

Study on Enhancement of Li Utilization and Cycle Stability of Anode in Li-0_2 Rechargeable Battery

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**Study on Enhancement of Li Utilization
and Cycle Stability of Anode in Li-O₂
Rechargeable Battery**

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Table of contents

Chapter 1 Introduction	1
1.1. Needs of high energy storage system	2
1.2. Rechargeable Li-oxygen batteries	2
1.2.1. Mechanism of non-aqueous Li-O ₂ battery	2
1.2.2. Current issues of Li-O ₂ batteries	3
1.3. Lithium metal as an anode	4
1.3.1. Solid Electrolyte Interphase (SEI) Layer	5
1.3.2. Morphology changes	5
1.4. Motivation and Outline of this study	6
 Chapter 2 Electrochemical Performance of Rechargeable Li-O₂ Batteries	 8
2.1. Introduction	9
2.2. Results and discussion	10
2.2.1. Electrochemical performance by different type of air electrodes	10
2.2.1.1. Poor cycle stability of carbon based air electrode	10
2.2.1.2. High capacity and stable cycleability of β -MnO ₂ based cathode	11
2.2.2. Li metal utilization in Li-O ₂ rechargeable batteries	11
2.2.2.1. Capacity and Li utilization rate	11
2.2.2.2. Cycle performance with different Li utilization	11
2.3. Conclusion	12
 Chapter 3 Li Utilization and Cyclability of Li-O₂ Batteries Incorporating a Mesoporous Pd/β-MnO₂ Air Electrode	 13
3.1. Introduction	14
3.2. Results and discussion	15
3.2.1. Effects of Li utilization on cell performance	15
3.2.2. Studies about the origin of low cycle stability	15

3.2.3. Li loss by needle-like dendrite and SEI layer	15
3.3. Conclusions	15

Chapter 4 Surface Coating on Li metal for Increased Cycle Stability of Li-O₂ Battery

4.1. Introduction	18
4.2. Results and discussion	18
4.2.1. Effects of surface coating of Li with polymers	18
4.2.1.1. Decreased interfacial resistance by suppressed dendrite formation	19
4.2.1.2. Study about Li loss by SEI layers	19
4.2.2. Much increased cycle retention rate under low Li utilization condition	19
4.2.3. Effects of polymer coating on the cycle stability at high rate	19
4.3. Conclusions	19

Chapter 5 Summery and Prospective

Acknowledgment

Chapter 1

Introduction

1.1. Needs of high energy storage system

Rapidly growing consumption of limited fossil fuels and global environmental problems have demanded for sustainable and clean energy. With the importance of energy production, efficient use of generated energy is very important. As a solution for efficient usage of energy, Li rechargeable battery has been investigated intensively. The commonly used cathode in Li ion battery is lithium cobalt oxide which has the theoretical capacity of 273 mAh/g. The energy density of current lithium ion battery is around 150 Wh/kg. From now, battery technology has been quiet developed and already used in several areas from stationary applications such as portable PC, mobile phone, e-Bike to vehicle application for hybrid vehicles. However, the maximum energy density of Li ion battery is too low and not sufficient to meet the demands of new markets such as electric vehicles.

Pike Research forecasts that cumulative sales of hybrid-electric vehicles (HEVs) will represent an additional 8.7 million vehicles by 2017. On the contrary, the increasing rate for battery-electric vehicles (BEV) and plug-in hybrid (PHEV) will be much faster by the same year. Currently, nearly all electric-powered vehicles on the market are hybrid-electric vehicles (HEVs). However, PHEV and EV are expected to gain a larger percentage of market shares over the next decade. As a result, considerable attention has given to advanced batteries which have high energy density. Because the maximum energy density of current lithium-ion batteries is limited owing to electrode materials having intercalation chemistry, battery system requires breakthroughs on fundamental level.

1.2. Rechargeable Li-oxygen batteries

1.2.1. Mechanism of non-aqueous Li-O₂ battery

The Li-O₂ batteries are commonly composed with Li metal anode, electrolyte with non-aqueous (aprotic) solvent. To use oxygen gas as a cathode material, porous carbon and catalyst composite usually added as a discharge product reservoir in the cathode. At the positive electrode during discharge, molecular oxygen is reduced by electrons and combines with lithium ions supplied from the negative electrode (metallic Li) to form lithium peroxide or lithium oxide with a thermodynamic voltage of 2.96 and 2.91(V_{Li}) respectively. Reverse reaction to decompose the precipitate is occurred during charge.

