

The Analysis of the Development and Improvement of Lithium-Air Batteries

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Abstract: Lithium-air batteries have been widely used by academia and industry because of their ultra-high theoretical energy density. The lithium-air battery uses lithium metal as the negative electrode and oxygen in the air as the positive electrode to achieve the conversion of chemical to electric energy. At present, the mainstream lithium-air battery design has four structures, respectively using an all-solid electrolyte, aqueous electrolyte, aprotic electrolyte and a mixed type to achieve ion migration. This paper mainly analyses and discusses the recent research on the performance improvements of the lithium-air battery. This paper finds that the development of lithium batteries is mainly hindered by the problems of catalyst efficiency, battery life and stability, so the focus of research is mainly to develop efficient catalysts, and improve electrode materials and electrolytes. After improvement and optimization, the lithium-air battery has considerable application prospects.

Keywords: Lithium-air battery, catalyst, electrolyte, electrode material

1. Introduction

With the accelerated development and utilization of renewable energy sources such as wind power, solar power, and tidal energy, along with the rapid growth of new energy industries like electric vehicles, most renewable energies are constrained by geographical factors and exhibit characteristics of discontinuity and instability. Therefore, there is an increasing demand for the development of energy storage and conversion technologies that are low-cost, safe, highly efficient, and have high energy density. After long-term development, the energy density of lithium-ion batteries has approached its theoretical limit. Currently, mainstream lithium-ion batteries, such as those using lithium iron phosphate and nickel-cobalt-manganese ternary cathode materials, have theoretical specific capacities that do not exceed 300 mAh g⁻¹, and the upper limit of the energy density of full cells is only around 400 Wh kg⁻¹.

Among various battery systems, lithium-air batteries have received extensive attention due to their exceptionally high energy density. Lithium-air batteries (also known as lithium-oxygen batteries) use metallic lithium as the anode and oxygen from the air as the cathode reactant to achieve the conversion between chemical energy and electrical energy [1]. The theoretical energy density of lithium-air batteries can reach up to 3463 Wh kg⁻¹ (and even up to 11680 Wh kg⁻¹ when the mass of external oxygen is excluded), making them one of the closest energy storage systems to fossil fuels in terms of energy density.

The paper starts with the principles of lithium-air batteries, summarizes the main challenges faced in their development, and briefly analyzes the corresponding solutions. It also looks forward to the future direction of lithium-air battery development, aiming to provide insights into the research and application of lithium-air batteries.

2. Principle of Lithium-Air Batteries

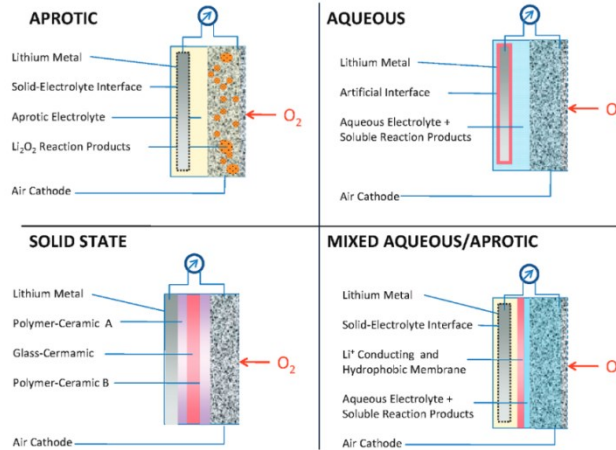
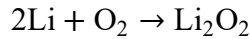


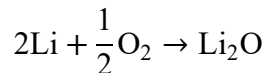
Figure 1: Four different architectures of Li-air batteries, which all assume the use of lithium metal as the anode [2]

Lithium-air batteries use lithium as the negative electrode and atmospheric oxygen as the positive electrode. Currently, lithium-air batteries' basic design structures can be mainly divided into four types: aprotic electrolytes, aqueous electrolytes, mixed aprotic and aqueous electrolytes, and all-solid-state electrolytes [2].

