Investigating the Factors for the Low Cycle Life of Sodium Oxygen
Batteries

Master Thesis

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By

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Abstract

Metal air (oxygen) batteries have recently attracted extensive research attentions due to the high theoretical energy density. Compared to lithium oxygen batteries, sodium oxygen batteries have much lower charging overpotentials which may offer longer cyclability and higher energy efficiency without losing much energy density ($\sim 1100 \text{ Wh kg}^{-1}$ vs. $\sim 3460 \text{ Wh kg}^{-1}$). However, the short cycle lives of sodium oxygen batteries greatly limit their applications in transportations or energy storage systems. The main reasons for the short cycling life of sodium oxygen batteries were primarily ascribed to be the accumulation of by-product during discharge and charge processes and/or electrolyte degradation. However, in our studies, both accumulation of by-product and electrolyte decomposition could not explain the failure of batteries for the first few cycles. In the first part of this thesis, sodium dendrite formation was identified to be 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. By solving the deadly short circuit problem of sodium oxygen batteries with Nafion membrane's physical preventing effect, cycle lives of 118 cycles in dimethoxyethane (DME) based electrolytes and 80 cycles in bis(2-methoxyethyl) ether (diglyme) based electrolytes were achieved with a current density of 0.16 mA cm^{-2} . In the second part of this thesis, the components of SEI layer on the sodium anode and by-product in the air electrode were identified. The sodium anode went through severe degradation process. It is proved that oxygen crossover was another factor to cause the failure of sodium oxygen batteries.

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.

Dedication

To my family

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Field of Study

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Table of Contents

Abstract.....	ii
Dedication.....	iv
Acknowledgment.....	v
Vita.....	vi
Table of Contents.....	viii
List of Tables.....	xi
List of Figures.....	xii
Chapter 1: Introduction.....	1
1.1 Metal oxygen batteries.....	1
1.1.1 Lithium oxygen batteries.....	2
1.1.2 Sodium oxygen batteries.....	5
1.2 Dendrite issue in the metal anode.....	7
1.2.1 Lithium anode.....	8
1.2.2 Sodium anode.....	10
1.3 Nafion membrane.....	12
1.4 Conclusion.....	14
Chapter 2: Experimental methods.....	15

2.1 Materials and batteries assembly.....	15
2.2 Characterization methods.....	16
2.2.1 X-ray diffraction (XRD)	16
2.2.2 Nuclear magnetic resonance (NMR)	17
2.2.3 Raman spectroscopy.....	17
2.2.4 Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS).....	18
2.2.5 X-ray photoelectron spectroscopy (XPS)	18
2.3 EIS method and battery performance tests.....	18
Chapter 3: Improved cyclability via an ion selective membrane in Na-O ₂ batteries	20
3.1 Dendrite issue in Na-O ₂ batteries.....	20
3.1.1 Electrolyte selection.....	20
3.1.2 Dendrite issue in Na-O ₂ batteries.....	24
3.2 Enhanced cycle life by Nafion-Na ⁺ membranes.....	29
3.2.1 Ionic conductivity of Nafion-Na ⁺ membranes.....	29
3.2.2 Enhanced cycling life of Na-O ₂ batteries.....	35
3.3 Conclusion.....	38
Chapter 4: The effects of electrolyte decomposition in Na-O ₂ batteries.....	40
4.1 Electrolyte decomposition.....	40
4.2 Sodium anode issues.....	43

4.2.1 The reactions between sodium and DME based electrolyte.....	43
4.2.2 The reactions between sodium and DME based electrolyte in Na-O ₂ batteries.....	45
4.2.2.1 Raman spectroscopy.....	45
4.2.2.2 XPS spectroscopy.....	46
4.2.3 Cycling efficiency of sodium metal in the sodium oxygen battery.....	49
4.3 Cathode issues.....	52
4.3.1 Raman spectroscopy.....	53
4.3.2 XPS spectroscopy.....	54
4.4 Conclusion	55
Chapter 5: Conclusion and future.....	56
5.1 Conclusion.....	56
5.2 Future.....	56
References.....	58

List of Tables

Table 3.1 Diffusion Coefficients Calculated from Oxygen Uptake Experiments.....	21
Table 3.2 Measurements of ionic conductivity of Nafion- Na^+ membrane.....	32
Table 3.3. Measurements of ionic conductivity of electrolyte in glass fibers.....	34
Table 3.4. Calculated ohmic loss from Nafion- Na^+ membrane and glass fibers.....	34

List of Figures

Figure 1.1 The gravimetric energy densities (Wh kg^{-1}) for various types of rechargeable batteries compared to gasoline. ⁷	2
Figure 1.2 The schematic diagram of lithium oxygen batteries. ⁷	3
Figure 1.3 The discharge/charge profiles of (a) a Li-O_2 battery and (b) a Na-O_2 battery. ²⁶	6
Figure 1.4 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/ LiPF_6 solution.) ³²	8
Figure 1.5 The chemical formula of Nafion film.	12
Figure 1.6 The cluster network model of Nafion.	13
Figure 2.1 The optical image of the Swagelok cell.	15
Figure 2.2 The optical image of air-tight sample holder for Raman spectroscopy.....	17
Figure 3.1 Schematic diagram of the Na-O_2 battery.	21
Figure 3.2 Discharge/charge profiles of Na-O_2 batteries in 0.5 M Na triflate (a) DME and (b) diglyme electrolytes.	22
Figure 3.3 (a) X-ray diffraction and (b) Raman spectra of discharge products on P50 carbon	

paper.	23
Figure 3.4 Discharge/charge profiles of Na-O ₂ 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.	24
Figure 3.5 The discharge/charge profiles after short circuit and after changing the separator.	25
Figure 3.6 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.	27
Figure 3.7 Na/Na sodium symmetric cells under argon (a) and under oxygen (b). (c) and (d) are the amplified images in (b).	28
Figure 3.8 (a) Equivalent circuit and (b) Nyquist plot of Nafion-Na ⁺ membrane in device. Insert of (b) is an amplified Nyquist plot of the blue square.	30
Figure 3.9 The curve angle of the Nyquist plot of Nafion-Na ⁺ membrane.....	31
Figure 3.10 SEM images of (a) Nafion-Na ⁺ membrane and (b) glass fibers.....	33
Figure 3.11 Nyquist plots and fitting data of Nafion-Na ⁺ membrane and glass fibers.....	33
Figure 3.12 The discharge/charge profiles of the first cycle of battery in DME based	

