Research on the Low-Temperature Stability of Anode and Electrolyte of Lithium-ion Battery

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Abstract. With the acceleration of technological progress, lithium-ion batteries (LIBs) have become one of the indispensable forms of energy in modern life and play a crucial role. However, its performance degradation in low-temperature environments remains a key factor restricting its further development. In particular, as the core components of LIBs, the stability of electrodes and electrolytes at low temperatures directly determines the overall performance of the battery. Specifically, the fluidity of the electrolyte is significantly reduced at low temperatures, while lithium-ions at the negative electrode are more easily precipitated, leading to the formation of lithium dendrites, which together affect the safety and life of the battery. This paper systematically analyses the latest advances in structural regulation and design of anode materials and electrolytes through an in-depth study of the low-temperature stability of LIBs. Modification methods for these key materials are described in detail, including strategies for optimising electrolyte additives and their positive effects on enhancing battery performance at low temperatures. In addition, the article discusses potential directions for future research in this area, aiming to provide guidance and reference for improving the performance of LIBs for applications in low-temperature environments.

1 Introduction

Against the backdrop of sustained global economic growth and increasing tension between energy supply and demand, environmental pollution issues need to be addressed urgently, thus giving rise to a rising demand for new energy technologies. In particular, with the rapid advancement of new energy technologies, LIBs has gained wide application in key areas such as automobiles and energy storage, owing to their high energy density, long lifespan, and environmentally friendly characteristics. Low-temperature LIBs can still provide power support in extreme cold environments and can be used in special areas such as polar regions and high altitudes to meet the power needs of a variety of harsh environments. However, LIBs face the challenge of reduced chemical stability at low temperatures, an issue that limits their potential application in cold environments. The stability of electrodes and electrolytes, which are the core components of LIBs, at low temperatures directly affects the overall performance of the battery (Figure 1 and Table 1). Therefore, improving the stability of electrodes and electrolytes in low-temperature environments has become the focus of the current research field of low-temperature performance. The article discusses the potential directions for future research in this field, with the aim of providing guidance and reference for improving the performance of LIBs for applications in cryogenic environments.

Table 1. Effect of temperature on the capacity of LIBs

Margin	25	55	0	-20	-40
Capacity (Ah)	11.818	11.954	9.632	7.238	4.746
Capacity Percentage (%)	100.00	101.16	81.43	61.24	40.16

Fig. 1. Effect of temperature on the state of LIBs [3]

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2 Low-temperature failure mechanism of LIBS

The optimal operating temperature range for LIBs is between 15°C and 35°C, with an acceptable range extending from -20°C to 60°C. At temperatures below -20 °C, the electrolyte's viscosity increases, slowing the rate of ion diffusion and consequently diminishing the rate of electrochemical reactions. This reduction in ion diffusion also decreases the electrical conductivity of the electrode material, leading to an increase in internal resistance due to hindered ion migration. As a result, the ionic conductivity decreases, reducing the battery's output power and efficiency. The primary limitation of the low-temperature performance of LIBs is the lithium plating reaction at the anode during the charging and discharging process. At low temperatures, substance transport slows, and the crystal lattice contracts, preventing the anode from incorporating sufficient lithium ions. Consequently, unincorporated lithium ions acquire electrons on the anode's surface, forming lithium metal monomers. Figure 2(a) shows the polarisation diagram of the anode at low temperatures [1], and Figure 2(b) shows the schematic diagram of lithium plating and lithium dendrite growth [2]

