text{O}_2^-$$  \hspace{1cm} (1.6)

$$\text{Li}^+ + \text{O}_2^- \rightarrow \text{LiO}_2$$  \hspace{1cm} (1.7)

$$2\text{LiO}_2 \rightarrow \text{Li}_2\text{O}_2 + \text{O}_2$$  \hspace{1cm} (1.8)

$$\text{Li}^+ + \text{LiO}_2 \rightarrow \text{Li}_2\text{O}_2$$  \hspace{1cm} (1.9)

During discharge, oxygen is first reduced to superoxide anion at the surface of the air electrode. The superoxide anions are soluble in the electrolyte so it first dissolves and then combines with lithium ions to form LiO\textsubscript{2} in the electrolyte (Equation 1.6 and 1.7).\textsuperscript{35} After the formation of LiO\textsubscript{2}, it could undergo either the disproportionation reaction to form Li\textsubscript{2}O\textsubscript{2} and release O\textsubscript{2} (Equation 1.8), or combine with another lithium ion to form Li\textsubscript{2}O\textsubscript{2} (Equation 1.9).

When LiO\textsubscript{2} is formed in the electrolyte, equilibrium would be reached between LiO\textsubscript{2} adsorbed on the cathode surface and LiO\textsubscript{2} dissolved in the electrolyte. Thus the solubility of LiO\textsubscript{2} in electrolytes is a key factor affecting the kinetics of the discharge process.\textsuperscript{35-37} The solubility is mainly based on the solvation of the cations by the solvent molecules and the ability of the solvation could be described by “donor number” (DN).\textsuperscript{38} In general, the higher the DN, the stronger the solvation ability and thus the higher solubility of Li\textsuperscript{+}. The different DNs of the solvents result in different morphology of the discharge products, shown in Figure 1.5. When the solvent has a high DN such as DMSO (DN=30), LiO\textsubscript{2} dissolves in the electrolyte and at high potential (low overpotential), Li\textsubscript{2}O\textsubscript{2} grows as micrometer-scaled toroidal particles, shown in Figure 1.5b. In contrast, if the
solvent has a small DN (e.g. CH₃CN, DN=14), Li⁺ is weakly solvated in the solvent. In this case, LiO₂ is present primarily on the surface of the electrode and then Li₂O₂ forms as a thin film, shown in Figure 1.5c. Therefore, the formation of the Li₂O₂ goes through a solution phase and correlated with the solvation ability of the solvent.

The charging reaction of Li₂O₂ in the air electrode is simpler than the discharge, shown in Equation 1.10:

\[ \text{Li}_2\text{O}_2 \rightarrow 2\text{Li}^+ + \text{O}_2 \quad (1.10) \]

where Li₂O₂ directly decomposes to oxygen and Li⁺ without superoxide formation. The decomposition starts from particle/thin film of Li₂O₂, and the insulating nature generates larger overpotential to the Li-O₂ cell. Electrocatalysts and additives in the electrolytes have been investigated to facilitate the decomposition of Li₂O₂.³⁹-⁴²

Since LiO₂ is first formed and acts as an intermediate at discharge, it co-deposits with Li₂O₂ and exists in the discharge product under certain conditions.⁴³-⁴⁷ Lu et al. investigate the magnetic properties of the discharge product in an ether-based Li-O₂ cell by electron paramagnetic resonance (EPR) and superconducting quantum interference device (SQUID) magnetometry. Although Li₂O₂ is the major product, their results show that the discharge product is paramagnetic, indicating the existence of superoxide due to its unpaired electron in the molecular orbital.⁴⁸ Further proofs were provided by transmission soft X-ray microscopy (TXM), which was conducted on a toroidal particle in a discharged electrode. In the map of the spatial distribution of various oxygen containing species, it shows that the core contains a mixture of superoxide-like species and peroxide species, and the shell has a layer of carbonate species. The formation of carbonates is likely
due to the side reactions either between the electrolyte and the discharge product or between the carbon materials and the discharge product, which was generally regarded as the solid electrolyte interface (SEI) at the air electrode.\(^{49}\)

Overall, the discharge product in Li-O\(_2\) batteries is composed of Li\(_2\)O\(_2\) (crystalline and amorphous), LiO\(_2\) species, and side products. The complexity of the product implies that multiple reactions occur at the discharge and each component contributes to the cell performance. The understanding of the discharge product in Li-O\(_2\) is not sufficient till now. The formation mechanism of crystal/amorphous Li\(_2\)O\(_2\) is not well-known and the effect of the solvent/salt and the side products also increase the difficulty to investigate the system. The study performed by Lu et al. shows that a reduced graphene oxide supported iridium (Ir-rGO) cathode could stabilize LiO\(_2\) during discharge.\(^{50}\) In the past decades, LiO\(_2\) was proved very difficult to be synthesized both in gas phase\(^{51}\) and in solid phase\(^{52}\). It was only isolated by co-depositing atomic Li metal and oxygen in inert gas matrix at low temperature.\(^{53}\) However, the existence of LiO\(_2\) is controversy since other study argues that the decomposition products of the binder PVDF shows the same Raman signals as the theoretical Raman vibrations of LiO\(_2\).\(^{54}\) In addition, the stability of the electrolyte has been a major obstacle for developing a long lasting battery with good cyclability and high specific capacity. A stable electrolyte could minimize the formation of side products, most of which are insulting and thus passivate the cathode surface. Hence, the study of the discharge products of li-O\(_2\) batteries still face many challenges that needs to be conquered in the future studies.

1.2.3 Problems and challenges in aprotic Li-O\(_2\) batteries
1.2.3.1 Decomposition of the electrolyte

The discharge products in aprotic Li-O\textsubscript{2} cells are very complex and contains side products. Those side products are mainly generated by the decomposition of the electrolyte in the system.\textsuperscript{55} The instability of electrolyte is a limiting factor for the development of aprotic Li-O\textsubscript{2} cells since none of the current salts and the solvents in the electrolytes are stable and could endure the attack from the superoxide species. At the beginning of the development of aprotic Li-O\textsubscript{2} batteries, carbonate-based electrolytes, which had been commonly used in LIBs, were considered as a candidate. However, Freunberger et al. and McCloskey et al. pointed out carbonate-based electrolytes could be easily attacked by the superoxide generated from the reduction of oxygen and finally form Li\textsubscript{2}CO\textsubscript{3}.\textsuperscript{49, 56} In contrast, ether-based electrolytes showed much-improved stability but the same group reported that they still suffered decomposition in oxygen-rich environment.\textsuperscript{57} The side products from the ether solvents are mainly Li\textsubscript{2}CO\textsubscript{3}, HCO\textsubscript{2}Li, CH\textsubscript{3}CO\textsubscript{2}Li, poly ethers/esters, CO\textsubscript{2} and H\textsubscript{2}O. Most side products are insulating and cannot be recharged, leading to large polarization at the charge and low capacity retention. Therefore, highly stable electrolytes need to be explored to fulfill the critical requirements for oxygen batteries due to the high reactivity of superoxide species.

1.2.3.2 Degradation of the carbon cathode
Figure 1.6 The schematic diagram of the product formation and the gas evolution at the carbon surface during one cycle. In the voltage profiles (the lower panel), at discharge the first step is forming Li$_2$CO$_3$ on the surface of carbon cathode and then it is covered by Li$_2$O$_2$ with carbonate species dispersed inside the product (upper right). At charge, more carbonate species are generated on the outer surface of the undischarged Li$_2$O$_2$ (upper middle). CO$_2$ is released at the end of charge when the voltage goes up to 4.2 V (upper left).\(^{49}\)

The instability of carbon cathode is another issue in aprotic Li-O$_2$ batteries. At discharge, the defects on the carbon surface is easily attacked by superoxide species, forming Li$_2$CO$_3$ (Figure 1.6). After coating a surface layer of Li$_2$CO$_3$, Li$_2$O$_2$ starts to accumulate on the electrode, accompanying with the formation of other carbonate species.
which is originated from the decomposition of electrolyte. At the early stage of charge (< 3.5 V vs. Li⁺/Li), the decomposition of Li₂O₂ mainly contributes to the charge capacity. With the increase of charge potential, electrolyte undergoes dissociation to form LiRCO₃ on the cathode surface. CO₂ is ultimately released from LiRCO₃ when the voltage reaches 4.2 V.⁴⁹ Similar results were obtained by Thotiyl et al. who performed DEMS measurement to monitor the evolution of CO₂ based on an isotopically labeled carbon (¹³C) cathode. The isotope replacement of the carbon electrode reveals that the source of CO₂ is from both the solvent and the carbon cathode.⁵⁸ evidencing the argument that both decomposition of electrolyte and the carbon cathode are attributed to the CO₂ emission.

In order to avoid side reactions from the carbon cathode, scientists made efforts to improve the stability of the air electrode. Peng et al. replaced the carbon material by a nanoporous gold (NPG) cathode, achieving capacity retention of 95% after 100 cycles. In addition, the content of Li₂O₂ in the product is 99% on discharge, effectively preventing the production of lithium carbonates at cathode.⁵⁹ Lu et al. designed a cathode of palladium (Pd) nanoparticles on a carbon surface by atomic layer deposition (ALD) with an alumina coating for passivating the carbon defect sites. A low charge potential of 0.2 V is achieved because of the defect free carbon surface and the improved OER kinetics in the presence of Pd catalysts.⁹

1.2.4 Challenges for exchanging O₂ to air

In most advanced Li-O₂ batteries, pure oxygen is used as the cathodic source instead of air not only due to its simpler kinetics during discharge/charge but also because many components in air have detrimental effects to the Li-O₂ cell. Moving “Li-O₂” to “Li-
“air” faces great challenges. Numerous advances were published in aprotic Li-O\textsubscript{2} in the past decades, the understanding of the air system is still in its infancy. Air contains 78% N\textsubscript{2}, 21% O\textsubscript{2}, ~0.04% CO\textsubscript{2}, and ~0.4% water vapor. N\textsubscript{2} could react with Li to form Li\textsubscript{3}N, which could become an issue when N\textsubscript{2} is dissolved in the electrolyte and crosses over to the metal anode. Both H\textsubscript{2}O and CO\textsubscript{2} have the same crossover effects and they are subjected to react with peroxide species at the cathode to form carbonate and hydroxide species, separately, shown as follows:

\begin{align*}
2\text{Li}_2\text{O}_2 + 2\text{H}_2\text{O} &\rightarrow 4\text{LiOH} + \text{O}_2 \\
2\text{Li}_2\text{O}_2 + 2\text{CO}_2 &\rightarrow 2\text{Li}_2\text{CO}_3 + \text{O}_2
\end{align*}

(1.11)  
(1.12)

Thus in Li-air batteries, the cell chemistry is completely different from the aprotic Li-O\textsubscript{2} batteries. On discharge, reactions in Equation 1.11 and 1.12 are thermodynamically favorable so that LiOH and Li\textsubscript{2}CO\textsubscript{3} are very likely to be the discharge products; while on charge, the dissociation of LiOH and Li\textsubscript{2}CO\textsubscript{3} experiences sluggish kinetics and requires high potential upon charge. Understanding the effects of H\textsubscript{2}O and CO\textsubscript{2} is essential to develop Li-air batteries under ambient air atmosphere, in order to implement rechargeable Li-air batteries toward practical applications.

\textit{1.2.4.1 Effect of water on discharge products}
Figure 1.7 SEM images of (a) pristine carbon fiber electrode, and electrodes discharged in electrolyte with (b) trace amount of H$_2$O (< 20 ppm), (c) 200 ppm H$_2$O, and (d) 1000 ppm H$_2$O. The electrolyte is 0.5 M LiTFSI in DEGDME and the applied current is 1 µA. (e) X-ray diffraction patterns of pristine carbon fiber electrode and electrodes discharged in electrolytes with trace amount of H$_2$O (< 20 ppm), 1% H$_2$O water, 1000 ppm H$_2$O, and 200 mM HClO$_4$. The vertical lines represent standard patterns of Li$_2$O$_2$ (PDF 09-0355), LiOH (PDF 32-0564), and LiOH·H$_2$O (PDF 24-0619). The inset shows an amplified diffractogram from 14.4-16.8° where all three compounds show their main diffractions. Reprinted from ref 56. Copyright 2015, The Electrochemical Society.

Since the formation of Li$_2$O$_2$ is through solution mediated pathway, the addition of water in aprotic electrolyte might change the electrochemical environment and show impacts on the formation of discharge product. Aetukuri et al. argued that in anhydrous electrolyte they have never observed toroidal Li$_2$O$_2$; while with small amount of H$_2$O (500 ppm), the discharge capacity was largely increased and the Li$_2$O$_2$ structure changed to
toroids\textsuperscript{60} They proves that even the water concentration is up to 25,000 ppm, Li$_2$O$_2$ is still the main discharge product, evidenced by XRD, FTIR and DEMS. This claim was further supported by Schwenke et al.\textsuperscript{61} They observed the morphology change of Li$_2$O$_2$ with water contents from anhydrous to 1000 ppm, shown in Figure 1.7. Thin-film like Li$_2$O$_2$ is formed on the surface of carbon (Figure 1.7b) with trace amount of H$_2$O with the pristine carbon fiber electrode as comparison (Figure 1.7a). The toroidal size expands with the increasing amount of H$_2$O in the electrolyte (Figure 1.7c and d), indicating that H$_2$O takes place in the discharge and contributes to the morphology change of the product. In addition, if the water concentration is beyond 1%, trace amount of LiOH-H$_2$O is observed in Figure 1.7e, indicating that Li$_2$O$_2$ reacts with the excessive water to form hydroxide. They proposed that the mechanism of the morphology change could be explained by Li$_2$O$_2$ solubilization by protons. In the presence of H$_2$O or acids, protons stabilize peroxide species by to form H$_2$O$_2$ in the solution and lead to the formation of toroid structure. They state that with the increase of the water concentration, the amount of Li$_2$O$_2$ decreases due to the continuous formation of H$_2$O$_2$ via the disproportionation of superoxide in electrolyte. A mechanism of the morphology change was proposed as three coupled kinetic processes: solution-mediated growth rate of Li$_2$O$_2$, the reverse rate that prevents the Li$_2$O$_2$ growth and the formation of defects and holes in the passivation layer. At low currents, toroidal particle are formed with sizes dependent on water concentration; while at high currents and low water concentration, oxygen diffusion becomes limiting factor and restrict the growth of Li$_2$O$_2$, resulting in a thin film like structure on the carbon surface.\textsuperscript{36}

1.2.4.2 Aqueous Li-O$_2$ batteries
Figure 1.8 (a) Discharge/charge profiles of a hybrid Li-air cell in 1 M LiClO$_4$ in EC-DEC/LATP/saturated LiOH with 10 M LiCl/KB aqueous solution with a current of 0.64 mA·cm$^{-2}$. (b) XRD patterns of the LiOH·H$_2$O reference and air electrode after discharged at 0.88 mA·cm$^{-2}$ for 240 h. Reprinted from ref 57. Copyright 2014, Elsevier.
With a trace amount of water applied in Li-O₂ batteries, the discharge product is still composed of mainly Li₂O₂, but replacing the aprotic electrolyte to an aqueous solution, different cell chemistry is applied and many issues need to be considered during the cell assembly. When aqueous solution is used as the electrolyte, a protection layer of lithium is generally applied on the anode given the drastic reaction between lithium metal and water. A typical aqueous Li-O₂ cell uses Li as the anode, solid-state Li⁺ conductive membrane as the separator/electrolyte, and gas diffusion layer as the cathode. The solid-state layer divides the cell into two parts, in which the anode usually uses aprotic electrolytes and the cathodic electrolytes are aqueous. Figure 1.8 shows a hybrid cell using 1 M LiClO₄ in EC-DEC as the anodic electrolyte, Li₁₊ₓ₊ₙAlₓ(Ti,Ge)₂₋ₓSiₓP₃₋ₙO₁₂ (LATP) membrane, and saturated aqueous solution of LiOH with 10 M LiCl as the cathodic electrolyte. The discharge voltage starts from 2.3 V and decreases to 1.7 V at the end of discharge, while the charge voltage shows a plateau at around 4.6 V (Figure 1.8a). XRD detects that the discharge product is mainly LiOH·H₂O compared to the standard pattern in Figure 1.8b. The different cell chemistry in aqueous solution suggests that the solvent participates in the discharge reaction and forms LiOH·H₂O as the final product. The reaction pathway is shown as follows:

\[
O_2 + 2H_2O + 4e^- \leftrightarrow 4OH^- \quad (1.13)
\]

\[
Li^+ + OH^- + H_2O \leftrightarrow LiOH·H_2O \quad (1.14)
\]

where the product is first in the form of Li⁺ and OH⁻, dissolved in the aqueous solution. It then precipitates out due to the limited solubility (12.8 g/100 g) of LiOH in H₂O. The
thermodynamic potential for the formation of LiOH·H₂O is 3.0 V vs. Li⁺/Li, similar to the reaction of Li₂O₂ (2.96 V vs. Li⁺/Li).

Currently, the key issue to aqueous Li-O₂ batteries is lacking of appropriate solid-state Li⁺-selective membranes. An ideal membrane should have the following features: 1) stable to the lithium metal, the electrolyte, and the highly reactive intermediate during discharge/charge; 2) sufficient Li⁺ conduction at room temperature; 3) good mechanical strength to accommodate the volume change of the anode and the cathode. Despite many efforts have been done on identifying the most desirable solid electrolyte, the ultimate one fulfilling all the requirements is yet to be explored.

1.2.4.3 Effect of CO₂ on discharge products

![Figure 1.9](image)

Figure 1.9 (a) Galvanostatic discharge profiles of Li cells discharged under three atmospheres: pure CO₂, pure O₂, and a 10:90 CO₂:O₂ mixture. The cathode is XC72-based electrodes and the current is 0.47 mA·cm⁻². (b) FTIR of cathodes discharged (0.9 mA·cm⁻², 4.7 mAh·cm⁻²) under pure O₂ and a 10:90 CO₂:O₂ mixture. In the pure O₂ spectra, peaks
at 1064, 1138, 1202, and 1340 cm\(^{-1}\) can all be attributed to the electrolyte salt (LiTFSI). P50 carbon was used as the cathode. The electrolyte is 1 M LiTFSI in DME. Reprinted from ref 67. Copyright 2013, American Chemical Society.

CO\(_2\) is another major contaminant in Li-O\(_2\) batteries. It is soluble in most organic solvents and reactive to Li (the anode), Li\(_2\)O\(_2\) (the major discharge product in aprotic Li-O\(_2\) cells) and LiOH (the major discharge product in aqueous Li-O\(_2\) cells) to produce Li\(_2\)CO\(_3\). The reaction between CO\(_2\) and Li\(_2\)O\(_2\) is thermodynamically favorable due to the standard formation Gibbs energies (\(\Delta G^\circ_{\text{Li}_2\text{O}_2} = -634.3\) kJ\(\cdot\)mol\(^{-1}\); \(\Delta G^\circ_{\text{Li}_2\text{CO}_3} = -1215.9\) kJ\(\cdot\)mol\(^{-1}\)).\(^66\) Gowda et al. studied the effect of CO\(_2\) on Li-O\(_2\) batteries and no capacity was obtained in pure CO\(_2\) atmosphere, shown in Figure 1.9a. In a mixture gas of CO\(_2\):O\(_2\) (10:90), the capacity was increased to 1.5 times larger than the capacity in pure O\(_2\). FTIR shows that the discharge products consist of mainly Li\(_2\)O\(_2\) and Li\(_2\)CO\(_3\), evidencing that the CO\(_2\) was involved in the cell reactions (Figure 1.9b and Equation 1.12).\(^67-68\) In the presence of CO\(_2\), the discharge voltage is similar to the cell in pure O\(_2\), but larger overpotential is observed at charge.\(^69\) Theoretical studies indicate that low concentration of CO\(_2\) (1\%) could block the nucleation sites at the cathode and thus change the formation mechanism of Li\(_2\)O\(_2\), inducing the high polarization on charge.\(^70\) However, experimental studies suggest that the electrolyte solvation effect plays a key role in yielding Li\(_2\)CO\(_3\). A low dielectric electrolyte tends to form Li\(_2\)O\(_2\) and then combine CO\(_2\) to form Li\(_2\)CO\(_3\), resulting in the co-existence of Li\(_2\)O\(_2\) and Li\(_2\)CO\(_3\). In contrast, a high dielectric electrolyte is more likely to produce superoxide anion and directly react with CO\(_2\), thus producing only Li\(_2\)CO\(_3\).\(^71\)
Moving oxygen to air is an important step for the practical application of Li-air batteries and is appealing to the researchers. More recently, many groups attempt to explore the rechargeable Li-air system at ambient air atmosphere. However, the cycle life and the capacity retention of current Li-air cells are far from satisfactory. Hence, more efforts are required to make the Li-air applicable:

(1) Seeking stable materials and electrolytes is the foundation for normal operation of Li-O\textsubscript{2} batteries. The instability of the materials and electrolytes causes many issues and prevents the development of Li-air batteries.