electrolyte.	34
Figure 3.13 The schematic diagram of Na-O ₂ batteries (a) with and (b) without using Nafion-Na ⁺ membrane.	36
Figure 3.14 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	36
Figure 3.15 The schematic diagram of a Na-O ₂ battery and optical images of glass fiber separators with using Nafion-Na ⁺ after cycles. (b) #2 glass fiber separator faced to the metal anode side and (c) faced to the Nafion-Na ⁺ membrane side. (d) #1 glass fiber separator faced to the Nafion-Na ⁺ membrane side.	37
Figure 4.1 (a) ¹ H-NMR and (b) ¹⁹ F-NMR spectra of the glass fiber separator tested after 6 cycles in a Na-O ₂ battery with DME based electrolyte.	41
Figure 4.2 ¹ H-NMR spectra of glass fiber separator faced to (a) the anode and (b) the cathode after 6 cycles in DME based electrolyte.	41
Figure 4.3 ¹⁹ F-NMR spectra of glass fiber separators faced to (a) the anode and (b) the cathode after 6 cycles in DME based electrolyte.	43
Figure 4.4 Optical images of sodium metal immersed in (a) pure DME and (b) 0.5 M sodium	

triflate in DME after one month. (c) and (d) are the Raman spectra of samples in (a) and (b), respectively.	44
Figure 4.5 Optical image of the sodium anode after 120 cycles.	45
Figure 4.6 Raman spectra of the sodium anode after 120 cycles.	46
Figure 4.7 (a) C1s, (b) F1s, (c) S2p and (d) Na1s XPS spectra of the sodium anode after 110 cycles.	47
Figure 4.8 Proposed mechanism of DME decomposition on the anode side with oxygen crossover. ⁶²	48
Figure 4.9 Discharge/charge profiles of Na-O ₂ battery in 0.5 M sodium triflate DME electrolyte.	49
Figure 4.10 (a) Cycling efficiency and (b) coulombic efficiency of the sodium oxygen battery.	50
Figure 4.11 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.	51
Figure 4.12 The SEM image of NaO ₂ from literature 50. SEM images of a cathode structure after discharge to 2 mAh at 80 $\mu\text{A cm}^{-2}$ at the oxygen/gas diffusion layer and gas diffusion layer/separator side.	52
Figure 4.13 Raman spectra of air electrode (P50) after 118 cycles in DME. Two references are	

NaO ₂ on P50 substrate and NaOH.	53
Figure 4.14 (a) C1s, (b) F1s, (c) S2p and (d) Na1s XPS spectra of the carbon cathode after 110 cycles.	54

CHAPTER 1: INTRODUCTION

Nowadays, more than 60% of the nation's energy was supplied by oil and natural gas, which are used to provide energies to the nation. However, the huge consumption of oil and natural gas not only pollutes the atmosphere but also generates large amount of carbon dioxide (CO_2), forming the major part of the total CO_2 emission.¹ In order to reduce the greenhouse effect, renewable sources such as wind, solar and waterpower 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.

Batteries with high volumetric and gravimetric energy density enable the storage of renewable energies without dissipation. Current battery technologies in the world are lithium ion (Li-ion), lead acid, sodium-sulfur (Na-S), nickel-metal hydride, flow batteries, etc.² However, those battery technologies suffer different kinds of problems such as high cost, environment hazardous, low energy density or low energy efficiency. Currently, lithium ion batteries are the dominant battery technology in the battery market, but the high cost and low theoretical energy density are major impediments for their applications in electric vehicles (EVs) or large-scale energy storage stations. Therefore, new battery technologies with high energy densities and low capital costs are imperative to be developed to fulfill the large energy demands.^{3,4}

1.1 Metal oxygen batteries

New battery technologies such as sodium ion batteries (NIB)⁵, lithium sulfur batteries (Li-S)⁶ and metal air batteries including zinc-air, lithium-air, sodium-air and potassium-air

batteries have attracted extensive research interests recently due to their high theoretical energy densities based on the air electrodes^{7,8,9}. The key of the high theoretical energy density is from the “air” because oxygen is used as the cathodic reactant, which largely lowers the weight of batteries. Among those battery technologies, sodium oxygen batteries have multiple benefits such as high round-trip efficiency and abundant in the world. However, few works have been reported on sodium oxygen batteries. In order to understand the chemical behavior of alkali metals in batteries and emphasize the importance of sodium oxygen batteries, metal oxygen batteries will be introduced and the issues from the metal anode will be discussed in this chapter.

1.1.1 Lithium oxygen batteries

Figure 1.1 The gravimetric energy densities (Wh kg^{-1}) for various types of rechargeable batteries compared to gasoline.⁷

Over the past few years, lithium air batteries have become one of the most promising batteries in the world. Compared to other battery technologies, lithium oxygen batteries display much higher theoretical energy density of 11700 Wh kg^{-1} , which indicate that they could store as much energy as gasoline (Figure 1.1). The oxygen used in metal air batteries

greatly reduces the weight and lowers the costs indicating the potential applications in EVs and large-scale energy storage stations. In a typical lithium oxygen battery, lithium metal is used as the anode, and porous carbon is used as a gas diffusion layer in the cathode. The schematic diagram of the lithium oxygen battery is shown in Figure 1.2. Upon discharge, lithium metal generates lithium ions transporting through the separator to the air electrode. Electrons move through the external circuit and meet oxygen in the air electrode to form superoxide. Then lithium ions react with superoxide to form lithium superoxide. Given the fact that lithium superoxide is thermodynamically unstable, it further forms to lithium peroxide (Li_2O_2) which deposits on the inert porous carbon cathode. Upon charge, Li_2O_2 is decomposed to lithium ions and oxygen and lithium ions diffuse through the separator to the Li metal and further deposit on the metal surface. The overall reaction in lithium oxygen batteries is shown in Equation 1.1:

Figure 1.2 The schematic diagram of lithium oxygen batteries.⁷

Lithium oxygen batteries were firstly demonstrated by Abraham and Jiang in 1996.¹⁰ They employed a mixture electrolyte consisting of two carbonate-based solid polymer solvents. The discharge potential was around 3 V and lithium peroxide (Li_2O_2) was detected as

the major discharge product in the solid-state battery. Abraham and Jiang's work opened a new field of batteries with high potential energy density. However, the follow-up studies were rare until recent years due to people's large demands of energy storage. At the beginning of the development, carbonates-based electrolytes which had been commonly used in LIBs were considered as a good candidate for lithium oxygen batteries. 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, forming lithium carbonates (Li_2CO_3) and other side products on the cathode instead of the desired product, Li_2O_2 .^{11,12} In contrast, ether-based electrolytes showed much higher stability in lithium oxygen batteries with Li_2O_2 as the major discharge product. However, the same group reported that ether solvents still suffered the decomposition in oxygen rich environment.¹³ The decomposition products from the ether solvents are mainly Li_2CO_3 , HCO_2Li , $\text{CH}_3\text{CO}_2\text{Li}$, poly ethers/esters, CO_2 and H_2O . Therefore, highly stable electrolytes need to be explored to fulfill the critique requirements for oxygen batteries due to the high reactivity of superoxide species. Ionic liquids with low vapor pressure and large electrochemical window have been regarded as a promising category of solvents for lithium oxygen batteries. Mizuno et al. reported that an ionic liquid (PP13-TFSA) with high stability increases the cycle life of the lithium oxygen battery¹⁴. However, ionic liquids suffer issues such as the high viscosity and low oxygen solubility. Lithium ion conduction can be affected by those issues, generating high discharge/charge polarizations. Therefore, looking for an electrochemical stable, thermal stable and highly ionic conductive electrolyte is the priority in lithium oxygen batteries.

In addition to the low stability of electrolytes, the insulating property of lithium peroxide is another major issue in lithium oxygen batteries. Lithium peroxide has an electronic conductivity of $5\text{e-}^{20} \text{ S cm}^{-1}$ leading to high polarizations ($> 1 \text{ V}$) during the charging process (lithium peroxide decomposition process).¹⁵ Due to the low electronic conductivity of lithium peroxide, the discharge capacity is generally limited by the air electrode. Based on calculating

studies, once the thickness of lithium peroxide reaches to 5 nm, it would prevent the further lithium peroxide deposition on the surface of air diffusion layer and thus stop the discharging process.^{16,17} Therefore, most researches have been focused on the air electrodes in lithium oxygen batteries. To facilitate the decomposition of lithium peroxide, different approaches were investigated to modify carbon materials and catalysts^{18,19,20}. Metal catalysts incorporated into the porous carbon air electrode could enhance the oxygen reduction kinetics and increase the specific capacity of the cathode. Peng et al. reported that using nanoporous gold (NPG) as the air diffusion layer and DMSO as the solvent in electrolyte, over 100 cycles were achieved in the lithium oxygen battery.²¹ NPG is stable to superoxide species and provides higher electronic conductivity than traditional carbon materials, further improving the kinetics of lithium peroxide formation and decomposition. Lu et al. designed a stable nanostructured carbon cathode for lithium oxygen batteries, which effectively protected carbon materials from the attack of superoxide.²² The cathode was made by porous carbon materials with a protective Al₂O₃ layer by atomic layer deposition (ALD) method attached with palladium nanoparticles. Alumina layer covered defect sites on the surface of porous carbon and palladium nanoparticles increased the electronic conductivity of the surface of porous carbon and provided more active sites for Li₂O₂ formation, reducing the charging overpotential to 3.5 V.

1.1.2 Sodium oxygen batteries

Sodium oxygen (Na-O₂) batteries were first reported by Peled et al. in 2011.²³ In sodium oxygen (Na-O₂) batteries, there are two possible products from the reactions of sodium and oxygen, sodium peroxide (Na₂O₂) and sodium superoxide (NaO₂). The overall reactions are shown as follows:

The free energies of the two reactions indicate that the formation of Na_2O_2 is more thermodynamically favorable. At the beginning of investigations on sodium oxygen batteries, since lithium and sodium were from in the same elementary group, people thought Na- O_2 batteries might have the same problem as Li- O_2 batteries with poor electronic conductivity of the product and low gravimetric energy density due to the heavier sodium metal. In the first study of sodium oxygen batteries, Peled et al. reported that using sodium as the anode and oxygen in the cathode, the sodium oxygen battery ran several cycles at the temperature of 105 °C.²³ However, the study did not include the characterization of discharge products and the high temperature brought up the safety issues. After that, Kim et al. investigated the discharge products and possible mechanisms of sodium oxygen batteries in carbonate-based electrolyte and ether-based electrolyte at room temperature. 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 found to be 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.²⁴

Figure 1.3 The discharge/charge profiles of (a) a Li- O_2 battery and (b) a Na- O_2 battery.²⁵

In 2013, Hartmann et al. reported that a sodium superoxide (Na- O_2) battery with 0.2 V voltage polarizations upon charge, which makes sodium air battery technology as a promising

competitor to lithium oxygen batteries.²⁵ The discharge/charge profiles of Li-O₂ and Na-O₂ batteries are shown in Figure 1.3.

In the lithium oxygen battery, the charging overpotential is generally larger than 1 V due to the low electronic conductivity of Li₂O₂ and multiple reaction steps. As shown in Figure 1.3a, the dashed line represents the standard potential, 2.96 V, for Li-O₂ battery. The distance between the dashed line and discharge/charge voltages shows the overpotential. The charging voltage is over 4.0 V vs. Li⁺/Li, leading to a low round-trip efficiency of the lithium oxygen battery. In contrast, Na-O₂ batteries show much lower overpotential (<200 mV), indicating that the product, NaO₂, forms a crystalline structure indicating better electronic conductivity than Li₂O₂. In addition, compared to the multi-step reactions in Li-O₂ batteries, Na-O₂ batteries undergo a reversible reaction with a single electron transfer process:

where sodium superoxide (NaO₂) is the discharge product and the equilibrium potential is 2.27 V. Although the reason for the formation of NaO₂ in the sodium oxygen battery is still not well understood, the high round-trip efficiency makes it a promising battery technology. Similar to the sodium oxygen 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.²⁶ However, the development of Na-O₂ batteries was greatly hindered by the poor cyclability, which was ascribed to by-product formation, instability of electrolytes, reactive anode and metal dendrite formation.