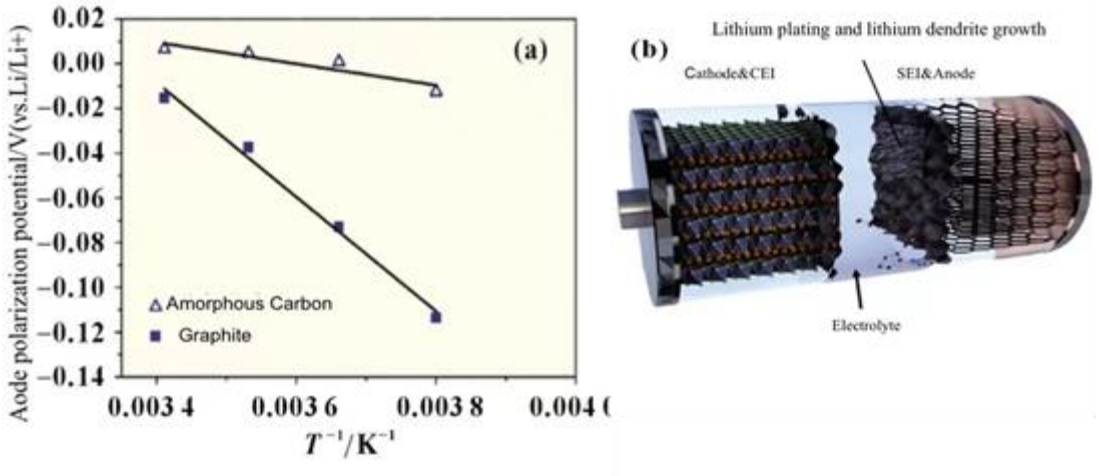

Fig. 2. (a) Polarisation diagram of the anode at low temperatures; (b) schematic diagram of lithium plating and lithium dendrite growth [1, 2]

Lithium metal is prone to dendrite formation due to its high activity and the high energy barrier for lithium ion diffusion at the SEI (solid electrolyte interface). The lithium battery anode undergoes unstoppable volume expansion during the charge/discharge process, resulting in the surface structure becoming loose and porous. With the increase in the number of charge-discharge cycles, the unstable lithium on the surface is gradually pulverised and detached, leading to the generation of a large number of dead lithium and the loss of electrons [3]. Studies have shown that regulating the liquid-phase mass transfer process can be achieved by operations such as changing the solvent molecules and concentration. In addition, screening for suitable lithium salts can help to stabilise the formation of SEI membranes, while the addition of specific additives can be targeted to improve the various processes of lithium deposition. All these methods can effectively promote the lithium ions to achieve uniform deposition on the lithium anode and inhibit the formation of lithium dendrites.

3 Low-temperature modification strategy for LIBs anode

3.1 Cycling performance of LIBs anodes

Li et al. discovered that optimizing the cathode and anode materials significantly enhances low-temperature charging performance. This improvement was achieved by reducing particle size and employing a carbon coating method. The morphology of lithium cobaltate and graphite was examined using scanning electron microscopy [4]. To address the need for low-temperature cycling, such as in-vehicle positioners used in cold regions, both the positive and negative materials of the battery need to be optimised to simultaneously improve low-temperature charge and discharge performance. Huang and colleagues demonstrated that the performance of LIBs at low temperatures is significantly influenced by the graphite anode. Particularly in cold conditions, the anode material impedes the complete solvation of lithium ions, resulting in heightened resistance to electrochemical transfer. This phenomenon adversely affects the battery's capacity and cycling performance [5].

3.2 Carbon-based and silicon-based composite electrode materials

In the realm of LIBs, traditional carbon and silicon electrodes undergo structural instability due to significant volume expansion during charging, altering their lattice structure. Addressing this issue, the

development of novel carbon and silicon-based electrode materials has emerged as a viable strategy to enhance battery performance at low temperatures. A key improvement approach involves augmenting the conductivity of electrode materials by combining active substances with conductive agents [1,2]. For carbon-based materials, adjusting the interlayer distance and doping with heteroatoms (such as nitrogen, sulfur, phosphorus) can refine their local electronic structure, thereby boosting conductivity. Despite silicon's potential as an anode material for LIBs, challenges related to its poor electrical conductivity and substantial volume changes during lithiation persist. However, research by Li and colleagues on various Si/Fe XSi_yNC/CNT composites as advanced anode materials has shown promise in preventing direct electrolyte-silicon contact during cycling and enhancing low-temperature lithium-ion transport performance [6]. Tan successfully synthesized artificially engineered graphite@nano-silicon@amorphous carbon materials using spray-drying technology. Incorporating a composite structure of nanosilicon with carbon and graphite significantly improves the cycling stability of silicon-based materials [7]. Moreover, the amorphous carbon layer minimizes direct silicon-electrolyte contact, thus mitigating the formation of a solid-electrolyte interphase (SEI) film. This composite design offers a novel approach to enhancing the performance of silicon-based electrode materials.

