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Zinc-Air Batteries

Fundamentals, Key Materials and Application

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Shengjie Peng
Department of Applied Chemistry
Nanjing University of Aeronautics
and Astronautics
Nanjing, China

Preface

Over the last few decades, electrochemical energy storage materials and devices have developed at an unprecedented rate, driven by consumer electronics, power tools and, more recently, automotive and renewable energy storage. Metal-air batteries represent one of the most efficient energy storage technologies due to outstanding features such as high round-trip efficiency, long life cycle, fast response during peak electricity demand/supply periods and reduced weight using atmospheric oxygen as one of the main reactants. Depending on the metal anode, metal-air batteries can be divided into several types, such as zinc-air batteries, magnesium-air batteries, aluminum-air batteries and lithium-air batteries. Zinc-air batteries are the preferred choice among all metal-air batteries for their low cost, lightweight, large scale, high energy density, safer battery technology and environmental friendliness. Rechargeable zinc-air batteries are regarded as very important rising energy storage systems due to their utility in portable electronics, grid management and electric vehicles.

This book titled *Zinc-Air Batteries: Fundamentals, Key Materials and Application* aims to discuss the cutting-edge materials and technologies for zinc-air batteries. From the perspective of basic research and engineering application, the principle innovation, research progress and technical breakthrough of key materials such as positive and negative electrodes, electrolytes and separators of zinc-air batteries are discussed systematically. This book also involves the theoretical calculation methods and advanced characterization techniques, which provides theoretical and technical references for the design and development and performance improvement of different zinc-air battery systems based on materials optimization. Current technologies, achievements and challenges and future development directions are further discussed, which can be used to guide and promote the development of zinc-air battery technology. This book is suitable to researchers at all levels in the energy area and provides them with a quick way of understanding the development of zinc-air batteries. Finally, we express our sincere thanks to all the contributors to this book, who are actively engaged in cutting-edge research on metal-air batteries.

Nanjing, China   Shengjie Peng

Contents

About the Author

Prof. Shengjie Peng (FRSC) received his Ph.D. degree at Nankai University (P. R. China) in 2010. Following a postdoctoral fellowship with Prof. Alex Yan and Prof. Seeram Ramakrishna in Nanyang Technological University and National University of Singapore, he is now working as a professor at Nanjing University of Aeronautics and Astronautics. His current research interests focus on development of rationally designed functional materials with finely tailored nanoscale architecture to tackle critical problems (such as energy density, power density, cycle and calendar life, safety and cost) in diverse energy-related applications, including ORR, water splitting, batteries, fuel cells, as well as clean and renewable energy. To date, he has co-authored 160 peer-reviewed publications with over 10,000 citations, 55 H-index.

Chapter 1
Overview of Zinc-Air Battery

1.1 History of Zinc-Air Battery

Energy is the material basis for the progress and development of human civilization. Since the industrial revolution, with the gradual consumption of fossil energy and the increasingly prominent environmental pollution problem, the demand for green, clean and renewable energy has grown rapidly, and the energy system has shown a trend of transformation from the absolute dominance of fossil energy to low-carbon and multi-energy integration [1, 2]. In recent years, electrochemical energy storage technology that has maintained a rapid growth momentum is considered as a sustainable and environmentally friendly green energy, and can be well used as a medium for energy storage and conversion, so it has aroused widespread concern in emerging markets and scientific research fields. This electrochemical energy storage technology is not limited by geographical environment, and can directly store and release electrical energy, mainly including various batteries, lead-acid batteries, lithium-ion batteries, sodium-sulfur batteries, flow batteries, etc. The market scale of these batteries is increasingly mature, and the application field is expanding, suitable for a wide range of occasions. Among them, metal-air batteries, as an emerging electrochemical energy storage technology, are expected to become a new generation of energy storage devices due to their abundant raw materials, low cost, high efficiency, and pollution-free characteristics.

Metal-air batteries use metals such as magnesium, aluminum, zinc, mercury, iron as the negative electrode, oxygen in the air or pure oxygen as the positive active substance. They play an important role in today's national economy and are widely used in industry, agriculture, transportation, post and telecommunications, etc. Among various metal anodes, zinc electrodes are considered to have very broad development prospects due to their abundant reserves, low price, good corrosion resistance, and ideal reaction kinetics in alkaline aqueous solutions. In 1879, Maiche et al. assembled the world's first zinc-air battery using metal zinc as the anode, platinum-plated carbon electrode as anode on the contrary of the manganese dioxide in Le Kronschie battery, in a slightly acidic aqueous solution of NH_4Cl as electrolyte.