1.2 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 lithium oxygen 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 reference the studies of dendrite in lithium ion batteries to understand the mechanism of dendrite formation and approaches to prevent dendrite growth.

1.2.1 Lithium anode

Figure 1.4 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.)³¹

The dendrite formation has been identified as a serious issue in lithium batteries many years ago.^{27,28} 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.²⁹ Orsini et al. used in-situ scanning electron microscopy (SEM) to observe morphology changes of the metal surface in lithium batteries.³⁰ They stated that at low current flow lithium had a moss structure while at high current flow 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 1.4).³¹ 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 flow could induce a rapid temperature increase leading to the explosion of batteries. In lithium dissolution process, the hollow area on lithium surface would be firstly dissolved to form deep valleys on the surface. With further dissolutions 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 appropriate SEI layer are key motivations to use lithium metal as the anode and reduce the safety hazards in lithium batteries. Currently, Sony's lithium ion batteries³² 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.³³ 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.³⁴ 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 LiAsF₆ 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.³⁵ Another method was reported by PolyPlus Battery Co.³⁶ 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 . 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-O₂ batteries, more complicated reactions could occur on the Li anode in the presence of O₂ crossed from the air cathode.³⁷

1.2.2 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.³⁸ 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 a problem 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)³⁹ 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 sodiation⁴⁰. 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⁻¹.⁴¹ Metal oxides anode materials such as SnO₂⁴², TiO₂⁴³ and Fe₂O₃⁴⁴ 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 structure changes.

In sodium oxygen batteries, Peled et al. reported a Na-O₂ battery operated at a temperature of 98 °C, which is slightly higher than the melting point of sodium, 97.72 °C.²³ 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-O₂ 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.⁴⁵ 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.⁴⁶

Regarding to 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-O₂ batteries have been focused on the air cathode such as investigating the formation of Na₂O₂ or NaO₂, and electrolyte decomposition. The studies on the anode need to be further explored in the future.

1.3 Nafion membrane

In our 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.

Figure 1.5 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.⁴⁷ The chemical formula of Nafion is shown in Figure 1.5. It consists of fluoroethylene polymer backbones with perfluorovinyl 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 1.6 The cluster network model of Nafion.

The cluster network model of Nafion is shown in figure 1.6. 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.⁴⁸ 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.⁴⁹ 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.⁵⁰ 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.

1.4 Conclusion

In conclusion, several promising battery technologies have been discussed in this chapter, within which sodium oxygen batteries with high round-trip efficiency and relatively high energy density have become one of the most promising batteries in the world. Although many works have been done in lithium batteries to investigate mechanism and solution of dendrite formation, limited studies have been reported in sodium batteries. The limited reports on the Na anode force us to explore the solution for Na dendrite formation. In our studies, dendrite penetration and oxygen crossover have been discovered to be the major issues for the low cycle life of Na-O₂ batteries. We will investigate the effects of dendrite formation on the battery cycle life and use sodium ion selective Nafion (Nafion-Na⁺) membranes as part of separators to inhibit dendrite penetration. In addition, to understand the underlying causes side reactions on both electrodes will be investigated.

CHAPTER 2: EXPERIMENTAL METHODS

2.1 Materials and batteries assembly

A sodium metal slice (Fisher Scientific, labgrade) was used as the metal anode and P50 (AvCarb®) was used as the air electrode in the Na-O₂ 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.

Figure 2.1 The optical image of the Swagelok cell.

Purchased Nafion® 211 membranes (25µm, 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.

The Swagelok cell setup is shown in Figure 2.1. The bottom stainless steel piece has a rod in the center as current collector and a support for the metal anode. The top piece with two valves allows the oxygen flow. The two stainless steel pieces were sealed by a Telfon® (DuPont) white holder with two O-rings on both sides isolating the cell from the air. A small oxygen reservoir with approximate 4 mL volume was linked to the cell for storing oxygen. A stainless steel mesh was used as the current collector and support for P50 carbon paper. A sodium oxygen battery was assembled by packing the sodium slice, separators, P50 gas diffusion layer, a stainless steel mesh and a washer in the Swagelok cell.

In the sodium oxygen batteries with Na^+ -Nafion membranes, the thickness of separators was well controlled. Without Nafion- Na^+ membranes, one piece of glass fiber (Whatman, 600 μm 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 μm thickness, 600 μm 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.

2.2 Characterization methods

2.2.1 X-ray diffraction (XRD)

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.

2.2.2 Nuclear magnetic resonance (NMR)

NMR spectroscopy was used to investigate the electrolyte decomposition products in sodium oxygen batteries. The separator samples with electrolyte were put in D₂O solvent (99.9%, Sigma-Aldrich). After dissolving in D₂O solvent, the electrolyte sample was transferred to an NMR test tube and ¹H-NMR and ¹⁹F-NMR spectra were tested by a 400 MHz NMR spectrometer (Bruker, Avance III).

2.2.3 Raman spectroscopy

Figure 2.2 The optical image of air-tight sample holder for Raman spectroscopy.

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 and shown in Figure 2.2. The holder is made by aluminum base with a quartz window. Two O-rings were used to seal it.

2.2.4 Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS)

The SEM and 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.

2.2.5 X-ray photoelectron spectroscopy (XPS)

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

2.3 EIS measurements and battery performance tests

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 10⁶ 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 ultrasonication for 5 min each and dried in the heating oven at 100 °C for 10 min. 50 μ L 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.