The oxygen reduction reaction proceeds in a stepwise fashion to form O₂⁻, O₂²⁻, and O²⁻ as products, and the first product of the reduction of oxygen is lithium superoxide, LiO₂, involving a one electron process. These reactions are kinetically irreversible or quasi-reversible electrochemical processes, resulting in high polarization for the oxygen evolution reaction. Understanding the reaction mechanism and the chemical/electrochemical stability of reaction products (and/or intermediate products) is imperative to enable development of highly efficient and long life Li-air batteries.

1.2.2. Current issues of Li-O₂ batteries

The Li-O₂ battery is the possibly the highest energy density electrochemical cell that can be configured today. The Li-O₂ cell has a theoretic energy density of 5.2 kWh/kg when oxygen mass is included. However, there are critical challenges that limit the practical application of Li-O₂ battery.

1) High overpotential on OER and ORR

During OER (Oxygen Revolution Reaction), the overpotential is positive on charging due to the extra energy required to reverse the reaction that occurs on discharging. On ORR (Oxygen Reduction Reaction) the lithium peroxide increases the internal resistance of the cell which is indicated by the negative overpotential. In addition, when the discharge products have clogged the pore of air cathode, reaction

will terminated. Usually, the round-trip efficiency of Li-O₂ batteries with uncatalyzed carbon electrode is below 70 %.

2) Irreversible reactions

To be rechargeable Li-air batteries detailed investigation of the chemistry of discharge and charge products is a critical issue. Although Li-air cells can be cycled several times by consuming some component, likely the electrolyte solvent, truly reversible electrochemical reactions need to be demonstrated. Several recent papers have specifically stated that in carbonated solvent Li₂O₂ is not a principal discharge products, and on charge CO₂ rather than O₂ is evolved. Some noncarbonate solvents have been investigated to be reversible in Li-O₂ cells including ethers, ionic liquids. However, to date there has been no report that clearly establishes truly reversible reaction during cycling.

3) Instability of air electrode

In nonaqueous Li-O₂ cells, carbon (such as Super P, Ketjenblack) has been widely used as the basis of porous air cathode. The discharge products should be formed in a porous conducting matrix, which has to combine sufficiently high conductivity with high surface area, low cost and ease of fabrication as a porous electrode. Stability of air cathode electrode during charge/discharge reaction is also a vital requirement. Recently, instability of carbon was investigated especially on the condition above 3.5 V during charge reaction. Also, in the presence of Li₂O₂, carbon promotes electrolyte decomposition during charge/discharge in Li-O₂ cell, giving rise to Li₂CO₃ and Li carboxylates. These side reactions could result in polarization on the subsequent reaction and capacity fading.

1.3. Lithium metal as an anode

As Li metal has a high specific capacity (3860 mAh/g) with the most negative electrode potential, its importance in high energy density storage systems is critically higher than any other anode candidates. Li metal used for anode in Li-air batteries and offered Li ion sources during cycles. However, there are several problems for capacity loss of Li metal including passivation layer (solid electrolyte interphase, SEI) and morphology changes. The growth of passivation layer and dendrite morphology on charging reaction requires excess Li, adding a severe penalty to the overall energy density of the system. Also, changes of morphology to needle like dendrite with cycle numbers could eventually penetrate the separator to reach the cathode, causing internal short-circuiting.

1.3.1. Solid Electrolyte Interphase (SEI) Layer

A passivation layer forms immediately on the surface of Li metal when Li contacted with non-aqueous electrolyte consisting of aprotic organic solvents and lithium salts. The passivation layer formed on the electrode surface due to reductive decomposition of electrolyte was named Solid Electrolyte Interphase (SEI) layer by Peled. The SEI prevents Li corrosion because Li is thermodynamically unstable with all organic solvents at the initial state; however, over time it leads to a gradual capacity fade as the SEI layer thickens. Also, properties of SEI including composition and morphology significantly affect battery performance. Thus, effective and stable SEI layers on electrolyte are mandatory for the long life time lithium rechargeable batteries.

