

Electrolyte composition for lithium-ion battery electrodes: progress and perspectives

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Abstract. Nowadays, finding more effective electrolytes is a key point in LIBs development. Researchers have considered the sulfone solvent as a potential electrolyte, but there are still some problems with the sulfone solvent that need to be addressed. Thus, this article emphasizes the effects of electrolytes on LIBs and focuses on the sulfone solvent effects. The author summarizes recent researchers' studies on sulfone solvent, analyzing the advantages and disadvantages of it. The sulfone solvent has better oxidation stability, high flash point, and a high dielectric constant. However, its high viscosity, melting point, and incompatibility with graphite anode hinder its application. The author studies on relevant research and finds several possible solutions to these problems. It is shown that modifying molecules is a good way to enhance sulfone performances, so the author suggests that future researchers can study other kinds of solvents and use their effective structures as references to modify sulfone molecules, which can blend different advantages to create more effective electrolytes.

1. Introduction

With the growing clean-energy vehicle market, the demand for green and renewable energy is rising, highlighting the promising future of lithium-ion batteries (LIBs). Since Sony successfully commercialized these batteries in 1991, they have been increasingly used in various applications, including electric vehicles and portable electronics [1]. The global market for lithium-ion batteries (LIBs) is projected to expand from approximately \$44 billion in 2021 to about \$193 billion by 2028, reflecting a substantial growth rate [2].

These batteries, typically comprising a metal oxide anode, a graphite cathode, a membrane, and an external circuit, operate through the migration and intercalation/deintercalation of lithium ions. However, under high temperatures, LIBs face challenges such as electrolyte decomposition and adverse reactions between the electrolyte and electrodes, which impair ion migration and reduce battery efficiency. Nowadays, Researchers have focused on new kinds of electrolytes, such as sulfone, ester, fluorinated, and so on, aiming to find a proper electrolyte to improve LIBs performance.

This review delves into how electrolytes affect LIB performance, summarizes recent research on various electrolyte compositions, and compares their respective advantages and disadvantages. This article aims to offer innovative ideas for selecting and designing more effective electrolytes in the future.

2. Effects of electrolytes on lithium-ion batteries (LIBs)

Understanding the properties of electrolytes requires knowledge of their components. Electrolytes in LIBs typically consist of carbonate solvents and conductive salts. The most common solvents are ethylene carbonate (EC) and dimethyl carbonate (DMC), while the widely used salt is LiPF₆.

During the initial charge cycle, carbonate solvents are reduced, forming a protective layer on both the anode and cathode surfaces. The layer on the anode is known as the solid-electrolyte interphase (SEI), and on the cathode, it is the chemical-electrochemical interface (CEI). Collectively referred to as the electrode-electrolyte interphase (EEI), these layers facilitate Li-ion passage while preventing direct electrode-electrolyte contact. This passivation reduces side reactions and extends battery life. However, extreme temperatures can compromise their effectiveness.

2.1. High-temperature conditions

Carbonates like EC and DMC have low thermal stability and decompose at high temperatures, producing CO₂ and other gases [3]. LiPF₆ also decomposes, forming LiF and HF [4]. LiF consumption reduces LIB capacity, while HF, being highly corrosive, and damages electrodes and crystal structures [5], diminishing battery performance.

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2.2. Low-temperature conditions

At low temperatures, reduced molecular motion increases intermolecular forces, so the viscosity of electrolytes increases as a result. Due to higher viscosity, it is difficult for ions to migrate between electrodes, so it lowers Li-ion conductivity and affects battery performance [6].

Low temperatures can promote the growth of lithium dendrites on the anode. Under low temperatures, Li-ion is more likely to be reduced on anode, forming lithium dendrites. These dendrites cause irreversible Li-ion loss and necessitate the continuous formation of new EEI layers, increasing electrode thickness and impedance [7]. Besides, the capacity of the battery decreases, and the growing dendrites may pierce the membrane, which destroys the battery.

3. Various electrolytes and their properties

3.1. introduction of various electrolytes

An appropriate electrolyte should have such characteristics: a wide electrochemical window, a high flash point, non-flammability, low viscosity, high dielectric constant, and so on. The advantages and disadvantages of different organic solvents can be seen in figure 1 [8]. Ester has excellent lithium salt solubility and high ionic conductivity, but it is limited in the electrochemical window. Sulfone has high oxidation stability, high dielectric constant and high flash point, but it also has a high viscosity, high melting point, and poor compatibility with graphite electrodes. The fluorinated solvent has high oxidation stability, non-flammable properties, and excellent wettability with a separator, but it also has high viscosity. Besides, the advantages and disadvantages of nitrile, ether, and ionic liquid are also shown in figure 1. This article focuses on one promising solvents: the sulfone solvents. Due to its high oxidation stability, high dielectric constant and high flash point, the sulfone solvent has a promising prospect. But there are also some disadvantages that need to be overcome.

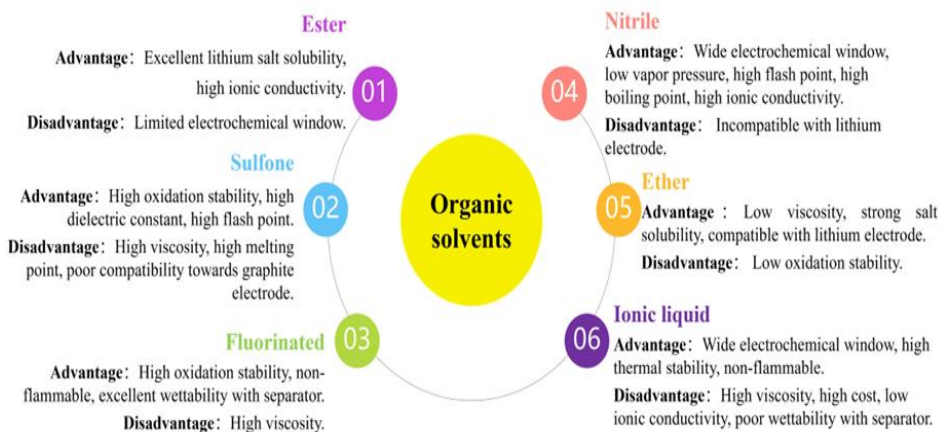


Fig 1. The advantages and disadvantages of different organic solvents [8].