CHAPTER 3: IMPROVED CYCLABILITY VIA AN ION SELECTIVE MEMBRANE IN Na-O₂ BATTERIES

3.1 Dendrite issue in Na-O₂ batteries

3.1.1 Electrolyte selection

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. To date, all the batteries suffer from the problem of electrolyte decomposition. 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 group^{Error! Bookmark not defined.} 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, NaO₂.²⁴ Therefore, seeking a stable solvent is the priority in metal oxygen batteries.

Ether solvents have been widely investigated in metal-oxygen batteries^{13,25,26} 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.⁵¹

Solvent/electrolyte	$D_{O_2}/10^{-5} \text{ cm}^2/\text{s}$	$H_{O_2}/\text{mol}/(\text{m}^3 \text{ bar})$
DME	6.0 ± 0.5	10.1 ± 0.3
Diglyme	4.4 ± 0.3	6.4 ± 0.2
0.5 M NaTfO/diglyme	3.9 ± 0.3	6.3 ± 0.2
Triglyme	3.2 ± 0.3	5.6 ± 0.3
Tetraglyme	2.6 ± 0.3	4.3 ± 0.2
DMAc	4.3 ± 0.3	5.4 ± 0.3

Figure 3.1 Schematic diagram of the Na-O₂ battery.

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 3.2 Discharge/charge profiles of Na-O₂ batteries in 0.5 M Na triflate in (a) DME and (b) diglyme electrolytes.

In Figure 3.2, DME based and diglyme based electrolytes show similar discharge and charge profiles. The equilibrium reaction voltage is 2.27 V in Na-O₂ batteries based on the reaction: $\text{Na} + \text{O}_2 \rightarrow \text{NaO}_2$. 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 NaO₂ formation in the cathode and the

sodium surface changes in the Na anode. Upon discharge, the accumulation of NaO_2 passives 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_2O_2 as the major discharge product^{52,53,54}. The low electronic conductivity of Na_2O_2 contributes a large charging voltage in sodium oxygen batteries, which is similar to Li-O_2 . Therefore, in our sodium oxygen battery, the low charging voltage shows that the decomposition of NaO_2 only contributes small polarization to the charging voltage indicating the high electronic conductivity of NaO_2 .

Figure 3.3 (a) X-ray diffraction and (b) Raman spectra of discharge products on P50 carbon paper.

Products in the Na- O_2 battery with DME based electrolyte were characterized by X-ray diffraction (XRD) and Raman spectroscopy (Figure 3.3). 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 3.3a, 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_2 , separately. There are no side products detected by XRD. Raman spectra further prove that NaO_2 is the major discharge product due to the unique peak from superoxide species at 1156 cm^{-1} which is consistent with the literature²⁵ with diglyme-based electrolyte. In conclusion, we prove that DME and diglyme-based electrolytes provide similar discharge/charge profiles in Na-O_2 batteries. NaO_2 is found to be the major discharge product in the sodium oxygen battery.

3.1.2 Dendrite issue in Na-O_2 batteries

Figure 3.4 Discharge/charge profiles of Na-O_2 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-O_2 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 11th and 12th cycles in DME based electrolyte are shown in Figure 3.4a. The 11th 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 NaO_2 ($\text{Na} + \text{O}_2 \rightarrow \text{NaO}_2$), as discussed above. In diglyme (Figure 3.4b), 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 3.4a). These observations are similar to Hartmann's results⁵³ showing that dendrite formation causes the premature death of Na- O_2 batteries.

Figure 3.5 The discharge/charge profiles of the cell with DME based electrolyte after short circuit and after changing the separator.

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, NaO_2 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.

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 3.5 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 short-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 3.4. 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 showing the recovery. The battery was further charged to 3.4 V to compensate the NaO_2 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 3.6 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 3.6a 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, Na₂SiO₃, which also contains sodium, so there are small amount of sodium signals obtained on the surface of glass fibers. In Figure 3.6b, 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 3.6c, 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 3.6d-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 μm which is consistent with the reported thickness from Whatman. From Figure 3.6d, 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-O₂ 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 3.6e 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-O₂ batteries.

Figure 3.7 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 3.7a, 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 3.7d. 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 3.7c (the amplified image of the first rectangle from Figure 3.7b) 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.

3.2 Enhanced cycle life by Nafion- Na^+ membranes

3.2.1 Ionic conductivity of 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 lives⁵⁰. 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.

Figure 3.8 (a) Equivalent circuit and (b) Nyquist plot of Nafion- Na^+ membrane in device. Insert of (b) is an amplified Nyquist plot of the blue square.

The Nafion- Na^+ membrane was made by changing the proton in purchased Nafion- H^+ membrane in 1 M NaOH DMSO: H_2O (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.

Figure 3.9 The curve angle of the Nyquist plot of Nafion-Na⁺ membrane.

Ionic conductivity was determined by a two-electrode Electrochemical Impedance Spectroscopy (EIS) method. A simplified equivalent circuit⁵⁵ and EIS data are shown in Figure 3.8. 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 (CPE₂) was used to model the capacitance of the two interfaces, shown in Figure 3.8a. The ionic resistance and capacitance of the membrane are represented by a parallel combination of an RC circuit (R_1 and CPE₁). R_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 3.8b), the intersection point at Z_{real} axis gives the value of R_0 . The semicircle at high frequencies corresponds to the ionic resistance (R_1) and capacitance (CPE₁) of the Nafion-Na⁺ membrane. At low frequencies, a straight curve with an angle of 82° is observed (Figure 3.9), which indicates that Nafion-Na⁺ 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 (CPE₂) of two Pt-FTO/membrane interfaces. R₁ 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 σ is the ionic conductivity, R is the AC resistance, L is the thickness and A is the area of Nafion-Na⁺ membrane.

Table 3.2 Measurements of ionic conductivity of Nafion-Na⁺ membrane

Samples (#)	R (Ω)	A (cm ²)	L (cm)	σ (S/cm)
1	242.1	0.42	2.5e-3	2.46e-5
2	65.32	1.54	2.5e-3	2.49e-5
3	66.49	1.54	2.5e-3	2.44e-5
4	381.5	0.27	2.5e-3	2.43e-5

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 μm , 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.