1.3.2. Morphology changes

All attempts to commercialize rechargeable lithium metal batteries since they were introduced in the early 1970s have failed due to low cycling efficiency and safety issues caused by rough Li deposits formed on the lithium during charge reaction. Deposition usually takes shape of branch or needle like morphologies referred to as dendrites. It is

known that local variations of SEI composition and thickness will lead to an uneven current distribution and thus morphology was changed. In the case of alkyl carbonate solutions, the major surface species are Li salts such as ROCO_2Li , Li_2CO_3 , LiF , etc., which cannot form highly cohesive surface films. Therefore, as the volume of the active metal changes due to a too-pronounced Li deposition, the protective surface films, composed of the above species, cannot accommodate the volume changes and thus crack. The cracks become the preferred locations for the electrochemical processes, and intensive Li deposition therefore occurs in these spots, thus leading to dendrite formation. The morphology change to dendritic lithium easily causes electrical or mechanical separation from a current collector. Li metal separated from a current collector is referred as “Dead lithium”. This could be an immediate cause of a rapid decrease in reversibility of the lithium anode.

1.4. Motivation and Outline of this study

Li-O₂ batteries have been extensively researched in recent years. In spite of potential for extremely high energy density of a Li-O₂ battery, scientific challenges have hindered the practical application such as capacity fading. Recently, many researchers have revealed that low cyclability of Li-O₂ batteries was mainly attributed to the following reasons; 1) Decomposition of an electrolyte on cycling 2) Blocked pores of cathode by lithium precipitates. Most Li-air cells have used Li metal as an anode to exploit its high energy density. However, a very few studies about Li metal were conducted. Previous studies so far showed high cathode capacity with very small amount (around 1mg) of active materials; therefore, the influence of anode was ignored due to a mass of Li metal. Thus, it is highly recommended to elucidate influence of Li metal anode on the cycle stability of Li-O₂ batteries in more detail. As explained in this chapter, Li metal has

scientific problems of Li loss by SEI and dendrite formation during cycling. To adopt Li metal as anode, more careful attention should be given than other anode candidates especially in the Li-O₂ battery system owing to the potential for high utilization ratio of Li metal. In this thesis, therefore, detail studies about influence of Li metal anode on electrochemical performance of Li-O₂ batteries are investigated. Furthermore, possible solution for increased cycle stability of Li-O₂ batteries will be proposed.

Chapter 2

Electrochemical Performance of Rechargeable Li-O₂ Batteries

2.1. Introduction

Rechargeable energy storage systems with high energy density and stable cycleability are urgently needed to accommodate emerging field such as renewable energy applications and electric vehicles. Lithium oxygen batteries have received tremendous attention recently due to their potential to provide energy density considerably higher than Li-ion batteries. The Li-O₂ battery is an advanced energy storage and conversion technology. During discharge, lithium is oxidized at the anode forming lithium ion and electrons. The electrons follow the external circuit to do electric work and lithium ions migrate across the electrolyte to reduce oxygen at the cathode. It is apparently simple reaction; however, there are many scientific challenges to be rechargeable Li-O₂ batteries for practical application. Addressing such challenges requires a deeper understanding of roles and effects of cell components including porous cathodes, electrolyte and Li metal as an anode. As explained in Chapter 1, most of the key components still cannot meet the requirements to be rechargeable. Furthermore, these components interplay with each other, which complicates the investigation on individual component. Considering that the Li-O₂ battery is still in its early stage of the development, each component should be studied in detail.

In this chapter, therefore, electrochemical performance of Li-O₂ batteries will be discussed. Generally, electrochemical performance was susceptible to various factors; therefore, we will select some important factors and investigate electrochemical performance of Li-O₂ batteries. At first, type of cathode candidate including solely carbon source and without carbon material were investigated as a one factor. Depending on the cathode, the mechanism of reaction will be changed and result in different performance. Secondly, factor related with electrolyte is going to be studied. Most

representative solvents for carbonate based and non-carbonated based electrolyte were examined using 1M LiTFSI. Lastly, the influence of Li metal anode will be investigated especially about Li metal utilization. Owing to the high capacity of Li-O₂ batteries which obtained between 400 and 5000 mAh/g based on cathode, researches about Li anode utilization for the capacity is critically important. Prior to study about Li metal utilization, we had to confirm whether 100 % Li on the anode can be consumed for the capacity. Thereafter, Li metal utilization for the capacity by decreasing Li metal amount and its effects on the electrochemical performance will be examined.