(2) The reaction mechanism and cell chemistry in Li-air batteries should be thoroughly understood, which could guide to provide new science and approaches to develop Li-air batteries.

(3) More effective catalysts or additives in electrolytes need to be explored in Li-air batteries because of the intrinsic low conductivities of the discharge products.

(4) Oxygen selective membranes benefit to the Li-O\textsubscript{2} batteries to eliminate the detrimental effects from water and CO\textsubscript{2} but they are not well developed to date. Since oxygen molecule is relatively smaller than most gases in air, designing a functionalized oxygen selective membrane could be a challenge.

1.3 Sodium oxygen batteries

Sodium oxygen (Na-O\textsubscript{2}) batteries were first reported by Peled et al. in 2011.\textsuperscript{72} In sodium oxygen (Na-O\textsubscript{2}) batteries, there are two possible products from the reactions of sodium and oxygen, sodium peroxide (Na\textsubscript{2}O\textsubscript{2}) and sodium superoxide (NaO\textsubscript{2}). The overall reactions are shown as follows:
The free energies of the two reactions indicate that the formation of \( \text{Na}_2 \text{O}_2 \) is more thermodynamically favorable. Regarding the studies on \( \text{Na}_2 \text{O}_2 \), it was not stable at ambient atmosphere and difficult to synthesize.\(^{73}\) During first attempts of sodium oxygen batteries, since lithium and sodium were from the same elementary group, people thought that Na-O\(_2\) batteries produced Na\(_2\)O\(_2\) and had similar problems to Li-O\(_2\) batteries: a low energy density of the cell was expected since Na\(_2\)O\(_2\) had poor electronic conductivity\(^{74}\) which requires higher energy to be charged. In the first study of sodium oxygen batteries, Peled et al. report that at an elevated temperature of 105 °C, the sodium oxygen battery ran several cycles using sodium as the anode and oxygen in the cathode.\(^{72}\) However, the study did not include the product characterization and just assumed Na\(_2\)O\(_2\) as the product. Then Kim et al. investigated the discharge products at room temperature in carbonate-based electrolyte and ether-based electrolyte, separately. They found that with carbonate-based electrolyte, sodium carbonate was the major discharge product resulted from the decomposition of electrolyte, while in ether-based electrolyte, sodium peroxide dihydrate and sodium hydroxide were the main products. Based on the poor electronic conductivity of the products, both batteries have large charging voltages over 3 V and poor Coulombic efficiencies.\(^{75}\) Na\(_2\)O\(_2\) was detected as the product in the early exploration of Na-O\(_2\) batteries.

In 2013, Hartmann et al. reported a sodium superoxide (NaO\(_2\)) based battery with 0.2 V voltage polarization upon charge, which makes Na-O\(_2\) cell technology a promising
competitor to Li-O₂ batteries.⁷⁶ The discharge/charge profiles of Na-O₂ batteries are shown in Figure 1.10.

Figure 1.10 The discharge/charge profile of the Na-O₂ battery with specific currents of 120, 200, 300, and 500 μA·cm⁻². Modified from ref 76. 2013 Nature Publishing Group.

In Li-O₂ batteries, the charging overpotential is generally larger than 1 V due to the low electronic conductivity of Li₂O₂ and the multiple steps in electrode reaction. In contrast, Na-O₂ batteries show much lower overpotential (<200 mV), indicating a faster kinetic process of NaO₂ dissociation. Additionally, it indicates a much-improved electronic
conductivity of the discharge product compared to Li$_2$O$_2$. In the NaO$_2$ based cell, a reversible reaction with a single electron transfer process occurs and is shown in Equation 1.17:

$$\text{Na} + \text{O}_2 \leftrightarrow \text{NaO}_2 \quad (E^0 = 2.27 \text{ V})$$

where sodium superoxide (NaO$_2$) is the discharge product and the equilibrium potential is 2.27 V. Although the reason for the formation of NaO$_2$ in the sodium oxygen battery is still not well understood, the high round-trip efficiency makes it a promising battery technology. Similar to the Na-O$_2$ battery, a one-electron potassium oxygen battery based on potassium superoxide has also been demonstrated in our group with a charge/discharge voltage hysteresis as small as 50 mV.$^{77}$

Based on the previous studies, the discharge products split to two parts: one is NaO$_2$ which was firstly reported by Hartmann et al. and then followed by other studies, and the other part is Na$_2$O$_2$ based product usually in the form of Na$_2$O$_2$·2H$_2$O. Bender et al. reviewed most studies in Na-O$_2$ batteries and summaries the major discharge products on account of results from different research groups.$^{78}$ They discussed multiple parameters that might affect the product formation and proposed that with excessive water, NaO$_2$ could combine water to form Na$_2$O$_2$·2H$_2$O. However, in our study, we discover that based on different cell setups, the product can be controlled to be NaO$_2$ and Na$_2$O$_2$·2H$_2$O. It is very unlikely that the cell with Na$_2$O$_2$·2H$_2$O as the product contains huge amount of water at the beginning of discharge. This study will be discussed in chapter 2.

We successfully prepared NaO$_2$ in a stainless steel cell. However, the NaO$_2$ based battery was greatly hindered by the poor cyclability, which was ascribed to by-product
formation, instability of electrolytes, reactive anode and metal dendrite formation. The background of dendrite formation of alkali metal will be introduced in the following section and the investigations of the dendrite issue and side reactions in Na-O$_2$ batteries will be discussed in chapter 3.

1.3.1 Dendrite issue in the metal anode

In alkali metal batteries, one significant problem is dendritic metal formation on the alkali metal anode. It could grow into and penetrate the separator and reach to the cathode, causing short-circuits of batteries and generating serious safety problems. Lithium is the most common alkali metal that has dendrite issue in lithium ion, lithium sulfur and lithium polymer batteries. However, in Li-O$_2$ batteries, no failure mechanism on dendrite formation was reported. Due to the effect of oxygen crossover, the solid-electrolyte interface (SEI) layer formed in oxygen atmosphere might change to a more complicated composition avoiding dendritic lithium formation. Here, we refer the studies of dendrite in Li-ion batteries to understand the mechanism of dendrite formation and approaches to prevent dendrite growth.
Figure 1.11 A description of the morphology and failure mechanism of Li electrodes during Li deposition and dissolution describing selected phenomena: the beginning of dendrite formation and non-uniform Li dissolution accompanied by breakdown and reparation of the surface films. (Li electrodes in an EC-DMC/LiPF₆ solution.) Reprinted from ref 79. Copyright 2002, Elsevier.

The dendrite formation has been identified as a serious issue in lithium batteries for decades.\textsuperscript{80,81} Many studies have been done in lithium batteries to probe the mechanism of dendrite formation. Brissot et al. claimed that there were excess positive charges at the metal anode, generating a high electrical field and facilitating the dendrite formation.\textsuperscript{82} Orsini et al. used in-situ scanning electron microscopy (SEM) to observe morphology changes of the metal surface in lithium batteries.\textsuperscript{83} They stated that at low current lithium
had a moss structure while at high current it formed dendrite structure. Aurbach et al. proposed a mechanism on the influence of SEI breakdown and reparation by surface reactions of Li with solution species on dendrite formation (Figure 1.11). Based on the uneven metal surface, the accumulation of metal ions was different from site to site generating different current density. During lithium deposition, SEI layer could not accommodate the surface change of lithium metal and break down to pieces, which allow Li\(^+\) directly growing on the metal surface and forming dendritic structure. The needle-like dendrite grows into pores of the separator and then comes to directly contact with the cathode. The dendrite penetration would lead to the batteries short-circuited and the high current could induce a rapid temperature increase leading to the explosion of batteries. In lithium dissolution process, the hollow area on lithium surface would be first dissolved to form deep valleys on the surface. Along further dissolution, the SEI layer breaks down and the fresh metal surface is revealed.

To date, there is no pure lithium metal that can be directly applied in lithium batteries due to the high reactivity and the dendrite formation. Preventing dendrite growth and forming durable SEI layer are key motivations to use lithium metal as the anode and reduce the safety hazards in lithium batteries. Currently, Sony’s Li-ion batteries\(^\text{84}\) are the dominant commercial batteries in the world market and they use graphite as the anode material. Graphite has a layered structure which accommodates lithium ions intercalated between the layers. The utilization of graphite instead of pure lithium metal in the anode reduces the risks of LIBs such as the high reactivity of lithium and dendrite formation induced shorting problem.\(^\text{85}\) Other approaches have been employed to solve the dendrite
issues in lithium ion batteries. Adding additives to the electrolyte could change the composition of SEI layer and control the dendrite morphology. Ding et al. reported a self-healing method to alter the dendrite formation mechanisms in lithium ion batteries. They stated that additional cations were added into the electrolyte to block the accumulation of lithium ions on the protuberant tips of lithium and thus form a uniform surface. However, the SEI layer grew continuously during cycles, which consumed Li metal and the electrolyte. Aurbach et al. used a 1,3-dioxolane solvent and a LiAsF$_6$ conducting salt as the electrolyte to form a flexible SEI layer that accommodated surface change during cycles, which protected the lithium metal from forming dendrites. Another method was reported by PolyPlus Battery Co. They used a lithium ion conductive glass ceramic with a decent ionic conductivity in a solid-state lithium ion battery. The ion conductive ceramic was directly pasted to the lithium metal and thus effectively suppressed the dendrite formation. Those methods could improve the possibility of utilization of lithium metal in lithium batteries, reaching to higher energy density compared to the presently used graphite materials. Another issue is the reaction between Li anode and the electrolyte in the presence of oxygen. Although a stable solid electrolyte interfaces (SEI) layer could be formed on the surface of Li-ion battery anode, it was recently reported that in Li-O$_2$ batteries, more complicated reactions could occur on the Li anode in the presence of O$_2$ crossed from the air cathode.

1.3.2 Sodium anode

In sodium batteries, the studies of sodium dendrite and its influence on cyclability are very limited. Sodium batteries such as sodium-sulfur batteries (Na-S) and ZEBRA
(Zero-Emission Battery Research Activities) batteries operated at high temperature (>300 °C) eliminates the influence of dendrite due to the molten state of the sodium metal. For sodium ion batteries, since they were directly derived from lithium ion batteries without using pure sodium metal, no failure mechanisms of pure metal have been reported. However, the nature of dendrite formation of pure sodium is still problematic for sodium ion batteries. Varieties of anode materials have been investigated in the past few years. Since the cation radius of sodium (1.06 Å) is larger than that of lithium ion (0.76 Å) indicating that the commonly used lithium intercalation materials are no longer applicable in the sodium system. For example, the graphite is regarded as a good anode material due to its appropriate interlayer distance with 0.34 nm for lithiation. Nevertheless, sodium ions with larger size cannot intercalate into graphite because of the larger interlayer distance 0.37 nm required. To use graphite in sodium ion batteries, Wen et al. expanded the interlayer space of graphite from 0.34 nm to 0.43 nm, making graphite applicable for sodiation. The batteries run over 2000 cycles and have good capacity retention after long cycles. In addition to graphite, other materials such as alloy and metal oxides anodes have also been investigated. Zhu et al. reported an ultra-small tin nanoparticles embedded in carbon matrix which accommodates the large volume expansion and achieves 200 cycles with a capacity retention of 720 mAh g⁻¹. Metal oxides anode materials such as SnO₂, TiO₂ and Fe₂O₃ could achieve higher discharge capacity due to multiple charge transfer process. However, the stability of metal oxides is not satisfied because two reactions including oxidation reaction and alloying process occurred during discharge inducing huge structural changes.
In sodium oxygen batteries, Peled et al. reported a Na-O$_2$ battery operated at a temperature of 98 °C, which is slightly higher than the melting point of sodium, 97.72 °C. However, in sodium sulfur batteries, the molten form of sodium grows into the solid-state separator forming dendrite and showing the degradation of the battery performance. Overall, in high-temperature batteries, the thermal stability of the battery is a challenge and the high operation temperature increases the risks during utilizations and operations in a Na-O$_2$ battery. Hartmann et al. observed the grayish dendrite penetrated through the polymer separator with a cycle life of 30 cycles. After replacing the polymer separator with a solid-state electrolyte, sodium-beta-alumina, they found the dendrite penetration was suppressed. However, the battery performance was not discussed in their work. Moreover, beta-alumina solid separator was brittle and could generate large internal resistance in the battery.

Regarding the limited studies, dendrite formation and its influence on the electrochemical performance of sodium oxygen batteries have not been well investigated. Due to the fact that the cathode is the main problem of lithium oxygen batteries, most works in Na-O$_2$ batteries have been focused on the air cathode such as investigating the formation of Na$_2$O$_2$ or NaO$_2$, and electrolyte decomposition. The studies on the anode need to be further explored in the future.

1.4 Conclusion

In this chapter, we reviewed the current status of the studies of discharge product in Li-O$_2$ and Na-O$_2$ batteries. We first introduced the discharge product in aprotic Li-O$_2$ batteries, which contains mainly Li$_2$O$_2$ (crystalline and amorphous), LiO$_2$ species, and side
products such as lithium hydroxide and carbonates. The structure and intrinsic properties of Li$_2$O$_2$ was also included owing to the major role of Li$_2$O$_2$ in electrochemical reaction. Secondly, the major issues in Li-O$_2$ batteries was discussed in terms of the instability of electrolyte and carbon cathode. Thirdly, we summarized the effects of carbon dioxide and water on the cell chemistries of Li-O$_2$ batteries considering exchanging the oxygen to air atmosphere. Given the infancy status of Li-O$_2$ batteries, there is still a long way to go for seeking the practical application of Li-O$_2$ batteries and moving to real air atmosphere.

For Na-O$_2$ batteries, recent advances on the stabilization of NaO$_2$ open a new door for improved kinetics during charge of metal oxygen batteries. However, the formation mechanism of NaO$_2$, or Na$_2$O$_2$·2H$_2$O is still unclear at this stage. In chapter 2, we perform the study on different cell setups, successfully controlling the formation of the two different products. Multiple parameters are compared for the two cell setups to reveal the mechanism of the formation of NaO$_2$ and Na$_2$O$_2$·2H$_2$O.

NaO$_2$ was obtained in a stainless steel cell. However, NaO$_2$ based batteries have many issues such as the unstable environment for the product and the electrolyte. Moreover, they suffered short-circuits within few cycles due to dendrite formation. The dendrite issue was reviewed in this in the alkali metal anodes. Lithium dendrite had been thoroughly explored but the sodium dendrite formation was lacking. In chapter 3, the instability of NaO$_2$ will be investigated and the behavior of the dendrite and investigation of the effect to the electrochemical performance will be investigated. The dendrite issue can be eliminated by adding a physical barrier, thus greatly improving the cycle life. With
the barrier, the side reactions occurred in the cell were explored, revealing the instability of the sodium metal and the electrolyte.

In chapter 4, the discharge product of a mixed salt based electrolyte in Li-O$_2$ batteries is studied. Other than most studies in Li-O$_2$ batteries, the sodium-ion added electrolyte changes the cell chemistry and leads to the formation of LiOH. Moreover, the formed LiOH is charged at a low overpotential. The discharge product is conducted by characterization methods such as scanning electron spectroscopy, transmission electron spectroscopy, Raman spectroscopy, and x-ray diffraction.

The last chapter introduces an advanced differential electrochemical mass spectroscopy (DEMS) which is very helpful for investigating mechanism in metal oxygen batteries. I first build a manual DEMS system based on a mass spectrometer and then update to an automatic system by changing the manual valves to solenoid valves. The studies of Li-O$_2$ batteries and Na-O$_2$ batteries have been conducted by the DEMS instrument.
Chapter 2: The Instability of Sodium Superoxide and Investigation of Different Discharge Products in Sodium Oxygen Batteries

2.1 Introduction

Recently, metal air batteries have received great research interests due to their high theoretical energy densities compared to lithium ion batteries, enabling the applications in electric vehicles or large energy storage systems.\textsuperscript{76-77, 99-100} The high theoretical energy density benefits from the light weight of alkali metal in the anode and the oxygen in the cathode. In a typical lithium oxygen battery, the overall reaction follows: $2\text{Li} + \text{O}_2 \leftrightarrow \text{Li}_2\text{O}_2$, ($E^0 = 2.96$ V), where lithium peroxide is generally observed as the discharge product.\textsuperscript{100-101} However, the sluggish kinetics during decomposition of Li$_2$O$_2$ is a major obstacle for the development of Li-O$_2$ batteries. As an alternative, Na-O$_2$ batteries have theoretical gravimetric energy density of 1602 and 1105 Wh·kg$^{-1}$ based on the mass of Na$_2$O$_2$ and NaO$_2$, respectively.\textsuperscript{102-103} The formation of peroxide-based products could benefit to the larger capacity and higher energy density while the formation/decomposition of NaO$_2$ is more kinetically favorable in an electrochemical environment, generating low overpotentials.\textsuperscript{104-105}

In 2014, Hartmann et al. first reported a Na-O$_2$ battery based on the formation of NaO$_2$.\textsuperscript{76} The study has overturned the traditional understanding of Na-O$_2$ batteries since
NaO₂ has poor stability at ambient atmosphere and is hard to be formed by chemical synthesis methods. While in the study of Hartmann et al., they discover that through an electrochemical reaction, NaO₂ was formed during discharge indicating a kinetically controlled reaction pathway. Cubes are a typical morphology for NaO₂ produced in ether-based electrolytes. The scale of NaO₂ cubes is generally in the micrometer range. Considering the insulating nature of NaO₂, the fast formation and decomposition kinetics imply that the growth mechanism is not a simple pathway for crystal growth/decomposition. Two formation mechanisms of NaO₂ have been proposed through the surface- or solution-mediated growth. On the one hand, in surface mediated growth mechanism, oxygen is firstly reduced to superoxide and then bonds with Na⁺ on the surface of the carbon. All the reaction pathways are completed on the electrode surface. While in solution mediated growth mechanism, the superoxide anion migrates to the electrolyte after forming on the carbon surface. When the solubility of NaO₂ reaches to its up limit, it is precipitated out on the electrode surface and further grows as cubes. The latter agrees with the reaction mechanism proposed by Xia et al.. They proposed that superoxide was initially stabilized by protons (H⁺) in the electrolyte in the form of HO₂. The protons were supplied by residual H₂O molecules which act as phase-transfer catalysts. Then the Na⁺ replaces the proton to produce NaO₂ in the solution. The formation of NaO₂ opens a new door for the development of Na-O₂ batteries with high energy efficiency.

While at the beginning of Na-O₂ studies, there were no criteria for each research group for cell testing and analysis parameters, leading to a wide range of discrepancies on the cell chemistry such as discharge product and electrochemical performance. Bender et
al. reviewed the recent studies on Na-O2 batteries and categorized them by the discharge products and voltage profiles, shown in Figure 2.1.

Figure 2.1 Summary of discharge/charge profiles of various reports on Na-O2 batteries. The discharge products are categorized as three parts: NaO2, Na2O2, and Na2O2·2H2O. Reprinted from ref 78. Copyright 2016, John Wiley & Sons, Inc.

Based on the summary, three possible products, sodium peroxide (Na2O2), sodium peroxide dihydrate (Na2O2·2H2O)112-113 and sodium superoxide (NaO2)111, 114-117, were detected in sodium-oxygen batteries. The overall reactions are shown as follows:

\[
Na + O_2 \leftrightarrow NaO_2 \quad (E^0 = 2.27 \text{ V}) \quad (2.1)
\]

\[
2Na + O_2 \leftrightarrow Na_2O_2 \quad (E^0 = 2.33 \text{ V}) \quad (2.2)
\]

The similar free energies of the two reactions (refer to Equation 2.1 and 2.2) imply that it is difficult to determine which product is more thermodynamically favorable.
The varied discharge products originate from different cell chemistries of Na-O_2_ batteries. The intrinsic properties such as the crystal structure and electron/ionic conductivity of sodium peroxide and sodium superoxide greatly affect the kinetics of cells, resulting in different electrochemical behaviors at the oxygen evolution reaction (OER) process.\textsuperscript{74, 118} As can be seen from Figure 2.1b and c, most studies with Na_2O_2 or Na_2O_2·2H_2O as the product show sluggish kinetics during OER and over 1 V charge overpotential was observed on bare carbon air electrode.\textsuperscript{119-120} Multiple OER catalysts was investigated to reduce the charging polarization, which is similar to the scenario in Li-O_2 batteries.\textsuperscript{121-122} In contrast to the peroxides based Na-O_2 batteries, the NaO_2 based batteries show steady voltages during discharge/charge and display a low charge potential, shown in Figure 2.1a. Based on the review by Bender et al., they reviewed the characterization methods of each study and concluded that the results of NaO_2 and Na_2O_2·2H_2O were solid while the results of Na_2O_2 were either ambiguous or incorrect.\textsuperscript{78}

Here, we first investigate the stability of NaO_2 after a period of time of formation and reveal that the resting of NaO_2 would not convert it to Na_2O_2·2H_2O. We use two different cell setups to control the formation of NaO_2 and Na_2O_2·2H_2O. Interestingly, the two cells use exactly the same sodium anode, glass fiber separator, carbon paper cathode, electrolyte, and oxygen gas supply system but the products are completely different. Our study reveals that in a stainless steel cell, NaO_2 is observed as the only discharge product, while in a glass chamber cell, Na_2O_2·2H_2O was formed as the only discharge product. Based on the formation of peroxide, in-situ XRD was carried out to investigate the discharge/charge process to understand the cell chemistry in the glass chamber cell. Our
results indicate that the formation of the discharge products in Na-O₂ batteries greatly rely on the sealing method of the cell. The formation of NaO₂ is guaranteed in a well-sealed, pressure tolerance device while a small amount of air leaking will lead to the peroxide formation. The work provides insights to understand the electrochemical process in peroxide-based Na-O₂ cells and brings up the importance of the cell design for Na-O₂ batteries.

