Research Status of Lithium Oxygen Battery and Its Components

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Abstract. Before the large-scale use of electric energy, fossil energy has been the main energy supply. The phenomenon of pollution and lack of supply caused by excessive consumption of fossil energy is becoming increasingly obvious. With the continuous consumption of fossil energy, electric energy is regarded as the replacement object of fossil energy. The task of storing electricity requires the support of batteries. In recent years, the battery industry has developed rapidly, including a battery with a high energy density. One of the materials needed for the reaction can be directly obtained from the air; This is a lithium-oxygen (Li-O_2) battery. Since its invention, the battery has opened a new way of energy storage for people. This paper will briefly introduce the design concept, reaction principle, selection, and improvement of each part of the Li-O_2 battery including anode, cathode and electrolyte. This paper provides a basic understanding of lithium oxygen battery.

Keywords: Lithium oxygen battery, Mechanism of battery, Anode, Cathode, Electrolyte.

1. Introduction

Starting with the release of the most ancient gravitational potential energy, storing energy has been a solution to overcome the difference between the time and place of energy generation and the time and place of demand for energy supply. After the Industrial Revolution, many advanced ways of storing excess energy were created. More advanced forms of energy storage are also needed. An obvious feature of energy storage is that all kinds of energy can be transformed in the process of storage and release [1]. With the passage of time and the advancement of technology, thermal, chemical, electrical, hydrogen, and other forms of energy storage are already available. For a long time, the chemical energy stored in fossil fuels has been powering human production, development, transportation, and other activities. However, the overuse of fossil fuels has caused many problems. The burning of many fossil fuels will produce harmful gases and greenhouse gases to pollute the atmosphere and aggravate the greenhouse impact. It can result in acid rain and other risks due to the sulfur and nitrogen oxides in it. Alternative energy, rational use of fossil energy and renewable energy are urgently needed now. Energy storage is a vital component in making renewable energy sources more dependable [2]. Battery storage is highly prized because electricity is the most widely used and easily converted form of energy. In 1799 Volta concluded experimentally that there is always an electrical imbalance in the contact of two different conductors. If both were class II (wet conductors), the imbalance was very small; if one was Class I (metallic), the imbalance became larger; if both were class I (metallic), the result would be the same larger. Based on these phenomena, Volta invented the first battery, opening the way of electric energy storage [3]. Among them, lithium-ion batteries (LIBs) are the mainstream style today. Lithium was discovered in 1817 by Arfwedson, a student of the Swedish chemist Berzlius, through an analysis of feldspar. Lithium is the least dense metal, it also has a very high charge density, and the metal is very active. Based on these excellent physical properties, lithium is gradually used in batteries. Lithium-ion batteries and lithium-polymer batteries are the two main types. The research on LIBs started in the 1970s and was commercialized in the 1990s after more than ten years of development, in which Michel Armand played a prominent role. In the battery positive electrode, negative electrode and electrolyte are outstanding contributions [4]. During following years, Li batteries have been the focus of research in the battery field. Lithium oxygen battery as one of the branches stand out, lithium oxygen battery has a higher energy density. In 1996, lithium-oxygen batteries were first reported by Abraham and Jiang [5]. Li-O_2 batteries theoretically have a very high energy density, but water-containing electrolytes tend to corrode metal electrodes, and the development of appropriate electrolytes is still ongoing. The structure of cathode still needs to be improved and optimized. The anode needs to become more stable to ensure its longevity. This paper will focus on the structural components of lithium oxygen battery such as anode, cathode, electrolyte, working principle. This paper will then go over the improvement potential of pertinent solutions and present potential directions for the advancement of lithium-oxygen batteries in the future. Mechanism

The core structure of lithium oxygen battery consists of several parts: positive electrode, negative electrode, electrolyte, and separator. Oxygen on the air electrode through a redox reaction, shown in Eq1:

$$2Li + O_2 \rightarrow Li_2O_2 \tag{1}$$

Eq1 is the reaction principle of lithium-oxygen batteries. In the discharge process, the positive electrode will generate Li_2O_2 which will decompose during the charging process.

When the electrolyte is hydrated, the reaction forms hydroxide. The discharge response equation is as follows in Eq2:

$$4Li + O_2 + 2H_2o \rightarrow 4LiOH \tag{2}$$

However, Li reacts easily with water, reducing the efficiency of the Li-O_2 battery in aqueous electrolyte. In addition, non-aqueous electrolytes are gradually developed and applied.

