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Research on the Low-Temperature Performance of Lithium Iron Phosphate Batteries

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Abstract. Lithium iron phosphate ($LiFePO_4$, LFP) batteries have become a cornerstone technology in the new energy industry, widely recognized for their superior safety, long cycle life, and environmental benefits, which have driven extensive adoption across various fields. The unique olivine-structured cathode material, LFP, provides exceptional thermal and chemical stability, effectively maintaining structural integrity under high temperatures and ensuring enhanced safety over other battery types. Furthermore, these batteries demonstrate remarkable durability, often exceeding 3000 full charge-discharge cycles, coupled with significant cost efficiency and a minimal ecological footprint. This combination of advantages solidifies their role as the leading choice for electric vehicle powertrains and large-scale energy storage systems. The present paper systematically investigates the mechanisms responsible for low-temperature performance degradation and comprehensively reviews four primary improvement strategies: innovative material synthesis, electrolyte formulation optimization, advanced electrode engineering, and intelligent thermal management. Finally, emerging industrial applications and promising future research directions toward broader electrification are also critically discussed.

Keywords: Lithium iron phosphate battery, low-temperature performance, Nano structuring, low-temperature electrolyte, thermal management

1. Introduction

The widespread adoption of lithium iron phosphate (LFP) batteries in the new energy landscape is rooted in their unique set of advantages, which have solidified their position as a cornerstone technology. By 2025, projections indicate that LFP batteries will capture over 70% of the global power battery market, with an even higher penetration rate exceeding 85% in China. This dominance stems from two core strengths: first, the exceptional stability of their olivine-type $LiFePO_4$ structure, which has a decomposition temperature above 500°C-far higher than that of cobalt-based cathodes-greatly reducing the risk of thermal runaway. Second, their ultra-long cycle life, often exceeding 3000 charge-discharge cycles, makes them highly cost-effective for long-term applications such as electric vehicle (EV) powertrains and stationary energy storage systems.

However, despite these merits, the low-temperature performance of LFP batteries remains a critical barrier to their adoption in cold climates. This limitation is particularly pronounced in regions with harsh winter conditions. To quantify this degradation, experimental data from Wang

Suijun’s team provide clear insights. Their studies reveal a sharp performance decline when temperatures fall below 0°C. At -10°C, the discharge capacity of LFP batteries drops to 67.7% of the room-temperature value under standardized testing conditions (0.2C rate, 25°C baseline). As the temperature further decreases to -20°C, capacity retention plummets to 40–50%, while internal resistance increases fourfold—this rise in resistance not only reduces output power but also leads to more heat generation during operation, creating a vicious cycle. At -30°C, the situation worsens: electrolyte solidification occurs, with the ionic conductivity of EC-based electrolytes (commonly used in LFP batteries) dropping to as low as 0.01 mS/cm, effectively halting ion transport and rendering the battery inoperable [1].

Beyond capacity loss, low-temperature operation also introduces safety risks. After 50 charge-discharge cycles at -10 °C, Wang Suijun’s team found that the thermal runaway onset temperature of LFP batteries decreases by over 10°C, and the risk of gas evolution rises significantly—with increased production of flammable gases such as CO and H_2 [1]. These gases can accumulate within the battery casing, leading to swelling and potentially triggering thermal runaway, especially if combined with internal short circuits caused by dendrite growth.

This "low-temperature anxiety" has become a key concern for users in cold regions, driving urgent research into mitigation strategies. In recent years, innovations such as material nanostructuring, bio-inspired electrolyte design, and pulsed self-heating systems have shown promising results in improving low-temperature performance. For instance, nanostructuring the LFP cathode shortens lithium-ion diffusion paths, while optimizing electrolyte formulations with low-freezing-point solvents reduces viscosity at low temperatures. Advanced electrode engineering, such as low-impedance architectures and modified binders, enhances structural stability under cold conditions, and integrated thermal management systems enable rapid preheating to maintain optimal operating temperatures. This paper aims to systematically review the mechanisms underlying low-temperature degradation in LFP batteries and summarize the latest advancements in these enhancement strategies.

2. Mechanisms of low-temperature performance degradation

To effectively address the low-temperature challenges of LFP batteries, it is essential to first understand the underlying mechanisms driving performance degradation. These mechanisms are interconnected, involving the electrolyte, cathode, and anode, and collectively lead to reduced ion transport efficiency and increased electrochemical polarization.

2.1. Electrolyte viscosity surge

The electrolyte serves as the "bloodstream" of a battery, facilitating the transport of lithium ions between the cathode and anode. Conventional LFP batteries typically use $LiPF_6$-based electrolytes, with a solvent blend of cyclic carbonates (e.g., ethylene carbonate, EC) and linear carbonates (e.g., dimethyl carbonate, DMC).

At low temperatures, the most significant issue arises from the behavior of the solvent components. EC, a key cyclic carbonate, has a melting point of 36°C. As temperatures drop below 0°C, EC begins to crystallize, causing a sharp increase in electrolyte viscosity. At -20°C, the viscosity of EC-based electrolytes can increase by several orders of magnitude compared to room temperature, while ionic conductivity drops to less than 5% of its 25°C value. This drastic reduction in ionic conductivity severely impairs lithium-ion mobility.