2.2 Experimental section

Materials and cell assembly: Sodium metal slice (Fisher Scientific, labgrade) was used as the metal anode and H23 (Freudenberg) carbon paper was used as the air electrode. The electrolyte was bis (2-methoxyethyl) ether (diglyme, Sigma-Aldrich, 99.5%) containing 1 M sodium trifluoromethanesulfonate (sodium triflate, Sigma-Aldrich, 98%). The sodium triflate salt was dried in a vacuum oven at 120 °C overnight. Separators and carbon papers were dried in the vacuum oven at 100 °C for 20 h. The solvent was dried with 3 Å molecular sieves (Sigma-Aldrich) before use. The water content in the electrolyte was tested using a Mettler Toledo C20 Karl Fischer Coulometer. Two pieces of glass fiber paper (Whatman, 300 um thickness) were used as the separator. The gas supply is ultrahigh purity oxygen gas (99.993%, UHP). The titration solution is diluted Titanium(IV) oxysulfate (TiO(SO₄)) solution (~2%, Sigma-Aldrich).

Before each battery performance test, oxygen gas was flowed into the sodium oxygen battery and stored in the oxygen reservoir. All the cells were assembled in the glove box under high purity Argon (O₂ content < 0.1 ppm, H₂O content < 0.5 ppm) and stayed
for 1 h to reach equilibrium before tests. The battery performance tests were performed by a Maccor testing station (model: 4000). The current density was set to 0.1 mA cm$^{-2}$.

Characterization methods: Ex-situ XRD was performed by high energy x-ray diffraction (HE-XRD) with a wavelength of 0.117418 Å at experimental station 11-ID-C of the Advanced Photon Source (APS), Argonne National Laboratory. In order to compare with the normal XRD, we converted the wavelength to 1.54059 Å (Cu Ka) in consistent with most studies. The samples were placed in a tiny holder (inner diameter: 3 mm) and sealed by Kapton tape on each side to avoid the contact with air.

In-situ powdered XRD was carried out at the experimental station 13-BM-C at APS. The X-ray beam was monochromated with silicon 311 crystal to 28.6 keV (0.434 Å), with 1 eV bandwidth. The wavelength was converted to Cu Ka (1.5418 Å). A Kirkpatrick-Baez mirror system was used to obtain a vertical × horizontal focus spot size of 20 µm × 30 µm, measured as full width at half maximum (FWHM). The diffraction pattern was collected in a transmission way, and the MAR165 Charge Coupled Device (CCD) detector (Rayonix) was placed about 170 mm away from the sample. LaB$_6$ powder was used to calibrate the distance and tilting of the detector. The typical exposure time was 120 seconds for each diffraction pattern. The diffraction patterns were integrated and analyzed by the DIOPTAS software (Prescher and Prakapenka, 2015). A home-made in-situ XRD holder similar to the glass chamber cell was used in the test. The transmission x-ray went across two well-sealed Kapton tape windows on each side of the holder. A 2032 coin cell was assembled with the same materials and same electrolyte as above. During the XRD test, a
Maccor (model: 4301) testing machine was gathering the galvanostatic results in the meantime. The XRD data were collected at the same point every 30 min.

The battery products and surface layer components on the air electrode were characterized by Raman spectrometer (iN Via, Renishaw) with an excitation wavelength of 633 nm (laser power 6 mW). An airtight sample holder was made by an aluminum base with a quartz window and sealed by two O-rings.

Scanning electron microscopy (SEM) was performed by a Hitachi S4700 SEM. Glass vials sealed in the Mason jar were used to store samples before tests. The samples were quickly transferred from the Mason jar to the SEM sample chamber exposing to air within 10 s.

2.3 Results and discussions

2.3.1 Instability of sodium superoxide

Figure 2.2 Galvanostatic cycles of three different cells that were let resting for 0 (black), 24 (blue), and 48 h (orange) between first discharge and charge.
In contrast to Li-O$_2$ batteries, where Li$_2$O$_2$ is reported as the discharge product, the chemical nature of NaO$_2$ is still under debate.$^{108, 115, 118, 123}$ In order to analyze the stability of NaO$_2$, we rest three cells with different resting periods after discharge and then observe the behavior during charge. The three cells were discharged to capacity of 1.5 mAh at a current density of 0.2 mA·cm$^{-2}$ with three resting periods of 0, 24 and 48 h. After the resting periods, the cells were charged at the same current. The voltage profiles are shown in Figure 2.2. The Coulombic efficiencies are 84.7% for no resting time, 70.6% for resting time 24 h, and 57.3% for 48 resting time. The lower Coulombic efficiency for the longer resting time indicates the change of the formed NaO$_2$. Moreover, this behavior is extended to further cycles as shown in Figure 2.3.

![Figure 2.3](image)

**Figure 2.3** Evolution of the Coulombic efficiency of the galvanostatic cycles with a resting period of 4 hours (grey), 30 minutes (orange) and without resting (blue) at a current density of 0.05 mAh limiting the discharge to 0.5 mAh.
Figure 2.4 (a), (b), (c), and (d) SEM images of discharge products generated during discharge. Electrode in (a) and (b) was directly disassembled and analyzed after discharge.
while electrode in (c) and (d) was kept in the cell for 30 h after discharge. (e) Atom percentage obtained by EDX in the electrode after discharge (blue) and after 30 h resting (gray).

To reveal the underlying effect, the discharged air electrodes of the two cells with 30 h resting time and without resting time were characterized by SEM, EDX analysis, and Raman. Figure 2.4 shows SEM images of the discharge products in cells without resting (Figure 2.4a and b) and with 30 h resting time (c and d). The product shows a cubic structure, consistent with the morphology of most studies in NaO$_2$ based cells.$^{76, 111, 124}$ Without resting time, the product shows a smooth surface with sharp edge of the cubes, while the one after 30 h resting time shows uneven surface, indicating the structural evolution of the discharge product.

EDX analyses were carried out to observe the change of element distribution of the cubes, shown in Figure 2.4e. Since the air electrodes were carefully washed by the solvent, no residue salt was left on the electrode surface. The main contribution to the total composition came from C ($\sim$70%) that principally belongs to the carbon electrode. Four percent of element F was detected in both samples reveals the possible formation of NaF as a side product since no S coupled to the F was discovered in the conducting salt.$^{97}$ After 30 h resting time, almost no percentage change was found on C and F. However, the ratios of Na and O show an obvious change. The content of Na rose from 10.5% to 20.2% during the resting period while the oxygen percentage fell from 14.1% to 5.8%. Although the EDX technique is unlikely to reveal the composition of the cubes, the Na/O ratio clearly shows the surface change after 30 h resting period, indicating that the product probably experience
chemical reactions during resting. Recently, Kim et al. argue that NaO₂ could convert to Na₂O₂·2H₂O during resting and ascribed the formation of Na₂O₂·2H₂O in many groups as the resting of the cell.¹²⁵ However, in our study we observe an increase of Na/O ratio but the transformation from NaO₂ to Na₂O₂·2H₂O does not increase the Na/O ratio and it is supposed to maintain at 1:2. Moreover, for the formation of Na₂O₂·2H₂O, a large amount of water needs to be present in the electrolyte, and this is not likely to occur under the closed conditions in this study. In addition, this compound usually exhibits several charge plateaus, which are neither observed in this study.¹⁰²,¹²⁶ Thus we conclude that the change of the Na/O ratio is ascribed to the formation of other species such as Na₂CO₃ and NaOH instead of or in addition to Na₂O₂·2H₂O.

To further probe the detailed composition of the product, Raman spectroscopy was performed on the air electrode without resting period and after resting period. In Figure 2.5a and b, Raman spectrum of the air electrode without resting period shows that NaO₂ is the sole product during discharge with a single peak located at 1156 cm⁻¹. Nevertheless, the one after 30 h resting period shows two additional peaks at 1080 cm⁻¹ and 1136 cm⁻¹. The signal at 1080 cm⁻¹ is from Na₂CO₃, which is probably generated from the reaction between NaO₂ and the carbon cathode. This is similar to the study in Li-O₂ cell where the defects on carbon electrode reacts with Li₂O₂ to form Na₂CO₃.¹⁰¹ Interestingly, we assemble a cell without applying any current but the signal of Na₂CO₃ is still observed, shown in Figure 2.5d, indication that Na₂CO₃ could form without the presence of NaO₂.
Figure 2.5 (a) Raman spectra (400-2000 cm\(^{-1}\)) obtained focusing the laser beam on a discharge particle in an oxygen electrode analyzed after the discharging the cell (blue) and an oxygen electrode letting rest inside the cell for 30 h after discharge (orange). (b) Detail of the previous Raman spectra (1000-1200 cm\(^{-1}\)). (c) Normalized FTIR spectra (650-3500 cm\(^{-1}\)) of the discharged electrode (blue), the discharged electrode stored in the cell for 30 h (orange), the pristine carbon electrode (black), and the Na triflate in DEGDME soaked separator (gray). (d) Raman spectra of a carbon electrode stored in the electrochemical cell for 64 h with oxygen (orange line). Spectrum of the pristine C (blue), Na\(_2\)CO\(_3\) (grey) and Na triflate (black) were also collected.
Based on previous study, Kim et al. report that the reason for the formation of Na$_2$O$_2$·2H$_2$O could be ascribed to the duration of resting between discharge and charge. However, Ortiz-Vitoriano et al. argue that they only observe Na$_2$O$_2$·2H$_2$O when NaO$_2$ is exposed to air and claim that the peak at 1136 cm$^{-1}$ which was attributed to Na$_2$O$_2$·2H$_2$O.$^{115}$ In their work, simple Na$_2$O$_2$ showed two peaks at 740 and 790 cm$^{-1}$, and the dihydrate phase showed an additional peak at 1136 cm$^{-1}$. In our work, however, none of these peaks at 740 and 790 cm$^{-1}$ were detected, suggesting that no peroxide was formed in our electrode. Consequently, the band at 1136 cm$^{-1}$ was unlikely to be Na$_2$O$_2$·2H$_2$O. Moreover, a detailed Raman study of peroxides and hydrated peroxides$^{127}$ attributed this peak to superoxide impurities, probably in a slightly different chemical environment, while suggesting just a small shift in the bands of hydrated peroxides (~800 cm$^{-1}$). These data are consistent with our results, but also point out the necessity of clarifying the chemical nature of hydrated peroxides (see also comments on the analysis of discharge products in ref$^{78}$). Finally, FTIR of the electrodes (Figure 2.5c) exposed to the cell environment for 30 h after discharge to 1.5 mA h evidenced signals at 1422 and 1589 cm$^{-1}$, which can be ascribed to the presence of Na$_2$CO$_3$.

2.3.2 Different discharge products in two cell setups
Figure 2.6 Optical images of (a) Swagelok cell sealed in a glass chamber (GC), and (b) stainless steel (SS) cell sealed by two bulk stainless steel pieces and a poly ethylene holder.

The optical images of the two different setups are shown in Figure 2.6. The glass chamber cell setup, shown in Figure 2.6a, used a Swagelok cell containing a 1/2" stainless steel rod and a 1/2" stainless steel tube tightly scrolled by the Swagelok nylon parts. The stainless steel rod served as the current collector of the metal anode, while the tube was open to the oxygen allowing gas diffusion through the air electrode. A stainless steel mesh was used as the support material and current collector for the air electrode. After the cell was assembled, it was placed in a home-made glass chamber (GC) was used as the oxygen reservoir with two adjustable valves for gas flow. Two clips wired out of the chamber serving as the electric connection to the testing machine. The top piece and the bottom
piece of the glass chamber were sealed using high vacuum grease and then tighten by a large snap ring.

The stainless steel cell setup (SS) is shown in Figure 2.6b. The bulk stainless steel base and the top piece were sealed by two O-rings on both sides of a poly ethylene holder (inner diameter: 1/2”), isolating the cell from air. The rod in the center of the stainless steel base served as the support for the sodium anode. A stainless steel mesh, the same as that in the GC cell, was used as the current collector for the cathode and a stainless steel spring washer used as a buffer to the pressure from the top piece of the SS cell. An SS oxygen reservoir was attached to the cell for oxygen storage.

The two cell setups share similarities but there are differences between the cell configurations. For the similarities, all the materials including the sodium metal, glass fiber separators, carbon paper cathodes, and the electrolytes were completely identical and prepared at the same time. For both cells, the diameter of the separator was 1/2”, and the size of the carbon electrode was 7/16” converting to the surface area of around 1 cm$^2$. The current was 0.1 mA for all galvanostatic tests, which was equivalent to a current density of 0.1 mA·cm$^{-2}$. Furthermore, the same gas supply line connected by high-pressure PVC clear tubing was applied for oxygen flow and both cells used static oxygen stored in the oxygen reservoir. In addition, for comparison, the two cells were assembled simultaneously and the electrodes were characterized after the same duration. Nevertheless, differences exist in two cells based on the different cell configurations. The GC cell used glass as the oxygen reservoir and vacuum grease for the sealing; while the SS cell used stainless steel oxygen reservoir and O-rings for the sealing material. The different sealing method might allow
air leaking into the system and result in different cell chemistries. Other parameters such as oxygen partial pressure, oxygen flow time and water content in the electrolyte were also investigated in this study but these factors were not able to change the cell chemistry (shown in the following section).

The first discharge/charge profiles of the Na-O₂ batteries based on the two cell setups are shown in Figure 2.7. The voltage window is set from 1.8 V to 4.0 V. For the GC cell (Figure 2.7a), the discharging voltage shows a steady plateau at 2.16 V; while the charge process displays three plateaus at 2.5 V, 3.4 V and 3.6 V, respectively. The high polarization upon charge indicates the formation of peroxide-based products, consistent with previous studies.\textsuperscript{112, 119-120} Nevertheless, in the SS cell, the discharge/charge profile is more reversible. The discharge voltage is 2.09 V and it is slightly lower than that in the GC cell.

\textbf{Figure 2.7} Discharge/Charge profiles of Na-O₂ cell in (a) glass chamber (GC) cell and (b) stainless steel (SS) cell. The current density is 0.1 mA·cm\textsuperscript{-2}.
cell. Moreover, the charging plateau stays at 2.31 V followed by a dramatically increase till the limiting voltage of 4.0 V. The low charging voltage shows that the decomposition of NaO₂ only contributes small polarization to the charging voltage resulted from a kinetic favorable process. The voltage increase at the end of charge implies that the depletion of the rechargeable product.

When the GC cell and SS cell were discharged for 10 h, they were disassembled and the air diffusion layers were characterized by SEM, high energy x-ray diffraction (HE-XRD) and Raman spectroscopy. For SEM measurements, the samples were protected in a Mason jar under argon atmosphere during the transfer to the chamber. Figure 2.8a shows the morphology of the discharge product in the GC cell. It shows an irregular shape with rod-like structure and unevenly disperses on the surface of carbon fibers, which is very different from the sodium peroxide dehydrate (Na₂O₂·2H₂O) reported in previous studies. In contrast, the discharge product in the SS cell displays a typical cubic structure with sharp edge (Figure 2.8b), indicating the formation of NaO₂. The size of the cube is around 7 to 10 µm. Interestingly, although the two cells use the same materials and electrolytes, the morphologies are completely different. To further identify the crystalline structure and the composition of the discharge products, He-XRD and Raman spectroscopy were carried out. For HE-XRD, the discharged air diffusion layers were sealed by Kapton tapes and were tested in transmission mode. Figure 2.8c shows the XRD patterns of the discharge product (blue curve) formed in the GC cell and the standard patterns of Na₂O₂·2H₂O (red vertical lines) from the crystal phase database (JCPDS reference card number 15-0064). The diffractions of the discharge product match well with the standard
Figure 2.8 (a) SEM images, (c) high energy XRD (HE-XRD) and (e) Raman spectra of the discharge product in GC cell. (b) SEM images, (d) high energy XRD (HE-XRD) and (f) Raman spectra of the discharge product in SS cell.
Na$_2$O$_2$·2H$_2$O and there is no superoxide detected. However, in the SS cell, the main discharge product is proved to be NaO$_2$ (Figure 2.8d) compared to the standard patterns obtained by JCPDS reference card number 01-077-0207. Raman spectrum further proves that NaO$_2$ is the major discharge product due to the unique peak from superoxide species at 1156 cm$^{-1}$ (Figure 2.8f).$^{76}$ The broad peak at 1335 cm$^{-1}$ is from the D-band of the carbon substrate.

Figure 2.8e shows the Raman spectrum of the discharged air diffusion layer in the GC cell and purchased Na triflate salt is used as the control material. From the Raman spectra, multiple peaks of sodium salt are observed due to the precipitation out of the electrolyte. Besides, we observe an additional peak at 860 cm$^{-1}$ instead of standard signals from Na$_2$O$_2$ located at 735 and 791 cm$^{-1}$. The same experiments had been repeated for multiple times and the peaks range from 860 to 864 cm$^{-1}$ were observed each time. Yang et al. and Kim et al. report that the vibration of Na$_2$O$_2$·2H$_2$O is located at 1,136 cm$^{-1}$ but the peak is not observed here.$^{115-116, 125}$ It should be noted that the formation of Na$_2$O$_2$·2H$_2$O in the previous studies were from the decomposition of NaO$_2$, while in our study Na$_2$O$_2$·2H$_2$O was directly formed at the beginning of the discharge. The different formation pathways might generate different form of the products. In addition, Sayed et al. argue that the peak at 1141 cm$^{-1}$ might come from the Na$_2$O$_2$ or the CH$_3$O and C-O groups.$^{126}$ It is likely that during the aging of NaO$_2$, it reacts with the electrolyte to form side products. The signal at 860 cm$^{-1}$ is most likely from hydrogen peroxide (H$_2$O$_2$) since Giguere et al. report that the stretch of O-O bond in H$_2$O$_2$ is located at 865 cm$^{-1}$.$^{14, 129-131}$ To further confirm the presence of peroxide in the discharge product, a titration method was
performed using the titanium oxysulfate (TiOSO$_4$) aqueous solution, which is selective to both superoxide and peroxide-based compounds.$^{97}$ The solution changed color from transparent to dark yellow when immersing the discharged air electrode (inset in Figure 2.8e). Since there is no superoxide detected in XRD and Raman for the GC cell, the color change results from the peroxide in the discharge product. Given that the detailed structure information of Na$_2$O$_2$·2H$_2$O is still missing to date,$^{132-133}$ and the Raman spectra show the presence of H$_2$O$_2$ in the discharge product, we cautiously suggest that the structure of the peroxide-based product is 2NaOH·H$_2$O$_2$ which share the same chemical formula as Na$_2$O$_2$·2H$_2$O.

![Figure 2.9](image.png)

**Figure 2.9** The in-situ XRD of the Na-O$_2$ battery tested in GC cell. From the top to the bottom, the cell first discharges and then charge. The current density is 0.1 mA·cm$^{-2}$. 

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In order to understand the structure evolution of the peroxide-based product during discharge/charge of the Na-O\textsubscript{2} battery, in-situ XRD was performed by high energy x-ray at Advanced Photon Source (APS), Argonne National Laboratory. The detailed experimental parameters are included in the experimental section. The in-situ cell has a large oxygen reservoir similar to the glass chamber and two Kapton sealed windows for the transmission of x-ray. Moreover, a coin cell replaced the Swagelok cell to minimize the cell thickness. Small holes were pre-punched in the middle of the coin cell cases, washers and sodium metal, and thus only the carbon electrode, glass fiber separator soaked with electrolyte were exposed to x-ray. The voltage profiles of the in-situ cell are shown in Figure 2.9 corresponding to the XRD patterns during the discharge/charge process. The discharge shows one plateau at 2.17 V while the charge process displays three plateaus. The red vertical lines at the top represent the standard patterns of peroxide-based product and the green lines at the bottom are the standard patterns of sodium hydroxide (NaOH, JCPDS reference card number 35-1009). At the beginning of the discharge, the diffraction of peroxide-based product is observed and no NaO\textsubscript{2} is formed, confirming that it is the only discharge product detected in XRD. With the increase of the depth of discharge, the peak intensity increases, indicating the expanding particle size of the product. For the charging process, the first plateau at \(~2.7\) V corresponds to the decomposition of the peroxide-based product, converting to a charge overpotential smaller than 0.5 V\textsuperscript{134} With the increase of the state of charge, the signals of NaOH at 38.3°, 54.0°, and 55.6° start to emerge at the end of the first plateau and keep increasing till the end of charge. At the second and the third plateaus, the decomposition of the peroxide-base discharge product continues but a
prominent signal at 48.0° is observed, which is very likely to be sodium carbonate (Na₂CO₃). The presence of additional peaks indicate that side products are formed during charge especially when the voltage exceeds 3.3 V. They might originate from the decomposition of the electrolyte. The formation of side products are probably the major obstacle for the low capacity retention of peroxide-based Na-O₂ batteries.