2.2. Results and discussion

2.2.1. Electrochemical performance by different type of air electrodes

It has been shown that the energy storage capacities of Li-air batteries are strongly influenced by air electrodes. In Li-O₂ batteries, all reactions between Li ion and oxygen (OER and ORR) occur on the cathode substrate, therefore it is critical to first build an ideal host cathode for Li-O₂ batteries by using appropriate materials. Also, it is generally believed that electrocatalysts are critical to improve the power, cycling capability and round trip energy efficiency of Li-O₂ batteries. Therefore, it is very important to determine what kinds of cathode material and electrocatalysts were used for air electrode. To elucidate the influence of cathode air electrode we prepared various types of cathodes.

2.2.1.1. Poor cycle stability of carbon based air electrode

When carbon based air electrode was used for Li-oxygen batteries, the plateau of charge and discharge voltage is 4.129 and 2.694 respectively and the overpotentials are positive on charging and negative on discharging. It would present the specific energy efficiency about 65 % during first round trip. The high charge and discharge

overpotentials were possibly attributed to insoluble reduction products, thus poor cycle stability was confirmed.

2.2.1.2. High capacity and stable cycleability of β -MnO₂ based cathode

Structure and morphology of prepared mesoporous β -MnO₂ were investigated. Much improved cycleability of Li-O₂ battery could be obtained compared to KB based cell with reasonably high capacity.

2.2.2. Li metal utilization in Li-O₂ rechargeable batteries

The theoretical specific energy density (excluding oxygen) of a Li-O₂ battery is 11,140 Wh kg⁻¹, which is much higher than that of other advanced batteries. The use of metallic lithium could make it possible to have high theoretical specific energy density value with very simple mechanism.

2.2.2.1. Capacity and Li utilization rate

In order to investigate the Li amount effects on the discharge capacity of Li-O₂ batteries, various amounts of Li metal were used as the anode and Ketjenblack was used as the cathode electrode mixed with EMD and PTFE.

2.2.2.2. Cycle performance with different Li utilization

In case of the cell with enough amount of Li which meaning low Li utilization, the capacity decreased excepting for initial few cycles. This decrease in discharge capacity was also reported by several groups and it is considered that poor cycle stability was attributed to Li₂CO₃ formation and electrolyte decomposition.

2.3. Conclusion

In this chapter, electrochemical performances of Li-O₂ batteries were investigated. Various factors were chosen to be examined. First, types of cathode materials including carbon based Ketjenblack and without carbon sources. When mesoporous β -MnO₂ based electrode was used for cathode in the carbonate based electrolyte, we could reduce charge voltage to 4 V by eliminating the carbon in air cathode and consequently the most stable cycleability could be obtained. Utilization of Li metal anode for capacity was studied. By calculating the Li amount from capacity and measuring the ICP, we could confirm that almost 100 % Li could be utilized as a capacity during discharge. Further, under high utilization condition, needle-like dendrite formation was accelerated and consequently poor cycle stability was obtained. More detail studies are needed about influence of Li utilization on the electrochemical performance in Li-O₂ batteries.

Chapter 3

Li Utilization and Cyclability of Li-O₂ Batteries Incorporating a Mesoporous Pd/ β -MnO₂ Air Electrode

3.1. Introduction

The Li-O₂ battery, however, has been faced with challenges such as low energy efficiency and poor stability on cycling. Recent studies have shown that electrolyte decomposition during the battery discharge reaction results in the irreversible formation of discharge products such as Li carbonate and Li alkyl carbonates. These products accumulate in the cathode on cycling, resulting in diminished capacity and eventual failure of the cell. It is therefore obvious that significant effort needs to be applied to gaining a better fundamental understanding of the Li-O₂ reaction.