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

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

Samples (#)	R ()	A (cm ²)	L (cm)	(S/cm)
1	32.89	1.33	4.0e-2	4.58e-4
2	32.40	1.33	4.0e-2	4.65e-4

Table 3.4. Calculated ohmic loss from Nafion-Na⁺ membrane and glass fibers.

Samples in battery	Average (S/cm)	A (cm ²)	L (cm)	R ()	I (mA cm ⁻²)	Ohmic loss (mV)
Nafion-Na ⁺	2.46e-5	0.636	2.50e-3	1.60e2	0.100	16.0
Glass Fibers	4.62e-4	0.636	4.00e-2	1.35e2	0.100	13.5

Figure 3.12 The discharge/charge profiles of the first cycle of battery in DME based electrolyte.

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^+ 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 $4.62\text{e-}4 \text{ S cm}^{-1}$ based on two trials.

In Na- O_2 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- O_2 battery, without Nafion- Na^+ membrane the thickness of glass fiber separator was measured as 400 μm in the Swagelok cell under the mechanical pressure. This thickness is maintained in the testing device by adding a 400 μm polyethylene spacer around the glass fiber separator. Thus, in all calculations, 400 μm 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} 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.

3.2.2 Enhanced cycling life of Na- O_2 batteries

Figure 3.13 The schematic diagram of Na-O₂ batteries (a) with and (b) without using Nafion-Na⁺ membrane.

Figure 3.14 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.

Figure 3.15 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 anode side and (c) faced to the Nafion-Na⁺ membrane side. (d) #1 glass fiber separator faced to the Nafion-Na⁺ membrane side.

The addition of Nafion-Na⁺ membranes greatly improves the cyclability of Na-O₂ batteries in both DME and diglyme based electrolytes as shown in Figure 3.14. Prior to assembly, the membrane was soaked in electrolyte for two days. Discharge/charge profiles of 1st, 50th, 118th cycles in DME based electrolyte are shown in Figure 3.14a. 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 80th cycle to 2.65 V in 118th 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 3.14b). After the cycled battery was disassembled, the Nafion-Na⁺ membrane

and glass fiber separator in the air electrode were removed for analysis. Figures 3.14c and 3.14d 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 3.14d) compared to DME indicating that diglyme might have lower stability than DME. Even so, 90 cycles were still achieved (Figure 3.14c). Good reproducibility and high Coulombic efficiency prove that the Nafion- Na^+ membrane efficiently prevents dendrite penetration and increases cycling performance of Na- O_2 batteries.

To show the effect of Nafion- Na^+ 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^+ membrane. Figure 3.15b 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 3.15c, which is faced to the Nafion- Na^+ 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^+ membrane. However, in the other electrode, the glass fiber separator shows a clean surface faced to the Nafion- Na^+ membrane (Figure 3.15d). As expected, there is no indication of dendrite penetrating through the Nafion- Na^+ membrane and glass fiber separator in the cathode side. The results prove that Nafion- Na^+ membranes effectively block sodium metal penetration through the separator and increase the cycle life of Na- O_2 batteries.

3.3 Conclusion

Sodium dendrite formation has been identified as a major issue for the poor cyclability of sodium-air batteries. Dendrites that ultimately penetrate through the glass fiber separator to the air electrode cause short-circuiting which leads to the premature death of the battery.

Using a Nafion- Na^+ membrane as part of a composite separator, 110 cycles in DME based electrolyte and 90 cycles in diglyme based electrolyte have been achieved at a current density of 0.16 mA cm^{-2} . The 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.

CHAPTER 4: THE EFFECTS OF ELECTROLYTE DECOMPOSITION IN NA-O₂ BATTERIES

In the last chapter, it is proved that dendrite penetration issue is solved by employing an ion selective membrane. However, it should be noticed from the voltage profiles (Figure 3.14a and 3.14c) that the last few cycles of batteries have larger discharge/charge voltage windows than the previous cycles. In the battery performance tests, after 110 cycles in DME based electrolyte and 90 cycles in diglyme based electrolyte, the discharge time of both batteries gradually decreased from cycle to cycle and ultimately reached to zero (not shown here). In ten decayed discharge/charge cycles, both batteries stopped working. In this chapter, we will investigate the reason why the batteries are not able to work after 110 cycles in DME based electrolyte by investigation side reactions. Raman, XPS, NMR will be used as the characterization techniques to characterize side products. Both effects on metal anode and air electrode will be discussed in this chapter.

4.1 Electrolyte decomposition

The stability of electrolyte has been discovered as the priority in sodium oxygen batteries. After Peter G. Bruce pointed out that carbonate-based electrolytes was not applicable for metal oxygen batteries, ether-based electrolytes are considered as good candidates due to the higher durability with superoxide species. Freunberger et al.^{Error! Bookmark not defined.,13} report that carbonate solvents in lithium oxygen batteries can be attacked by superoxide species which is reduced from oxygen, thus forming lithium carbonate in air diffusion layer instead of lithium peroxide. Ether solvents have higher stability but it still suffers decomposition in lithium oxygen batteries even though lithium peroxide is the major product formed in the air

electrode. In our study, electrolyte decomposition was found to be a significant issue which affects the cycle life of sodium oxygen batteries.

Figure 4.1 (a) ^1H -NMR and (b) ^{19}F -NMR spectra of the glass fiber separator tested after 6 cycles in a Na- O_2 battery with DME based electrolyte.

Figure 4.2 ^1H -NMR spectra of glass fiber separator faced to (a) the anode and (b) the cathode after 6 cycles in DME based electrolyte.

NMR was performed to detect the side products in a sodium oxygen battery with DME based electrolyte. After 6 cycles, the glass fiber separator was immersed in D_2O solvent and tested by NMR. In ^1H -NMR spectra (Figure 4.1a), peaks at 3.3 ppm and 3.5 ppm represent the chemical shifts of DME and signal at 4.7 ppm is related to the water molecule in the D_2O solvent. Signals at 1.8 ppm and 8.4 ppm are related to acetate and formate species, which are most likely from the electrolyte decomposition. In ^{19}F -NMR, (Figure 4.1b), the peak at -7.9

ppm is the characteristic peak of SO_3CF_3^- from the pristine conducting salt, sodium triflate. At -122 ppm, the peak is related to F^- . Since triflate is the only source of fluoride, it indicates the decomposition of conducting salt in electrolyte. The results show that even after 6 cycles both DME solvent and conducting salt experience decomposition and side products are detected to be mainly sodium formate, sodium acetate and sodium fluoride.