The structure and principle are as follows:

$$Zn|NH_4Cl|O_2(C)$$
$$Zn + 2NH_4Cl + \tfrac{1}{2}O_2 \rightarrow Zn(NH_3)_2Cl_2 + H_2O$$
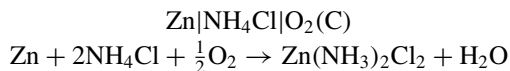
The structure and appearance of this zinc-air battery are similar to zinc-manganese dry batteries, but its capacity is more than twice that of the latter, so it has attracted people's close attention once it came out. Zinc-air batteries were mass-produced during World War I, but had a very low discharge current density of about 0.3 mA cm^{-2}. At that time, France applied them in railways, post and telecommunications and other fields, but has not fully demonstrated their superiority.

By the 1920s, a lot of research and improvement had been done on zinc-air batteries, and the direction had been shifted to alkaline zinc-air batteries. In 1932, Heise and Schumadcher changed the slightly acidic NH$_4$Cl electrolyte to alkaline to improve the conductivity of the electrolyte, which significantly reduced the internal resistance of the battery. It used zinc amalgam as the anode, porous carbon treated with paraffin waterproofing as the cathode, and 20% sodium hydroxide aqueous solution as the alkaline electrolyte, which greatly improved the discharge current, and the current density can reach 7 ~ 10 mA cm^{-2}. This zinc-air battery exhibited high energy density, but low output power, and was mainly used for the power supply of railway signal lights and beacon lights. In the 1940s, due to the successful development of zinc-silver batteries, it was found that powdered zinc electrodes in alkaline solutions could discharge under high current conditions, which provided conditions for the further development of zinc-air batteries. Subsequently, the development of zinc-air batteries encountered a bottleneck for a long time due to the lack of suitable air electrode structures and effective catalysts.

After the 1960s, owing to the rapid development of normal temperature fuel cells, the research enthusiasm for high-performance gas electrodes was stimulated, which brought an opportunity to the development of zinc-air batteries and made another breakthrough in their performance. After 1965, the excellent gas diffusion electrode, prepared with PTFE as a binder and a hydrophobic agent, gradually replaced other gas electrodes. Such new type of gas diffusion electrode had a good gas/liquid/solid three-phase structure. Its electrode thickness was 0.12 ~ 0.5 mm, and the discharge current density could reach 1000 mA cm^{-2} in pure oxygen state. In 1967, the above electrodes were further modified with a breathable and waterproof film to form a gas diffusion air electrode of a fixed reaction layer, so that they can work under normal pressure. Since then, commercialized zinc-air batteries have entered the market. By the end of the 1960s, high-efficiency zinc-air batteries had entered the stage of industrial production. At present, zinc-air batteries have played an irreplaceable role in many important fields.

1.2   Other Metal-Air Batteries

Metal-air batteries use relatively active metals such as magnesium, aluminum, zinc, cadmium, and iron as the anode, cooperating with the air electrode of the fuel cell, which uses the oxygen in the air as the cathodic active substance. The electrolyte generally uses alkaline or neutral electrolyte aqueous solution. If using more active lithium, sodium, potassium, etc. as anodes, it is necessary to match with non-aqueous organic or inorganic electrolyte solution. This kind of battery can be used as both a primary battery and a secondary battery. Due to its abundant raw materials, high cost performance, and pollution-free, metal-air batteries are called "green energy for the twenty-first century".

Since the air used in the air electrode is available everywhere and inexhaustible without cost, it is highly valuable to match with many metals with negative potential to form a series of metal-air batteries. The main feature of metal-air batteries is high specific energy [3]. In theory, the capacity of the cathode is infinite, and the active substance is outside the battery, which makes the theoretical specific energy of air batteries much larger than that of general metal oxide electrodes. The theoretical specific energy of metal-air batteries is generally above $1000\,\mathrm{Wh\,kg^{-1}}$, and the actual specific energy is above $100\,\mathrm{Wh\,kg^{-1}}$, belonging to high-energy chemical power sources. In addition, metal-air batteries are made of common and cheap materials and exhibit stable performance. If pure oxygen is used instead of air, the discharge performance can be greatly improved.

Metal-air batteries can be designed as primary batteries, reserve batteries, electrochemically rechargeable batteries, and mechanically rechargeable batteries. Metal-air batteries also have inherent shortcomings, that is, the battery cannot be sealed, which is easy to cause the electro-hydraulic to dry up and swell, and affects the capacity and life of the battery. If using alkaline electro-hydraulic, there exists carbonation effects, which increases the internal resistance of the battery and affects the discharge of the battery. In addition, wet storage performance is poor because the diffusion of air in the battery to the cathode will accelerate the self-discharge of the negative electrode. In order to reduce the self-corrosion of zinc, whether in alkaline or acid dry batteries, mercury or mercury compounds are generally added during production. However, mercury not only harms the health of workers but also pollutes the environment, so it needs to be replaced by a non-mercury corrosion inhibitor.

