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The Fundamentals and Mechanisms of Electrolytes

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Abstract. Batteries, with their high efficiency, are increasingly recognized because of an indispensable function that is used as sustainable energy storage, and versatility, they can also reduce carbon emissions. While lithium-ion batteries (LIBs) currently dominate commercial applications with high energy density and stable cycling performance, their limitations—including material scarcity, safety risks, and limited voltage ranges—have driven exploration into alternative chemistries. This review highlights the structural and mechanistic differences between different kinds of electrolytes, with particular emphasis on the role of electrolytes as a critical component in determining stability, safety, and performance. Electrolytes are composed of salts, solvents, and additives, each playing a distinct role in ion conduction, interfacial stability, and overall efficiency. We further discuss key requirements for electrolytes, including ionic conductivity, electrochemical stability, electrode compatibility, and thermal resistance. Special focus is given to electrolyte design strategies such as the selection of anion species, development of solvent systems, and the use of additives like fluoroethylene carbonate (FEC) and lithium nitrate ($LiNO_3$), which stabilize interfaces and suppress detrimental side reactions. By comparing inorganic and organic systems, this paper provides insights into the mechanisms of ion transport, challenges in electrolyte engineering, and strategies for enabling next-generation batteries with improved energy density, safety, and long-term cycling stability.

Keywords: mechanism of electrolytes; requirements of electrolytes; mechanism of batteries.

1. Introduction

Nowadays, batteries, as a technology for storing sustainable energy, have received widespread attention because of zero tailpipe emissions and lower cost compared to burning fuels to provide energy. However, the containments such as raw material scarcity, environmental pollution of recovery, low operation voltage and short lifecycle show that many aspects of batteries can be improved to match more energy storge applications. In general, a battery system consists of three necessary components, which are the cathode, anode and electrolyte. In detail, the promotion in the energy density of the battery system can be completed by changing the materials of the electrode (cathode/anode), so most of the research of batteries has been done on the materials of the electrode in few years. In addition, the electrolyte plays an important role because it acts as a medium during charging and discharging, allowing ions to move between the anode and cathode. It can conduct ions but block electrons so that the short circuits can be prevented. The selection of electrolytes determines the operational voltage window, safety and lifespan of the battery, as it must remain stable while the battery is in working. The absence of electrolytes makes energy storage impossible. They are usually composed of ionic liquids or mixtures of solvents and salts, enabling ions to be transported between electrodes. The function of electrolytes varies by system: in lithium-ion batteries, it serves as the medium for the transfer of lithium ions during charging and discharging, while in electrochemical capacitors, it can act as an active material, directly storing charges at the electrode-electrolyte interface [1]. In this review, different electrolytes (organic liquid electrolytes, aqueous electrolytes, inorganic solid electrolytes, polymer-based electrolytes) and their operating principle will mainly be discussed.

2. Functions of Electrolytes in Batteries

In general, batteries can broadly be divided into inorganic and organic types. Inorganic batteries mainly use metals, metal oxides, or inorganic salts as electrode materials (e.g., Li-ion, Na-ion, Zn-air). These dominate the commercial market today because of their high energy density and stability. Organic batteries use carbon-based molecules or polymers as electrodes (e.g., quinones, conductive polymers, radical polymers). These are still mostly in the research stage but are attractive for their flexibility, sustainability, and potential low cost [2].

2.1. The Structure of Batteries

Typically, the structure of fundamental metal-based batteries consists of two electrodes (cathode - positive electrode, anode - negative electrode), and the electrolyte used for ionic conduction but is insulating for electrons. Moreover, there is a separator between the electrodes, which is a polymer film that allows ion transmission while preventing electrical short circuits [3], as shown in Figure 1. [4] The crystal framework of inorganic electrode materials provides clear channels for ion insertion and extraction, ensuring mechanical stability during the cycling process. This structure supports the high energy density and long lifespan of inorganic batteries.