Table 2.1 The discharge products in the GC cell and SS cell based on multiple factors. The discharge products are confirmed by XRD and Raman.

<table>
<thead>
<tr>
<th>Products</th>
<th>GC Cell</th>
<th>SS Cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>Factors</td>
<td>O₂ Flow Time</td>
<td>Na₂O₂·2H₂O</td>
</tr>
<tr>
<td>1 min</td>
<td>Na₂O₂·2H₂O</td>
<td>NaO₂</td>
</tr>
<tr>
<td>10 min</td>
<td>Na₂O₂·2H₂O</td>
<td>NaO₂</td>
</tr>
<tr>
<td>30 min</td>
<td>Na₂O₂·2H₂O</td>
<td>NaO₂</td>
</tr>
<tr>
<td>O₂ Partial Pressure</td>
<td>Na₂O₂·2H₂O</td>
<td>NaO₂</td>
</tr>
<tr>
<td>0.5 atm</td>
<td>Na₂O₂·2H₂O</td>
<td>NaO₂</td>
</tr>
<tr>
<td>1 atm</td>
<td>Na₂O₂·2H₂O</td>
<td>NaO₂</td>
</tr>
<tr>
<td>2 atm</td>
<td>------</td>
<td>NaO₂</td>
</tr>
<tr>
<td>Water Content in Electrolyte</td>
<td>Na₂O₂·2H₂O</td>
<td>NaO₂</td>
</tr>
<tr>
<td>~20 ppm</td>
<td>Na₂O₂·2H₂O</td>
<td>NaO₂</td>
</tr>
<tr>
<td>~300 ppm</td>
<td>Na₂O₂·2H₂O</td>
<td>NaO₂</td>
</tr>
<tr>
<td>~4000 ppm</td>
<td>Na₂O₂·2H₂O</td>
<td>NaO₂</td>
</tr>
</tbody>
</table>

The comparisons of the two cell configurations such as oxygen flow time, oxygen partial pressure, and water content in electrolyte are investigated, shown in Table 2.1 (the XRD and Raman data are not listed here). However, those factors are not the major reasons
for the formation of different discharge products. Pinedo et al. have considered multiple factors such as current density, size effect, oxygen pressure and gas moisture, and discovered that gas moisture is the key issue for the formation of Na$_2$O$_2$·2H$_2$O, which was probably from the gas/water leaking.\textsuperscript{135} Ortiz-Vitoriano et al. discovered that even the water content is as high as 6000 ppm, NaO$_2$ is still the major discharge product except exposing NaO$_2$ to air.\textsuperscript{110, 115} It is very unlikely that the GC cell has a huge amount of water (>> 6000 ppm) from the air before discharge since the peroxide-based product is observed at the beginning of the discharge. Nevertheless, the formation of peroxide-based product requires water either from the air atmosphere or the decomposition of the solvent. In our study, the vacuum grease sealed glass chamber might cause a significant issue for air leaking. The impurities from air could contribute to the formation of peroxide-based product but the mechanism is not clear at this stage. More experiments and calculations are required in the future work.

2.4 Conclusion

In this work, the evolution in the cell environment of the superoxide formed in the ORR has been analyzed. NaO$_2$ is unstable in the cell environment and Na/O ratio of the cubes formed during discharge is decreased, proving that chemical reactions occurred. In addition, the gas pressure of the cell is increased during these resting periods and coupled to the Na/O ratio decrease, it can be deduced that oxygen is being released from these NaO$_2$ cubes. This instability leads to the reduction of both the Coulombic efficiency and the battery life.
We apply two cell setups in Na-O$_2$ cells and different discharge products are obtained. In the GC cell the discharge product is peroxide-based product while in the SS cell it is superoxide-based product, which are confirmed by HE-XRD and Raman spectroscopy. In-situ XRD for the GC cell shows that the single plateau during the discharge is only related to the formation of peroxide-based product, while the three charge plateaus correspond to the decomposition of the peroxide-based product (2.7 V) and side reactions (> 3.3 V). Our results reveal that the environment for the formation of NaO$_2$ is critical and even a small portion of air leaking might lead to a completely different discharge product. This work could help to guide for the future application of superoxide based Na-O$_2$ batteries especially for large scale application.
Chapter 3: Investigating the Factors for the Low Cycle Life of Sodium Oxygen Batteries

3.1 Introduction

Sodium superoxide based sodium oxygen batteries not only possess high theoretical energy density but also have benefits of high energy efficiency that can be attributed to the fast kinetics of the cell reaction. Despite the promising round-trip efficiency gained from the lower charging potential, the development of Na-O\textsubscript{2} batteries was greatly hindered by the poor cycle life which was ascribed to dendrite formation, instability of electrolytes and by-product formation.

Inspired by the complex by-product formation reactions at the cathode side of Li-O\textsubscript{2} batteries,\textsuperscript{9,44,57,59} most of the research studies have been focused on the characterization of cathodes, e.g., effects of cathode morphology and by-products on cyclability. Hartmann and Bender et al. observed that the conducting salt decomposed to sodium fluoride and sodium sulfite on the carbon fiber cathode in Na-O\textsubscript{2} batteries.\textsuperscript{97,123} Zhao et al. detected sodium hydroxide and sodium carbonate as decomposition products on vertically aligned carbon nanotubes.\textsuperscript{124} However, McCloskey et al. pointed out that the cleaner cathode reactions in Na-O\textsubscript{2} compared to Li-O\textsubscript{2} were less concerned and the low cycle life was perhaps caused by the Na anode.\textsuperscript{136} The possible contribution to the cyclability from the Na anode has rarely been reported in Na batteries.\textsuperscript{137-139} It is well known that the lithium
dendrite is a safety concern in lithium ion batteries but with complicated effects of an oxygen rich environment, there has been no report on the dendrite formation in Li-O\(_2\) and K-O\(_2\) batteries\(^{77,99}\) Hartmann et al. observed growth of dendrites into the polymer separator, which had a detrimental effect on the Na-O\(_2\) battery. By replacing the polymer separator with a solid-state electrolyte (sodium-beta-alumina) dendrite penetration was suppressed; however, the battery performance was not shown in their work and the effect of dendrite formation was not clearly understood\(^{97}\). On the other hand, the reaction of a metal anode with the electrolyte was not fully investigated. Although a stable solid electrolyte interface (SEI) layer could be formed on the surface of a Li-ion battery anode, it was recently reported that in Li-O\(_2\) batteries, more complicated reactions could occur on the Li anode in the presence of O\(_2\) crossing from the air cathode\(^{89}\).

In this study, sodium dendrite formation was found to be the major issue for the premature death of in sodium oxygen batteries. To solve the dendrite penetration problem, ion selective polymer membrane was considered as a good candidate of separator to prevent dendrite penetration.

\[
\begin{align*}
\text{OCF}_2\text{CFOCF}_2\text{CF}_2\bigg|_{x} & \text{SO}_3\text{H} \\
\text{CF}_3 & \bigg| \\
\text{CF}_2\text{CF}_2 & \bigg(\text{CF}_2\text{CF}_2\bigg)_n
\end{align*}
\]

**Figure 3.1** The chemical formula of Nafion film.
Nafion was first invented by Walther Grot of DuPont in 1960s by a copolymerization of tetrafluoroethylene (TFE) (the monomer in Teflon) and a derivative of a perfluoro (alkyl vinyl ether) with sulfonyl acid fluoride. The chemical formula of Nafion is shown in Figure 3.1. It consists of fluoroethylene polymer backbones with perfluovinyl ether groups terminated by sulfonate groups. Since Nafion was synthesized from Teflon, it has some similar properties to Teflon such as high mechanical strength, thermal and chemical stabilities. Besides, good ionic conductivity and ion selectivity are the outstanding properties of Nafion, which have attracted a considerable amount of research interests in fuel cells, electrochemical devices, water electrolysis plating, etc.

**Figure 3.2** The cluster network model of Nafion.

The cluster network model of Nafion is shown in Figure 3.2. In Nafion membrane, the sulfonate groups linked with fluoroethylene backbones are evenly distributed in 40 Å diameter ion channels. The size of the channels between clusters is around 10 Å. Before
water uptake, protons could not move in the network due to the electrostatic effect with negative charged sulfonate groups. Once Nafion soaks in water, protons are solvated by water molecules, which provide the diffusion pathway and enable the proton conduction. In addition, the negative charged network only allows cations passing through resulting in good ion selectivity. Due to the electrostatic effect between cations and negative charged sulfonate groups, the ion diffusion mechanism for proton in Nafion can also be applied to other cations such as lithium ion, sodium ion and potassium ion.

Nafion membrane with high mechanical strength, high ionic conductivity and high ion selectivity is promising to be used for alkali metal protection. Cao et al. fabricated a sodium ion exchange polymeric membrane with high ionic conductivity. The membrane with good mechanical strength avoided dendrite penetration from anode to cathode, increasing the battery cycle life. In our study, sodium dendrite formation was found to be a serious issue in Na-O₂ batteries. A thin layer of sodium ion selective Nafion membrane can be used to prevent dendrite penetration without introducing high internal resistance of the battery.

Here we show that dendrite formation in Na-O₂ batteries is the primary reason for the failure of batteries while the reaction of the Na anode with the electrolyte in the presence of O₂ plays a vital role in the decline in cycling performance. To address the dendrite issue, the first use of a sodium ion selective polymer membrane incorporated as part of a separator into a Na-O₂ battery is reported in this work. Using a geometric current density of 0.16 mA·cm⁻², cycling lives of 110 cycles in 1,2-dimethoxyethane (DME) and 90 cycles in diglycol methyl ether (diglyme) were achieved. Additionally, the by-products
were investigated in both electrodes. Since the Nafion-Na\(^+\) membrane selectively blocks the diffusion of anions through the batteries, it helped distinguish the anode side reactions from the cathode ones, which proved that the decomposition occurred mostly in the Na anode instead of the cathode. These results highlight the significance of solving anode issues in sodium–oxygen batteries and potentially pave the way for further improving the performance and cyclability of the batteries.

3.2 Experimental Section

A sodium metal slice (Fisher Scientific, labgrade) was used as the metal anode and P50 (AvCarb\(^\circledR\)) was used as the air electrode in the Na-O\(_2\) battery. The electrolytes were 1,2-dimethoxyethane (DME, Novolyte Tech.) or bis (2-methoxyethyl) ether (diglyme, Sigma-Aldrich, 99.5%) containing 0.5 M sodium trifluoromethanesulfonate (sodium triflate, Sigma-Aldrich, 98%) conducting salt. Both solvents and oxygen gas (99.993%, UHP) were dried with 3 Å molecular sieves (Sigma-Aldrich) before use.

Purchased Nafion\(^\circledR\) 211 membranes (25\(\mu\)m, DuPont) were stirred in a solution of 1 M NaOH in dimethyl sulfoxide (DMSO) (>99.9%, Sigma-Aldrich) and water with 1:1 volume ratio at 65 °C for 2 h to convert protons to sodium ions. Then the Nafion-Na\(^+\) membranes were washed by stirring in distilled water at 90 °C for 2 h. The residual water in the membrane was removed by evacuating in a vacuum oven at 100 °C for 20 h. After pretreatment, dry Nafion-Na\(^+\) membranes were transferred into a glove box and stored under high purity Argon for future use. Before characterizations and battery tests, Nafion-Na\(^+\) membranes were immersed in electrolytes for 48 h. A sodium oxygen battery was
assembled in stainless steel cell setup by packing the sodium slice, separators, P50 gas diffusion layer, a stainless steel mesh and a washer together.

In the sodium oxygen batteries with Nafion-\( \text{Na}^+ \) membranes, the thickness of separators was well controlled. Without Nafion-Na\(^+\) membranes, one piece of glass fiber (Whatman, 600 um thickness) was used as the separator soaked with saturated electrolytes (0.5 M sodium triflate in DME or diglyme). Nafion-Na\(^+\) membrane was sandwiched by two pieces of glass fibers (Whatman, 300 um thickness, 600 um thickness in total). Symmetric cells were assembled by packing a sodium slice, glass fiber separator and another sodium slice in the same cell setup. The electrolyte was 0.5 M sodium triflate in DME. All the cells were assembled in the glove box under high purity Argon and stayed for 2 h to reach equilibrium before tests.

X-ray diffraction (XRD) was performed by a Bruker d8 advance X-ray powder diffractometer on flat plate mode. An airtight sample holder made by Poly (methyl methacrylate) (PMMA) was used to isolate the sample from the air. After placing the sample in the holder, the PMMA holder was sealed by a water barrier film (Scotchpak HB-P, 3M) by a hot heating iron.

Nuclear magnetic resonance (NMR) spectroscopy was used to investigate the electrolyte decomposition products in sodium oxygen batteries. The separator samples with electrolyte were put in D\(_2\)O solvent (99.9\%, Sigma-Aldrich). After dissolving in D\(_2\)O solvent, the electrolyte sample was transferred to an NMR test tube and \(^1\text{H}\)-NMR and \(^19\text{F}\)-NMR spectra were tested by a 400 MHz NMR spectrometer (Bruker, Avance III).
The battery products and surface layer components on both electrodes were characterized by Raman spectrometer (inVia, Renishaw) with an excitation wavelength of 633 nm (laser power 6 mW). An airtight sample holder was used, which is made by aluminum base with a quartz window. Two O-rings were used to seal it.

The Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) mappings were performed by a FEI/Philips Sirion Field Emission SEM. The samples were placed on an aluminum holder. When transferring the air sensitive sample, a glove bag was used to seal the small SEM chamber and filled with high purity Argon.

An airtight chamber module was used in X-ray photoelectron spectroscopy (XPS) tests by a Kratos Axis Ultra XPS spectrometer. The XPS spectra were collected using monochromatic Al Kα radiation. In XPS analysis, all spectra were calibrated by referencing the binding energy of carbon-carbon bond at 284.8 eV.

Ionic conductivity of Nafion-Na⁺ membrane was determined by a two-electrode AC impedance method using an EIS600 potentiostat. The frequency range was set from $10^6$ Hz to 1 Hz at 21 °C (room temperature). Before every test, the Nafion-Na⁺ membrane was sandwiched by two blocking electrodes made by platinum coated conductive fluorine-doped tin oxide (Pt-FTO) glass. FTO conductive glass was washed with soap water, water, ethanol, acetone and water by ultrasonicating for 5 min each and dried in the heating oven at 100 °C for 10 min. 50 uL 5 mM H₂PtCl₆ isopropanol solution was slowly dropped to the surface of FTO conductive glass and dried at 21 °C for 1 h. FTO was heated from room temperature to 385 °C at a rate of 5 °C/min and stayed at 385 °C for 15 min. DC bias was 0 V vs. open circuit potential and the AC amplitude was 10 mV. EIS data were fitted by
Gamry Echem Analyst software. The ionic conductivity of electrolyte in glass fiber was tested by the same method. One piece of glass fiber was immersed in electrolyte for 5 min and then sandwiched by the blocking electrodes. Filter paper was used to remove the extra electrolyte.

Before every battery performance test, oxygen gas was flowed into the sodium oxygen battery and stored in the small oxygen reservoir. 2 mL DME solvent was added to the reservoir to avoid the battery degradation by depletion of electrolyte. The battery performance tests were performed by a Maccor testing station (model: 4304). The testing voltage window was 1.6 V-3.4 V (vs. Na⁺/Na) and the current density was set to 0.16 mA·cm⁻² based on the area of 0.64 cm². Six-hour discharge was set in the battery performance tests.

3.3 Results and Discussions

3.3.1 Dendrite issue in Na-O₂ batteries

The rechargeable Na-O₂ batteries have received great research interests recently due to high round-trip efficiency and large theoretical energy density. However, the low cycling life and the low practical capacity suggest that they are remaining far from the practical applications. In Na-O₂ batteries, electrolytes play a significant role providing the stable environment for ion diffusion. However, all the batteries suffer from the problem of electrolyte decomposition to date. In lithium ion batteries, people spent decades to seek stable electrolytes. The electrolyte using LiPF₆ in carbonate-based solvent guarantees the continuous and durable operations in lithium ion batteries. However, the carbonate-based solvents were not applicable to metal oxygen batteries. Peter G. Bruce group⁵⁷ investigated
the decomposition of carbonate-based electrolyte in Li-O₂ batteries. They reported that during discharge of the battery, superoxide species reduced from oxygen would attack the polyethylene carbonate and the products were dominated by Li₂CO₃ accompanied with Li propyl dicarbonate, Li formate, Li acetate, H₂O and CO₂. The products can be partially charged back and evolve CO₂ during the charging process. Similar to Li-O₂ batteries, superoxide would attack carbonate-based electrolytes in Na-O₂ batteries to form Na₂CO₃ instead of the ideal product, NaO₂.⁷⁶ Therefore, seeking a stable solvent is the priority in metal oxygen batteries.

Ether solvents have been widely investigated in metal-oxygen batteries⁷⁷, ⁸⁰, ⁱ⁴⁴ since they are relatively stable compared to other non-aqueous solvents and produce favorable metal oxides products. Although ether solvents can still be attacked by superoxide species, more stable electrochemical environment was provided compared to carbonate solvents.

### Table 3.1 Diffusion coefficients Calculated from oxygen uptake experiments.¹¹⁴

<table>
<thead>
<tr>
<th>Solvent/electrolyte</th>
<th>Do₂/10⁻⁵ cm²/s</th>
<th>Ho₂/mol/(m³ bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DME</td>
<td>6.0±0.5</td>
<td>10.1±0.3</td>
</tr>
<tr>
<td>Diglyme</td>
<td>4.4±0.3</td>
<td>6.4±0.2</td>
</tr>
<tr>
<td>0.5 M NaTfO/diglyme</td>
<td>3.9±0.3</td>
<td>6.3±0.2</td>
</tr>
<tr>
<td>Triglyme</td>
<td>3.2±0.3</td>
<td>5.6±0.3</td>
</tr>
<tr>
<td>Tetraglyme</td>
<td>2.6±0.3</td>
<td>4.3±0.2</td>
</tr>
<tr>
<td>DMAc</td>
<td>4.3±0.3</td>
<td>5.4±0.3</td>
</tr>
</tbody>
</table>

DME and diglyme were selected as the two ether solvents utilized containing 0.5 M sodium triflate due to the higher reported stabilities compared to other non-aqueous
solvents in metal air batteries. This is because DME and diglyme have higher oxygen solubility and oxygen diffusion coefficients than other commonly used ethers such as triglyme and tetraglyme, as shown in table 3.1. The selection of solvents is to minimize the interference of the testing results from the air electrodes, namely oxygen diffusion, electrolyte decomposition, and pore blocking. These characteristics of DME and diglyme not only improve oxygen diffusion in the air diffusion layer but also facilitate the formation of sodium superoxide.

The sodium oxygen battery was assembled by packing sodium metal foil, glass fiber separator and P50 carbon paper in a Swagelok cell. One stainless steel mesh and a washer were placed on the air cathode as current collector and the buffer to the pressure from the cell setup. To avoid blocking of air diffusion by the discharge product in the porous carbon electrode, shallow discharging conditions (0.16 mA·cm⁻² for 6 hours) were used. Before every test, the battery was allowed to rest for 2 h to reach equilibrium.