In addition to the zinc-air batteries introduced earlier, common metal-air batteries include magnesium-air batteries, aluminum-air batteries, and lithium-air batteries. Figure 1.1 shows a comparison chart of the theoretical mass energy density, volume energy density, and theoretical voltage of several metal-air batteries [4].
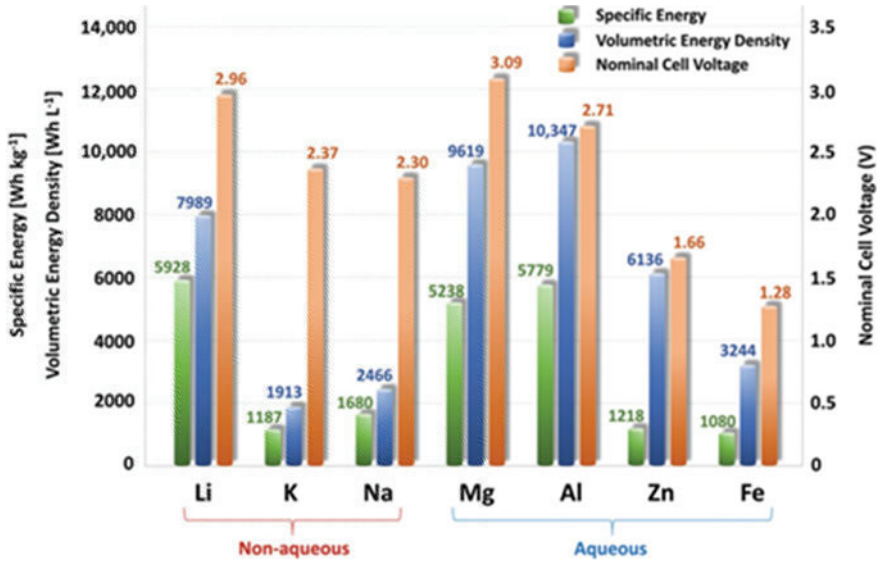
Fig. 1.1 Comparison of theoretical mass energy density, volume energy density, and theoretical voltage of several metal-air batteries [4]

1.2.1 Magnesium-Air Battery

Magnesium-air batteries use metal magnesium or magnesium alloys as the anodic active substance, and oxygen in the air as the cathodic active substance.

1. Overview of magnesium-air batteries

Magnesium and magnesium alloys are excellent anode materials for metal-air batteries, with large crustal reserves, high stability to air and moisture, low density, high theoretical specific capacity, and high energy density [5]. Compared with the overly active lithium mental, the electrode potential of magnesium is relatively negative, which makes it more suitable for battery systems with electrolyte than lithium, also reduces the difficulty of production and storage, and no dendrites are generated during the cycling. Furthermore, the usage of magnesium not only reduces the cost, but also improves the safety [6]. Magnesium with low electrochemical equivalent can be paired with an air electrode to form a magnesium-air battery. The electrochemical equivalent of magnesium is 0.454 g $(Ah)^{-1}$, and $\varphi^{\Theta} = -2.69$ V in alkaline solution. The theoretical specific energy of the magnesium-air battery is 3910 Wh kg^{-1}, which is three times higher than that of the zinc-air battery.

Although magnesium-air batteries have these advantages, there are still several unsolved problems that limit their wide applications [7–9]. First, magnesium is used as the anode of the air battery, and self-corrosion occurs in the electrolyte. The loss of this part of the electrode cannot be used for discharge, which reduces

its anode efficiency; second, the magnesium anode will have undissolved particles fall off during the discharge process (called block effect). This weight loss also cannot be used for discharge, and it will also reduce its anode efficiency; third, many corrosion products will be formed on the surface of the magnesium anode during the discharge process. The corrosion products cover the anode surface and reeduuce the effective discharge area, which will hinder the further discharge and affect the dis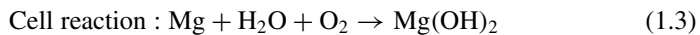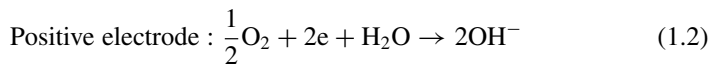charge performance. Therefore, proposing new type of magnesium anode material with good corrosion resistance and stable discharge has become a key issue in the development of new energy sources. Alloying is a very effective solution. The second phase is one of the important factors affecting the anodic corrosion behavior and discharge performance of magnesium alloys. Therefore, the second phase can be adjusted by alloying to improve the performance of magnesium alloy anodes. Appropriate addition of zinc and calcium to magnesium can obtain good corrosion performance. In addition, there are also ways such as plastic deformation and heat treatment.

