

Research progress of gel polymer electrolytes for lithium batteries

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Abstract. Due to their exceptional electrochemical properties, lithium-based rechargeable batteries have been the industry leaders in the energy storage field and have attracted substantial research attention. Electrolytes play an irreplaceable role in lithium batteries. Gel polymer electrolytes (GPEs) not only hold the potential to ameliorate the risks associated with liquid electrolytes and solid electrolytes but also show further applications as additives, activators, and membranes, enhancing the properties of many electrochemical systems. Moreover, their processibility and flexibility make them a promising application on wearable and biomedical devices. This article first briefly introduces the basic structure and working principle of lithium batteries. After that, the characteristics of several lithium-based batteries, including LSB, LMB, LIBs, and LOB, were compiled. Finally, this paper emphasizes several traditional gel polymer electrolytes for lithium batteries, including PAN-based GPE, PEO-based GPE, PMMA-based GPE, and PVDF-based GPE. The critical role they play in enhancing the performance and safety of lithium battery systems was illustrated by presenting the most recent research advancements.

Keywords: Lithium battery, gel polymer electrolyte, matrix material.

1. Introduction

Nowadays, energy exhaustion and environmental pollution are becoming more and more severe and people should take effective methods to deal with it. One of the most feasible ways is to invent high-efficiency and portable energy storage devices. So, it leads to a rising demand for high-energy batteries, leading to the research of rechargeable lithium batteries (LB) growing faster.

The electrolyte is one of the essential components of lithium batteries. The ionic conductivity, mechanical flexibility, electrochemical stability, and safety are significant criteria of the electrolyte. Nowadays, gel polymer electrolyte is becoming more and more promising to industry and society. For its special physical characteristics, it is widely used in portable and wearable devices, biomedical devices, storage batteries, et cetera. In previous studies, liquid electrolytes and solid electrolytes both show gorgeous properties in certain areas. The liquid electrolytes have excellent performance in electrode wetting and have outstanding ionic conductivity. However, the mechanical strength and safety of liquid electrolytes are inferior. Figure 1 shows the comparison between different electrolytes [1]. Solid electrolytes, for example, ceramic electrolytes, perform high mechanical strength and safety. Moreover, it's worth mentioning that it has a perfect Li^+ transference number (nearly 1). But it also has an unavoidable drawback, it can't wet the electrode. However, gel polymer-based electrolytes (GPEs) are a moderate choice to solve those problems. GPEs' ionic conductivity and characteristics of physical phase are between liquid electrolytes and solid electrolytes. What's more, using GPEs can productively decline liquid electrolytes' potential risks such as electrolyte leakage and flammability.

For its useful characteristics, GPEs have already been applied in the industry. The low migration number of lithium ions, vulnerability to macroscopic phase separation during long-term cycling, and poor ion conductivity are only a few of the severe issues that GPE still encounters in reality. As an emerging research focus, gel polymer electrolytes show bright prospects in application. The gel polymer electrolytes can enhance the properties of electrodes. They can improve the active mass load of cathodes of LCO and the cycle stability of solid-state lithium batteries with LCO and LFP as cathodes at room temperature and high current density [2]. However, their ion conductivity and electrochemical stability are still unavoidable drawbacks. If this breakthrough is completed, it is

expected to promote the emergence of a new generation of lithium batteries that show high flexibility, safety, and energy density.

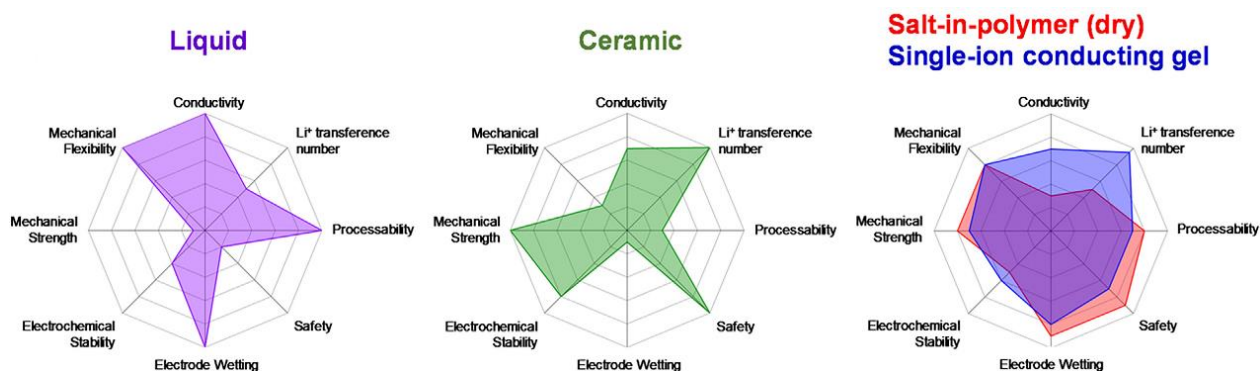


Figure 1. Comparison between different electrolytes [1]

