Electrolyte Challenges in Achieving Ultimate Energy Density in Lithium-Ion Batteries

Jingqin Zhang *

Pennon Education Group, Qingdao, 266104, China

* Corresponding Author Email: jdzhangzhiliang@tzc.edu.cn

Abstract. Lithium-ion batteries (LIBs) represent a pivotal technology in the advancement of electric vehicles, driving the transition from traditional fuel-powered cars to more sustainable alternatives. The continuous demand for higher energy density in LIBs is essential for improving vehicle range, performance, and overall competitiveness in the automotive market. Central to this goal is the role of the electrolyte, which functions as a charge carrier within the battery's internal circuit. The electrolyte's properties directly impact the battery's ability to achieve higher energy densities. However, several challenges arise in optimizing electrolytes, including issues related to thermal stability, ionic conductivity, and compatibility with high-capacity electrodes. This paper delves into these critical challenges, analyzing the factors that currently hinder the achievement of ultimate energy density in LIBs. By exploring potential advancements in electrolyte design and formulation, this study provides insights into future strategies for enhancing the performance and energy density of LIBs, thereby supporting the broader adoption of electric vehicles.

Keywords: Lithium-ion battery; electrolyte; energy density.

1. Introduction

A typical LIB is mainly composed of the electrolyte, the separator and electrodes, as shown in Fig. 1 [1]. The electrolyte is a substance that conducts electric current as a result of a dissociation into cations and anions, which serves as a carrier of the ion transport in the battery between the two electrodes. The separator is a polymeric membrane placed between the electrodes, serving as a physical blockade. Electrodes are two terminals that conduct current into and out of it. The positive electrode is the terminal from which electrons are absorbed, and electrochemical reduction takes place. The negative electrode is the terminal that releases electrons to the external circuit, and electrochemical oxidation takes place. The positive electrode is also called a cathode, and the negative electrode is called an anode although their polarity will reverse during the charging-discharging process.

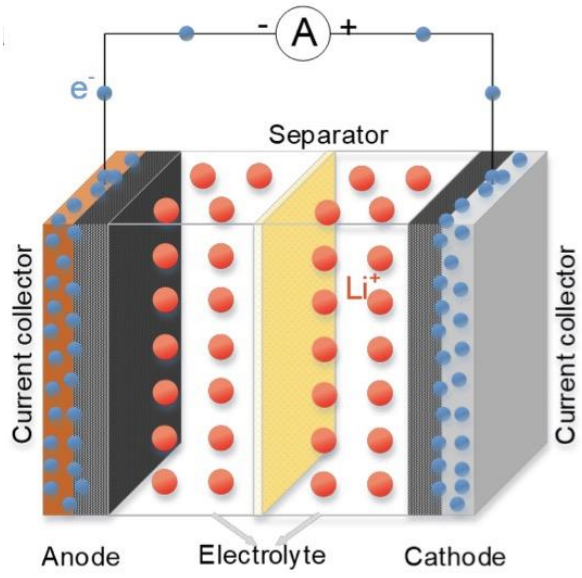


Fig. 1 The structure of a typical LIB [1].

Lithium metal is the lightest metal and offers a high specific capacity and a low electrode potential. From this perspective, it is a promising negative electrode material for batteries required in electric vehicles. However, lithium metal batteries suffer from safety concerns related to the formation of lithium dendrites. To avoid safety issues, the LIBs using two different intercalation hosts were suggested by Armand in 1980 [2]. After that, LIBs came into the public's view and were gradually used in various applications such as electric devices, electric vehicles and energy storage stations.

Energy density is a volumetric measurement of the battery capacity in vehicles, which is energy per unit volume, and its unit is often MJ/m^3. Improving the energy density of LIBs has a significant influence on everyday life. It dramatically extends the usage time of portable electronic devices so that they can run for longer periods without charging, providing convenience for consumers. Enhancing the energy density of LIBs also helps to increase the driving range of electric vehicles, reducing their dependence on charging stations, which will promote the popularization of electric vehicles. In addition, LIBs with high energy density impact a lot on energy storage systems which are key to addressing the intermittent power supply.

2. Fundamentals of Electrolytes used in LIBs

2.1. Key Role of Electrolytes

An electrolyte is a material that conducts electricity when it is dissolved in an aqueous solution or a molten state. In a circuit, the electrolyte functions as a carrier for the movement of ions. It conducts current due to dissociation into cations and anions, which move towards and discharge at the positive electrode and negative electrode, respectively.