2. Structure and working principle of magnesium-air battery

Magnesium-air batteries are generally rectangular in structure, with air electrodes on both sides of the battery, magnesium electrodes in the middle, and a separator between the positive and negative electrodes, and KOH solution as electrolyte.

The magnesium-air battery in alkaline solution reacts as follows during discharge:

$$\text{Negative electrode}: \text{Mg} - 2e + 2OH^- \rightarrow \text{Mg(OH)}_2 \tag{1.1}$$

$$\text{Positive electrode}: \frac{1}{2}O_2 + 2e + H_2O \rightarrow 2OH^- \tag{1.2}$$

$$\text{Cell reaction}: \text{Mg} + H_2O + O_2 \rightarrow \text{Mg(OH)}_2 \tag{1.3}$$

Since magnesium-air batteries use sheet-like magnesium electrodes, the vacuum surface area is much smaller than that of porous powdered Zn electrodes in zinc-air. Therefore, when the same current passes through, the current density of magnesium electrodes is large, and the polarization is serious. At the same time, from the reaction formula, magnesium-air battery consumes water and it needs more electrolyte than Zn-air battery. For Zn-air battery, electro-liquid mass is 30 ~ 35% of the mass of active substance, while magnesium-air battery is 80 ~ 85%. The open circuit voltage of the magnesium-air battery is 1.6 V, and it can work between – 26 ~ 85 °C although the corrosion reaction is serious when discharging at high temperature. For example, only 40% of the rated capacity can be released at 52 °C. When discharging current density is higher than 40 mA cm^{-2}, the electro-hydraulic needs to be cooled. When working at low temperature, it can be changed to a neutral electrolyte, releasing 33% of its room temperature capacity at − 26 °C with electrohydraulic $NH_4Cl + CaCl_2$.

Due to the small electrochemical equivalent of magnesium and the high electromotive force of the battery, its theoretical specific energy is high, but in fact magnesium electrodes are easily passivated in an alkaline medium, so the actual specific energy is much lower than the theoretical value. It is of great significance for the development of magnesium secondary batteries to control the interlayer spacing of new layered materials and realize new layered cathode materials with high specific capacity, excellent rate performance and cycle stability [10].

1.2.2　Aluminum-Air Battery

The aluminum-air battery uses high-purity aluminum (Al) as the anode, oxygen as the cathode, and potassium hydroxide or sodium hydroxide aqueous solution as the active substance of the electrolyte.

1. Overview of aluminum-air battery

Aluminum-air batteries have very high energy density and consist of an air cathode, an electrolyte, and a metallic aluminum anode (Fig. 1.2) [11]. The theoretical specific energy reaches 800 Wh kg^{-1}. Aluminum, rich in raw materials, is harmless to the human body, and can be recycled with no pollution to the environment, and the method of replacing aluminum electrodes can solve the problem of slow charging of aluminum-air batteries. Therefore, aluminum-air batteries have also received a lot of attention. Low-power aluminum-air batteries have been used in mining lamps, radio stations, and marine lighthouses. Developed countries led by the United States and the United Kingdom have carried out a lot of research and development on aluminum-air batteries. In the 1980s, The United States Aluminum Power Company studied the application of aluminum air battery in the power supply of deep-sea vehicle, unmanned exploration vehicle and AIP submarine. Using alloy Aluminum electrode and high efficiency air electrode, aluminum-air batteries have a specific energy of 400 Wh kg^{-1} and a power of more than 20 W kg^{-1}, and their energy density and volumetric energy density are several times higher than those of Cd-Ni batteries. The U.S. Department of Energy cooperated with Lawrence Livermore Laboratory in California to develop metal-air batteries for electric vehicles. Later, Lawrence Livermore Laboratory and other companies jointly established Voltek, firstly applying aluminum-air batteries to electric vehicles, and the efficiency of the aluminum-air battery pack is more than 90%. In 2015, Alcoa and Israel's Phinergy demonstrated that a 100 kg heavy aluminum air battery can drive a racing car for 1600 km.