Another factor which makes a major contribution to poor stability on cycling is the Li metal anode which is used in Li-air batteries to produce extremely high capacity in combination with the cathode. Although Li has an extremely large columbic capacity of 3860 mAh g⁻¹, and thus enables the construction of Li-O₂ batteries with high energy densities, metallic Li exhibits poor cycling stability due to the formation of a surface passivation layer and dendrites. The reaction of the dendrites with the electrolyte as well as with various impurities results in corrosion and the subsequent isolation of lithium (so-called dead Li), which in turn produces a gradual loss of cycling capacity. In addition, the loss of Li to the solid-electrolyte interphase (SEI) is thought to be the most common and fundamental source of capacity loss in Li metal batteries. The SEI layer is initially advantageous since it protects the Li metal from decomposition by the solvent. Over time, however, the SEI thickens, leading to a gradual loss of capacity. Considering the pronounced negative effect of Li metal electrodes, it is of course suspected that the Li anode may also play a significant role in the poor cycle stability of Li-air batteries. In spite of this, only a few studies have focused on the contribution of the Li metal anode to the poor cycling performance of Li-air batteries, and the current theory is that reductions in battery capacity on cycling are due to the accumulation of discharge

products such as Li_2CO_3 or Li_2O_2 on the air electrode. It therefore stands for a reason that the influence of Li metal on capacity retention should also be investigated. Because Li- O_2 battery usually showed extremely excess amount of Li based capacity; the amount of Li metal for the capacity will be much larger than other battery systems and the utilization of Li is generally less than 20% in the conventional study. Therefore, influence of Li utilization on discharge capacity and cycle stability of Li- O_2 battery under high Li utilization condition is required to be studied.

3.2. Results and discussion

3.2.1. Effects of Li utilization on cell performance

The electrochemical properties of lithium-air batteries were measured using a cathode catalyst composed of Pd mixed with mesoporous $\beta\text{-MnO}_2$ to examine the effects of Li utilization.

3.2.2. Studies about the origin of low cycle stability

In order to determine the origin for degradation of the Li-air cell under conditions of high Li utilization, two cells were prepared, both employing reused electrodes taken from the cell after 10 charge/discharge cycles at 100 % Li utilization.

3.2.3. Li loss by needle-like dendrite and SEI layer

To verify the growth of Li dendrites, the microstructure of the Li metal anode surface was examined after various discharge cycles.

3.3. Conclusions

The influence of high utilization of Li anode for the capacity on cycle stability was investigated. Under anode limited condition, the cycle stability of the cell significantly decreased over the first few cycles. The main reason for the low cycle stability is a

decrease in usage of Li at the anode for discharge, which is attributed to the formation of a surface passivation layer in conjunction with the formation of needle-shaped Li dendrites which significantly increases the anode surface area. Therefore, improvements in the cyclability of lithium-air batteries could be realized by increasing the stability of the Li metal anode rather than by improving the stability of the air electrode or preventing organic electrolyte with O₂.

Chapter 4

Surface Coating on Li metal for Increased Cycle Stability of Li-O₂ Battery

4.1. Introduction

A nonaqueous liquid electrolyte commonly used in Li ion rechargeable battery is unstable when it contact with Li metal, and as a result, SEI layers were immediately formed on the surface of Li metal. The SEI prevents Li corrosion at the initial state; however, over time it leads to a gradual fading of discharge capacity as the SEI layer thickness increased. Also, due to the poor kinetics of ions on the Li electrode surface, lithium ions are preferentially deposited and removed from the electrode in areas where SEI is the thinnest. This behavior results in the morphology change to dendrite which could easily cause electrical and mechanical separation from a current collector. This could be an immediate cause of a rapid decrease in reversibility of the lithium anode ^[10]. Therefore, when Li metal is used as an anode, these disadvantages should be considered and managed properly. Much efforts have been devoted to prevent these problems by electrolyte additive, surface modification, and polymer coating especially in Li-metal and Li-S batteries system. In contrast, limited number of studies focused on the influence of Li metal anode to the electrochemical performance in the Li-air batteries, in spite of their poor cycle stability. Thus, it is highly required to increase Li cycle efficiency by suppressing amount of Li loss in Li anode which may be related with the dendrite formation and SEI layer for increasing the cycle stability of Li-O₂ battery.

4.2. Results and discussion

4.2.1. Effects of surface coating of Li with polymers

Although the surface was coated with polymer, observed initial discharge capacity was almost the same with that of the cell using pristine Li suggesting that surface polymer may not seriously disturb Li dissolution into electrolyte.

4.2.1.1. Decreased interfacial resistance by suppressed dendrite formation

The effects of polymer coating on cycle stability in Li-O₂ batteries were demonstrated by impedance spectroscopic measurements. In order to distinguish the resistance originated from both electrodes in our study, lithium reference electrode was placed between cathode and anode.