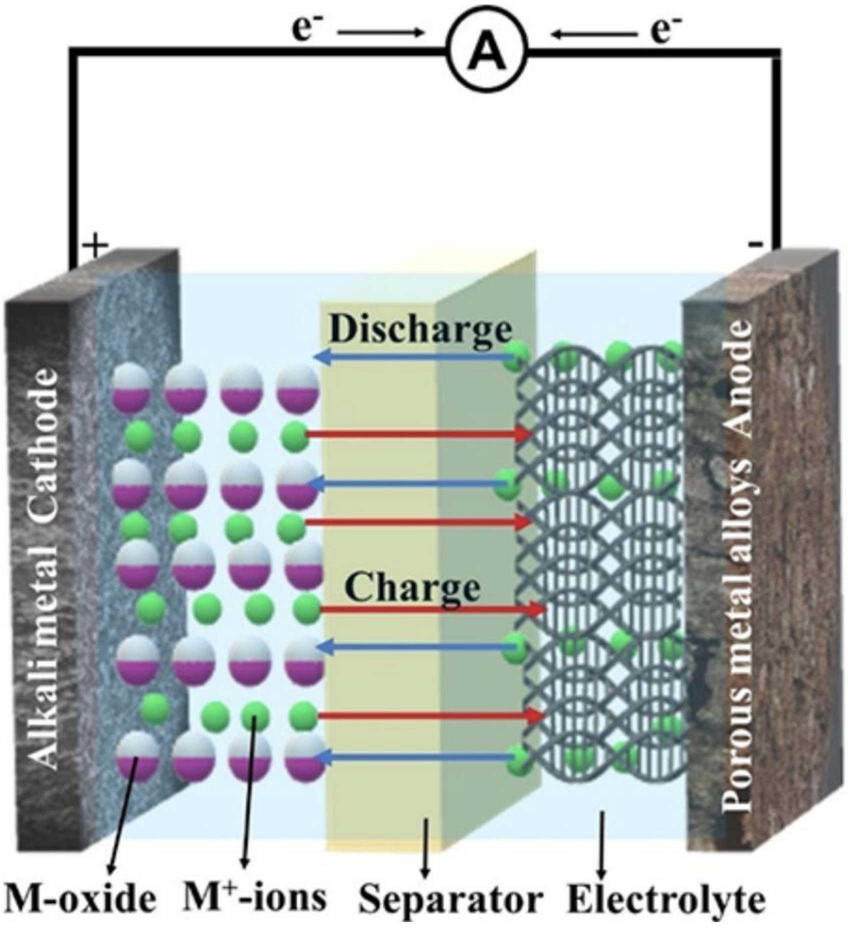

Fig. 1 The structure of a fundamental metal-based battery. For the discharging process, metal ions will move from the anode to the cathode, then electrical power is generated as electrons flow from the negative to the positive electrode through an external circuit [4].

2.2. The Mechanism of Batteries

In conventional inorganic batteries, charge storage is mainly achieved through the intercalation and deintercalation of ions such as Li^+, Na^+, or Mg^{2+} into and out of crystalline electrode structures. During this process, transition metal atoms within the cathode undergo valence changes to balance the inserted or removed ions. This mechanism depends strongly on the ionic radius of the charge carrier and the available interlayer spacing within the crystal lattice, which restricts the variety of ions that can be stored efficiently. While intercalation enables high energy densities, repeated ion insertion often causes lattice deformation, slow diffusion kinetics, and reduced cycling stability, especially under high current densities or low-temperature conditions.

2.3. Requirements for Electrolytes

Electrolytes are essential to improve the electrochemical performance of batteries, which is responsible for electrochemical stability window, compatibility with the electrode and so on [5]. There are four types of electrolytes in total, which are organic liquid electrolytes, aqueous electrolytes, inorganic solid electrolytes and polymer-based electrolytes [5].

First, an ideal electrolyte in a battery must combine high ionic conductivity with low electronic conductivity. High ionic conductivity ensures that ions can move quickly between the electrodes, supporting fast charge and discharge. Nevertheless, the electronic conductivity should be as low as possible so that short circuits and self-discharge can be prevented. For Liquid electrolytes, they are preferred to have low viscosity and good solvation properties to enable rapid ion transport. However, solid polymer electrolytes often suffer from low ionic conductivity, which can be overcome by adding solvents or inorganic padding, as well as by operating at higher temperatures. For inorganic solid-state electrolytes, the ionic conductivity can be improved by increasing sintering density and reducing grain boundaries [6]. Moreover, recent studies highlight that suppressing electronic conductivity in solid electrolytes is crucial to avoid dendrite growth within the electrolyte, which can compromise both safety and performance.