The concentration of ions in an electrolyte determines its conductivity. Based on the ability of conductivity, electrolytes are divided into weak and strong electrolytes. When strong electrolytes dissolve, they almost completely dissociate into ions. Among the strong electrolytes are strong acids, bases, active metal oxides and most salts. For example, sulfuric acid, sodium hydroxide and copper sulfate are strong electrolytes. Weak electrolytes are substances that partially dissociate into ions. Typical weak electrolytes are weak acids, bases and a few salts such as acetic acid, ammonia monohydrate, mercuric chloride, etc.

2.2. Main Types

2.2.1 Non-aqueous electrolytes

Non-aqueous electrolytes in LIBs are electrolytes that consist of a lithium salt dissolved in an organic solvent or solvent mixture. Lithium hexafluorophosphate ($LiPF_6$) is the most common salt used in LIBs. The widely used organic carbonates that $LiPF_6$ dissolved in are mixtures of ethylene carbonate (EC) with dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), diethyl carbonate (DEC), and propylene carbonate (PC) [3]. Table 1 lists the formula weight, melting point and boiling point of the organic carbonates. Non-aqueous electrolytes, with great electrochemical stability, have been widely used in LIBs in many applications, including electric devices and power storage stations. Nevertheless, they suffer from flammable problems in large-scale LIBs.

Table 1. Properties of several common organic solvents applied in LIBs [4].

Solvent	FW	T_m /°C	T_b /°C
EC	88	36.4	248
DMC	90	4.6	91
EMC	104	-53.0	110
DEC	118	-74.3	126
PC	102	-48.8	242

2.2.2 Aqueous solution electrolytes

Aqueous solution electrolytes contain water as the solvent. Non-flammable and higher ionic conductivity are the advantages of using aqueous solution electrolytes over non-aqueous electrolytes [5]. The construction of an aqueous rechargeable lithium-ion battery (ARLB) by the Dahn group in 1994 involved the use of lithium nitrate ($LiNO_3$), the first aqueous electrolyte [6]. However, it has attracted little attention because this electrolyte has the problem of low cyclability as a result of the limited electrochemical stability window of water. After that, a number of ARLB systems with appropriate electrodes and various aqueous electrolytes, such as lithium sulfate (Li_2SO_4) and some lithium transition metal oxides, have been reported to have improved cycle abilities.

2.2.3 Ionic liquid electrolytes

Ionic liquids (ILs) are compounds that only consist of ions with melting points below 100 ˚C [7]. In LIBs, IL electrolytes are composed of lithium salt and ILs. Ethylammonium nitrate ($C_2H_8N_2O_3$), the combination of equimolar amounts of ethylamine and nitric acid, is one of the first IL electrolytes reported by Paul Walden in 1914 [8]. Since then, ILs received wide attention. The chemical properties of ILs vary dramatically with their constituent cations and anions. With further experiments and studies, the chemical properties of ILs have been deeply discovered, and they have many categories. There are various types of ILs, including room-temperature ionic liquids (RTILs), task-specific ionic liquids (TSILs), polyionic liquids (PILs) and supported ionic liquid membranes (SILMs) [9]. RTILs are the most popular ones used in LIBs due to their nonvolatile and non-flammable features that contribute to green design potential. In an RTIL electrolyte, quaternary ammonium salts are used as cations. Apart from halides (F, Cl, Br, etc.), common negative ions are tetrafluoroborate (BF_4^-), hexafluorophosphate (PF_6^-) and so on [10]. Fig. 2 lists some common cations and anions.

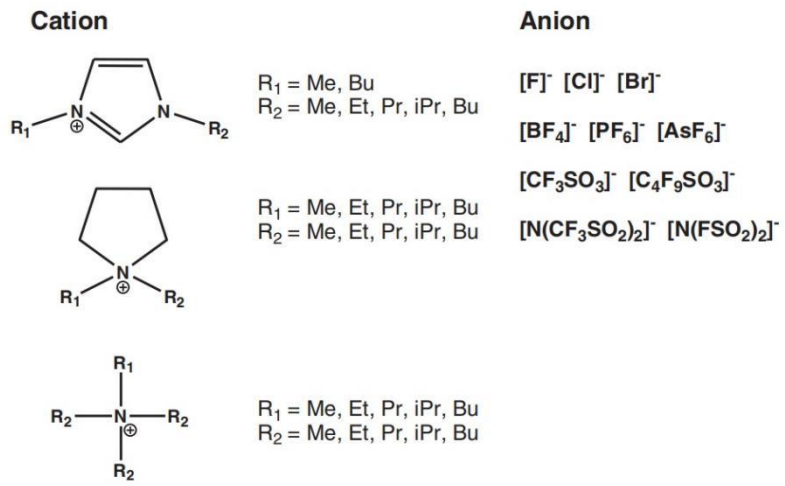


Fig. 2 Several typical cations and anions of RTILs [10].