4.2.1.2. Study about Li loss by SEI layers

Surface sensitive ATR type measurement set was applied for the surface analysis of SEI layer after 10 cycles.

4.2.2. Much increased cycle retention rate under low Li utilization condition

Cycle performance under specific capacity limited condition at 1111 mAh/g of Li (corresponding 28% of theoretical capacity of Li) was presented for investigating the polymeric coating effects under the assumption of cathode capacity limited condition.

4.2.3. Effects of polymer coating on the cycle stability at high rate

In Li-O₂ batteries, poor rate performance should be improved for commercialization and it is well known that the specific capacity strongly depends on the current density. To study the effects of coating on Li diffusion in more detail, discharge capacity was studied as a function of current density. For this experiment, charge was always performed at 0.1 mA/cm².

4.3. Conclusions

Increase in cycle stability of Li-O₂ batteries was achieved by a polymer coating onto the Li anode under anode capacity limited condition.

Chapter 5

Summary and Prospective

Recently, Li-O₂ battery has emerged as a promising energy storage technology with the potential for very large energy density without contamination of the environment. Extensive researches have been conducted mainly on cathode and electrolyte. Along with the cathode and electrolyte of Li-O₂ batteries, the Li metal anode is a critically important component that should be investigated in more detail, particularly with respect to lithium utilization in a Li-O₂ battery.

In chapter 1, a literature review of lithium-air batteries was presented. In this chapter, the basic concepts and principles with introduction of various types of lithium-air batteries were presented. Current issues of Li-O₂ batteries including high over-potential, irreversible reaction and instability of cathode carbon were reviewed. In addition, the phenomenon related with Li metal as an anode was explained.

In chapter 2, electrochemical performance of Li-O₂ batteries were investigated. In general, electrochemical performance was susceptible to various factors. Various factors were chosen to be examined. First, types of cathode materials including carbon based Ketjenblack and without carbon sources were measured. When mesoporous β -MnO₂ based electrode was used for cathode in the carbonate based electrolyte, we could cut-off charge voltage to 4V by eliminating the carbon in air cathode and consequently the most stable cycleability could be obtained. In addition, utilization of Li metal anode for capacity was studied. Under high utilization condition, needle-like dendrite formation was accelerated and consequently poor cycle stability was obtained. More detail studies are needed about influence of Li utilization on the electrochemical performance in Li-O₂ batteries

In chapter 3, we reports critical effects of Li utilization on the cycle stability of Li-O₂ batteries. In our study, we give a difference in the Li metal amount, which used as

anode in lithium oxygen rechargeable batteries. By reducing the Li metal amount, Li metal utilization for the capacity could be increased and the effects of anode were magnified. Under high utilization condition, much serious needle-like dendrite formation with thicken SEI layer was confirmed. Consequently, we could confirm the critical importance of Li anode on cycle performance in a Li-O₂ battery. This result is highly important for further research of the lithium air battery systems for improving the cycle stability.

In chapter 4, various solutions for increased cycle stability of Li-O₂ batteries were proposed. Mainly, effects of surface coated polymer on cycle stability of Li-O₂ battery under a condition of high utilization of Li were investigated. Impedance analysis suggested that the interfacial resistance on anode compartment was the main reason for low cycle stability with increasing cycle numbers in the cell using pristine Li. By coating, interfacial resistance could be suppressed when cycled at 0.1 mA/cm² and even at high current density. From the microscopic study, the lithium morphology deposited on the polymer coated electrode showed a suppressed needle-like dendrite formation which is main reason for enhanced cycle stability of Li-O₂ batteries.

At present, lithium–air batteries have received much attention as advanced energy storage systems. Although this technology has the potential to provide higher energy density than current lithium-ion system, it is still in the developmental stages, and far away from its practical application due to many challenges. Intensive studies are required for cathode and electrolyte stability for oxygen radical, electro-catalysts for oxidation of discharge products. Fundamental studies about Li metal in Li-air batteries are strongly requested including utilization rate, compatibility with various solvents and

salts, and control for morphology during cycling. Furthermore, owing to air in Li-air batteries, Li metal seems to be much vulnerable and thus much attention should be given to anode. Coating Li metal with polymer is one of promising directions for research. Realization of the Li-air batteries will require a long-term research. However, it is worthy to invest time and passion in those advanced energy storage systems.

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