However, there are also some problems to be solved in the aluminum electrode of aluminum-battery. First, when the anode is dissolved, a passivation film is formed on the surface of metal aluminum, which inhibits the electron-loss oxidation reaction of aluminum, thereby increasing the potential of the aluminum electrode and causing the voltage drops of battery. Secondly, after the oxide film on the surface of aluminum is destroyed, a large amount of hydrogen will
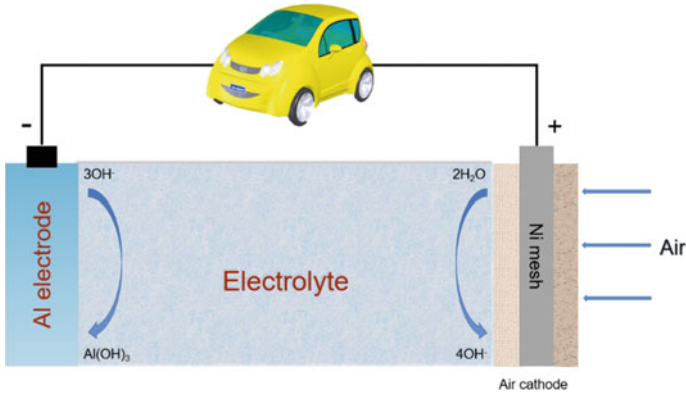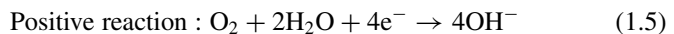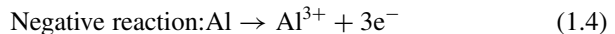
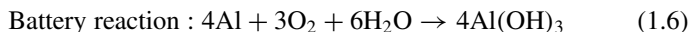**Fig. 1.2** Schematic diagram of aluminum-air batteries

evolve, and the dissolution of aluminum itself is difficult to stop, which eventually leads to serious battery self-corrosion discharge. Furthermore, commercial ultra-pure aluminum containing trace elements with low hydrogen evolution overpotential such as copper, iron and silicon will also aggravate the self-corrosion of aluminum. For example, the hydrogen evolution overpotential of copper is 0.59 V, and the hydrogen evolution overpotential of iron is 0.41 V [12]. Moreover, the metal-air battery represented by aluminum-air battery has a high theoretical energy density, but in the non-working state such as storage and standby, the anode often undergoes irreversible corrosion, resulting in the loss of energy density and the decrease of battery life. At present, there are many strategies to inhibit the corrosion of the anode of aluminum-air batteries, including anode alloying, electrolyte additives, gel electrolytes, non-aqueous electrolytes, etc. These strategies did alleviate the corrosion of the anode to a certain extent, but mostly at the expense of reducing the power density and energy density, and it is still necessary to find more effective strategies to improve the electrochemical performance of the system.

2. Structure and working principle of aluminum-air battery

The anodic active material of the aluminum-air battery is aluminum or aluminum alloy, and the cathodic active material of the is oxygen in the air. The aluminum electrode can use a neutral (salt-containing) solution or an alkaline solution, depending on the acidity and alkalinity of the electrolyte medium. The principles of electrochemical reactions are as follows:

1. Under neutral conditions

$$\text{Negative reaction:} Al \rightarrow Al^{3+} + 3e^- \tag{1.4}$$

$$\text{Positive reaction}: O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \tag{1.5}$$

$$\text{Battery reaction}: 4Al + 3O_2 + 6H_2O \rightarrow 4Al(OH)_3 \qquad (1.6)$$

2. Under alkaline conditions

$$\text{Battery reaction}: 4Al + 3O_2 + 6H_2O \rightarrow 4Al(OH)_3 \qquad (1.7)$$
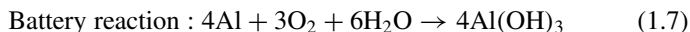
The actual electrode potentials of aluminum electrodes and air electrodes deviate greatly from the theoretical electrode potentials, and water is consumed during the reaction, but the actual energy density of aluminum-air batteries still exceeds that of most battery systems. In aqueous electrolyte, aluminum anode is prone to self-discharge and regassing. As a result, aluminum-air battery sources are often added with electrolyte just before use, or designed to mechanically rechargeable batteries that replace the aluminum anode after each discharge. Aluminum-air batteries emit a lot of heat when discharging, and the battery heats up so badly that a thermal management system is needed to prevent damage. At present, researchers are also exploring the possibility of combining oil and electrolyte to reduce the corrosion of the electrode and improve the performance and stability [13].

1.2.3 Lithium-Air Battery

Lithium-air battery uses lithium metal as the anode and oxygen in the air as the active substance of the cathode reactant.