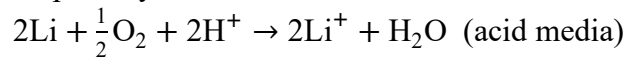
In aprotic electrolytes, the primary reactions in lithium-air batteries are as follows:



In addition to the primary reactions, other side reactions can occur in lithium-air batteries with aprotic electrolytes:



In aqueous electrolytes, the primary reactions in lithium-air batteries are as follows:



The reaction mechanisms of all-solid-state electrolytes in lithium-air batteries have not yet been fully elucidated, but it is generally accepted that they are similar to those observed in aprotic electrolytes.

Currently, research on the four main types of electrolyte structures has progressed to varying degrees, but there is no consensus on which structure represents the optimal choice for lithium-air batteries. Each of the four electrolyte structures offers distinct advantages, but also presents unique challenges that require further investigation. The following sections will detail these aspects.

3. Problems And Solutions in Lithium-Air Batteries

Currently, lithium-air batteries face challenges such as low efficiency and poor stability, which hinder their large-scale application. Therefore, the main research directions focus on developing efficient catalysts, improving electrode materials, and optimizing electrolytes.

Table 1: Comparison of specific discharge capacities of different positive catalysts.[3]

Catalyst	Discharge voltage(V)	Capacity of cycle 1(mAh g ⁻¹)	Capacity of cycle 5(mAh g ⁻¹)	Capacity of cycle 10(mAh g ⁻¹)	Capacity retention per cycle(%)
Pt	2.55	470	60	60	1.28
La _{0.8} Sr _{0.2} MnO ₃	2.6	750	75	40	0.53
Fe ₂ O ₃	2.6	2700	500	75	0.28
Fe ₂ O ₃ -carbon loaded	2.6	2500	280	75	0.3
NiO	2.6	1600	900	600	3.75
Fe ₃ O ₄	2.6	1200	1200	800	6.67
Co ₃ O ₄	2.6	2000	1900	1300	6.5
CuO	2.6	900	900	600	6.67
CoFe ₂ O ₄	2.6	1200	900	800	6.67

3.1. Catalysts

Catalysts at the cathode of lithium-air batteries play crucial roles in enhancing charge-discharge capacity, reducing overpotentials (especially during charging), and influencing cycle performance. The choice and performance of catalysts significantly impact the overall performance of lithium-air batteries, making selecting catalysts with good oxygen reduction activity particularly important.

The primary catalysts currently used in lithium-air batteries include Fe, NiO, CoO₄, CuO, MnO₂, Au, and Pt. Table 1 shows that Fe catalysts exhibit the highest initial discharge capacity, while NiO, Fe₃O₄, CoO₄, CuO, and CoFe₂O₄ maintain certain capacity retention rates. Among these, Co₃O₄ demonstrates the best overall performance. However, different catalysts have minimal impact on the discharge plateau voltage.

Studies on the catalytic performance of Au and Pt indicate that Au facilitates the oxygen reduction reaction (ORR), while Pt promotes the oxygen evolution reaction (OER). Different catalysts show little variation in their effect on ORR, possibly because ORR is inherently insensitive to catalysis, or because carbon materials themselves already exhibit good ORR catalytic properties, masking the effects of the studied catalysts.

Considering both performance and cost, MnO₂ currently exhibits the best catalytic performance. Research shows that among different sizes, morphologies, and crystal structures of manganese oxides, α -MnO₂ has the best catalytic performance, with an initial discharge capacity exceeding 3000 mAh g⁻¹. Avoiding deep polarization (deep discharge) can improve battery cycle performance. α -MnO₂ can react with the discharge product LiO₂ to form Li₂MnO₃, which is a reversible reaction product, thereby enhancing charge capacity and cycle performance. Data indicate that cathodes using MnO₂ as a catalyst show a slight increase in initial discharge capacity with increasing cycle numbers, possibly due to the inherent capacity of MnO₂. Due to the density differences between catalysts and carbon materials, direct mixing often results in uneven catalyst distribution, leading to a higher proportion of catalysts in the electrode. To achieve uniform catalyst distribution, in-situ synthesis methods can be employed to prepare lithium-air battery cathodes using mesoporous carbon

frameworks with nano-sized MnO_2 particles as catalysts. This method has demonstrated excellent discharge performance, with an initial discharge capacity reaching 4750 mAh g^{-1} .