Secondly, conventional organic solvents will generate flammable steam at high temperatures, which means batteries are not able to operate at high temperatures. Therefore, electrolytes should have good thermal stability. In order to prevent the decomposition of electrolytes, the operating voltage of the battery should be narrower than the electrochemical window of an electrolyte. During the first charge/discharge process, the formation of protective layers would occur while the electrolyte is partially decomposed. These interphases help stabilize the system by extending the effective stability window of the electrolyte in practical operation. However, for long-term cycling, a chemically and electrochemically stable electrolyte is essential to prevent continuous side reactions, which would otherwise lower Coulombic efficiency and reduce the lifespan of batteries. More importantly, compared to inorganic electrodes, organic electrode materials typically operate at lower potentials, which allows for compatibility with a broader range of electrolytes, including aqueous, organic liquid, and solid-state systems that are not suitable for high-voltage inorganic batteries. On the other hand, for high-voltage organic electrodes, specially designed electrolytes with strong oxidation resistance are required to match the electrode potential and ensure stability without degradation [5].

The compatibility between electrolyte and electrode is a fundamental requirement for the development of high-energy density batteries. A well-aligned interface facilitates efficient ion transport across the electrolyte-electrode boundary, thereby reducing resistance and suppressing undesirable side reactions. This requirement is especially critical in solid-state batteries, where the absence of liquid contact complicates the establishment of intimate interfacial contact. In such systems, achieving uniform and effective ion conduction at the electrolyte/electrode interface is essential for fully utilizing the active material. Conversely, poor interfacial compatibility can lead to elevated resistance and uneven ion distribution, ultimately compromising both the performance and safety of high-energy density batteries.

2.4. Organic Liquid Electrolytes

2.4.1. Salts

Three main components for electrolytes are salts, solvents and additives [7]. The requirements for salts in electrolytes are stringent [8]:

Generally, the salt must exhibit high solubility in the chosen solvent to ensure sufficient ionic conductivity. Second, it should be chemically stable with other electrolyte components, as well as electrochemically compatible with the electrodes and current collectors, to avoid unwanted side reactions. Third, the salt should have adequate oxidation and reduction stability, since this defines the electrochemical stability window and thereby the operating voltage range of the battery. Finally, safety considerations are essential to minimize risks during operation and improve the overall sustainability of the battery.

More importantly, the performance and stability of batteries are often more strongly influenced by the anion species in the electrolyte salt than by the cation [9, 10]. In fact, much of the progress in designing electrolytes for sodium-ion, potassium-ion, and calcium-ion batteries has been guided by insights gained from lithium-ion battery research. Commonly investigated anions include ClO_4^-, BF_4^-, PF_6^-, $CF_3SO_3^-$, (Tf)- and $TFSI^-$. However, each of these presents specific drawbacks [11]. For example, ClO4- is highly oxidizing, which makes it erosive and unsuitable for practical cell applications. BF_4^-, while stable, forms strong ion pairs with cations, which reduces the number of free charge carriers and thus lowers ionic conductivity. PF_6^-, it is one of the most widely used anions in lithium-ion batteries, suffers from safety concerns because it can decompose in the presence of moisture or under elevated temperatures. Similarly, Tf- and $TFSI^-$, despite being popular in advanced electrolyte designs, often exhibit low ionic conductivity and can corrode aluminum current collectors [11], which limits their long-term reliability. These issues highlight the ongoing challenge of identifying and engineering new anions that can provide high conductivity, wide electrochemical stability, and robust compatibility with electrodes and current collectors for next-generation battery systems.

2.4.2. Solvents

For batteries to operate safely and efficiently, the choice of solvent is crucial. A suitable solvent should combine chemical stability with low toxicity and reasonable cost [7], while also dissolving enough electrolyte salt to supply sufficient charge carriers for ion transport. In addition to these general requirements, solvents influence how the electrolyte interacts with the electrode surfaces and help define the electrochemical stability window of the system. To meet these needs, researchers have explored different classes of solvents. Organic solvents can offer a broad stability window, though they often raise safety concerns. Ionic liquids provide non-volatility along with excellent thermal and electrochemical stability. Polymer-based solvents make it possible to design flexible solid or gel electrolytes with improved safety. Each class brings its own strengths, and together they represent different strategies for balancing conductivity, stability, and safety in modern battery technologies.

2.4.3. Additives

Additives are the last component of functional electrolytes, introduced in small proportions (usually <5 wt%) to compensate for the limitations of primary electrolytes. They primarily act at the electrolyte/electrode interface, where they can stabilize or modify the solid electrolyte interphase (SEI), improve surface wetting, and provide protection against overcharging. In addition, additives enhance electrolyte performance by serving as flame retardants, viscosity modifiers, or radical scavengers [7], contributing to both safety and efficiency. Some additives also promote the formation of stable SEIs, improving cycle life and overall electrochemical performance. For sodium-ion batteries (NIBs), fluoroethylene carbonate (FEC) is the most commonly used, while blends with prop-1-ene-1,3-sultone (PST) and 1,3,2-dioxathiolane-2,2-dioxide (DTD) have shown excellent results [12].