3.2. analysis of sulfone solvent

The sulfur atom of the sulfonyl connects with two carbon atoms, forming the sulfone.

Sulfone solvents, taking Tetramethylene Sulfone (SL) as an example, have better oxidation stability ($>6.35\text{V}$), high flash point (166°C), and high dielectric constant ($\epsilon=43.4, 303.2\text{K}$) [9], offering them a promising future in LIBs researching field.

According to frontier molecular orbital theory, the ability of molecules/ions to gain/loss electrons determines the stability of the electrolyte [8], that is, the lower the HOMO (highest occupied molecular orbital), the weaker the tendency to lose electronic, and the better the oxidation stability. Correspondingly, the higher the LOMO (lowest unoccupied molecular orbital), the weaker the tendency to gain electrons and the better the reduction stability. Using methods called MP2/PCM, Shao, etc. examined and calculated the oxidation potential of sulfone solvents, finding it to be around 5.5V [10]. Xue etc. inferred it is the strong electron-withdrawing sulfonyl that reduces the HOMO energy level, which increases the oxidation stability of sulfones and gets a wider electrochemical window [11].

In the burning experiment, both with 1M LiPF_6 , the SL-EMC group, compared to the EC-EMC group, performed a weaker flame [12], indicating that the SL has a low flammability, which can protect the LIB's safety during usage.

However, sulfones have a pretty high viscosity, and a high melting point, and are not compatible with graphite anode well. These problems limit their applications.

To solve the incompatibility. Cui etc. used SL as a model to study its properties. They found, that in the same environment and with the same dosage, LiBOB/SL/DMC/GBL, compared to LiBOB/GBL/DMC, had a higher oxidation potential [13]. They speculated that SL formed a protective film on the cathode during the initial charge circle, so the electrolyte stability was enhanced [14].

In fact, whether sulfones can form a film depends on lithium concentration. When LiPF_6 concentration is low ($\sim 1\text{mol/L}$), sulfone solvents such as TMS and EMS, cannot form a SEI. But in higher concentrations ($>4\text{mol}$, 4M), they can form a dense and stable SEI [15].

The viscosity relates to temperature and the type and concentration of substances. Focusing on SL viscosity, there are two methods to solve the problems. One is using a diluent or a cosolvent, and another is modifying sulfone molecular. Wang etc. [16] used stable diluent-HFE, combined with $\text{LiNO}_3/\text{LiTFSI-SL}$ to run multiple cycles, getting a high coulombic efficiency (CE). On Li anode, NO_3^- involved in the formation of $\text{Li}_n\text{O}_y\text{-LiF}$ SEI, inhibited lithium dendrite growth and made Li condensed finer. On the NMC811 cathode, NO_3^- involved in the formation of CEI, inhibited the decomposition of electrolytes under high temperature. Thus, after adding diluent to sulfone solvents, the low conductivity can be improved, ensuring the battery capacity and prolonging the battery life span. Plus, He etc. [17] added cosolvent to the sulfone solvent system, and successfully reduced the viscosity as well as formed a dense SEI on Li anode. The LIB remained at a high capacity and CE after 500 charge cycles, which shows an outstanding performance. Besides, based on high concentrations of lithium, fluorinating β -position can decrease sulfone solvents viscosity and make them present good reduction stability [18].

The melting point can be adjusted through molecule modification. Shao etc. [19] added side chains such as nitrile and carbonic ester to α position of sulfone molecules, which efficiently reduced the melting point and maintained oxidation stability. Additionally, Angell, etc. [20] found that breaking molecular symmetry can also lower melting points. They synthesized a kind of ether sulfone-MEMS, which represented a lower melting point (2°C) and good oxidation stability in the lab.

However, molecule modification has not been developed systematically, and research on this method is insufficient. Besides, because this technique is on molecule aspect, the procedure is complicated the accuracy needs to be improved, and the cost is pretty high. So future researchers can focus on this technique and make it more suitable for mass production. Using the enhanced technique, researchers can better improve electrolyte properties, which may highly promote LIBs applications.

4. Conclusion

This article summarizes the effects of electrolytes on LIBs and states the main disadvantages of electrolytes. Moreover, it also selectively analyses a kind of new solvent-sulfone solvent and points out its advantages, and disadvantages, as well as measures for improvement.

Nowadays, problems such as the high viscosity, the high melting point, and the incompatibility with graphite anode, prevent sulfone solvents from further applications. There are two main kinds of methods to improve this. One is the indirect method, which means using diluent, cosolvent, or modifying lithium concentration, cooperating with sulfone solvents, to improve the whole performance of the LIBs system. Another is a direct method, which means directly modifying sulfone molecules by adding side chains or fluorinating the β -position of sulfones to enhance their properties, therefore getting good-performance sulfone solvents.

The author suggests that future researchers can study other kinds of solvents, such as nitriles, fluorinated, ether, and so on, analyze their advantages and effects, and use their structures as a reference to modify sulfone molecules. Blending their advantages together may help researchers to develop excellent-performance solvents for future applications.

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