1. Overview of lithium-air batteries

Lithium-air batteries use metal lithium with minimum density and maximum electronegativity as the anode, porous air electrode as the cathode, and oxygen in the air as the anodic active material. Usually, a catalyst is used to promote the oxygen reduction reaction of the cathode. Therefore, the most prominent advantage of lithium-air batteries is that they have a very high theoretical energy density, with a theoretical specific energy of 11,140 Wh kg^{-1} (based on the mass of lithium metal), including the reaction product Li_2O_2, whose theoretical specific energy is 3505 Wh kg^{-1}. It has been considered as the most promising secondary battery system with an actual specific energy expected to reach 600 Wh kg^{-1}. With the development of the electric vehicle industry, more and more attention has been paid to power batteries. As a new type of chemical power system, lithium-air batteries are easier to meet the cruising range requirement of electric vehicles than other chemical power systems due to their outstanding energy density advantages. However, there are still many problems in current lithium-air batteries, such as high charge–discharge overpotential, poor cycle and rate performance, especially the metal lithium anode is faced with the fact that metal lithium is easily decomposed by various substances, resulting in many by-products, and using metallic lithium as the anode, lithium dendrites are generated during the
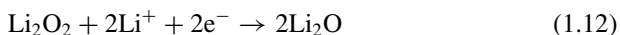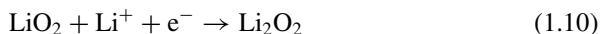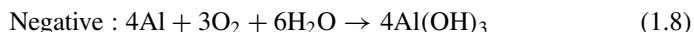
repeated electroplating/stripping of lithium ions. Therefore, metal lithium-air batteries still need to be further explored.

Lithium-air batteries mainly include battery types such as aqueous systems, organic systems, solid electrolyte systems and hybrid systems. Aqueous lithium-air batteries use a protective lithium metal composite anode and an aqueous electrolyte, which can work in an air environment, and the discharge products are usually LiOH or LiOAc. In the solid-state lithium-air battery, a solid-state electrolyte is used to separate the air electrode and the lithium anode, which avoids the direct reaction of moisture in the air with lithium metal, so that the battery can operate in the air. In theory, the solid-state electrolyte system battery can fundamentally solve the issues of security and stability. However, the lithium-ion conductivity of solid-state electrolytes is generally lower than that of liquid aqueous and non-aqueous electrolytes, the interfacial impedance between lithium metal and cathode is larger, resulting in the relatively lower energy utilization efficiency and output power of solid-state lithium-air batteries. At present, more research focuses on non-aqueous system (organic system) lithium-air battery, which was first reported by K. M. Abraham and Jiang in 1960.

2. Structure and working principle of lithium-air battery

Non-aqueous lithium-air batteries are mainly composed of metal lithium anode, organic electrolyte, and air electrode. During the charging and discharging process, the anode is mainly based on oxygen reduction (ORR) and oxygen evolution (OER) reactions, and the anode is based on the dissolution and deposition of lithium. During discharge, the lithium anode dissolves and transforms into Li^+, which migrates to the cathode (air electrode) through the electrolyte, and the electrons flow to the cathode through the external circuit to supply power to the load; meanwhile, oxygen is reduced at the cathode and combines with lithium ions to form Li_2O_2, which is deposited inside the porous air electrode.

The reaction mechanism of the lithium-air battery during the discharging process is as follows:

$$\text{Negative} : 4Al + 3O_2 + 6H_2O \rightarrow 4Al(OH)_3 \tag{1.8}$$

$$\text{Positive} : Li^+ + e + O_2 \rightarrow LiO_2 \tag{1.9}$$

$$LiO_2 + Li^+ + e^- \rightarrow Li_2O_2 \tag{1.10}$$

$$2LiO_2 \rightarrow Li_2O_2 + O_2 (\text{chemical process}) \tag{1.11}$$

$$Li_2O_2 + 2Li^+ + 2e^- \rightarrow 2Li_2O \tag{1.12}$$

The specific way that LiO_2 generates Li_2O_2 mainly depends on the properties of the electrode and electrolyte system. Theoretically, both Li_2O and Li_2O_2 may be

the cathode discharge products of lithium-air batteries, but the main product in the actual system is still Li_2O_2. Under certain conditions, a small amount of Li_2O may be produced by a four-electron reaction pathway. The lithium-air battery system based on the four-electron reaction pathway can increase the theoretical energy density by more than 50% compared with the conventional system based on the two-electron reaction mechanism. In organic phase lithium-air batteries, the discharge product is solid Li_2O_2. Due to its own insulating properties, the cathode exhibits slow reaction kinetics, low energy efficiency, poor rate performance, and limited cycle stability. Similar effects can be weakened by controlling the nucleation and growth of Li_2O_2, such as the morphology and structure of Li_2O_2. Structural doping is an effective route to adjust the properties of materials, which can change the density of states, band gaps, and electrical conductivity of compounds, and endow new compounds with unique properties. This is an ideal way to improve the electrocatalytic activity of lithium-air batteries. Designing efficient catalysts to catalyze the cathodic reaction according to the four-electron reaction pathway is also the optional way to greatly advance the further development of lithium-air batteries.
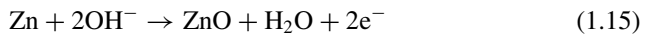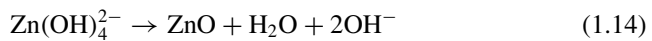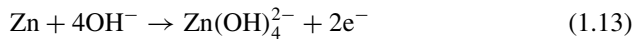
1.3 Fundamental Principles