The Solid Electrolyte Interphase (SEI) forms when a lithium electrode meets an electrolyte solution. Lithium ions can embed and depart easily due to the material's characteristics as a solid electrolyte. SEI film protects the electrodes from solvents while passivating them. SEI formation is affected by temperature and will continue to grow. The stable SEI layer is a key guarantee for the long-term use of the battery. Well-designed structures and components of artificial SEI can effectively inhibit dendrite development and electrolyte corrosion. Adhesives can also stabilize SEI properties, and layers that prevent SEI from forming dendrites such as alcohol-containing coatings and bilayer Li_4SiO_4 are also being developed. Fluorinated additives also help to form stable SEI for increased performance due to their bi-polarity [6]. The composition of SEI is very complex and has important relationship with substrate and electrolyte type. Taking $LiPF_6$ and as an example, the SEI of $LiPF_6$ is includes little to no carbonate and is mostly made up of Li and F [7]. Solvent reduction product is a major factor in the SEI investigation. However, the electrolyte type affects the result of the solvent reduction, so the SEI components of lithium batteries with different solvents are also very different.

In addition, dendrite growth of lithium battery is also a factor to be considered. In a battery, dendritic crystals slowly form on the surface of the negative lithium electrode during charging. Its formation is the result of lithium nucleation and growth. This phenomenon may be caused by uneven coating on the electrode surface, mixed with impurities of active substances, lithium-ion concentration gradient, limited absorption capacity of the deep discharge negative electrode and so on. The higher the surface roughness is, the more favorable the formation of lithium dendrites will be. Lithium dendrites can cause batteries to fail. For example, lithium dendrites are not easy to grow in solid polymer electrolyte (SPE), so research into dendrites in lithium batteries using SPE as the electrolyte is important [8]. Dendrite growth may result in contact between positive and negative poles, causing the battery to heat out of control and catch fire and explode. Secondly, a series of side reactions will be caused by the dendrites breaking the SEI film, leaving the lithium directly exposed to the electrolyte, contributing to the irreversible consumption of lithium. Moreover, dendrites can cause the metal to take on a more empty state, impeding the safe operation of the anode [9]. At present, different methods are adopted for dendrites according to their different morphology. Using two dimensional materials or three dimensional scaffolds to inhibit dendrite growth and non-dendritic lithium deposition is a solution. In addition, dendrite regulation is also an effective way to guide dendrites by adjusting the position of lithium nucleation, growth route and direction. Third, dendrite elimination is also a solution. However, this method has some challenges at present, which uses Lorentz force and increasing yield stress to eliminate dendrites. More types of forces and processes are still under development and need more development and research [10].

2. Anode

The design concept of lithium-oxygen battery is that it can directly obtain O_2 from the environment as cathode materials and Li as the anode materials. All Li-O_2 batteries have lithium metal as a negative electrode. Therefore, there are few researches on anodes in Li-O_2 batteries. Nevertheless, normally, the surface of Li metal is coated with SEI. Lithium-oxygen batteries come into direct contact with oxygen, water vapor, carbon oxide, etc. This is a test of lithium anode electrolytes. However, the accumulation of lithium hydroxide in lithium anode is considered. The concept of lithium silicon alloy anode has been proposed. Li-Si-C composite electrode can successfully replace lithium metal. At present, the capacity of the anode is stable through testing. The successful development of the electrode also suggests that it is feasible to reduce the energy loss caused by lithium metal anode using nanotechnology in the future [11]. In the case of pure lithium anodes, the electrolyte will corrode Li and thus dendrite growth. The current idea is to use artificial SEI to protect pure lithium electrodes. Another new design is associated with carbon nanotubes (CNTs). A type of carbon nanostructured cathode material with regular sequence is the carbon nanotube [12]. According to their structure, carbon nanotubes are classified as single-walled and multi-walled varieties. The classification standard is the number of layers of graphene sheets in the nanotubes. Multiwalled carbon nanotubes are closed cylinders rolled up by graphite sheets. Single-walled carbon nanotubes are cylindrical structures constructed of rolled-up sheets of graphene that can contain lithium.Carbon nanotubes possess the highest reversible capacity theoretical value of 1116Ahg-1 among carbon-based active materials [13]. By using lithium metal and carbon nanotubes as composites, which have the appearance of microspheres and interweave carbon nanotubes to form a network. This design can enhance the electrochemical reversibility and extend the cycle life, which is significant for developing the next generation Li-O_2 batteries [14]. For now, lithium is the dominant electrode, but new designs are emerging. It is believed that in the future there will be a higher performance lithium oxygen battery negative electrode to be developed to improve the maturity of lithium oxygen battery.