Low viscosity and relatively high electrical conductivity can be found in ILs that contain imidazolium. However, they have the problem of cathodic instability. ILs containing quaternary ammonium possess greater electrochemical stability than ILs containing imidazolium, so they can withstand lithium deposition and dissolution without self-reduction. They can be used for high-voltage LIBs, but the large size of cations, high viscosity and low ionic conductivity limit their applications [3].

2.2.4 Polymer electrolytes

Polymer electrolyte (PE) is made up of dissolution salts within a polymer matrix that has a high molecular weight. PEs are divided into two types based on sources and origins, as shown in Fig. 3. Chitosan, rice starch and corn starch are a few examples of natural PEs that are frequently applied in research. According to the material physical state and composition, PEs are categorized as solid polymer electrolytes (SPEs), gel polymer electrolytes (GPEs) and a combination of the two.

GPE, also known as plasticized PEs, has a plasticized or gelled polymer matrix featuring the addition of plasticizers. GPE combines the diffusive property of liquids as well as the cohesive property of solids. GPE offers high ionic conductivity and low reactivity, resulting in good electrochemical stability and operating safety. However, they suffer from low mechanical strength, making them incapable of withstanding the stress between electrodes, which limits their application. The addition of nanomaterials optimizes this problem.

SPEs are often based on polymers like polyethylene oxide (PEO) that can establish semi-crystalline structures. SPEs own many attractive characteristics, including solvent-free, leak-proof, low volatility, high thermal stability and electrochemical stability. Nevertheless, SPEs indeed have some limitations which affect their performance in electrochemical devices. Two major drawbacks are their low conductivity at room temperature and high interfacial resistance [11].



Fig. 3 Different types of PEs [11].

One of the most crucial subjects in PEs is ionic conductivity, which has a direct bearing on the degree of polymer crystallinity and viscosity [12]. With higher levels of crystallinity, ionic conductivity is reduced due to the poor mobility of the ions in crystalline regions. A PE with reduced viscosity has higher ionic conductivity, resulting from a higher proportion of amorphous (non-crystalline) regions. Ions can move more freely in amorphous regions due to the lack of an ordered lattice structure, which acts as a barrier in crystalline areas. Several attempts have been reported, including the use of inorganic fillers, plasticizers and nanomaterials, as well as polymer blending and the use of comb-branches copolymers [11].

2.2.5 Hybrid electrolytes

ILs and PEs both exhibit a number of benefits but they still possess certain drawbacks. In order to overcome the disadvantages of them, hybrid electrolytes are artificially synthesized. There are two primary categories: one based on PEs and the other on ILs. ZrO_2, TiO_2 and SiO_2 are typical nanoparticle types that have been utilized to create IL-nanoparticle hybrid electrolytes. It has been reported that IL-ZrO_2 hybrid electrolytes exhibit good interfacial stability and can modify their mechanical properties [13]. A majority of PE hybrid electrolytes contain both organic and inorganic components. Common inorganic materials are nanoparticles and polymers are used as the organic composition [3].

3. Key Factors Contributing to Ultimate Energy Density

Aiming for a higher energy density of LIBs, electrode-specific capacity and cell voltage are key factors. The former factor does not directly depend on electrolytes due to the similar performance of the specific capacity of most electrode materials in both aqueous and non-aqueous electrolytes. Therefore, in order to improve energy density, searching for materials contributing to high battery voltage becomes a main topic [14]. When designing high-voltage electrolytes, electrolyte quantity and thermal stability are important factors.

3.1. Liquid Electrolyte Quantity

The liquid electrolyte quantity is an important factor worth considering because it affects the wetting rate of electrodes and separators and reduces the battery capacity. Hence, the cycle life of the battery is reduced [15].