Figure 3.3 Discharge/charge profiles of Na-O₂ batteries in 0.5 M Na triflate in (a) DME and (b) diglyme electrolytes.
In Figure 3.3, DME based and diglyme based electrolytes show similar discharge and charge profiles. The equilibrium reaction voltage is 2.27 V in Na-O\textsubscript{2} batteries based on the reaction: \( \text{Na} + \text{O}_2 \leftrightarrow \text{NaO}_2 \). In DME based electrolyte, the discharging voltage starts with 2.2 V and then decreases to 1.9 V at the end of the discharge timeframe; while in diglyme the discharging voltage is relatively stable with minor decrease from 2.1 V-2.0 V. The decreasing voltage indicates the combination effects from both NaO\textsubscript{2} formation in the cathode and the sodium surface changes in the Na anode. Upon discharge, the accumulation of NaO\textsubscript{2} passivates the carbon surface and increases the resistance of the cathode, resulting in the increasing overpotential. Moreover, the morphology change of the Na anode surface contributes to the increase of the discharge overpotential. On the other hand, the reactions between Na metal, oxygen and electrolyte form SEI layer on the Na surface. The ionic resistance of SEI layer contributes the discharging overpotential voltage. Upon charge, in both electrolytes the charging voltages are around 2.4 V with a dramatically increase at the end of charging process, indicating the fully decomposition of the discharge product. In previous studies, most works observed Na\textsubscript{2}O\textsubscript{2} as the major discharge product\textsuperscript{112, 119-120}. The low electronic conductivity of Na\textsubscript{2}O\textsubscript{2} contributes a large charging voltage in sodium oxygen batteries, which is similar to Li-O\textsubscript{2}. Therefore, in our sodium oxygen battery, the low charging voltage shows that the decomposition of NaO\textsubscript{2} only contributes small polarization to the charging voltage indicating the high electronic conductivity of NaO\textsubscript{2}. 
Products in the Na-O\textsubscript{2} battery with DME based electrolyte were characterized by X-ray diffraction (XRD) and Raman spectroscopy (Figure 3.4). The samples for XRD were the air diffusion layer in the cathode prepared by discharging the batteries for 2 h, 4 h, 6 h and 20 h respectively. The sample for Raman spectroscopy is the carbon cathode with discharge time of 30 h. P50 was rinsed by DME solvent for 5 min by 3 times and dried in a vacuum oven to remove extra solvents. In XRD tests, the airtight sample holder made by PMMA has a broad peak at 25°, so the region under 30° was cut off. In Figure 3.4a, the diffraction peak at 56° is related to the P50 carbon paper substrate. The peaks at 33°, 47°, 54° and 58° are the (200), (220), (311) and (222) planes from NaO\textsubscript{2}, separately. There are no side products detected by XRD. Raman spectra further prove that NaO\textsubscript{2} is the major discharge product due to the unique peak from superoxide species at 1156 cm\textsuperscript{-1} which is consistent with the literature\textsuperscript{76} with diglyme-based electrolyte. In conclusion, we prove that
DME and diglyme-based electrolytes provide similar discharge/charge profiles in Na-O₂ batteries. NaO₂ is found to be the major discharge product in the sodium oxygen battery.

**Figure 3.5** Discharge/charge profiles of Na-O₂ batteries for the last two cycles in (a) DME and (b) diglyme. The insert images are the glass fiber separators facing the sodium electrode. Dashed lines are the equilibrium potentials of sodium oxygen batteries with superoxide as the product.

In our study, dendrite penetration in Na-O₂ batteries has been found to be the primary issue causing the premature death of batteries. In ether-based electrolytes, the shorting of the batteries was displayed within few cycles. The discharge/charge profiles of 11ʰ and 12ʰ cycles in DME based electrolyte are shown in Figure 3.5a. The 11ʰ cycle is characterized by a smooth discharge curve around 2.2 V with a charging voltage close to 2.4 V. The small voltage gap between discharge and charge indicates the reversible one electron reaction process to form NaO₂ (Na + O₂ ↔ NaO₂), as discussed above. In diglyme
(Figure 3.5b), the same scenario is observed in the 6th cycle. However, after the 11th cycle in DME (after the 6 cycle in diglyme), voltage fluctuations during the charging process are observed which are then followed by a charging voltage around 2.4 V that never reaches the cut-off voltage (3.4 V) within the preset charging timeframe. Based on the battery tests, cycle life in DME and diglyme based electrolytes fluctuate from 6 to 12 cycles. The discrepancy is likely due to different dendrite growth rates on varying sodium surfaces in each cell or on different mechanical compressions. The results indicate that dendrite formation is selective by different solvents. After disassembly inside a glove box, spots were observed at the surface of glass fiber facing the metal anode (insert in Figure 3.5a). These observations are similar to Hartmann’s results showing that dendrite formation causes the premature death of Na-O2 batteries.

During the last charging process, abrupt voltage drops suggest that both batteries were short-circuited. After the transient short circuit, the voltage recovered to the previous values, which were followed by subsequent voltage drops. Upon charge, NaO2 is oxidized into oxygen and sodium ions that subsequently deposit on the Na anode. The uneven deposition of sodium metal induces metal dendrite growth which penetrates the porous glass fiber separator ultimately contacting the air electrode. After the short is established, the large current flowing through dendrite would generate heat sufficient to melt the sodium dendrite cutting off its contact to the air electrode, which will restore the battery to its previous working potential. Furthermore, Na dendrites reaching the air electrode could induce reactions with oxygen to form by-products in the cathode.
Figure 3.6 The discharge/charge profiles of the cell with DME based electrolyte after short circuit and after changing the separator.

To further prove that Na dendrites penetrate the separator resulting in the short circuit, the glass fiber separator was replaced after encountering the shorting problem. Figure 3.6 shows the voltage profiles of the sodium oxygen battery with DME based electrolyte. In order to observe the effect of dendrite growth, previous 9 cycles were omitted and only the shot-circuit region was selected. The battery runs 11 cycles followed by voltage fluctuations occurred in the following charging process, which is consistent with the charge profiles in Figure 3.5. After 182 h’s testing, the battery was disassembled and the glass fiber separator was replaced by a new piece. The target of changing separator is to remove the sodium dendrite formed in the separator in order to recover the battery. As can be seen, after replacing the separator the battery was discharged for 6 h, and during the next charging process from 190 h to 196 h, the charging curve maintains smooth.
the recovery. The battery was further charged to 3.4 V to compensate the NaO₂ generated during 178 h and 182 h. The following charging process shows that the battery no longer suffers the shorting problem. The results prove that dendrite penetration induces the voltage fluctuations during the charging process and causes the premature death of the sodium oxygen battery.

**Figure 3.7** SEM and EDS mapping images of (a-c) the top-view and (d-f) the cross-section of the glass fiber separator after 6 cycles.

SEM images show the morphology of sodium dendrite in the glass fiber separator. Figure 3.7a shows the top-view of glass fibers (faced to the air electrode) on which a thin layer of glass fibers was peeled off in order to catch sight of the tip of Na dendrite. The morphology of sodium dendrite in Na-O₂ batteries is very different compared to the needle-like structure of lithium dendrite in lithium ion batteries. The large diameter of sodium
dendrite is probably caused by oxygen crossover by passivating the sodium surface instead of forming needle-like structure. EDS mappings show distributions of sodium and silicon elements. The dense distribution of sodium element represents the sodium dendrite or the SEI layer on the dendrite. The silicon element is from the glass fibers, Na$_2$SiO$_3$, which also contains sodium, so there are small amount of sodium signals obtained on the surface of glass fibers. In Figure 3.7b, the major sodium area can be assigned to the sodium dendrite. Moreover, the large area at the right bottom side of sodium under the glass fibers was also observed standing for the root of the dendrite tip. For the rest of the area in the image, the evenly distributed sodium is related to the glass fiber separator. In Figure 3.7c, the signals of silicon element are from glass fibers. In the middle region of the image, the missing silicon signals can be assigned to the sodium dendrite but little amount of silicon signal can still be observed, which indicates that the glass fibers are cross-linked inside of the dendrite. Figure 3.7d-f shows the cross-section of the glass fiber separator. The topside of the separator in the image was attaching to the anode and the bottom side was facing to the cathode. The thickness of the separator is around 600 um which is consistent with the reported thickness from Whatman. From Figure 3.7d, the structure of glass fibers changes from a layered structure to a porous structure with the metal growth, and the sodium metal almost reaches the other side of the separator. From our previous data, the cycle lives of Na-O$_2$ batteries fluctuate from 6 to 12 cycles. In this battery, after 6 cycles, the sodium metal grows more than 80% of the thickness of the separator predicting short-circuit in few cycles. Figure 3.7e and f show the distributions of sodium and silicon proving the dendrite
penetration situation of the battery. The results clearly show that sodium metal grows inside and penetrates the glass fibers inducing the shorting of Na-O$_2$ batteries.

![Figure 3.8](image)

**Figure 3.8** Na/Na sodium symmetric cells under argon (a) and under oxygen (b). (c) and (d) are the amplified images in (b).

To investigate the effects of oxygen on the cycle life of the battery, two symmetric cells were assembled by packing sodium metals, glass fiber separators and sodium metals in Swagelok cells. The current was set to 0.16 mA cm$^{-2}$ and the reduction/oxidation time was set to 1 h. In Figure 3.8a, the Na/Na symmetric cell under argon was short-circuited after 30 cycles. The voltage of the cell decreases from 0.03 V to 0.005 V followed by...
voltage fluctuations indicating that the sodium metal have penetrated through the glass fiber separator. The low voltages generated after the shorting is related to the series resistance in the cell. In contrast, the cell in the oxygen environment runs 195 cycles after which the voltage drops from 0.8 V to 0.005 V. The amplified image after the shorting is shown in Figure 3.8d. By comparison, cell under oxygen generates larger polarizations than the cell under argon which could be assigned to the effect of oxygen on Na. The presence of oxygen induces the reactions between sodium metal and electrolyte, which will be discussed in the next chapter, creating low ionic conduction of the more complicated SEI composition. In addition, in Figure 3.8c (the amplified image of the first rectangle from Figure 3.8b) the reduction/oxidation voltages have two plateaus with a difference of 0.2 V, which is probably from the combination effects on the dendrite and Na SEI layer.

3.3.2 Enhanced cycle life by Nafion-Na$^+$ membranes

Nafion, with its good ion selectivity, high mechanical and chemical stability has been widely applied in fuel cells, sensors, chemical productions etc. Nafion membranes in lithium ion and sodium ion batteries have demonstrated good chemical stability and providing high cycling lives$^{143}$. In our study, the inclusion of the Nafion-Na$^+$ membrane serves to inhibit dendrite penetration through the porous separator. The good mechanical strength of Nafion membranes is postulated to prevent dendrite penetration to the air electrode. Moreover, good thermal and electrochemical stability may prevent side reactions in an oxygen rich environment. The ionic conductivity of the Nafion-Na$^+$ membrane presents an important parameter in battery efficiency since it introduces Ohmic loss thereby increasing the overpotential in discharge/charge.
The Nafion-Na⁺ membrane was made by changing the proton in purchased Nafion-H⁺ membrane in 1 M NaOH DMSO:H₂O (volume ratio=1:1) solutions. After protons were exchanged to sodium ions, the membrane was washed by distilled water and dried in the vacuum oven overnight. Before ionic conductivity tests, Nafion-Na⁺ membranes were stored in the glove box and immersed in the electrolyte for two days. In the testing device, platinum coated FTO conductive glass was used as the current collector and sandwiched one piece of Nafion-Na⁺ membrane in between.
Ionic conductivity was determined by a two-electrode Electrochemical Impedance Spectroscopy (EIS) method. A simplified equivalent circuit\textsuperscript{145} and EIS data are shown in Figure 3.9. In the testing device, the Pt-FTO electrode was used as a blocking electrode/membrane interface with no faradic current flow, so the charge transfer resistance of the electrode/membrane interface was eliminated resulting in a simplified circuit. A constant-phase element (CPE\textsubscript{2}) was used to model the capacitance of the two interfaces, shown in Figure 3.9a. The ionic resistance and capacitance of the membrane are represented by a parallel combination of an RC circuit (R\textsubscript{1} and CPE\textsubscript{1}). R\textsubscript{0} represents the series resistance of the device that is assigned to the sheet resistance of the Pt-FTO layers and the circuit contacts. From the Nyquist plot (Figure 3.9b), the intersection point at $Z_{\text{real}}$ axis gives the value of R\textsubscript{0}. The semicircle at high frequencies corresponds to the ionic resistance (R\textsubscript{1}) and capacitance (CPE\textsubscript{1}) of the Nafion-Na\textsuperscript{+} membrane. At low frequencies, a straight curve with an angle of 82° is observed, which indicates that Nafion-Na\textsuperscript{+} membrane has an infinite capacitor behavior other than diffusion behavior with an angle of 45°. Therefore, the region of low frequencies can be assigned to the non-ideal capacitance (CPE\textsubscript{2}) of two Pt-FTO/membrane interfaces. R\textsubscript{1} is the ionic resistance of membrane and is used to calculate the ionic conductivity. Detailed calculations and the values of ionic conductivities are listed below and are in Table 3.2.

The equation for ionic conductivity calculation is shown as follows:

$$\sigma = \frac{L}{R \cdot A} \quad (3.1)$$

where $\sigma$ is the ionic conductivity, $R$ is the AC resistance, $L$ is the thickness and $A$ is the area of Nafion-Na\textsuperscript{+} membrane.
Table 3.2 Measurements of ionic conductivity of Nafion-Na\(^+\) membrane.

<table>
<thead>
<tr>
<th>Samples (#)</th>
<th>R (Ω)</th>
<th>A (cm(^2))</th>
<th>L (cm)</th>
<th>σ (S·cm(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>242.1</td>
<td>0.42</td>
<td>2.5e-3</td>
<td>2.46e-5</td>
</tr>
<tr>
<td>2</td>
<td>65.32</td>
<td>1.54</td>
<td>2.5e-3</td>
<td>2.49e-5</td>
</tr>
<tr>
<td>3</td>
<td>66.49</td>
<td>1.54</td>
<td>2.5e-3</td>
<td>2.44e-5</td>
</tr>
<tr>
<td>4</td>
<td>381.5</td>
<td>0.27</td>
<td>2.5e-3</td>
<td>2.43e-5</td>
</tr>
</tbody>
</table>

Four trials have been performed in the conductivity tests. Before every test, Nafion-Na\(^+\) membranes have been soaked in 0.5 M Na triflate in DME electrolyte and stored in the glove box for two days. All four tests are measured at room temperature (21 °C). As can be seen in the Table 3.2, the results are repeatable and consistent based on the different sizes of membranes. The average ionic conductivity of Nafion-Na\(^+\) is calculated to be 2.46e-5 S·cm\(^{-1}\).

Figure 3.10 SEM images of (a) Nafion-Na\(^+\) membrane and (b) glass fibers.
The morphologies of Nafion-Na\(^+\) membrane and glass fibers are compared in Figure 3.10. In Figure 3.10b, the diameter of glass fibers ranges from 200 nm to 2 \(\mu\)m, which generates large and unevenly distributed pores. Na metal could choose the loose packed region and grow in the pores. Compared to the loose structure of glass fibers, Nafion-Na\(^+\) membrane has more uniform surface and more dense structure which could prevent dendrite formation. Additionally, the tetrafluoroethylene backbone is very rigid.

![Nyquist plots and fitting data of Nafion-Na\(^+\) membrane and glass fibers.](image)

**Figure 3.11** Nyquist plots and fitting data of Nafion-Na\(^+\) membrane and glass fibers.

As a comparison, the ionic conductivity of the electrolyte within the glass fiber separator was measured. The Nyquist plots and fitting data are shown in Figure 3.11. At
high frequencies, the small semicircle indicates the smaller ionic resistance of glass fibers due to the large pores that could facilitate the sodium ion diffusion. Similar to the Nafion-Na\textsuperscript{+} membrane, at low frequencies the large angle curve represents the capacitance behavior of the two electrode/membrane interfaces. As shown in Table 3.3, the average value of electrolyte in glass fibers is calculated to be 4.62e-4 S cm\textsuperscript{-1} based on two trials.

**Table 3.3** Measurements of ionic conductivity of electrolyte in glass fibers.

<table>
<thead>
<tr>
<th>Samples (#)</th>
<th>R (Ω)</th>
<th>Λ (cm\textsuperscript{2})</th>
<th>L (cm)</th>
<th>σ (S/cm)</th>
</tr>
</thead>
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<tr>
<td>1</td>
<td>32.89</td>
<td>1.33</td>
<td>4.0e-2</td>
<td>4.58e-4</td>
</tr>
<tr>
<td>2</td>
<td>32.40</td>
<td>1.33</td>
<td>4.0e-2</td>
<td>4.65e-4</td>
</tr>
</tbody>
</table>

**Table 3.4** Calculated ohmic loss from Nafion-Na\textsuperscript{+} membrane and glass fibers.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Average σ (S/cm)</th>
<th>Λ (cm\textsuperscript{2})</th>
<th>L (cm)</th>
<th>R (Ω)</th>
<th>I (mA cm\textsuperscript{-2})</th>
<th>Ohmic loss (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion-Na\textsuperscript{+}</td>
<td>2.46e-5</td>
<td>0.636</td>
<td>2.50e-3</td>
<td>1.60e2</td>
<td>0.100</td>
<td>16.0</td>
</tr>
<tr>
<td>Glass Fibers</td>
<td>4.62e-4</td>
<td>0.636</td>
<td>4.00e-2</td>
<td>1.35e2</td>
<td>0.100</td>
<td>13.5</td>
</tr>
</tbody>
</table>
In Na-O₂ batteries, resistances generated from separators are important to the Ohmic loss, which greatly affects the battery performance. Therefore, the influence of separator on the resistance is discussed below. In a Na-O₂ battery, without Nafion-Na⁺ membrane the thickness of glass fiber separator was measured as 400 um in the Swagelok cell under the mechanical pressure. This thickness is maintained in the testing device by adding a 400 um polyethylene spacer around the glass fiber separator. Thus, in all calculations, 400 um were used as the thickness of the separator. The Ohmic losses from Nafion-Na⁺ and glass fibers are 16.0 mV and 13.5 mV, respectively (Table 3.4). The total Ohmic loss from the separator/membrane is calculated from the sum of the individual losses and is approximately 30 mV. Although this number is relatively low at 0.16 mA·cm⁻²...

Figure 3.12 The discharge/charge profiles of the first cycle of battery in DME based electrolyte.
current density compared to 200 mV total overpotential, it cannot be neglected under higher current densities. The comparison of the discharge/charge profiles of Na-O$_2$ batteries with and without Nafion-Na$^+$ membrane is shown in Figure 3.12. The slightly increase overpotential during discharging and charging processed can be assigned to the Ohmic loss from Nafion-Na$^+$ membrane. As the increase of the current, larger overpotential will be obtained. Therefore, developing new membranes with high ionic conductivity will be essential to reduce the Ohmic loss from the separators.

Figure 3.13 (a) Discharge/charge profiles and (b) Coulombic efficiency with Nafion-Na$^+$
membrane in DME. Insert is the glass fiber separator in air electrode faced towards the Nafion membrane. (c) Discharge/charge profiles and (d) Coulombic efficiency with Nafion-Na$^+$ membrane in diglyme. The voltage window is 1.6-3.4 V with current density of 0.16 mA·cm$^{-2}$.

As described above, the thickness of glass fiber separator changes from 600 um to 400 um after packing in Na-O$_2$ Swagelok cell. After adding Nafion-Na$^+$ membrane (25 um) in two pieces of glass fiber separators (300 um), the total thickness of separator is around 425 um. Therefore, the 25 um difference after adding Nafion-Na$^+$ membrane barely changes the physical distance between anode and cathode, avoiding introducing more errors to the system.

The addition of Nafion-Na$^+$ membranes greatly improves the cyclability of Na-O$_2$ batteries in both DME and diglyme based electrolytes as shown in Figure 3.13. Prior to assembly, the membrane was soaked in electrolyte for two days. Discharge/charge profiles of 1$^{st}$, 50$^{th}$, 118$^{th}$ cycles in DME based electrolyte are shown in Figure 3.13a. The first discharge and charge voltages are around 2.0 V and 2.4 V, respectively. The discharge/charge voltages are very reproducible for the first 80 cycles, after which the charging voltage gradually increased from 2.50 V in 80$^{th}$ cycle to 2.65 V in 118$^{th}$ cycle. The expanded voltage gap results from increased polarization most likely due to the accumulation of side products in the air electrode and the growth of a SEI layer on metal surface. Although larger polarization is observed after 80 cycles, Coulombic efficiencies of over 95% were maintained throughout the tests (Figure 3.13b). After the cycled battery
was disassembled, the Nafion-Na⁺ membrane and glass fiber separator in the air electrode were removed for analysis. Figures 3.13c and 3.11d display the discharge/charge curves and Coulombic efficiency vs. cycle number for cell utilizing a diglyme based electrolyte, respectively. It further confirms that increased cyclability is obtained using the composite separator. However, the Coulombic efficiencies in diglyme were relatively low (Figure 3.13d) compared to DME indicating that diglyme might have lower stability than DME. Even so, 90 cycles were still achieved (Figure 3.13c). Good reproducibility and high Coulombic efficiency prove that the Nafion-Na⁺ membrane efficiently prevents dendrite penetration and increases cycling performance of Na-O₂ batteries.

Figure 3.14 The schematic diagram of a Na-O₂ battery and optical images of glass fiber separators with using Nafion-Na⁺ after cycles. (b) #2 glass fiber separator faced to the metal
To show the effect of Nafion-Na\textsuperscript{+} membrane for blocking dendrite penetration, optical images of glass fibers in both electrodes were detected. After 110 cycles, two pieces of glass fiber separators were peeled off from the Nafion-Na\textsuperscript{+} membrane. Figure 3.14b show the #2 glass fiber separator faced to the metal anode side, dendrite with a light grey color is observed on the surface of glass fibers. The other side of the same piece of this separator is shown in Figure 3.14c, which is faced to the Nafion-Na\textsuperscript{+} membrane. Similar dendrite distribution was display on both sides of the separator proving that the sodium dendrite penetrates the glass fibers and reaches to the Nafion-Na\textsuperscript{+} membrane. However, in the other electrode, the glass fiber separator shows a clean surface faced to the Nafion-Na\textsuperscript{+} membrane (Figure 3.14d). As expected, there is no indication of dendrite penetrating through the Nafion-Na\textsuperscript{+} membrane and glass fiber separator in the cathode side. The results prove that Nafion-Na\textsuperscript{+} membranes effectively block sodium metal penetration through the separator and increase the cycle life of Na-O\textsubscript{2} batteries.