2. Brief introduction of Lithium batteries

2.1. Mechanism and structure

Different types of lithium batteries have different operating mechanisms, but all of them are based on the moving of lithium ions. The initial potential is provided by electrode materials. When discharging, lithium transforms from anode to cathode, forming electric currents. When charging, lithium ions back to the anode and proceed reductive reaction. After that, the product—lithium metal, is inserted into anodes. The structure of lithium batteries containing GPEs usually has four major components: cathode, anode, GPEs, and separators.

2.2. Lithium-sulfur batteries (LSBs)

LSBs have both high specific capacity (1675 mAh g^{-1}) and high theoretic energy density (2600 Wh kg^{-1}), and the main resources are plenty in nature. However, the shuttle effect of lithium polysulfides—the most well-known issue of Lithium-sulfur batteries—impedes the future application of LSBs. In the discharge process, some cyclic S_8 is reduced, producing liquid lithium polysulfides (Li_2S_x , $2 \leq x \leq 8$). Those lithium polysulfides will be further reduced and finally produce the solid Li_2S . Figure 2 shows the typical discharge-charge curves in the first cycle of LSBs. The dissoluble component shuttle between cathode and anode, causing serious capacity fading issues and low CE.

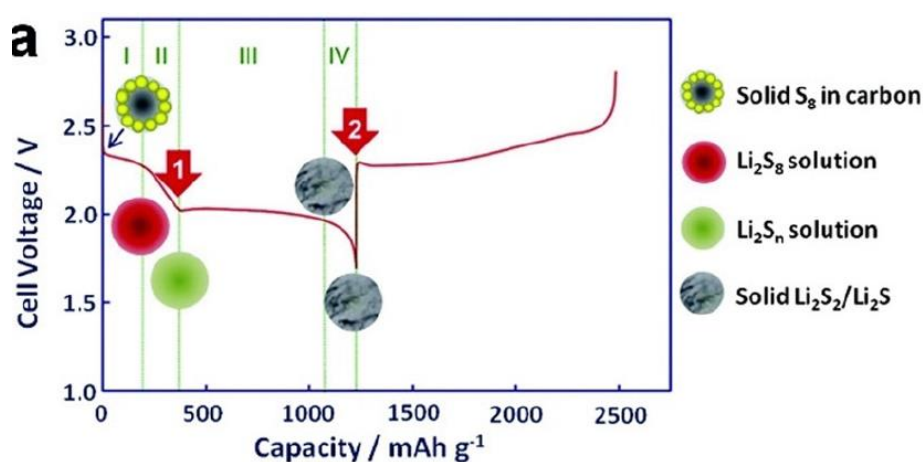


Figure 2. Typical discharge-charge curves in the first cycle of LSBs [3]

2.3. Lithium metal batteries (LMBs)

Although the theoretical capacity of lithium metal batteries is extremely high, issues with safety and cycling stability have emerged as significant roadblocks to their development. Both of these

roadblocks are connected to the ongoing growth of lithium dendrites on the lithium-negative electrode. Lithium dendrites are dendritic metal lithium that occur during the deposition and precipitation of lithium ions on the surface of lithium-negative electrodes. One of the major challenges to the development of metal lithium batteries is the presence of lithium dendrites. It is difficult to build lithium metal batteries because of their low Coulombic efficiency, rapid capacity decay, electrolyte use, and safety concerns. The lithium dendrites also decline the available lithium for electrochemical reaction, called the formation of 'dead lithium', leading to capacity loss. What's more, dendrite growth brings mechanical stress to the lithium batteries which causes the degradation of cycle life. However, GPEs are awarded as a potential solution to remit the risk of dendrite due to their physical barrier, and mechanical conformity, and they can also help lithium deposit uniformly.