In order to enhance battery energy density, electrolyte quantity needs to be as precise as possible. Fig. 4 presents the relationship between electrolyte volume and energy density. There exists a unique optimal number of electrolytes filling into the battery. Adequate electrolytes are required to wet the electrode surface to keep good contact between the electrolyte and the electrode, ensuring efficient ion transport. Therefore, the electrolyte deficiency causes poor wetting and low ionic conductivity and eventually leads to lower energy density of the battery. In addition, energy density increases with electrolyte amount, and the charging rate of the battery is also increased. However, after reaching a peak value, increasing electrolyte quantity causes a drop in energy density. The reason is that excess electrolyte does not contribute to the battery capacity but adds weight and hence limits the energy density and increases the manufacturing costs needlessly [16].

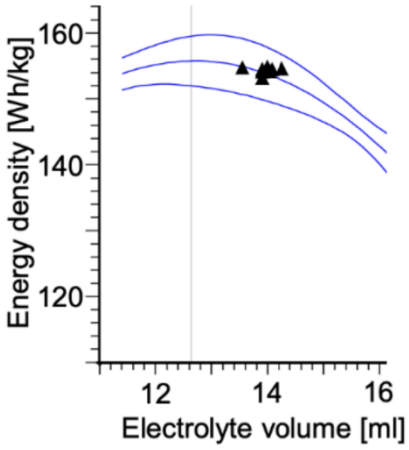


Fig. 4 A plot of energy density against electrolyte volume. The optimal electrolyte volume regarding energy density is marked by a grey line [16].

Additionally, the concentration of electrolytes at optimal quantity is important. Generally speaking, higher concentration increases electrolyte ion conductivity since there are a larger number of charge carriers. From this perspective, it makes battery energy density increase. However, increasing concentration also leads to the increase of viscosity of electrolytes, especially for some organic solutions. In this case, the movement of ions is slowed down, and charge transport is retarded. Thus, the internal resistance of the battery increases, which in turn reduces battery energy density. As shown in Fig. 5, a high electrolyte concentration leads to poorer performance compared to a lower concentration. The normalized charge and discharge curves do not overlap at different concentrations, and the increased viscosity of the electrolyte with its concentration is the cause [17].

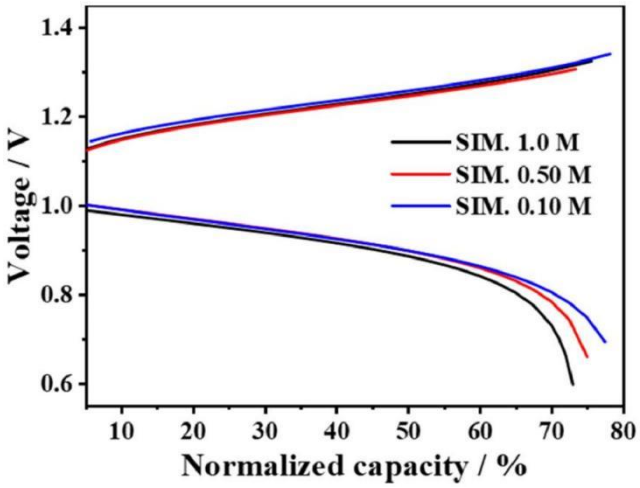


Fig. 5 Charge and discharge curves vary depending on the initial concentration at 60 mA/cm^2 [17].

3.2. Electrolyte Thermal Stability

Electrolytes with better thermal stability are less likely to undergo decomposition reactions and side reactions with active electrode materials or cause thermal runaway, which leads to hazards. From this perspective, enhancing the stability of electrolytes currently used or looking for novel electrolytes with higher thermal stability is important for cell energy density since electrode materials with greater energy density can be applied in LIBs with fewer safety risks. In addition, the thermal decomposition of electrolytes leads to some by-products with lower ionic conductivity. Hence, the energy density of batteries will decrease.