3.3.3 The effects of electrolyte decomposition in Na-O\textsubscript{2} batteries

After the failure of the Na-O\textsubscript{2} battery with Nafion-Na\textsuperscript{+} in DME (after 120 cycles), the battery was taken apart and no metallic Na was observed in the anode. The leftovers show a light grey color without metallic luster, which indicates the depletion of sodium. To measure the depletion rate of Na, cycling efficiencies of Na in the anode were calculated and the cycling efficiency for each cycle ranged from 60\%–80\%, as shown in Figure 3.15.
Cycling efficiency for the metal anode is a very important factor to represent the anode performance of metal air batteries. In the battery assembly, the anode used small amount of Na (1.5 mg) corresponding to 17.5 h discharge (1.75 mAh based on the current of 0.1 mA). The separator was glass fiber/Nafion-Na+/glass fiber composite and the cathode was P50 carbon fiber paper. The electrolyte was 0.5 M Na triflate in DME and the battery operated in 1 atm oxygen atmosphere with current of 0.1 mA. The voltage window was set to 1.2-3.4 V with no discharge time limit. In this case, the end of discharge indicates the depletion of Na in the anode and the charge capacity shows how many Na is obtained from the decomposition of NaO$_2$. The cycling efficiency of the first cycle is determined by the first discharge capacity divided by the theoretical capacity. The cycling efficiency of the second cycle was determined by the second discharge capacity (consumed Na) divided by the first charge capacity (formed Na). The cycling efficiency for each cycle ranges from
60%-80% which indicates Na metal undergoes a severe decay in the anode. Errors could lead to an underestimate of the cycling efficiency. Since limited Na was used in the anode, the ion diffusion is more difficult than the large amount of Na used in the anode, resulting in larger overpotentials in the cell.

Figure 3.16 (a) 1H-NMR and (b) 19F-NMR of DME based electrolyte in GF separators from the anode side and the cathode side after 6 cycles. (c) Raman spectra of reference materials and electrodes after 120 cycles. Nafion-Na\textsuperscript{+} membranes were used in the cells.
In order to get more insight into the underlying causes, the side products were investigated in both the anode and the cathode. With the Nafion-Na\textsuperscript{+} membrane as a part of separator, anion diffusion between the two electrodes has been blocked, giving us the opportunity to explore the decomposition of the electrolyte separately. 0.5 M sodium triflate in DME was used as electrolyte. After 6 cycles, the GF separators from both sides were peeled off from the Nafion-Na\textsuperscript{+} membrane and then immersed in D\textsubscript{2}O, respectively, for NMR measurement. 1H-NMR spectra of the electrolyte from the anode are shown in Figure 3.16a. The peaks at 8.5 ppm and 1.9 ppm are assigned to formate (HCOO\textsuperscript{-}) and acetate (CH\textsubscript{3}COO\textsuperscript{-}) respectively.\textsuperscript{56} At 3.8 ppm, the signal is assigned to methoxyacetate (CH\textsubscript{3}OCH\textsubscript{2}COO\textsuperscript{-}).\textsuperscript{146} The small peak at 3.2 ppm is for the conducting salt, sodium triflate.\textsuperscript{147} Interestingly, compared to the anodic electrolyte, the cathodic electrolyte only shows a small peak of CH\textsubscript{3}COO\textsuperscript{-}. This is consistent with the argument that the cathode experiences less decomposition than in Li-O\textsubscript{2}.\textsuperscript{136} From the 19F-NMR spectrum, as shown in Figure 3.16b, the peak at 79 ppm is the characteristic peak of triflate species (SO\textsubscript{3}CF\textsubscript{3}\textsuperscript{-}) and the peak at 122 ppm is for fluoride species (F\textsuperscript{-}).\textsuperscript{148} The missing peak at 122 ppm in the cathode side indicates that Na triflate is barely decomposed in the cathode. The results indicate that both DME solvent and Na triflate were decomposed in the Na anode. Since all the by-products were detected to be oxidative compounds, it can be explained that oxygen crossover induces the decomposition of the electrolyte in the presence of Na. The light grey colored solids in the anode were detected by Raman spectroscopy. Figure 3.16c shows the Raman spectra of both electrodes and the standard peaks of reference materials. In the case of the sodium anode, the peaks at 1080 cm\textsuperscript{-1}, 1156 cm\textsuperscript{-1} and 3638 cm\textsuperscript{-1} are for
sodium carbonate ($\text{Na}_2\text{CO}_3$), sodium superoxide ($\text{NaO}_2$) and sodium hydroxide ($\text{NaOH}$), respectively. The peak located at 750 cm$^{-1}$ is most likely for sodium peroxide ($\text{Na}_2\text{O}_2$). Other small peaks cannot be clearly identified but they suggest the complex products on the sodium surface. $\text{Na}_2\text{CO}_3$ and $\text{NaOH}$ are related to the decomposition of the electrolyte in the presence of oxygen. For the carbon cathode, only the signals of $\text{NaO}_2$ and $\text{NaOH}$ were detected. $\text{NaOH}$ may originate from the decomposition of the electrolyte or from possible moisture contamination. The remnant peak of $\text{NaO}_2$ shows that not all $\text{NaO}_2$ was accessible during charging, which is consistent with the previous report. The built-up sodium superoxide would lead to low apparent Coulombic efficiency and passivation of the cathode surface.
Figure 3.17 (a) C1s, (b) F1s, (c) S2p and (d) Na1s XPS spectra of the sodium anode after 120 cycles.
To understand the decomposition products in the SEI layer, C1s, F1s, S2p and Na1s spectra on the metal anode were obtained in XPS, as shown in Figure 3.17. The spectra were calibrated by the standard position of carbon-carbon bond at 284.8 eV. In C1s spectrum, the peak at 284.8 eV from the carbon-carbon bond in DME solvent. The peaks at 286.7 eV and 292.9 eV are related to C-O bond from DME solvent and C-F bond (-CF3 group) from the sodium triflate salt. The large peak at 289.2 eV is most likely from -CF2, ester or carbonate groups114,148. These groups are generated either by solvent decomposition (ester or carbonate groups) or by conducting salt decomposition (-CF3). In F1s spectra, peaks at 683.9 eV and 688.9 eV are related to fluoride species (NaF) and -CF3 group of the salt. The small peak of F- indicates that a small portion of the conducting salt decomposes. There is additional peak at approximately 691.2 eV which is hard to be assigned. In S2p spectra, the peak at 166.7 eV is probably from the sulfite species (SO3). In Na1s spectra, there are two peaks at 1071.1 eV and 1073.1 eV. According to the literature 119, the two peaks could be assigned to sodium metal, sulfite and/or carbonate species, and oxide compounds or sodium fluoride separately. Since the decomposition of salt is not severe in the metal anode due to the F1s and S2p spectra, the large peak observed in C1s spectra is likely due to the decomposition of the electrolyte.

The mechanism of solvent decomposition has been proposed in lithium oxygen batteries7 and potassium oxygen batteries146. Here, we borrow the proposed mechanism of oxygen crossover in DME based electrolyte in potassium oxygen batteries to understand the electrolyte decomposition in sodium oxygen batteries. In the DFT calculations, during charging process, DME molecules combine with electrons and to form DME radical and
further interact with oxygen in the anode. The DME oxygen complex went through C-O bond cleavage without undergoing high barrier. The side products can be obtained from the decomposition of DME solvent.

In conclusion, decomposition of electrolyte occurs in the sodium anode causing the degradation of sodium. The high reactivity of sodium metal induces side reactions with electrolyte and oxygen in the anode and the compositions of SEI layer are $\text{Na}_2\text{CO}_3$, $\text{NaO}_2$, $\text{NaOH}$ and probably $\text{Na}_2\text{O}_2$. The depletion of sodium is likely to be major issue to cause the death of sodium oxygen batteries.

**Figure 3.18** The sodium metal electrode (a) before and (b) after 5 cycles by using limited sodium. (c) The stainless steel rod after scraping the side products. (d) The glass fiber separator faced to the metal anode after 5 cycles.
Figure 3.18a shows the pristine 3.0 mg sodium pasted on the stainless steel rod. After five cycles, the surface of the metal changes to light grey colored solids which are similar to Figure 3.18b. When the solid is scraped off, only a small amount of sodium was left in the middle of the rod (Figure 3.18c). Side products were also observed on the glass fiber separator faced to sodium anode (Figure 3.18d). It indicates that dendrite has grown into the glass fibers and due to the large surface area of sodium dendrites more severe decomposition occurs on the dendrites converting sodium metal to the side products.

Although the formation of sodium dendrite and high reactivity of sodium metal are the major issues in sodium oxygen batteries, the carbon cathode still suffers many problems. In lithium oxygen batteries, the major issue is the high overpotential during charging process generated by the insulating Li$_2$O$_2$. However, the product in sodium oxygen batteries, sodium superoxide, is not a significant problem due to the small polarization upon charge. Sodium superoxide is grown on the surface of carbon and shows a cubic morphology. Different from the amorphous structure of lithium peroxide in Li-O$_2$ batteries, sodium superoxide has a good crystalline structure. Although there were no reports on the experimental or calculation studies of electronic conductivity of NaO$_2$ to date, it indicates that NaO$_2$ might have higher electronic conductivity than Li$_2$O$_2$. Although the electronic conductivity of products in sodium oxygen batteries is not a big concern, in Hartmann’s study, they observed that after cycles part of sodium superoxide couldn’t be recharged. To understand the discharge products and the effects of electrolyte
decomposition on cathode, Raman and XPS were performed to detect the products on the air diffusion layer.

![Raman spectra of air electrode (P50) after 118 cycles in DME. Two references are NaO$_2$ on P50 substrate and NaOH.](image)

**Figure 3.19** Raman spectra of air electrode (P50) after 118 cycles in DME. Two references are NaO$_2$ on P50 substrate and NaOH.

After 120 cycles in a sodium oxygen battery, P50 carbon paper was tested by Raman spectroscopy. In Figure 3.16c, Raman spectra show peaks of NaO$_2$ and NaOH at 1150 cm$^{-1}$ and 3634 cm$^{-1}$, separately. Sodium hydroxide may originate from the decomposition of electrolyte or from the moisture contamination. The remnant peak of NaO$_2$ shows that not all NaO$_2$ was removed during cycling. The built-up sodium superoxide would lead to low apparent Coulombic efficiency and passivation of the cathode surface. Those results indicate that in addition to dendrite growth, other factors such as moisture, electrolyte stability, and incomplete of NaO$_2$ decomposition can also affect the cyclability of Na-O$_2$ batteries.
Figure 3.20 (a) C1s, (b) F1s, (c) S2p and (d) Na1s XPS spectra of the carbon cathode after 110 cycles.
Four spectra including C1s, F1s, S2p and Na1s were tested in XPS on the air electrode after cycling, as shown in Figure 3.20. The spectra were calibrated by C-C bond at 284.8 eV. In the C1s spectrum, the large peak at 289.1 eV is related to -CF2, ester or carbonate groups. F1s spectra show the peak at 683.9 eV which is related to fluoride indicating the decomposition of the conducting salt. S2p spectra show the peak of sulfite species at 166.7 eV, which proves that the salt is not stable in the air electrode. This is contrast to the NMR results in the carbon cathode. This is probably because for a short period the amount of side products decomposed from electrolyte are small so it is hard to be detected. After 120 cycles, both decompositions of conducting salt and DME solvent were detected in XPS. In Na1s spectra, only one peak at 1071.1 eV is observed. The XPS spectra show similar results with the metal anode.

Figure 3.21 Proposed mechanism of DME decomposition on the anode side with oxygen crossover.
A proposed electrolyte decomposition mechanism was reported by our group in K-O_2 batteries, shown in Figure 3.21. Given the similar products detected in the anode, the decomposition mechanism of DME solvent can be applied in Na-O_2 batteries. The solvated electrons generated from the alkali metal react with DME solvent to form DME anions. It further reacts with oxygen and undergoes the C-O bond cleavage to form different oxidative products. The investigation of side products in both electrodes implies that the Na anode brought up more issues than the carbon cathode. In addition, different from K-O_2 batteries, the side products formed in the Na SEI layer are ion conductive and the accumulation of side products does not cause the failure of the battery only if the sodium is fully depleted. Hence, metal protection and oxygen crossover prevention are critical for improving the cyclability of Na-O_2 batteries.

3.4 Conclusion

Na dendrite formation has been identified as a major reason for the poor cyclability of sodium-air batteries. Dendrites that ultimately penetrate through the glass fiber separator to the air electrode cause short-circuiting of batteries. Using a Nafion-Na^+ membrane as part of a composite separator, 110 cycles in DME and 90 cycles in diglyme have been achieved at a current density of 0.16 mA cm^-2. These results not only demonstrate the significant enhancement of cyclability of Na-O_2 batteries by physically preventing dendrite penetration, but also offer the possibility of investigating further structure-performance-durability relationships of the batteries without the interference of short-circuiting.
However, after cycling sodium oxygen batteries stopped working due to the depletion of sodium. Oxygen crossover and the instability of electrolyte have been proved to be the major problems for the decay of sodium anode. It suffers more severe decompositions than the carbon cathode. NMR, Raman and XPS techniques were employed to characterize the side products in both electrode. By characterizing the side products in both electrodes, sodium anode induces more side reactions than the air cathode. In the anode, major side products are Na$_2$CO$_3$, Na$_2$O$_2$, NaO$_2$, NaOH, sodium formate and sodium acetate. Our results show that even there are accumulations of side products but they did not affect the cycle life of sodium oxygen batteries only if the sodium is exhausted. Based on the side products, the electrolyte decomposition mechanism has been discussed. On the other hand, the cathode still has issue of electrolyte decomposition. In addition, small portion of NaO$_2$ cannot be recharged back to sodium and oxygen. It is critical to develop stable anode materials and explore stable electrolytes for sodium oxygen batteries.

Although the cycle life of sodium oxygen batteries could be improved by using ion exchange membranes in the separator, the limited ionic conductivity and the stability of membranes require further enhancement. For Nafion-Na$^+$ membrane, the relatively small ionic conductivity of sodium ions (~2.5e-5 S·cm$^{-1}$) compared to the proton exchange membranes (1e-2~10 S·cm$^{-1}$)$^{149}$ would meet more challenges when higher current is applied. As reported by DuPont, Nafion membrane is not fully stable with sodium metal so the dendrite of sodium might induce the decay of Nafion membrane. In the future, sodium ion exchange membrane with higher stability should be explored avoiding reactions of sodium metal. In addition, the ionic conductivity would be improved by
adjusting side groups in the ion diffusion channels of the membrane, e.g. increasing the concentration of sulfonate group sites. Furthermore, Nafion membrane could be modified to block oxygen crossover. In fuel cells, lower gas permeability of the Nafion membrane can be achieved by incorporating miscellaneous fillers and polymers such as SiO$_2$, zeolites, zirconium, and polypyrrole. In addition, graphene oxide/Nafion membrane composite is also a promising material that has higher ion conductivity than the inorganic and organic fillers. In the future, we can develop Nafion membrane/advanced materials composites similar to the materials in fuel cells to achieve lower gas crossover. Other methods such as using alloy, metal oxides or adding additives to the electrolyte would change the surface morphology of sodium metal, avoiding dendrite formation and metal depletion.
Chapter 4: Unveiling the Effects of Sodium Ions on Aprotic Lithium Oxygen Batteries

4.1 Introduction

Rechargeable lithium air (oxygen) batteries have recently attracted extensive research interests due to their ultrahigh theoretical energy density of 3500 Wh·kg\(^{-1}\), five-to seven-fold higher than the state-of-the-art lithium ion (Li-ion) batteries.\(^9\), \(^99\), \(^155\) In a typical lithium oxygen (Li-O\(_2\)) cell, oxygen is reduced at the air electrode and forms superoxide at discharge. It further reacts with Li\(^+\) to initially form LiO\(_2\) which then undergoes disproportionation reaction or combines with another Li\(^+\) to ultimately produce the final discharge product (typically, Li\(_2\)O\(_2\)). At charge, the discharge product is oxidized and removed from the electrode surface. Many efforts were made to investigate the cell chemistry and a solution-mediated mechanism was established. The ability of Li\(^+\) solvation by the solvent, defined by donor number (DN), determines the morphology and the composition of the discharge product. Therefore, the choice of solvents and additives to electrolytes plays critical roles in the cell chemistry of Li-O\(_2\) batteries.

Recent progress focuses on investigating the effects of the electrolyte solution to understand the cell chemistry of Li-O\(_2\) batteries. Johnson et al. investigated the effect of DN of various solvents and discovered that stronger Li\(^+\) solvation leads to Li\(_2\)O\(_2\) formation.
in the solution and continuously growth as toroids on the electrode surface, while weaker Li\(^+\) solvation results in forming surface Li\(_2\)O\(_2\) film.\(^{156}\) Additives such as 2,5-di-tert-butyl-1,4-benzoquinone (DBBQ) serve as assistants to tune the solution-mediated pathway. Gao et al. report that DBBQ first generates DBBQO\(_2\) in the electrolyte instead of LiO\(_2\), and then produces Li\(_2\)O\(_2\) as the final product.\(^{157}\) The addition of the additive avoids the formation of the highly reactive LiO\(_2\) and film-like Li\(_2\)O\(_2\) by eliminating the interference from the solvent, thus achieving high rates and long cycle life. Liu et al. added water and additive LiI into an ether-based electrolyte to finally produce LiOH which was thought to be an insulator and a side product in Li-O\(_2\) cells. In addition, it was proved to be rechargeable at a very low overpotential of 0.2 V in the presence of reduced graphene oxide electrode additive LiI. Since the formation and growth of the discharge product is greatly dependent on the solution, the investigation of additives to the electrolyte becomes significant by tuning the cell chemistries to achieve high efficient Li-O\(_2\) cells.\(^{158-161}\)

In order to get insight of the solution-mediated mechanism, we employ other cations in addition to Li\(^+\) in the electrolyte to investigate the new cell chemistry of Li-O\(_2\) batteries. The addition of the cations may compete with Li\(^+\) solvation and change the discharge product. Here, we investigate the cell chemistry of lithium oxygen batteries by tuning the solution phase reaction with sodium ions, which have the same valency of Li\(^+\) and share similarities in electrochemical environment. To avoid the parasitic reactions from binder involved in most cathode materials, a pure carbon air diffusion layer was employed in our system. We observed that with the addition of sodium ions in the electrolyte, the electrochemical performance of Li-O\(_2\) cells show a remarkable decrease of charge
overpotential from over 4 V to 3.3 V and the morphology of the discharge product has a drastic change. The product is identified as LiOH, which could be reversibly charged during cycles. Interestingly, we did not observe any sodium-based products on the carbon surface. NMR results indicate that sodium ions change the solvation environment of lithium ions in the electrolyte, thus forming LiOH.

4.2 Experimental Section

Materials and cell assembly. The Li-O₂ cell was assembled by using Li foil (99.9%, MTI Corporation) as the anode, glass microfiber filters (420 um, Whatman™ GF/F) as the separator and H23I6 carbon fiber paper (Freudenberg FCCT) as the air electrode in a stainless steel cell setup (shown in Figure 4.1). The electrolyte was comprised of 1 M lithium trifluoromethanesulfonate (Li triflate, 99.995%, Sigma-Aldrich) in triethylene glycol dimethyl ether (TEGDME, ReagentPlus®, 99%, Sigma-Aldrich) with different concentration of sodium trifluoromethanesulfonate (Na triflate, 98%, Sigma-Aldrich). TEGDME solvent was dried with 3 Å molecular sieves (Sigma-Aldrich) and the salts were dried in a vacuum oven at 100 °C overnight before use. 1 M Na triflate in TEGDME was also used as a control electrolyte. The other set of electrolytes was comprised of the total concentration of 1 M conducting salts of Li triflate and/or Na triflate in TEGDME. The water contents in electrolytes were tested around 50 ppm by using a Mettler Toledo C20 Karl Fischer Coulometer. A stainless steel grid window was employed as the current collector in the air electrode and two O-rings were used to seal the stainless steel setup. The testing cell was assembled in an argon filled glove box (oxygen < 0.1 ppm, water < 0.5 ppm) and then stayed in 1 atm oxygen atmosphere for 30 min to reach equilibrium. The
Electrochemical performance of Li-O$_2$ cells was evaluated by a Maccor cycler (model-4000). A voltage window of 2.2-4.8 V (vs. Li$^+/\text{Li}$) and a current of 0.05 mA cm$^{-2}$ were applied in the cells.

![Schematic diagram of the stainless steel cell setup.](image)

**Figure 4.1** Schematic diagram of the stainless steel cell setup.

Characterization. Scanning electron microscopy (SEM, Hitachi S4700) were performed to identify the discharge product. A Mason jar was used to store samples before test. The samples were quickly transferred from the Mason jar to the SEM sample chamber exposing to air within 10 s.