To investigate electrolyte decomposition in both metal anode and air electrode, a Nafion- Na^+ membrane was used as a part of separator in a Na-O_2 battery to block the anions diffusion through the two electrodes informing us the place where the electrolyte could be decomposed. The electrolyte was a solution of DME solvent containing 0.5 M sodium triflate conducting salt. In Na-O_2 batteries, decomposed products in glass fiber separators from both sides of the electrodes were characterized by NMR. After 6 cycles, the glass fiber separators from both sides were peeled off from the Nafion- Na^+ membrane and then immersed in D_2O respectively. ^1H -NMR spectra of the glass fiber separator from the anode is shown in Figure 4.2a. The peaks at 8.5 ppm and 1.9 ppm are related to formate and acetate species respectively, indicating the decomposition of the DME solvent. Figure 4.2b shows the ^1H -NMR spectra of the separator in the P50 carbon paper cathode side. Interestingly, only a small peak of acetate is shown at 1.9 ppm without the presence of formate species. This shows that more side products are generated from metal anode instead of the cathode. This can be explained that oxygen dissolved in the electrolyte could diffuse from the air electrode to the metal anode through the glass fiber separator. It could induce the reaction between sodium metal and oxygen or the reactions between the electrolyte, sodium metal and oxygen. In the cathode, superoxide species generated from the reduction of oxygen molecules would attack the DME solvent inducing the degradation of DME molecules and forming acetate species. Compared to Figure 4.1a, we can conclude that sodium formate species are mainly formed in the anode instead of the cathode. Therefore, the reactivity of sodium is more significant than the activation of carbon cathode in sodium oxygen batteries.

Figure 4.3 ^{19}F -NMR spectra of glass fiber separators faced to (a) the anode and (b) the cathode after 6 cycles in DME based electrolyte.

^{19}F -NMR spectra of the glass fiber separators from both sides are shown in Figure 4.3. In Figure 4.3a, the peak at -79 ppm is the characteristic peak of triflate species (SO_3CF_3^-) and the peak at -122 ppm is related fluoride species (F^-). The missing peak at -122 ppm in Figure 4.3b indicates the conducting salt in electrolyte is barely decomposed at the carbon cathode. The result indicates the presence of sodium metal decomposes the conducting salt in electrolyte.

In conclusion, NMR results prove that both conducting salt and DME solvent are decomposed in the sodium anode. While in cathode, although the acetate species was detected, it is relatively stable in sodium oxygen batteries.

4.2 Sodium anode issues

As discussed in the last chapter, dendrite penetration is the primary issue to cause the premature death of sodium oxygen batteries. After solving the dendrite penetration problem, the reactivity of sodium becomes a significant issue for the low cycle life of sodium oxygen batteries. In this section, the reaction between sodium and electrolyte will be discussed and the characterizations of side products on the sodium surface will be performed.

4.2.1 The reactions between sodium and DME based electrolyte

Figure 4.4 Raman spectra of sodium metal immersed in (a) pure DME and (b) 0.5 M sodium triflate in DME after one month.

Figure 4.4 shows the comparison between sodium metal in DME and sodium metal in 0.5 M sodium triflate in DME. Two pieces of sodium metal with the mass of 30 mg were placed in two 4-ml test vials containing 1.5 mL solvent or solution. The vials were sealed by Parafilm and stayed in the glove box for one month. Three trials have been performed and similar results were obtained. The sodium metal in pure DME solvent after one month becomes a white colored solid and no metallic luster of sodium was found in the middle of the solid after cutting it in half. Figure 4.4a is the Raman spectra of the white colored solid after dried in the oven. There is one strong peak shown at 3638 cm^{-1} which is related to sodium hydroxide. It shows that sodium was converted to sodium hydroxide, indicating that the reaction between sodium and DME is severe. However, after the presence of sodium triflate conducting salt in the DME solvent, the reaction between sodium and electrolyte was inhibited. As can be seen from Figure 4.4d, a smaller peak of sodium hydroxide was detected. In lithium oxygen batteries, lithium fluoride is the decomposed product from the conducting salt and it protects lithium from further reactions with electrolytes⁵⁶. Here, similar results were observed in DME based electrolyte. In sodium oxygen batteries, sodium triflate reacts with sodium metal and forms sodium fluoride in the SEI layer protecting sodium from reacting with DME solvent. In conclusion, the reaction between sodium metal and DME solvent is detrimental. The sodium

triflate reduces the reactivity of the sodium metal but the decomposition of electrolyte and the depletion of sodium metal cannot be completely inhibited.

4.2.2 The reactions between sodium and DME based electrolyte in Na-O₂ batteries

Oxygen crossover has been discovered as a serious issue in lithium oxygen batteries³⁷ and potassium oxygen batteries⁵⁷. In sodium oxygen batteries, at the anode oxygen accompanied with superoxide species will exhibit high reactivity to sodium metal inducing more side reactions in the highly reducing environment. Side products were observed in sodium anode and characterized by Raman and XPS.

4.2.2.1 Raman spectroscopy

Figure 4.5 Optical image of the sodium anode after 120 cycles.

The morphology of sodium metal anode after 120 cycles is observed in Figure 4.5. The battery used a Nafion-Na⁺ membrane between two glass fiber separators with 0.5 M sodium triflate in DME electrolyte. As can be seen from figure 4.5, the original sodium disk changes to light grey colored solids without metallic luster on the surface. The branches around the disk indicate the dendrite grows in the gaps between the stainless steel rod and the sealed Teflon piece. The sample was scraped off from the stainless steel rod and no sodium was found underneath the solids. It indicates that the death of the sodium oxygen battery after 120 cycles is due to the depletion of sodium.

Figure 4.6 Raman spectra of the sodium anode after 120 cycles.