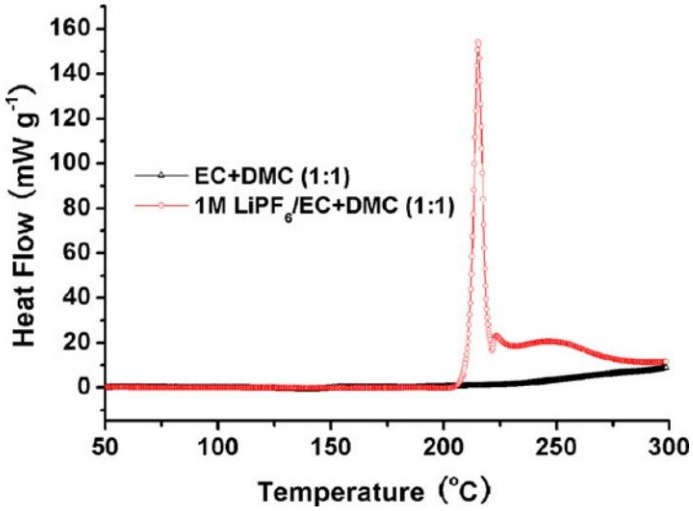


Fig. 6 C80 heat flow curves for 1 M $LiPF_6$/EC+DMC electrolyte at a heating rate of 0.2 ˚C/min. The sample mass is 1.0 g [18].

Fig. 6 reveals the heat flow of the $LiPF_6$/EC+DMC electrolyte. The electrolyte is initially set at approximately 202 ˚C. After that, the emergence of an exothermic peak implies that some decomposition reactions have taken place at 215 ˚C. A lower heat flow occurs in a wide temperature range with temperatures above 225 ˚C. The former strong heat release due to decomposition reactions is the dominant factor influencing electrolyte thermal stability [18]. The exothermic decomposition of $LiPF_6$ can contribute to thermal runaway in the battery, especially if the heat generated cannot be dissipated effectively. Under fast charging and high voltage conditions, a greater operating current leads to a greater heat generation rate [19]. This can lead to a rapid temperature increase, which can accelerate the decomposition reactions and compromise the battery's safety and energy density.

4. Challenges with Ultimate Energy Density

4.1. Processing Challenges

Aiming for a higher energy density, the requirements for a lower percentage of inactive materials in a battery lead to the tendency of thinner separators and thicker electrodes. The large-format batteries suffer from mainly processing challenges [16]. The process of filling liquid electrolytes is a crucial part of the battery's performance. When filling a LIB, the quantity of electrolytes should be minimized to reach the optimal wetting state of cell components. Due to the sensitivity of battery energy density to dosing accuracy, improving dosing accuracy in the production process is the main challenge.

4.2. Safety Problems

Electrolytes for commercial LIBs are mostly organic liquid electrolytes composed of lithium salts and organic solvents, which are flammable. The internal temperature of the battery will increase

during the charging-discharging process. The excess accumulation of heat may lead to a hazard. Electrolyte thermal stability is directly correlated to battery safety. With the pursuit of safer batteries, the thermal stability of electrolyte materials should be improved [20]. Improving thermal stability generally involves the application of more stable, but sometimes less conductive, materials. This can lead to reduced ionic conductivity, which affects the battery's overall performance, reducing the energy density.

Different kinds of practical abuse usually cause thermal runaway. During the process of intense energy release, the thermal runaway of LIBs usually takes place due to smoke, fire, or explosion. The propagation of thermal runaway from an initiating cell to its neighbors can result in damage to the whole system. Therefore, it is of great significance to mitigate thermal runaway. Several methods are reported including designing cells with improved cooling systems and incorporating current interrupt devices. However, the challenges come from performance trade-offs and manufacturing costs. The addition of safety enhancements may pose a negative impact on the performance of the batteries. Additionally, these enhancements also lead to an increase in cost, which may limit the application of batteries in price-sensitive markets [21].

5. Conclusion

In summary, key factors influencing the energy density of LIBs come down to electrolyte quantity and thermal stability. Electrolyte quantity should be accurate to an optimal volume. Either excess or insufficient electrolytes leads to decreased energy density. Also, the concentration of the electrolyte at this optimal volume is considerable since it is related to ionic conductivity and viscosity. Another key factor worth consideration is electrolyte thermal stability. Electrolytes with greater thermal stability can adapt to a wider operating voltage range and severe circumstances with less risk of thermal runaway. Challenges faced with the ultimate energy density of LIBs can be classified in terms of processing challenges and safety problems. Processing challenges are related to dosing electrolytes with high accuracy, while safety problems are mainly due to the thermal runaway of electrolytes. One of the most promising future electrolytes is solid-state electrolytes. Solid-state electrolytes are attractive due to their potential for higher energy density in terms of higher thermal stability. In this case, the application of higher-voltage electrodes, such as lithium metal anodes, is allowed, which can increase battery energy density. With ongoing research, the energy density of LIBs is expected to increase further in the future, bringing more possibilities for the development and promotion of electric vehicles.

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