3. Cathode

Lithium oxygen battery has a very high energy density because oxygen is inexhaustible, and lithium oxygen battery has a special electrode mechanism - air cathode. The carbon, catalyst, and polymer binder that make up the air cathode. The lithium ions move through the electrolyte and eventually form a precipitate with the oxide ions. This Li2o2 precipitate attaches to the air electrode. In order to maintain its service life, the cathode is required to have a high surface area for attachment. In addition, the thickness of the air electrode also has a certain effect on its performance. Thicker electrodes have lower specific capacity as oxygen enters the electrolyte [15]. A high performance air electrode should ensure a fast diffusion rate of oxygen, a higher surface area of carbon, good conductivity, and high electrode integrity. Graphene nanosheets (GNSs) stand out among many carbon-based materials because of the high discharge capacity displayed by their unique form. Its discharge capacity is up to 8705.9mAhg^{-1}. Currently GNSs electrodes can be used in alkyl carbonate electrolyte lithium oxygen batteries. The 3D structure of GNSs creates wide channels for the passage of electrolytes and oxygen [16].

In addition to GNSs, porous carbon, carbon oxide, and carbon-based precious metals can also be used as air electrodes. Each of these materials has its own advantages. However, the related attribute characteristics still need to be further studied for practical use and production in the future. Promising cathode systems need the right electrolytes to realize their essential role in battery operation. The electrolytes for lithium oxygen batteries are described in the following section.

4. Electrolyte

The current lithium-oxygen battery has four electrolyte systems. There are three kinds of liquid electrolyte systems: non-aqueous, aqueous, and mixed electrolyte system; A solid electrolyte system. Water containing electrolytes is generally not recommended due of the water and lithium parasitic interaction. In order to prevent the electrode from being affected by water, a solid electrolyte of Li^+ conductorcan be used to improve the water resistance of the lithium electrode [17]. $Li–Al–Ti–PO_4$ (LATP) membrane is an excellent ceramic membrane with satisfactory stability in the water electrolyte of Li-oxygen battery. Although water electrolyte lithium air battery still has some defects, it can operate normally and has certain stability [18]. Besides, it also indirectly promoted the development of non-aqueous electrolytes. Both solutions can avoid some undesirable reactions between lithium metal and water. When organic matter is used as electrolyte in Li-oxygen battery, the reduced product is insoluble in electrolyte. It can be configured to increase oxygen concentration to improve its ability to transport oxygen. There are many electrolytes currently used in non-aqueous lithium oxygen batteries. For example, alkyl carbonate was initially promising, but later it was proved that carbonates would be attacked by superoxide radicals and then oxidized; it does not match the electrochemical reaction characteristics of the cell [19]. Although it has excellent lithium ion transport performance and lithium salt solubility, it cannot be used safely due to its instability. The mixed electrolyte system is more like a combination. These include one aqueous electrolyte and one non-aqueous electrolyte. These two electrolytes are in the cathode and anode. The scheme draws on the best of both systems, but more research is needed on how to find compatible partners. The last solid electrolyte, again, is the highly touted electrolyte. It has the advantages of safety, low cost, wide range of operating temperature and stable electrochemical properties. More importantly, the electrolyte can impede the development of lithium dendrites.Therefore, solid electrolyte has a high potential for development. Currently the two main solid electrolytes are ceramic solid electrolyte (CSE) and solid polymer electrolytes (SPE) [20]. The CSE has high thermal stability, which is the fundamental reason for its extended battery life. However, there are not many types of CSEs that are compatible with lithium-oxygen batteries, and these two systems are the most compatible. CSE has high thermal stability, which is the fundamental reason for its extended battery life. There are not many kinds of CSE matching lithium oxygen battery, among which $Li–Al–Ge–PO_4$ and LATP systems are the most suitable [21].

Although solid electrolytes have been criticized for their low current density, this new concept has just been born, and the future of solid electrolytes is very bright. Armand was the first to use SPEs in lithium batteries and lithium-ion polymer batteries have attracted a lot of attention [21]. Although many different systems have been developed, the problem of poor contact between solid electrolytes and carbon-based conductors has not been completely solved. If the contact between the two can be closer, then the internal resistance will be reduced even more.

5. Conclusion

This article introduces the development history of $Li-O_2$ battery and expands the introduction. As a highly anticipated high-performance battery, lithium-oxygen battery is the key to solve the problem of battery energy storage capacity.Currently, lithium-oxygen batteries have a substantially larger energy storage capacity than LIBs. The operating principle and main structure of lithium oxygen battery are also introduced. SEI, lithium dendrites and other details are also elaborated. In recent years, the development of lithium oxygen battery is relatively smooth, and some theoretical ideas have been realized one by one. However, many architectures still have more performance options to develop. This article holds a positive attitude towards the future development of $Li-O_2$ batteries. It is anticipated that lithium oxygen batteries' great performance in the future can be used right away, so that the anticipated stage of design such as electric aircraft can become a reality.

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