3.3 Nanostructured electrode materials

Due to structural deformation caused by volume expansion, the performance of conventional electrode materials gradually deteriorates during cycling. In particular, some materials (e.g., lithium-cobalt oxides) may undergo phase transformation at low temperatures. Nanostructured electrodes show high cost-effectiveness in practical applications due to their high stability in harsh environments and relatively low cost. These materials increase the active sites by providing a large specific surface area, which improves the efficiency of electrochemical reactions. Li's research on the carbon nanotubes and Sn-Ni composite as an anode material demonstrates that the superior electrical conductivity of carbon nanotubes, combined with the high-capacity density of Sn-Ni, endows the composite with commendable electrochemical performance at low temperatures [8]. By optimising the thickness, porosity, and other parameters of the electrodes, the nanostructured electrodes provide a fast transfer channel for lithium ions, effectively reducing the resistance to lithium-ion transport at low temperatures, thus improving the low-temperature performance of the battery [1].

4 Low temperature modification strategies for electrolytes

4.1 Cycling performance of LIB s anodes

4.1.1 Optimisation of electrolyte

The conventional electrolyte composition for LIBs, comprising organic solvents like ethylene carbonate, propylene carbonate, and dimethyl carbonate, exhibits increased viscosity and internal resistance at low temperatures, adversely affecting safety and performance. At reduced temperatures, electrolyte conductivity diminishes, and lithium metal tends to precipitate during charging, reacting with the electrolyte. This reaction leads to the thickening of the Solid Electrolyte Interface (SEI) film, further impairing low-temperature performance. Employing higher molecular weight amorphous polymers as solvents or incorporating cationic ligands such as 15-crown-5 ether, which offers superior cycling stability compared to 12-crown-4 ether, can mitigate the formation of lithium dendrites on the anode at low temperatures, thereby enhancing charging and discharging efficiency [9]. In addition, $LiBF_4$ has good thermal stability, which avoids the problem of electrolyte performance degradation at low temperatures. Adding a small amount of $LiBF_4$ can improve the battery discharge platform and capacity retention rate (retention rate increased from 80% to 85%) [10]. Hu et al. reviewed the study of film-forming additives and donated the use of vinyl sulfite (ES), sulfite (DES) and lithium difluoro-oxalate borate (LiODFB) and other substances can be used to improve the low-temperature performance of the material, and the application of these additives is expected to play an important role in the relevant fields [11].

4.1.2 Optimisation of organic solvents

Currently in LIBs commonly used organic solvent is EC, based on the strong dissociation of lithium ions, when the LIBs electrolyte contains a high concentration of EC has a high melting point, so there is a risk of crystalline solidification at low temperatures. Liu discovered that a high concentration of Ethyl Methyl Carbonate (EMC) and a low concentration of Ethylene Carbonate (EC) can significantly reduce the common melting point to -60 °C or lower. The inclusion of EMC aids in decreasing the electrolyte's viscosity, thereby enhancing its conductivity. Liu designed a series of electrolytes optimized for low-temperature operation and found that at -45 °C, utilizing an electrolyte composition of 1.2mol/L (80 % $LiPF_6$ + 10 % $LiBF_4$ + 10 % LiBOB)-EC/EA/EMC/DMC (10:20:35:35wt%) + 1.5 % VC (vinylidene carbonate) + 0.5% Dimethyl Sulfoxide (DMS) enables charging and discharging of lithium batteries. This formulation resulted in a battery capacity retention of 89% compared to its performance at room temperature (25°C) [12]. Liang introduced a novel formulation for low-temperature electrolytes in LIBs, optimizing the ratio of methyl acetate to vinyl carbonate and incorporating lithium difluoro(oxalato)borate as an inorganic film-forming agent. This composition, within a specific proportional range, facilitates the formation of a stable

Solid Electrolyte Interface (SEI) film. It has been demonstrated that a 9:1 ratio of methyl acetate to vinyl carbonate enables the battery to achieve a capacity retention rate exceeding 80% [13].