In summary, effective catalysts not only reduce overpotentials (especially during charging) and improve charge-discharge efficiency but also influence discharge capacity and cycle performance.

3.2. Electrode Materials

Cathode materials play a critical role in the performance of lithium-air batteries, primarily due to the significant voltage drop occurring at the cathode. Currently, porous carbon materials are widely used as cathode materials due to their excellent conductivity and oxygen-reduction activity. Lithium-air batteries require high porosity, pore size, and active surface area in cathode materials.

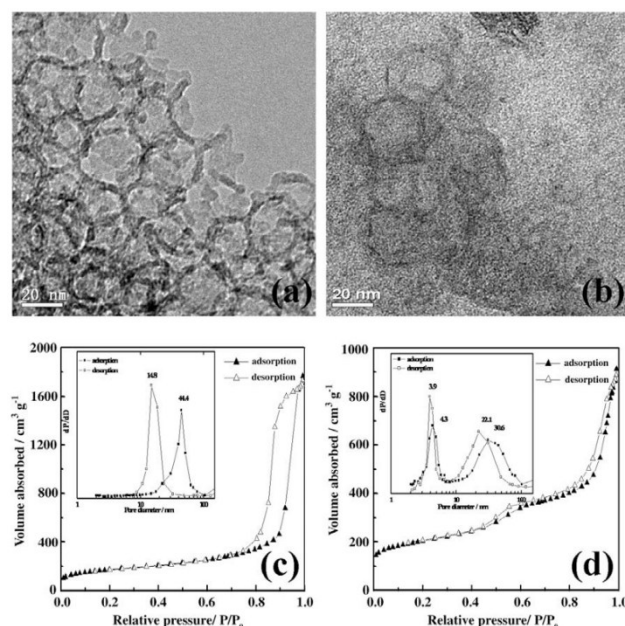


Figure 2: TEM graphs of (a) MCF silica and (b) MCF-C. Nitrogen adsorption isotherms and corresponding pore size distributions (inset) for (c) MCF silica and (d) MCF-C [4]

Figure 2 shows that mesocellular carbon foam (MCF-C) prepared using a silica hard-template method, when used as a cathode material in lithium-air batteries, exhibits better performance compared to other common carbon materials.[4] Experimental results indicate that mesopore size is more important than specific surface area. Cathodes with more mesopores exhibit better discharge performance. Additionally, the open-shell structure of mesoporous carbon foam allows for product deposition, resulting in higher discharge capacity. Higher mesopore ratios result in greater specific capacities of the prepared electrodes [5].

Furthermore, composite cathode materials have been explored. One study used single-walled carbon nanotubes (SWCNTs) and carbon nanofibers (CNFs) as composite cathode materials for lithium-air batteries and investigated the effects of different electrode thicknesses and discharge currents on cathode performance. The results showed that thicker electrodes and higher discharge currents result in lower discharge capacities [6].

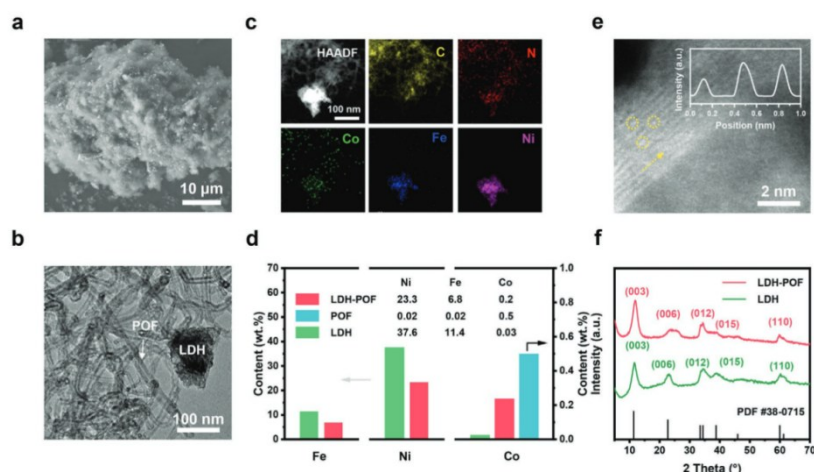


Figure 3: Characterizations of LDH-POF [6]