2.4. Lithium ion batteries (LIBs)

In the area of energy storage, LIBs have the broadest range of use. The significant mechanisms of LIBs are the intercalation and de-intercalation of lithium ions and lithium ions' migration through the electrolyte. Although it has already been applied in society, multiple issues still need to be solved, such as the extreme temperature performance and the high-voltage performance. GPEs can make contributions to solving those questions by improving their stability.

2.5. Lithium oxygen batteries (LOBs)

Lithium oxygen batteries use air or oxygen as their cathodes and metallic lithium as their anodes. They have a high specific energy density ($\sim 3500 \text{ Wh kg}^{-1}$) [4]. They usually use porous materials to make Li^+ and O_2 contact. During the discharge process, O_2 produces lithium superoxide by receiving transferred electrons and reacting with solute lithium. There are two different mechanisms of LOBs separated by a reaction zone, involving the solution-mediated mechanism and the surface-mediated mechanism.

3. Gel polymer in LBs

3.1. PAN-based GPEs

PAN-based GPEs (polyacrylonitrile gel polymer electrolytes) are one of the widest-applied gel polymers in our society. The interaction between PAN polymer chains and lithium salts is comparatively weak because they lack oxygen atoms and are thus unable to coordinate with them. However, the PAN matrix has CN groups that are quite polar. Lithium batteries' cycling performance is substantially impacted by the interface impedance's large rise and the pair's poor compatibility when lithium is employed as the battery electrode. In other words, PAN-based gel polymer electrolyte has a lot of issues with actual application, and it has to be changed to be used effectively with lithium batteries. Recently, Dong et al. discovered a special use of PAN-based GPEs. By using PAN-based GPEs as a separator, the performance of lithium batteries has been significantly improved by about 20%. This is because the flexibility of PAN can release internal stress, increase electrode contact, and thus improve the recyclability of the system [5]. Figure 3 shows the charging and discharging curves of lithium batteries using PP and PAN as separators, respectively. It can be found that compared to traditional PP polymer materials, using PAN as the battery separator improves the reversible capacity of the battery. In addition, PAN-based GPEs, as a separator, also exhibits good processability and electrochemical stability, which is outstanding in terms of LBs' safety.

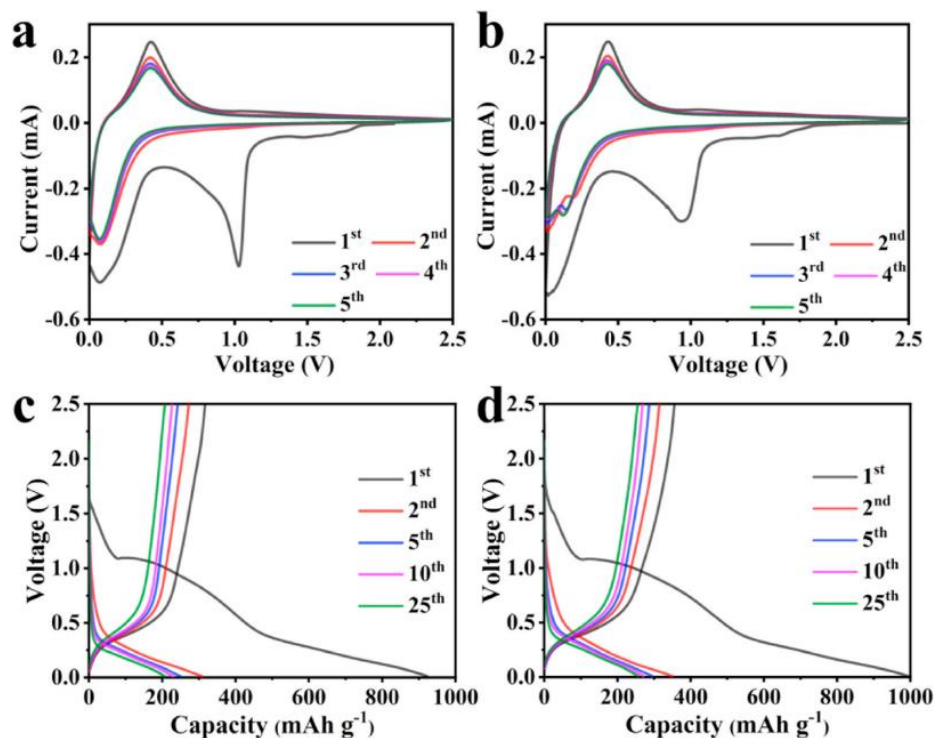


Figure 3. The charge-discharge curves of (a) & (c) PP separator, and (b) & (d) PAN separator [5]