X-ray diffraction (XRD) was performed by a Rigaku benchtop miniflex X-ray diffractometer with a Cu Ka radiation at ambient temperature. The sample was sealed by Kapton tape (Micronova™) before measurement. The discharged air electrode was characterized by Raman spectrometer (inVia, Renishaw) with an air-tight holder at an excitation wavelength of 633 nm (laser power 6 mW).

High-angle annular dark-field (HAADF) STEM was conducted on a JEOL JEM-ARM200CF equipped with a cold field emission source. 22 mrad probe convergence angle
and 90 mrad inner-detector angle was used for the image collection. The discharge product was collected by scratching the prepared air electrode, dispersing it in the solvent, and loading to the copper mesh. NMR experiments were performed using Bruker AV-III 300 MHz NMR Spectrometer. For the sample preparation, one piece of carbon electrode and one piece of glass fiber separator faced to the air electrode were immersed in 1 mL D$_2$O solvent. After 5 min, 900 µL was taken out to 5 mm tubes for the testing.

4.3 Results and Discussions

4.3.1 Electrochemical performance

The electrochemical performance of Li-O$_2$ cells was evaluated by a stainless steel-type cell\textsuperscript{162} composed of lithium metal anode, glass microfiber filter separator and carbon fiber air diffusion layer. The configuration of the cell setup is shown Figure 4.1. In order to investigate the effects of sodium ions on the Li-O$_2$ cells, we applied a range of concentrations of sodium trifluoromethanesulfonate (Na triflate) to 1 M lithium trifluoromethanesulfonate (Li triflate) in tetraethylene glycol dimethyl ether (TEGDME) electrolyte, listed in Table 4.1.

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<th>(a) 1 M Li$^+$ based electrolyte</th>
<th>(b) 1 M overall concentration of metal ions</th>
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Figure 4.2 Voltage profiles of (a) 1 M Li\(^+\) based electrolyte, (b) 1 M overall concentration of ions and (c) first 20 cycles of the Li-O\(_2\) cell with electrolyte of 1 M Li\(^+\) and 0.5 M Na\(^+\) with limited capacity.
Figure 4.2a shows voltage profiles of the cells four electrolytes based on 1 M Li⁺ electrolyte. Since there was no catalysts involved and only carbon substrate was used in the air electrode, the capacity delivered in the cell is represented based on the specific apparent area. In 1 M Li⁺ electrolyte (black curve), the discharge shows a plateau around 2.7 V, while the charging curve starts with a short plateau at 3.6 V and then quickly increases over 4.0 V till the end of charge, which is similar to most of the previous studies based on carbon substrates. When 0.1 M sodium ions are present in the cell, the charging voltage shows a stable plateau at 3.8 V. For the electrolyte with 1 M Li⁺ and 0.5 M Na⁺, the charge voltage further decreases to 3.4 V, exhibiting a low charge overpotential smaller than 0.5 V. If we replace all the lithium ions by sodium ions in the electrolyte, the charge potential shows a little increase to 3.6 V. The results show that sodium ions could largely decrease the charge overpotential in Li-O₂ cells, especially with 0.5 M Na⁺ in the electrolyte. Since the ultralow charge voltage is observed, it represents that the cells experiences fast kinetics during oxygen evolution reaction (OER). The cells with Na⁺ in the electrolyte deliver high capacity, as shown in Figure 4.3. In the pristine Li-O₂ cell without Na⁺, the discharge capacity is 2.08 mAh·cm⁻²; while the cell with 0.1 M Na⁺ delivers a high discharge capacity as large as 4.11 mAh·cm⁻². As the increase of Na⁺ concentration, the discharge capacity changes from 4.11 mAh·cm⁻² for 0.1 M Na⁺, 3.36 mAh·cm⁻² for 0.5 M Na⁺, and 1.84 mAh·cm⁻² for 1 M Na⁺.
Figure 4.3 The first full cycle of the cells with the four electrolytes. The voltage window is set to be 2.2 V to 4.5 V.

Given that the total concentrations of conducting salts in the solvent might cause discrepancies on the electrochemical performance such as capacity and cell stability\(^{163-164}\), we use another set of electrolytes based on the total concentration of 1 M triflate salts to eliminate the effects from the higher salt concentration (Table 4.1b). For this set of electrolytes, similar scenario is observed as shown in Figure 4.2b. With 1 M salt in the electrolytes, the charge overpotential still shows a large decrease after the addition of sodium ions. The result rules out the possibility that the low overpotential results from higher salt concentration and further confirms that sodium ions influence the OER process.
and thus lowers the charge overpotential in Li-O₂ cells. Then we test the cycle stability based on the mixed salt electrolyte, as shown in Figure 4.2c. In the cell with 1 M Li⁺ and 0.5 M Na⁺, the discharge voltage during the first cycle maintains at 2.7 V and the charge voltage is close to 3.6 V which is higher than the following cycles. This is probably due to the formation of the SEI layer or irreversible parasitic reactions during first cycle. The cell runs over 50 cycles and the charge overpotential maintains below 0.5 V over 20 cycles, exhibiting a decent stability.

4.3.2 Characterization of the discharge product

![SEM images of the discharge product with electrolytes (a) 1 M Li⁺, (b) 1 M Li⁺ + 0.1 M Na⁺ (c) 1 M Li⁺ + 0.5 M Na⁺ (d) 1 M Na⁺. Scale bars in the image are 10 um and the scale bars in the inset are 1 um.](image)

Figure 4.4 SEM images of the discharge product with electrolytes (a) 1 M Li⁺, (b) 1 M Li⁺ + 0.1 M Na⁺ (c) 1 M Li⁺ + 0.5 M Na⁺ (d) 1 M Na⁺. Scale bars in the image are 10 um and the scale bars in the inset are 1 um.
Figure 4.5 (a) XRD of the discharged air electrodes based on the four electrolytes compared with the standard patterns of LiOH and Li$_2$O$_2$. (b) Raman spectra of pristine carbon, triflate salts and discharged cathode in 1 M Li$^+$ and 0.5 M Na$^+$ electrolyte.

The discharge products were examined by scanning electron microscope (SEM) and the morphology is strongly dependent on the concentration of sodium ions. Figure 4.4a shows the air electrode after the first discharge in 1 M Li$^+$ electrolyte. The SEM image reveals that the toroids are evenly deposited on the carbon substrate and the dimension ranges from 300 nm to 800 nm, implying the formation of Li$_2$O$_2$. While in the presence of sodium ions, the morphology of the discharge products were greatly changed. In Figure 4.4b, the particles are like toroids but they have an irregular shape with rough surface. In addition, the diameter of particles ranges from 2 to 3 microns, which is much larger than the toroids formed in lithium electrolyte. The larger scale of the discharge product may contribute to the larger discharge capacity shown in Figure 4.3. With the increase of sodium ion concentration, the discharge product becomes spherical, as shown in Figure 4.4c and 4.4d. Clearly, the results show that the morphology of the discharge
product depends on the concentration of sodium ions, indicating that the sodium ions take part in the pathway of the product formation.

![Raman spectra of the discharged and recharged electrodes in 1 M Li^+ electrolyte.](image)

**Figure 4.6** Raman spectra of the discharged and recharged electrodes in 1 M Li^+ electrolyte.

The discharge product on the carbon substrate was characterized by x-ray diffraction (XRD) shown in Figure 4.5a. The black dots represent the signals from the aluminum holder. Since the samples were attached to the surface of Al holder, there is a minor displacement of the Al peaks due to the distance between the samples and Al holder. The black XRD pattern (in 1 M Li^+) shows the signals at 32.8°, 35.0° and 58.9°, corresponding to the (100), (101) and (104) planes of Li_2O_2, separately. The Raman spectrum of the cathode discharged in 1 M Li^+ electrolyte is shown in Figure 4.6. The peak at 790 cm^{-1} confirms that the discharge product is Li_2O_2. Nevertheless, once sodium ions...
Figure 4.7 (a) TEM image of a local particle grown on the surface of the carbon fiber. (b) SAED diffraction on the particle collected on the position of the cross shown in (a). (c) TEM image on another local particle on carbon surface formed in 1 M Li$^+$ and 0.5 M Na$^+$ electrolyte. (d-f) EDS mapping of the local particle in (c).
are present in the electrolyte, LiOH is identified to be the only discharge product. The peaks at 32.5°, 51.4°, 55.9° and 62.1° match the (101), (200), (112), and (211) planes of LiOH in Figure 4.5a. Raman spectra (Figure 4.5b) show a peak at 3662 cm⁻¹ corresponding to the standard peak of LiOH. There are no other signals except the standard triflate salts and the carbon substrate, which further prove that LiOH is the only discharge product. It is interesting to see that although sodium ions are present in the electrolyte, there is no sodium based product observed on the carbon fiber paper.

To better understand the function of sodium ions on the formation of the discharge product, we employed TEM to look at the local particle and further probe the composition of the discharge products. Figure 4.7a shows TEM image of a local particle grown on the surface of the carbon fiber and Figure 4.7b shows SAED diffraction on the particle. From the SAED result, the lattice distances are converted from the pattern and match well with LiOH. It further confirms that the composition of the particle on the carbon surface is LiOH. In addition, as can be seen in Figure 4.7c to f, we focus on another single particle located on carbon fiber and collect EDS mapping. There is almost no sodium signal (0.1% content from EDS mapping compared to 97% of carbon and 2.9% of oxygen) detected on the particle. It excludes the possibility that sodium ions are present in the discharge products. Except sodium based products, we also checked the formation of Li₂O₂ by adding TiOSO₄ solution to the discharged air electrode. We hardly see the color change after the addition of 0.5 mL TiOSO₄, indicating that Li₂O₂ is not the main discharge product in the system (Figure 4.8). Given that the addition of sodium ions changes the discharge product to LiOH but no sodium based products are observed, it suggests that sodium ions compete
with lithium ions in the solution phase. The results further proves that the formation of the discharge product is in the solution phase instead of directly reduced on the carbon electrode surface.

**Figure 4.8** Air electrode discharged 20 h in 1 M Li\(^+\) and 0.5 Na\(^+\) electrolyte after adding 0.5 mL TiOSO\(_4\) solution.

**Figure 4.9** (a) XRD of the pristine air electrode, discharged and recharged electrodes in 1 M Li\(^+\) and 0.5 M Na\(^+\) electrolyte. (b) Raman spectra of the discharged and recharged electrodes in 1 M Li\(^+\) and 0.5 M Na\(^+\) electrolyte.
In our study, we surprisingly found that the discharge product, LiOH, could be reversibly charged at the low voltage. The reversibility of the product was investigated by discharging the cell to 0.3 mAh and recharging to the equivalent capacity. Figure 4.9a shows the XRD results of the pristine carbon, discharged and recharged electrodes in 1 M Li$^+$ and 0.5 M Na$^+$ electrolyte. No peaks of LiOH are detected after one cycle evidencing that LiOH has been reversibly charged in the cell. Additional evidences of the reversibility of LiOH are provided by Raman after a galvanostat cycle. The missing peaks at 3662 cm$^{-1}$ indicates the decomposition of LiOH during charge (Figure 4.9b).

![Figure 4.10 XRD of the discharged air electrodes based on electrolytes with 1 M triflate salts. XRD of air electrodes (a) after the first discharge and (b) after recharge.](image)

To further confirm the reversibility of LiOH, another set of the electrolytes were investigated. The six set of electrolytes are 1 M Li$^+$, 0.8 M Li$^+$ and 0.2 M Na$^+$, 0.6 M Li$^+$ and 0.4 M Na$^+$, 0.4 M Li$^+$ and 0.6 M Na$^+$, 0.2 M Li$^+$ and 0.8 M Na$^+$, and 1 M Na$^+$ with the
overall salt concentration of 1 M. In Figure 4.10a, the XRD results shows that expect the product in 1 M Li$^+$ electrolyte which is Li$_2$O$_2$, the discharge products for the other five electrolytes are all LiOH compared to the standard pattern of LiOH. Nevertheless, after one cycle, the peaks for both Li$_2$O$_2$ (1 M Li$^+$) and LiOH (Na$^+$ added electrolytes) disappear. The results confirm that LiOH decomposes during charge of the cell, further proving the good reversibility of LiOH.

Figure 4.11 SEM images of the recharged air electrodes in (a) 1 M Li$^+$, (b) 1 M Li$^+$ + 0.1 M Na$^+$ (c) 1 M Li$^+$ + 0.5 M Na$^+$ (d) 1 M Na$^+$.
Figure 4.12 (a-d) 1H-NMR spectra of the comparison of the discharge products after the first discharge and after 5 cycles for the electrolytes with (a) 1 M Li⁺ (b) 1 M Li⁺ and 0.1 M Na⁺, (c) 1 M Li⁺ and 0.5 M Na⁺, and (d) 1 M Na⁺. (e-h) 19F-NMR spectra of the comparison of the discharge products after the first discharge and after 5 cycles for the
electrolytes with (e) 1 M Li$^+$ (f) 1 M Li$^+$ and 0.1 M Na$^+$, (g) 1 M Li$^+$ and 0.5 M Na$^+$, and (h) 1 M Na$^+$.

In addition to the XRD results, SEM was performed after one cycle of the four electrolytes based on 1 M Li$^+$. Compared to Figure 4.4, the discharge products with particles on the carbon fibers disappear. As can be seen from Figure 4.11a and 4.11b, for 1 M Li$^+$ and 1 M Li$^+$+0.1 M Na$^+$ electrolytes, almost all the products are removed from the carbon surface and the carbon fiber maintains clean. Nevertheless, when the concentration of Na$^+$ increases to 0.5 M or to 1 M, the surface of carbon is no longer smooth and becomes fluffy. It is probably from the side product such as carbonates that could not be recharged and thus stay on the electrode surface.

In order to prove the formation of LiOH did not result from the decomposition of the solvent in the electrolyte, proton and fluorine NMR were employed to detect the change of the electrolytes after the first discharge and after five cycles. We precisely controlled the experiment parameters (explained in the experimental section) in order to quantitatively measure the side products in electrolyte. Without sodium ions in the electrolyte, we observe that the 1H-NMR spectra (the black line in Figure 4.12a) show one peak at 8.4 ppm which is assigned to formate (HCOO$^-$), the side product from the decomposition of the TEGDME. The small peak at 3.2 ppm is for the conducting salt, triflate. It indicates that even without sodium ions, the solvent undergoes decomposition during discharge. After 5 cycles, there is no apparent increase of the peak intensity of formate. Similar results are observed in the electrolytes with 1 M Li$^+$ and 0.1 M Na$^+$, 1 M Li$^+$ and 0.5 M Na$^+$ 1 M
Li\(^+\) and 1 M Na\(^+\) (the green lines). It should be noted that even in 1 M Li\(^+\) electrolyte, the solvent decomposes after the first discharge, but the discharge product is still Li\(_2\)O\(_2\), which is consistent with the literature. Aetukuri et al. argue that even adding H\(_2\)O to 4000 ppm, Li\(_2\)O\(_2\) remains the major discharge product on a carbon paper cathode although drastic morphology change is observed.\(^{36}\) Similar results were reported by Schwenke et al. and they argue that the formation of LiOH in most studies comes from the binder used in the air electrode.\(^{168}\) Hence, we conclude the formation of LiOH in our system is due to the sodium ions but neither the decomposition of the solvent nor trace water in the solution. However, we do see the decomposition of triflate salt in the cell with 1 M Li\(^+\) and 0.5 M Na\(^+\). From the 19F-NMR spectrum, the peak at -79 ppm is the characteristic peak of triflate species (SO\(_3\)CF\(_3\)) and the peak at -122 ppm is for fluoride species (F\(^-\)), the side product from the decomposition of triflate.\(^{148}\) After the first discharge, the cell with 1 M Li\(^+\) shows no signals of fluorine species, while after 5 cycles, there is a small peak observed. Nevertheless, even after the first discharge, the cells with electrolytes of with 1 M Li\(^+\) and 0.1 M Na\(^+\), 1 M Li\(^+\) and 0.5 M Na\(^+\) 1 M Li\(^+\) and 1 M Na\(^+\) has already shown the signals of fluorine species. Moreover, the peak intensity keep increasing after 5 cycles, indicating the degradation of the triflate salt in the electrolyte. With the loss of triflate anions, lithium ions and sodium ions would be more likely to coordinate with the solvent-TEGDME. The change of solvation could drag the diffusion of the metal ions in the solution. Considering the limited sodium ions in the solution, the excess of lithium ions diffuses faster than the sodium, resulting in the formation of lithium based products instead of sodium based products.
The reaction of the formation of LiOH follows $4\text{Li} + 2\text{H}_2\text{O} + \text{O}_2 \rightarrow 4\text{LiOH}$, ($E^0 = 3.35 \text{ V}$). However, the charging voltage of the sodium ion based cells is very close to the standard electrode potential, indicating that the reaction pathway does not follow this reaction. We propose the reaction pathway starts with the reduction of oxygen to superoxide, after which sodium ions and lithium ions undergoes competition with the superoxide. Considering the hard-soft acid-base (HSAB) theory, the reaction between Na$^+$ and O$_2^-$ is more favorable so it’s more likely that Na$^+$ first interact with O$_2^-$ in the solution phase. However, the solvation effects may play an important role, for which sodium ions only serve as a catalyst, redirecting the reaction pathway to form LiOH. Additionally, sodium ion accelerates the removal of LiOH from the carbon substrate at a low overpotential, benefit to the OER process. The theoretical calculation and investigation of solvation mechanism are ongoing and will be included in the future work.

For the formation of LiOH, the proton source must come from the trace water in the electrolyte or the decomposition of the TEGDME solvent. As can be seen from Figure 4c, even without Na$^+$ in the electrolyte the solvent decomposes after the first discharge. However, once H$_2$O is generated in the cell, superoxide is more likely to attack H$_2$O instead of less polarized solvent in the presence of sodium ions thus enabling the following cycles based on the formation/decomposition of LiOH. In the subsequent cycles, H$_2$O could be produced by the decomposition of LiOH with the action of sodium ions. Thus the increase of the side products is very little in the following cycles.

4.4 Conclusion
In conclusion, we explore the Li-O$_2$ cell system by using a range of concentrations of sodium ions in lithium electrolyte and investigate the influence of sodium ions on the cell chemistry. To avoid the parasitic reactions from binder involved in most cathode materials, a pure carbon air diffusion layer was employed in our system. We observed that with the addition of sodium ions in the electrolyte, the electrochemical performance of Li-O$_2$ cells show a remarkable decrease of charge overpotential from over 4 V to 3.3 V and the morphology of the discharge product has a drastic change. The product is identified to be LiOH, which could be reversibly charged during cycles. Interestingly, we did not observe any sodium-based products on the carbon surface, indicating that sodium ions serves as a catalyst facilitating the formation and removal of LiOH. Hence, selecting an appropriate additive could improve the cell performance to achieve high efficient and high durable Li-O$_2$ cells.
Chapter 5: The Design and Setup of Differential Electrochemical Mass Spectrometry for Metal Air Batteries

5.1 Introduction

Differential Electrochemical Mass Spectrometry (DEMS) is a comprehensive technique that combines electrochemical methods with mass spectroscopy. A brief diagram of DEMS is shown in Figure 5.1. If gases or volatile species are evolved in the electrochemical reactions, mass spectrometer could analyze the products simultaneously to give the components. In addition, if a multi-step reaction occurs, the intermediates and each step in the reaction could be identified by the operando mass spectrometry. By calculating the faradaic current flow and the consumed/generated gases, the elementary step in electrochemical reaction can be elucidated. Since most of times the gaseous product generated in electrochemical reaction is small amount, mass spectroscopy has the benefit of high sensitivity to detect the product.
Figure 5.1 A brief diagram of DEMS instrument based on a metal air batteries cell.

The concept of DEMS was first proposed by Wolter and Heitbaum in 1984. They were inspired by Electrochemical Mass Spectroscopy (EMS) for the analysis of gaseous reaction products by Bruckenstein and Gadde in 1971, and firstly measured the time derivative of the amount of the species produced in an electrochemical reaction, thus naming it “differential” electrochemical mass spectroscopy (DEMS).

The design of DEMS cells is critical for the various application. Till now, many kinds of cell setups were designed such as classic cell, thin layer cell, and dual thin layer cell. A classic cell composes of counter electrode, working electrode, and hydrophobic PTFE membrane on which the working electrode material is sprayed. Based on the direct contact of the membrane and the working electrode, the gas product could be detected right after generation, resulting in fast response time. However, this type
of cell setup is limited by the morphology and layer thickness of the porous working electrode so it is not appropriate for the measurement of other types of electrode materials such as single crystals. Furthermore, the generation of the gaseous product occurs near the surface of the membrane. Concentration polarization could be created due to the prompt evacuation of the gas in the classic cell.