The electrochemical reactions involved in zinc-air battery are three-phase reaction on air electrode and oxidation–reduction reaction of metal zinc on zinc anode. Zinc-air batteries can be divided into primary batteries and secondary batteries. The primary zinc-air battery only involves the discharge process of the battery, that is, oxygen reduction reaction (ORR) occurs in the positive air electrode, and metal zinc oxidation reaction occurs in the anode, which loses its use value after the discharge. Nowadays, it has been widely used in low-current portable wearable devices such as artificial hearing aids. With the serious consumption of energy and great pollution to the environment by traditional vehicles, new energy vehicles have attracted wide attention due to the excellent advantages of energy saving and cleanliness. The demand for new energy vehicles in the automobile industry is constantly rising, which further promotes the rapid development of rechargeable secondary zinc-air batteries. Besides the same discharge process as the primary zinc-air battery, the secondary zinc-air battery also involves a charging process, that is, oxygen evolution reaction (OER) occurs at the positive air electrode and reduction of metallic zinc occurs at the anode. The reaction mechanism is much more complicated than that of the primary zinc-air battery, and the requirements for the air electrode are also much more complicated. In the secondary zinc-air battery, the air electrode needs to have dual-function activity of catalyzing OER and ORR reactions simultaneously, and these two reactions are mutually inverse. The process of four-electron transfer is involved, but the reaction process is complicated, and the steps are tedious. Since the kinetic process is slow and a large energy barrier needs to be overcome in the reaction process, the requirements for the catalyst are very strict. Therefore, in order

to further study zinc-air battery, it is of great importance to deeply understand the mechanism of zinc-air battery.
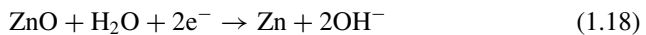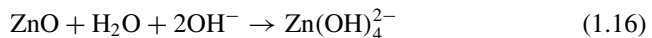
1.3.1 Zinc Anode Mechanism

The anode of zinc-air battery is mainly metal zinc, and the involved reaction process is mainly the reduction and oxidation of metal zinc, also with the side reactions such as corrosion of zinc anode by electrolyte. During the preparation of zinc anode, the corrosion of electrolyte and the growth of its own dendrite are often considered. In the reaction process, theoretically, the catalytic electrode will not be consumed, so the zinc anode of zinc-air battery will determine the output capacity of the battery, which is an important factor restricting the development of zinc-air battery. The specific capacity of zinc-air battery can be improved by increasing the amount of zinc anode. The degradation of the performance of most batteries after long-term charge–discharge cycles is ascribed to the degradation of the metal anode, not the air electrode. However, the passivation of zinc electrode in alkaline solution will prevent the normal reaction, while the corrosion of zinc electrode will occur in acidic solution. Only when it is in neutral solution, the effect on zinc electrode is relatively small. The most common electrolyte is alkaline solution because the activity of catalyst in alkaline solution is high.

In an alkaline solution, the reaction process on the anode of zinc-air batteries can be divided into charging process and discharging process. When discharging, an oxidation reaction occurs on the anode, and metal Zn is oxidized to Zn^{2+}. The reaction equations are,

$$Zn + 4OH^- \rightarrow Zn(OH)_4^{2-} + 2e^- \tag{1.13}$$

$$Zn(OH)_4^{2-} \rightarrow ZnO + H_2O + 2OH^- \tag{1.14}$$

$$Zn + 2OH^- \rightarrow ZnO + H_2O + 2e^- \tag{1.15}$$

When charging, a reduction reaction takes place on the anode of zinc, and Zn^{2+} is reduced to metal Zn. The reaction equation are,

$$ZnO + H_2O + 2OH^- \rightarrow Zn(OH)_4^{2-} \tag{1.16}$$

$$Zn(OH)_4^{2-} + 2e^- \rightarrow Zn + 4OH^- \tag{1.17}$$

$$ZnO + H_2O + 2e^- \rightarrow Zn + 2OH^- \tag{1.18}$$

The two reactions in the charging and discharging process are inverse reactions to each other. However, in the primary battery, there is no reversible process, which is unique to the secondary battery.