3.2. PEO-based GPEs

PEO-based GPEs (polyethylene oxide gel polymer electrolyte) have shown great potential as an electrolyte for LIBs. One of the first materials employed as a polymer electrolyte matrix was PEO, which primarily took advantage of the stability of the electrode materials and the coordination between the PEO matrix and alkali metals. The oxygen atoms in the ethylene oxide (EO) groups that make up the PEO chain segment have lone pair electrons that can coordinate with Li^+ in a 2s empty orbit. Li^+ may continually interact with the oxygen atoms on the PEO chain segment through a process of "complexation, de-complexation, and re-complexation" during the conductive process, producing the effect of fast Li^+ migration. The migration of Li^+ often takes place in the amorphous area of PEO, which has poor mechanical and ion conductivity capabilities. At present, the main methods used to improve its electrochemical performance include copolymerization, modification, blending, and composite. Li et al. recently discovered a novel hybrid GPE that introduces regenerated cellulose (RC) into PEO. Because cellulose forms a 3D porous cross-linked network structure in the electrolyte, its mechanical strength is significantly improved, and the ion conductivity is also improved with the addition of RC. In addition, the GPE also exhibits a high Li^+ migration rate. This is because the polar hydroxyl groups of cellulose can fix PF6 groups through hydrogen bonding interactions, thereby providing lithium-ion transport [6]. In addition, PEO-based GPE also demonstrates the potential to address the issue of electrolyte flammability. Wang et al. designed and prepared a new flame retardant GPE through one-step in-situ polymerization of ethylene phosphonate diethyl ester (DEVP) and polyethylene glycol diacrylate (PEGDA). This GPE not only exhibits high heat resistance and fire resistance but also exhibits good ionic conductivity [7].

3.3. PMMA-based GPEs

PMMA has emerged as one of the most dependable polymer matrices employed in the production of polymer electrolytes due to its exceptional thermal and dimensional stability, as well as its excellent optical properties and relatively low glass transition temperature. PMMA has a strong polar carbonyl group that can interact with the plasticizer's oxygen atom to enhance the gel polymer electrolyte's ability to absorb liquid and its conductivity. It is not possible to employ this sort of gel polymer electrolyte alone due to its weak mechanical qualities. To create polymer electrolytes with acceptable

conductivity and mechanical characteristics, it is typically necessary to copolymerize, mix, or cross-link with other polymer matrices. What's more, PMMA exhibits strong compatibility with lithium ions and a strong attraction to liquid electrolytes, thanks to the ester groups it contains. PMMA can be used as the activator of P(AN-VAc) to develop a new polymer matrix, which improves its compatibility with high-voltage electrode material and cyclic stability [8].

3.4. PVDF-based GPEs

PVDF has garnered the attention of numerous scientists because of its elevated dielectric constant, favorable mechanical characteristics, and robust electrochemical range. In contrast to the usual short-circuit problem seen in PEO-based electrolytes, PVDF-based solid polymer electrolytes (SPEs) display a tendency to remain open-circuited under high current density. Consequently, this characteristic helps prevent safety concerns stemming from over-currents [9]. Recently, Shi et al. found that a decrease in the thickness of the polymer electrolyte can increase the batteries' electrochemical performance. In this research, researchers prepared polymer electrolytes with thicknesses of about 20 μ m, 80 μ m, 140 μ m and 200 μ m. Among them, the 20 μ m group shows significant superiority in both battery rate property and cyclic stability [10].

4. Summary

GPEs have a promising future due to their unique flexibility, processability, and elasticity which are necessary to develop wearable and portable devices. Moreover, many functional types of GPEs have been researched by labs, such as GPEs with high thermal stability, thermally responsive ability, or self-healing ability. Although those functional GPEs have challenges in enhancing their electrochemical properties and realizing large-scale applications, there are still many further applications of them.

There are still many urgent issues of GPEs that need to be solved. Significantly, at ambient temperatures, most of the single-ion conducting GPEs have low conductivity and inferior interfacial properties. But the most important one is to handle the safety problem. In our expectation, GPEs will be mainly used in portable devices, and biomedical devices, which are highly associated with users' safety. Predictably, GPEs will gradually replace liquid electrolytes as further research steadily prompts their electrochemical properties.

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