3.3. Electrolytes

To ensure the stability and safety of lithium-air batteries, the development of reliable and high-performance electrolytes is a crucial direction. Solid-state electrolytes offer several advantages, such as preventing lithium dendrite growth and avoiding electrode corrosion and contamination, fundamentally enhancing the stability and safety of lithium-air batteries.

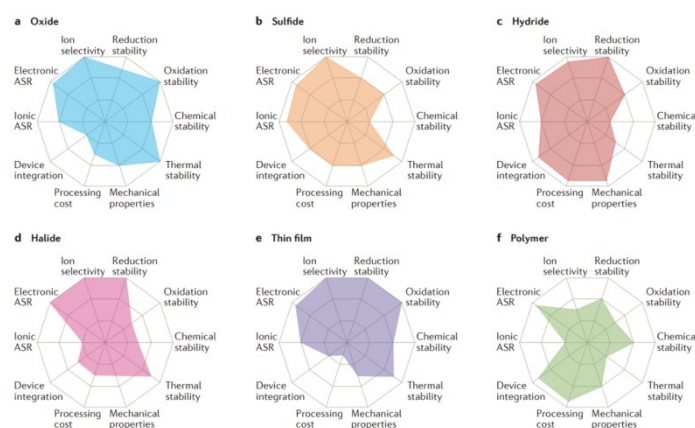


Figure 4: Comparison of different types of solid electrolyte materials [7]

Currently, the main types of solid-state electrolytes can be broadly classified into inorganic solid-state electrolytes (including oxide, sulfide, halide, and thin-film solid-state electrolytes), organic polymer-based solid-state electrolytes, and organic-inorganic composite solid-state electrolytes (Figure 4). Key performance indicators for solid-state electrolytes include lithium-ion transference number, electrochemical stability window, thermal stability, chemical compatibility, solid-state electrolyte-electrode interfacial impedance, mechanical properties, device integration capability, environmental friendliness, and cost [7].

Inorganic solid-state electrolytes have advantageous ionic conductivities but face a common issue: high interfacial impedance between the electrolyte and electrodes. Additionally, most inorganic solid electrolytes are brittle, and cracking can lead to short circuits in the battery. In contrast, polymer electrolytes offer better flexibility and processability, but polymer electrolytes composed solely of polymer hosts and lithium salts typically have low ionic conductivities and low lithium-ion transference numbers, making them unsuitable for practical applications.

To address these issues, combining inorganic solid-state electrolytes with polymers is an effective approach. Composite solid-state electrolytes exhibit enhanced electrochemical performance, mechanical properties, and processability, achieving higher room-temperature ionic conductivities and suppressing unwanted side reactions.

In recent years, significant advancements have been made in the development of solid-state electrolyte materials across various systems. However, practical applications of solid-state electrolytes in lithium-air batteries still face challenges, such as interfacial contact and the construction of air cathodes. Systematic research is needed to advance solid-state lithium-air batteries.

4. Conclusions

This paper mainly analyses and discusses the recent research on the performance improvements of the lithium-air battery, pointing out the main research directions. Limited by the length, some contents of this paper are not deep enough, and some research directions are omitted.

Given the extremely high energy density of lithium-air batteries, addressing the key issues related to electrode materials, electrolytes, and catalysts could enable these batteries to meet the standards required for large-scale production and application. If these challenges are successfully overcome, lithium-air batteries have the potential to bring significant benefits to industries such as energy storage and electric vehicles.

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