Thin layer cell separates the material and the membrane so that the material is no longer limited to the morphology and the property of the membrane. In this case, the working electrode could be maintain its original morphology such as single crystal or porous structure. In the measurement of DEMS, it could correlate with the rotating disk electrode which is a common method for ORR/OER testing, eliminating the effect of diffusion. Nevertheless, the enlarged space between the working electrode and the membrane delays the response time of mass spectrometer. Moreover, the efficiency of the gas detection is sacrificed by the distance between the electrode and the membrane. This is caused by the flowing electrolyte that takes away the generated gases when they are not reaching to the membrane. Moreover, the gases in the electrolyte generate gradient and keep changing while testing, so the efficiency and the accuracy are not as good as the classic cell.

Dual thin layer cell completely divides the working electrode and the membrane into 2 chambers, where the electrolyte firstly passes through the working electrode and brings the product to the membrane, thus improving the gas detection efficiency. However, there is no static region in the cell and the response time is further delayed. Each cell has its benefits and drawbacks determined by the specific purposes of different systems.
A typical thin layer half-cell setup for catalytic studies is shown in Figure 5.2. The cell is composed of a working electrode, two outlets for electrolyte flow and a membrane which only allows gas products passing through and block the diffusion of liquids.

**Figure 5.2** The diagram of a traditional membrane based DEMS half-cell for materials and catalytic studies. The middle part of the cell is magnified in the picture on the right side. The cell in the picture was designed and draw by Hiden Analytical.

Electrolyte flows through the cell by filling the gap between the working electrode and the membrane. The membrane is typically made by PTFE and its hydrophobic nature block the passage of electrolytes. On the other side of the membrane, vacuum system is set up to absorb the gas products to the mass spectrometer. When our lab purchased a DEMS system from Hiden Analytical, the cell shown in Figure 5.2 comes with it and it is capable to perform the catalytic reactions in our lab based on this type of cell. An electrochemical
half-cell is similar to the cell shown in Figure 5.2, it has a counter electrode at the top of
the cell, wired to the electrochemical station. The working electrode is inserted at the
bottom of the cell. The electrolyte flows through the designed tunnel, first filling the space
between working and counter electrodes and then reaching the membrane.

![Figure 5.3](image)

**Figure 5.3** CV and MSCV of CO\(_2\) (m/z = 44) during CO-bulk oxidation at various different
electrolyte flow rates for the dual-cyclone thin-layer flow cell. The correlation of the QMS
mass ion current with the electrode current improves with increasing electrolyte flow rate. The residence of the electrochemical reaction species in the electrochemical cell also decreases. Reprinted from ref 178. 2002 Springer-Verlag Berlin Heidelberg.

The response of the mass spectrometric cyclic voltammogram (MSCV) is correlated with the electrolyte flow rates and the scan rate. Figure 5.3 shows a sample of the CO$_2$ detection based on the oxidation of CO on a platinum electrode at m/z=44. The more fast of the flow rate, the more accurate the MSCV response. At low flow rate the generated CO$_2$ is tend to diffusion in the thin layers leading to a poor collection efficiency.

In the study of metal air batteries, the gas consumption and evolution make DEMS perfect for the investigation of the electrochemical reactions occurred in the electrode and identification of the side products generated from the system. However, the half-cell designs introduced former were not suitable for the study in metal air batteries. Firstly, the current applied in metal air batteries is small, usually in range of 1e$^{-5}$ A. Such a small amount of gas evolution may be hard to reach the sensitivity of the mass spectrometer. Secondly, previous cell design focuses on the electrolyte flow and gas generation but metal air requires static environment for both gas and electrolyte since it stores air in the cell during discharge and releases gas during charge. Small amount of electrolyte is sufficient for avoiding excessive gas dissolution in electrolyte. Based on the considerations, metal air cell fits for the DEMS design. Hence, we applied a metal air cell in our DEMS system shown in Figure 5.4.
5.2 Materials

The gas supply lines were purchased from Swagelok and assembled mainly based on 1/16 and 1/4 in stainless steel tubing. The model of pressure transducers is PX419-050GV-USBH from OMEGA Engineering, INC. The 8-port, 2-position switch valve was purchased from Valco Instruments Co. Inc. The metal air cell was purchased from MTI Engineering. The mass spectrometer was purchased from Hiden Analytical with an oil free pump attached. The secondary dry pump, ISP-250C-SV, was from Anest Iwata. The known volume of tubings (250 µL, 500 µL, 1 mL, 2 mL, and 5 mL) were purchased from Valco Instruments Co. Inc. For the automatic system, two of the regular valves were updated to solenoid valves (Varian Direct Acting Electromagnetic Aluminum Block Valve) and a LabVIEW software was used to control the valves. C series relay output module (NI-9482) and cDAQ-9181 were employed to send/receive signals from the valves and the computer. The power signals were supported by a 24 Vdc power supply and the Valco valve was connected to the computer by using cable DB-9 (RS-232).
5.3 DEMS Instrument Setup and Calibration

Figure 5.5 The diagram of DEMS instrument for studies in metal air batteries. The dark yellow line represents the transfer line.

Figure 5.5 shows the diagram of the DEMS including the gas supplies, the 8-port, 2-position valve was wired to the gas inlet/outlet ports and linked to a metal air cell and transfer line which is marked as the dark yellow line. The design of the DEMS instrument is from Dr. Brian McCloskey and the specific information of the cell can be found in the supporting information of literature 179. The two positions of the 8-port valve determine the gas direction and help to gas injection during measurements, as shown in Figure 5.6. When the valve is at “A” position, the 8 ports were linked by 1-2,3-4,5-6 and 7-8 and the gas passes through the cell and enters the mass spec; while at “B” position, 2-3, 4-5,6-7,8-1 were linked and the gas bypasses the cell and isolates the cell.
Figure 5.6 Gas flow directions of two positions of the Valco valve. The two volumes separated by valves B are labeled red and green.

In order to quantitatively measure the gas, pressure transducers were applied to calculate the total amount of gas by ideal gas law, $PV = nRT$. In the gas law, the pressure
is read from the pressure transducer, R is the gas constant and T is the room temperature. Once volume is known, the n of the total gas can be obtained. The calibration of volumes of cell head space, the cross union and the transfer line could be achieved by using a number of known volume loops attaching to the corresponding space and calculated the volumes. The four valves in the system are labeled A, B, C and D in Figure 5.5. For the calibration of the volume of the cell head space, we placed the valve position to A. Firstly, one loop with known volume was attached to port 5 and 6, and Ar was purged through the system. All four valves were closed and the space in valves B, C and D was evacuated by the dry pump. Read the pressure transducer on the left (P1), and then open the valve and record the pressure (P2) again. As shown in position A in Figure 5.6, the volume of the red lines is labeled V1 and the green lines are V2. One equation can be created: \( P1V1 = P2(V1 + Vloop1 + V2) \). By replacing loop 1 by loop 2, the unknowns in the equation, V1 and V2, could be calculated based on the two equations. The calibration can be finished by attaching five loops with known volumes. After calibration, attach the metal air cell to the system, the volume of the cell head space can be easily calculated. Using the same method, we could calibrate the two volumes V3 (red lines) and V4 (green lines) in position B. For the volume of the transfer line, first purge Ar through the system. In position A, evacuate the green part by opening valve C and closing A, B and D. Then, close C and change to position B by allowing the gas in transfer line entering V4. Since V4 is already known, the volume of transfer line is known too. The volume of transfer line should be a little larger than the cell head space, in order to hold all the gas from the cell.
The Hiden mass spectrometer system was employed to detect the gas components from the cell. Before testing, the mass spectrometer requires one day to reach a constant background that the partial pressures for the target gases are below 1e-8 torr. The mass spectrometer was then calibrated by 1%, 5%, and 10% (O\textsubscript{2}, H\textsubscript{2}, and CO\textsubscript{2}) mixture gas in argon. The response time for each gas and the partial pressure calibration were obtained. From the calibration, the ratio of partial pressures that was measured in the mass spectrometer matches well to the standard gas. In Figure 5.7, different response time for Ar, CO\textsubscript{2}, and O\textsubscript{2} are observed from the mass spectrometer. In our study, we used the peak numbers of each gas after each sample injection since they matched partial pressure ratio.

![Figure 5.7](image_url)

**Figure 5.7** One of the mass spectrometer calibration data based on 1% O\textsubscript{2}, 5% CO\textsubscript{2} mixture gas in Argon.
After the calibration of the volumes and the mass spectrometer, we applied the DEMS instrument to perform Na-O$_2$ batteries and Li-O$_2$ batteries. The detailed experiments will be introduced in the following sections.

5.4 DEMS Investigation on Na-O$_2$ Batteries.

5.4.1 Cell assembly

The Na-O$_2$ cell was assembled by packing sodium metal, glass fiber separator, air electrode, and stainless steel mesh current collector together. Two pieces of glass fiber papers were used as the separator to guarantee the contact of anode and the cathode. The air electrode was using carbon fiber paper (H2315, Freudenberg) and the electrolyte was 1 M Na triflate in diglyme. The cell was assembled and sealed in the glove box with oxygen level smaller than 0.1 ppm and water level smaller than 0.5 ppm. It was wired to a MTI 8-channel battery analyzer. The current was set to 0.1 mA·cm$^{-2}$ and the voltage window was set to 1.8 to 4.2 V.

5.4.2 DEMS Measurement

The Na-O$_2$ battery was tested in DEMS instrument. Before the measurements, the mass spectrometer was on for one day to wait for the background reaching to equilibrium. The partial pressures of major gas components maintain at the scale of 1e-9 torr. During discharge, we used only pressure transducer to monitor the discharge since not much by-products in gas phase were formed. Before discharge, oxygen was purged through the system and valves A and B were closed. Since V1 (volume between valves A and B) was known, the pressure changes corresponding to the consumption of the oxygen in the cell
during discharge was also known. After discharge, the gas in V1 was injected to the mass spectrometer and no other signals were detected except oxygen. The second discharge profile of the Na-O_2 cell is shown in Figure 5.8a. Based on the discharge capacity, we simulated the one-electron transfer curve and compare with the experimental data in Figure 5.8b. The two overlapped curves proves that Na-O_2 goes through one-electron transfer reaction during discharge.

**Figure 5.8** DEMS tests of the Na-O_2 cell at discharge. (a) Discharge voltage profile of Na-O_2 cell. (b) Pressure change during discharge. The theoretical curve is calculated from the current flow of the cell.
During charge, argon gas was purged through the system and maintained certain pressure. The mass spectrometer can be used to detect if all the oxygen is removed from the system. In position B, valves A and C are open, and B and D are closed. In this case, V3 is filled with Ar and V4 is under vacuum. In the meantime, the cell is isolated for collecting the gas product. After 15 min, valve c was closed and then the Valco valve was switched to position B. In this case, the carrier gas, argon, pushed the gas in the cell head space to the transfer line. After 1 second, switch the Valco valve back to position A, pushing the gas in the transfer line to V4. Open valve D to let gas coming into the mass spectrometer. Once the data was collected, close valve D and open C. The data was collected every 15 min. The results are shown in Figure 5.9.
Figure 5.9 DEMS tests of the Na-O$_2$ cell at charge. (a) Charge voltage profile of Na-O$_2$ cell. (b) Pressure change during discharge. The theoretical curve is calculated from the current flow of the cell.

When switching position A to position B, the gas in the transfer line was injected to V2, while the pressure transducer recorded the pressure of the gas. In this case, the mols of the total amount of the gas was known by the ideal gas law. From the calibration and the partial pressure of each gas in the mass spectrometer, we could obtain the mols of each gas, shown in Figure 5.9b. As can be seen, in Na-O$_2$ cells, the gas evolution includes mainly
oxygen, hydrogen and carbon dioxide. From the capacity to the gas generation, the charge process consumes 1.13 electrons to 1 oxygen formation. At the end of the charge, we observe a quick increase of the partial pressure of hydrogen, indicating side reactions occurred. However, the generation of hydrogen in such a high voltage requires further investigation.

5.5 DEMS Investigation on Li-O₂ Batteries.

5.5.1 Cell assembly

The cell assembly of Li-O₂ battery is similar to Na-O₂ battery introduced in chapter 5.4.1. In the Li-O₂ cell, we applied a MoS₂/reduced graphite oxide/carbon electrode as the cathode. The electrode was cut into ½ inch diameter and placed in the stainless steel cell. The electrolyte was 1 M LiTFSI in TEGDME with 500 ppm LiI. The current was set to 300 mA·g⁻¹. The cell head space was calibrated every time before tests.

5.5.2 DEMS measurements

Based on the collaboration of University of California San Diego, they synthesized the air electrode, MoS₂/reduced graphite oxide (rGO)/carbon, for Li-O₂ batteries with additive of LiI and accomplished major characterization studies. They identified the discharge product is Li₂O₂ and it was mainly imbedded in the matrix of layer MoS₂ in the form of Li₂Mo₂SO₂. In order to reveal the role of MoS₂/graphene electrode and the additive LiI in the OER and ORR processes in Li-O₂ cells, DEMS measurement is performed to support the mechanism.
The discharge/charge procedure of the DEMS tests are similar to the trial explicated in chapter 5.4.2. The voltage profiles are shown in Figure 5.10. The voltage of the first discharge is around 2.65 V which is similar to that of a typical Li-O\textsubscript{2} cell without any additives. Interestingly, the charge voltage is only 2.95 V, converting to a very small charge overpotential. For the second discharge, the curve shows two plateaus, in which the first one is located at 2.95 V and the second one is around 2.70 V. The first discharge is more likely to be an activation process for the reaction of Li\textsubscript{2}O\textsubscript{2} and MoS\textsubscript{2}. For the following cycles, the lithiation/delithiation of MoS\textsubscript{2} becomes more reversible in the function of the additive, I\textsuperscript{-}. The DEMS results of the first two cycles are recorded in Figure 5.11.

Figure 5.10 Voltage profiles of the first 50 cycles of MoS\textsubscript{2}/rGO based Li-O\textsubscript{2} battery.
Figure 5.11 The results of DEMS measurements of the first cycle (a, b) and the second cycle (c, d) of the MoS$_2$/rGO based Li-O$_2$ cell.

There are discrepancies of the first two cycles, especially during discharge so the DEMS measurements are performed for the two cycles to reveal the oxygen consumption/evolution. The gas consumption during the first discharge is shown in Figure 5.11a. The black curve shows the change of gas during discharge, while the theoretical consumption of oxygen is also shown as the straight lines of 1-electron process and 2-electron process. As can be seen, from the first half hour, the reaction is more likely to be 1-electron process and the following discharge follows 2-electron process. However, the
reactions are not exactly 1 or 2 electrons, indicating the side reactions occurred in the system. For the 1st charge, shown in Figure 5.11b, the data are collected every 10 min and compares with the theoretical value. Based on the results, the oxygen evolution firstly experiences 1-electron process and then follows the 2-electron process. For the second cycle, the discharge process shows a neat curve, which first follows the 1-electron process for the first 1 h and then the 2-electron process for the following discharge. The 2nd charge shows similar result to the 1st charge.

A mechanism was proposed based on the results obtained, shown in equations 5.1 to 5.8. The oxygen firstly reduced to superoxide species which dissolves in the electrolyte. The superoxide species were then captured by iodide and water to form IO\(^-\) in the solution, which could react with MoS\(_2\) and form MoO\(_2\)S\(_2\) and iodide. The iodide plays a role of catalyst and it helps to stabilize superoxide in the matrix of MoS\(_2\).

Discharge:

\[
\begin{align*}
O_2 + e^- & \rightarrow O_2^- \quad (5.1) \\
2O_2^- + 3I^- + H_2O & \rightarrow 3IO^- + 2OH^- \quad (5.2) \\
2IO^- + MoS_2 & \rightarrow MoO_2S_2 + 2I^- \quad (5.3) \\
2Li^+ + MoO_2S_2 + 2e^- & \rightarrow Li_2MoO_2S_2 \quad (5.4) \\
2Li^+ + IO^- + 2OH^- & \rightarrow Li_2O_2 + I^- + H_2O \quad (5.5) \\
2Li^+ + e^- + O_2^- & \rightarrow Li_2O_2 \quad (5.6)
\end{align*}
\]

Total discharge reaction:

\[
\begin{align*}
O_2 + MoS_2 + 2Li^+ + 2e^- & \rightarrow Li_2MoO_2S_2 \quad (5.7) \\
2Li^+ + 2e^- + O_2^- & \rightarrow Li_2O_2 \quad (5.8)
\end{align*}
\]
From equation 5.2, the formed superoxide species is firstly stabilized by iodide to form IO⁻. This might explain why the first 1 h discharge is one electron process. The following discharge corresponds to the formation of Li₂O₂ which undergoes 2 electron reaction. Both formation of Li₂MoO₂S₂ and Li₂O₂ contributes to the discharge capacity. However, during the charge process, the additive is critical to the low charge overpotential and the oxygen evolution. The theoretical charge reactions are listed in equation 5.9-5.10, which follows two electron transfer reaction. However, from the DEMS results (Figure 5.11b and d), larger amount of oxygen evolves from the air electrode at the beginning of the charge. It is probably coming from side reactions which also includes oxygen evolution. At the end of the charge process, less oxygen than the theoretical value is generated which compensates the amount of the oxygen released at the beginning of the charge process, indicating the side reactions occurred at the beginning of the charge is from the chemical decomposition of Li₂O₂.

Charge:

\[ 3I^- \rightarrow I_3^- + 2e^- \] (5.9)

\[ \text{Li}_2\text{O}_2 + I_3^- \rightarrow 3I^- + 2\text{Li}^+ + \text{O}_2 \] (5.10)

Although the mechanism of the MoS₂/rGO based Li-O₂ cell requires further investigation, DEMS provides insights for understanding the mechanism and displays the information of electrochemical/chemical reactions for each step. As can be seen, the oxygen evolution did not follow the 2-electron pathway and more complicated reaction pathway occurred during charge by the addition of I⁻.

5.6 Conclusion
DEMS is a useful tool to be applied in metal oxygen batteries since they use oxygen as the cathode source, the amount of which could be monitored during the measurements. In our study, we successfully installed the DEMS system based on a purchased mass spectroscopy and calibrated the system by different ratio of gas components and known volume loops. The DEMS turns out to be reliable and functional based on the results on the sodium oxygen battery and lithium oxygen battery. It correlates the relationship between the electron flow through the system and the consumption/release of oxygen. In addition, based on the variation of the electron/gas ratio, we could conclude if chemical reactions occur and how they contributes to the overall reaction.

However, regarding to the procedure to build the DEMS instruments, some issues need to be addressed for the further design of DEMS system. The accuracy of the DEMS instrument is determined by many factors. Firstly, the error of the instrument is mainly from the reading of the pressure transducer. Certain amount of time is required to obtain a stable reading. It contributes error to the calibration of volumes and the measurements on the amount of gas. Secondly, the design of metal air cell also brings error to DEMS due to the dissolution of gases in the electrolyte, and thus the total amount of gas might be underestimated. Thirdly, the response time of the mass spectrometer is critical to the reading of partial pressure of each gas. The different response behavior of different gas component may affect the ratio of the reading, causing error to the data.
Chapter 6: Conclusion and Outlook

The discharge products in both Li-O\textsubscript{2} batteries and Na-O\textsubscript{2} batteries have been reviewed in chapter 1. The complexity of the discharge products indicates the complex electrochemical environments in metal air batteries. The instability of NaO\textsubscript{2} in Na-O\textsubscript{2} batteries was investigated, mainly due to the side reactions with the formed NaO\textsubscript{2} and the carbon substrate. Further studies could be performed by replacing the carbon substrate to more stable materials such as nanoporous gold or TiC which have been reported as stable electrodes. Moreover, we controlled the formation of two different products by two different cell setups. The preliminary data of the theoretical calculation study show that the structure of Na\textsubscript{2}O\textsubscript{2}·2H\textsubscript{2}O is instable and our study indicates it is more likely in the form of 2NaOH·H\textsubscript{2}O\textsubscript{2}. It is interesting to investigate the structure of 2NaOH·H\textsubscript{2}O\textsubscript{2} by chemical synthesis and theoretical study in the future study.

Other than the problem of the air electrode, the Na anode in Na-O\textsubscript{2} batteries brought more issues. The dendrite formation of sodium metal caused the pre-mature death of the cell and oxygen crossover from the air electrode to the anode also generates the side reactions between Na, oxygen, and the electrolyte. In our study, the dendrite formation can be suppressed by applying a separator as a physical barrier between the anode and the cathode. The cyclability of the Na-O\textsubscript{2} batteries was largely increased. In addition, we
performed the studies on the side products on the anode and the cathode separately, confirming that the oxygen crossover to the anode induced severe side reactions.

In Li-O\textsubscript{2} batteries, the discharge product in a mixed salt electrolyte was investigated. By applying Na\textsuperscript{+}-contained Li\textsuperscript{+} electrolyte, the discharge product was confirmed to be LiOH instead of Li\textsubscript{2}O\textsubscript{2}. It could be recharged at a low charge overpotential, enabling the application of LiOH based Li-O\textsubscript{2} batteries. Although the mechanism of the formation of LiOH is unclear at this stage, the addition of Na\textsuperscript{+} is very likely tuning the formation pathway of the discharge products in Li-O\textsubscript{2} batteries. Mechanism study will be performed such as DEMS study to monitor the oxygen consumption and evolution.
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