Lithium nitrate ($LiNO_3$), used as an electrolyte additive in lithium-based batteries due to its ability to stabilize the Li metal surface and improve battery performance. By forming a protective Li_xNO_y passivation layer, $LiNO_3$ effectively suppresses the shuttle effect caused by dissolved organic species, which otherwise react continuously with the anode and degrade performance. This protective film reduces unwanted side reactions, enhances the coulombic efficiency, and significantly improves the cycling stability of lithium secondary batteries [13-15]. When added in appropriate amounts, $LiNO_3$

ensures more controlled electrode–electrolyte interactions, making it a crucial additive for maintaining long-term stability in rechargeable Li systems [16].

2.5. Aqueous Electrolytes

2.5.1. Salts

Various electrochemical redox phenomena would be displayed by organic quinone electrodes, which depend on the type of water metal ion electrolyte used. In this electrolyte, carriers possess unique physicochemical characters, which directly affect the performance of the electrode. To investigate the ion pairing effect of these charge carriers on quinone-based electrodes, researchers used 9,10-anthraquinone (AQ) as a model compound and systematically studied its redox properties in various aqueous solutions [17].

2.5.2. Solvents

Generally, most salts do not directly participate in battery reactions but instead function primarily to stabilize the solvation sheath structure. Consequently, a major challenge for researchers is to develop cost-effective strategies that not only reduce the water percentage in aqueous electrolytes but also precisely tailor the coordination environment of metal ions.

2.5.3. Additives

The incorporation of organic solvents into aqueous electrolytes can lead to two distinct solvation effects. First, organic additives may interact with water molecules, disrupting the hydrogen-bonding network and altering the overall electrolyte structure. Second, they can insert into the inner solvation sheath of metal ions, partially replacing water molecules and thereby modifying the conventional solvation environment.

2.6. Inorganic Solid Electrolytes

Inorganic solid-state electrolytes not only provide high safety along with excellent thermal and mechanical stability, but also help mitigate issues such as organic electrode dissolution, thereby enhancing cycling stability. While they address many of the challenges faced by liquid electrolytes, they introduce new ones of their own. For example, although solid-state electrolytes are generally expected to suppress dendrite growth, recent studies have shown that dendrites can still form in certain systems. This phenomenon is often linked to the relatively high electronic conductivity of some inorganic solid-state electrolytes [18].

2.7. Polymer-based Electrolytes

Polymer-based electrolytes typically consist of organic polymer matrices combined with dissolved salts, and may also include liquid solvents. To further enhance their performance, inorganic fillers are often incorporated, ranging from inert materials like SiO_2 and Al_2O_3 to active fillers such as $Li_7La_3Zr_2O_{12}$ (LLZO) and $Li_{0.33}La_{0.557}TiO_3$ (LLTO).. In addition, ionic liquid (IL)-based ionogel electrolytes and poly (ionic liquid) (PIL) electrolytes have emerged as promising alternatives, offering excellent electrochemical and stability characteristics that continue to attract significant research attention [5].

3. Conclusion

Batteries represent a cornerstone technology of the sustainable energy systems, but their performance and safety remain highly dependent on electrolyte design. Inorganic batteries, such as LIBs, NIBs, and KIBs, benefit from established crystalline electrode structures and high energy densities. However, they still have many challenges, such as material availability, lattice stability, and interfacial degradation. Organic batteries can offer unique advantages, including structural flexibility, sustainability, and compatibility with a broader range of electrolytes, but their stability and scalability require further improvement. Across both types, the electrolyte plays a decisive role by governing ionic transport, electrochemical windows, and electrode compatibility. Salts, solvents, and additives must be carefully tailored to provide high conductivity, thermal and electrochemical stability, and controlled interfacial reactions. In particular, advances in electrolyte additives such as FEC and LiNO3 demonstrate the potential to suppress parasitic reactions, which can enhance Coulombic efficiency and extend battery lifespans. Moreover, the development of electrolytes with optimized anion chemistries, non-flammable solvents, and multifunctional additives will be critical to unlocking safer, high-performance, and scalable energy storage systems. By bridging fundamental understanding with material innovation, electrolyte engineering can enable the next generation of both inorganic and organic batteries to meet the diverse demands of future energy applications.

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