4.2 Novel polymer electrolytes

Polymer electrolytes serve a dual purpose as a replacement for both diaphragms and liquid electrolytes. The new polymer electrolytes exhibit high chemical stability and low risk of ignition at low temperatures and are environmentally friendly as they contain fewer toxic substances than traditional electrolytes. The flexibility and deformability of these electrolytes can help improve the mechanical strength and deformation resistance of batteries, inhibit the growth of lithium dendrites, and improve the life of lithium-ion batteries. Despite the current high cost of preparation, with technological advances and cost reductions, new polymer electrolytes are expected to become the first choice in the battery industry. Ge and others studied developed low-temperature additive containing fluorinated linear esters through patented technology, and by dropping into the diaphragm and thermally initiating the polymerisation, the solid electrolyte obtained has high conductivity at low temperatures [14]. Barbosa used a high dielectric constant polymer P (VDF-TrFE-CFE) and 40 wt% of ionic liquids (IL) with the same bis(trifluoromethylsulfonyl)imide [TFSI] anion and different cations to prepare a new solid polymer electrolyte [15]. It was found that the combination of high dielectric P (VDF-TrFE-CFE) with ILs for the development of solid polymer electrolytes (SPEs) has potential applications. This phenomenon depends on the interaction between the polymer matrix and the ionic liquid. Based on Figure 3 cyclic voltammetry curves [15], it was observed that the reduction potentials of all the blended samples were lower than 1V vs Li/Li+ and no oxidation potentials appeared. All the ionic liquids used show good stability and do not affect their electrochemical stability as SPEs in solid-state LIBs. This result also indicates the potential application of this electrolyte for higher voltage cathodes.

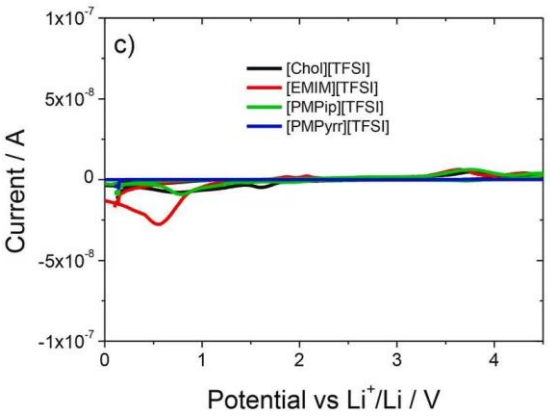

Fig. 3. Cyclic voltammetry curves [15]

5 Conclusion

The stability of LIBs in low-temperature environments represents a critical area of inquiry within battery science. This review aims to identify effective strategies for achieving high-performance LIBs under such conditions, focusing on the selection of innovative anode materials and electrolytes, among other approaches. It is demonstrated that novel silicon-based anodes and composite nanostructured electrode materials exhibit superior stability at low temperatures. Furthermore, the use of electrolyte additives and polymeric solid electrolytes not only lowers the electrolyte's freezing point but also markedly enhances its ionic conductivity and stability in cold conditions. Additionally, this review highlights the role of carbon nanotubes and Si-C composites as anode materials and the efficacy of incorporating $LiBF_4$ with a 0.5% molar ratio into ethyl carbonate electrolytes, in bolstering the applicability of LIBs in low-temperature settings.

Despite extensive research aimed at mitigating the performance decline of LIBs at low temperatures through electrode and electrolyte enhancements, gaps remain in our comprehensive understanding of the batteries' internal changes under such conditions, particularly regarding their electrochemical reaction mechanisms. Variability in testing methodologies and equipment across studies complicates the comparison of results. Moreover, further exploration into novel anode materials is warranted. Presently, most strategies for electrolyte improvement focus on singular aspects, such as introducing new solvents or modifying electrolyte compositions, without a holistic approach. Future research should delve deeper into these strategies to foster overall performance enhancements. These insights not only shed light on the mechanisms underpinning the performance of LIBs in cold environments but also guide the future development and optimization of LIB technology.

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