After 120 cycles, the light grey colored solids were tested by Raman spectroscopy. Before Raman tests, the sample was rinsed by DME to remove the conducting salt, dried in a vacuum chamber in the glove box and then sealed in an airtight holder. Figure 4.5 shows the Raman spectra of the sodium metal after 120 cycles and the standard peaks for references of sodium carbonate, sodium peroxide and sodium hydroxide. The peak at 750 cm^{-1} is most likely from sodium peroxide. The peaks at 1080 cm^{-1} , 1156 cm^{-1} and 3638 cm^{-1} are related to sodium carbonate, sodium superoxide and sodium hydroxide, respectively. The result shows that the sodium anode forms Na_2CO_3 , Na_2O_2 , NaO_2 and NaOH in the SEI layer in the presence of oxygen and electrolyte. The formation of NaO_2 and Na_2O_2 is probably originated from the reaction with oxygen due to the oxygen crossover, and Na_2CO_3 and NaOH are related to the decomposition of the electrolyte and the reaction with the trace water in the anode.

4.2.2.2 XPS spectroscopy

Figure 4.7 (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 4.7. 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 groups^{51,56}. These groups are generated either by solvent decomposition (ester or carbonate groups) or by conducting salt decomposition (-CF₂). 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 53, 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.

Figure 4.8 Proposed mechanism of DME decomposition on the anode side with oxygen crossover.⁵⁷

The mechanism of solvent decomposition has been proposed in lithium oxygen batteries³⁷ and potassium oxygen batteries⁵⁷. 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 Na_2CO_3 , NaO_2 , NaOH and probably Na_2O_2 . The depletion of sodium is likely to be major issue to cause the death of sodium oxygen batteries.

4.2.3 Cycling efficiency of sodium metal in the sodium oxygen battery

Figure 4.9 Discharge/charge profiles of Na-O₂ battery in 0.5 M sodium triflate DME electrolyte.

In order to test the extent of the loss of sodium in sodium oxygen batteries, cycling

efficiency is calculated based on the consumption of sodium. The sodium oxygen battery was assembled by using a limited amount of sodium (3.0 mg) in the anode in 0.5 M sodium triflate DME electrolyte. The discharge time was not limited, the voltage window is set to 0.2 V-3.2 V and the current is 0.16 mA cm⁻². The discharge/charge profiles of this battery are shown in Figure 4.9. The first discharge time is 34.23 h and the first charge time is similar to the first discharge which shows a high coulombic efficiency. However, the discharge time decreases as the cycle number increases. The cycling efficiency and the coulombic efficiency have been calculated and are shown in Figure 4.10.

Figure 4.10 (a) Cycling efficiency and (b) coulombic efficiency of the sodium oxygen battery.

The theoretical discharge time is calculated here.

$$t = \frac{0.0030 \text{ g s}}{22.99 \text{ g/m}} * \frac{96485 \text{ C}}{1 \text{ m}} * \frac{1 \text{ m h}}{3.6 \text{ C}} * \frac{1 \text{ h}}{0.1 \text{ m h}} = 34.97 \text{ h}$$

Cycling efficiency is calculated by using discharge time of each cycle divided by the theoretical discharge time, 34.97 h. The first discharge time is 34.23 h converting to 98% cycling efficiency (Figure 4.10b). However, the following cycles show a decreasing discharge time, and till the fifth cycle the discharge time decreases to 10 h. From Figure 4.10a, we can see the dramatic change of cycling efficiency from 98% to 18% indicating the depletion of the sodium metal. The coulombic efficiency is calculated using charge time divided by discharge time. The coulombic efficiencies maintain between 95%-100%, which indicates that less than

5% of NaO_2 cannot be charged back²⁵. The results show that the sodium metal decays quickly in sodium oxygen batteries by using DME based electrolyte. This will be detrimental to the application of sodium oxygen batteries. The protection of sodium metal is essential for the future use of this battery technology.

Figure 4.11 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 4.11a 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 4.5b. When the solid is scraped off, only a small amount of sodium was left in the middle of the rod (Figure 4.5c). Side products were also observed on the glass fiber separator faced to sodium anode (Figure 4.5d). 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. Raman spectra of collected solids show similar results as Figure 4.6, which are not shown here.

4.3 Cathode issues

Figure 4.12 The SEM image of NaO₂ from literature 50. SEM images of a cathode structure after discharge to 2 mAh at 80 $\mu\text{A cm}^{-2}$ at the oxygen/gas diffusion layer and gas diffusion layer/separator side.⁴⁵

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 Li₂O₂. However, the product in sodium oxygen batteries, sodium superoxide, is not a significant problem due to the small polarization upon charge. Figure 4.12 shows the SEM image of the discharged air electrode in a Na-O₂ battery⁴⁵. Sodium superoxide is grown on the surface of carbon and shows a cubic morphology. Different from the amorphous structure of lithium peroxide in Li-O₂ batteries, sodium superoxide has a good crystalline structure. Although there were no reports on the experimental or calculation studies of electronic conductivity of NaO₂ to date, it indicates that NaO₂ might have higher electronic

conductivity than Li_2O_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.

4.3.1 Raman spectroscopy

Figure 4.13 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 4.13, 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.

4.3.2 XPS spectroscopy

Figure 4.14 (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 4.14. 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.

4.4 Conclusion

In this chapter, the failure of sodium oxygen batteries was investigated after employing Nafion-Na⁺ membrane. 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 Na₂CO₃, Na₂O₂, NaO₂, NaOH, sodium formate and sodium acetate. 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 NaO₂ cannot be recharged back to sodium and oxygen. It is critical to develop stable anode materials and explore stable electrolytes for sodium oxygen batteries.

CHAPTER 5: CONCLUSION AND FUTURE

5.1 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. 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.

5.2 Future

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 ($\sim 2.5 \times 10^{-5} \text{ S/cm}$) compared to the proton exchange membranes

($1\text{e-}2\sim 10\text{ S/cm}$)⁵⁸ 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 ⁵⁹, zeolites⁶⁰, zirconium⁶¹, and polypyrrole⁶². In addition, graphene oxide/Nafion membrane composite is also a promising material that has higher ion conductivity than the inorganic and organic fillers.⁶³ 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.

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