1.3.2 Air Cathode Mechanism

The electrode is the core of zinc-air battery, which plays a vital role in the charging and discharging process of zinc-air battery. Oxygen precipitation reaction (OER) and oxygen reduction reaction (ORR) on the electrode belong to three-phase interface reactions, which occur at the interface of solid, liquid and gas, and are two indispensable reactions of zinc-air battery. In the secondary zinc-air battery, the ORR occurs on the air battery during discharge, while the OER occurs on the air electrode during charging, which requires that the air electrode has a higher reaction rate in ORR and OER. The catalysts on the air electrode are required to have good bifunctional activity and be able to reduce the energy barriers of the two reactions simultaneously. Therefore, the improvement of catalysts activity has now become a focus of research. Air electrode is often regarded as the energy converter of zinc-air battery, which determines the power output capacity of the battery. In the zinc-air battery, the process of three-phase reaction at the air electrode is as follows: when discharging, the oxygen in the air first diffuses through the diffusion layer of the air electrode to the catalytic layer, and then a three-phase electrochemical reduction reaction occurs at the interface between the catalytic layer and the electrolyte, just like the cathode process of hydrogen fuel cell.

OER is an anode reaction in water electrolysis for hydrogen production and air electrode charging in a reversible metal-air battery. During OER, oxygen molecules are produced by several proton/electron couplings. In order to produce oxygen molecules, a process with four electron transfers is required. However, the OER process is carried out through multi-step reactions in each step, so the potential energy barrier accumulated at each individual step will lead to the slow kinetics of OER reaction, resulting in a large overpotential. Different materials or crystal planes in the OER reaction will affect the formation of reaction intermediates, and then affect the reaction path. Figure 1.3 shows the mechanism of oxygen evolution reactions in acidic and alkaline electrolyte, respectively.

In alkaline electrolyte, the following two intermediate reactions first occur:

$$OH^- + * \rightarrow OH^* + e^- \qquad (1.19)$$

$$OH^* + OH^- \rightarrow O^* + H_2O + e^- \qquad (1.20)$$
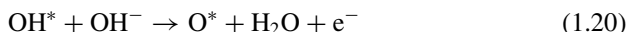
Then, O_2 can form in two possible ways. One is to combine two O* intermediates to produce O_2:

$$2O^* \rightarrow O_2 \tag{1.21}$$
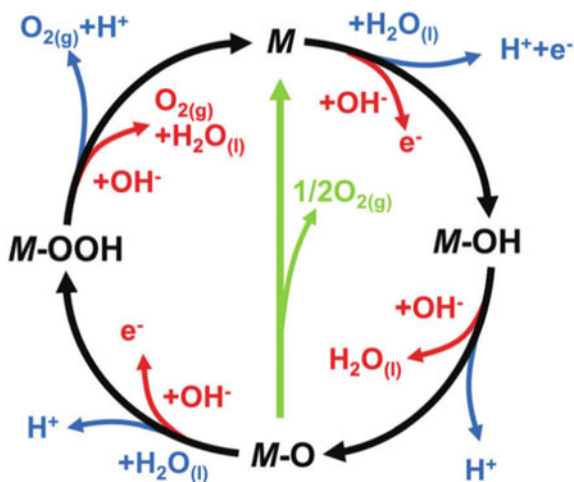
The other is that firstly O* reacts with OH⁻ to form OOH*, and then OOH* further combines with OH⁻ to form O_2 (therefore, the potential energy barrier of the reaction here is relatively large):

$$O^* + OH^- \rightarrow OOH^* + e^- \tag{1.22}$$

$$OOH^* + OH^- \rightarrow O_2 + H_2O + e^- \tag{1.23}$$
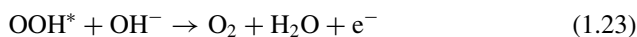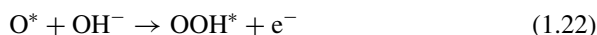
In acidic electrolyte, the reaction process is as follows:

$$H_2O + * \rightarrow OH^* + H^+ + e^- \tag{1.24}$$

$$OH^* \rightarrow O^* + H^+ + e^- \tag{1.25}$$

$$O^* + H_2O \rightarrow OOH^* + H^+ + e^- \tag{1.26}$$

$$OOH* \rightarrow * + O_2 + H^+ + e^- \tag{1.27}$$
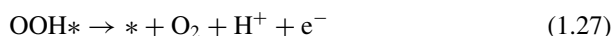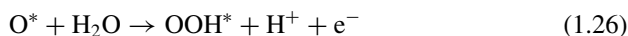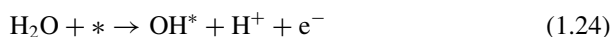
In which "*" represents the active sites on the catalyst surface, and O*, OH* and OOH* represent the adsorbed intermediates. It can be seen from the above reaction process that the formation and dissociation of intermediate adsorption products O*, OH* and OOH* run through the whole reaction path, so the activity of OER catalyst can be described by the adsorption oxygen reduction free energy.