Ma Ruijun et al. further verified this phenomenon through Antarctic simulation experiments, where temperatures were maintained at -30°C. They observed near-solidification of the electrolyte, with lithium-ion mobility reduced to a level insufficient to sustain normal battery operation. This electrolyte "freezing" directly blocks the ion transport pathway, making it the primary limiting factor for low-temperature performance.

2.2. Cathode ion diffusion hindrance

The LFP cathode's olivine structure inherently features one-dimensional lithium-ion diffusion channels, which are crucial for ion transport during charge and discharge. However, this structure is also sensitive to low temperatures, as slowed kinetics can induce irreversible structural changes. Wang Suijun's team conducted a detailed study on aged LFP power batteries (with 84% residual capacity) cycled at -10 °C. Through post-cycling analysis using transmission electron microscopy (TEM) and X-ray diffraction (XRD), they found that low-temperature cycling induces pronounced phase separation on the cathode surface.

This phase separation disrupts the continuity of the one-dimensional diffusion channels, increasing the resistance to lithium-ion transport. Additionally, the distorted interface region acts as a "barrier" that slows ion diffusion—TEM images showed that lithium ions take 3–5 times longer to traverse this interface compared to the bulk material.

2.3. Anode lithium plating

The graphite anode in LFP batteries is generally stable at room temperature, with capacity loss primarily attributed to gradual SEI film thickening and irreversible lithium consumption. However, at low temperatures, the kinetics of lithium intercalation into graphite slow dramatically. At -20°C, the lithiation rate (the speed at which lithium ions insert into the graphite lattice) is estimated to be ten times slower than at 25°C. This mismatch between the rate of lithium-ion transport (from cathode to anode via the electrolyte) and the rate of intercalation (into the graphite) creates a surplus of lithium ions at the anode surface.

Unable to be efficiently inserted into the graphite layers, these excess ions tend to deposit as metallic lithium on the anode surface—a phenomenon known as lithium plating. Wang Suijun's team quantified this effect: they found that the amount of lithium plating at -20°C is eight times higher than at room temperature under the same charging conditions. The plated lithium forms dendrites—needle-like structures that can pierce the separator, leading to internal short circuits and triggering thermal runaway.

Moreover, plated metallic lithium is highly reactive. It continuously reacts with the electrolyte to form by-products such as Li_2CO_3 and LiF, consuming active lithium ions and generating gas (e.g., CO, H_2). This not only causes rapid capacity fade but also leads to battery swelling, as the generated gas increases internal pressure. In extreme cases, this swelling can rupture the battery casing, posing safety hazards. Even if dendrites do not immediately cause short circuits, the irreversible loss of active lithium and thickening of the SEI film (due to continuous side reactions) further degrade battery performance over cycles.

3. Strategies for low-temperature performance enhancement

To mitigate the low-temperature degradation of LFP batteries, researchers have developed multi-scale strategies targeting the electrolyte, electrodes, and system design. These approaches aim to improve ion transport efficiency, accelerate reaction kinetics, and suppress harmful side reactions such as lithium plating.

3.1. Electrode optimization

The electrode structure and material properties directly influence ion and electron transport, making them key targets for low-temperature optimization. Strategies such as nanostructuring, surface coating, and bulk doping have been widely explored to enhance electrode performance under cold conditions.

3.1.1. Nanostructuring and morphology control

Nanostructuring involves reducing the size of LFP cathode particles to the nanoscale (typically 100–200 nm), which offers two critical advantages for low-temperature operation. First, smaller particles shorten the lithium-ion diffusion path within the cathode: for a 100 nm particle, the diffusion distance is ~50 nm, compared to ~500 nm for a 1 μm particle—this reduces the time required for ions to traverse the particle, mitigating diffusion limitations at low temperatures. Second, nanostructured particles have a larger specific surface area, increasing the electrode-electrolyte contact area and facilitating more efficient ion transfer at the interface.

Wattmar's research demonstrated the effectiveness of this approach: LFP cathodes with primary particle sizes of 100–200 nm retained 94% of their room-temperature capacity at -20°C (0.2C discharge), far outperforming micron-sized LFP materials (which retained only 40–50% under the same conditions) .To further enhance performance, nanostructuring is often combined with carbon coating (to improve electronic conductivity) and bulk doping (to modify the crystal structure). For example, Rao Mumin et al. reported that nanostructured LFP coated with 2% amorphous carbon and doped with 0.5% Mg^{2+} exhibited 92% capacity retention after 100 cycles at -10°C, compared to 65% for unmodified LFP. This synergy of nanostructuring and surface/ bulk modification addresses both ion and electron transport limitations, making it a promising strategy for low-temperature applications.

3.1.2. Surface coating and bulk doping

Surface coating is a complementary approach to nanostructuring, focusing on improving the electrode-electrolyte interface. By applying a thin layer of conductive and stable materials (e.g., amorphous carbon, carbon nanotubes (CNTs), or CeO_2) on the LFP particle surface, the interfacial impedance can be reduced, and side reactions between the cathode and electrolyte can be suppressed. For instance, amorphous carbon coatings not only enhance electronic conductivity but also act as a physical barrier, preventing direct contact between $LiFePO_4$ and the electrolyte-this reduces the formation of resistive surface films and stabilizes the interface at low temperatures.

Bulk doping involves introducing foreign ions (e.g., Mg^{2+}, F^-, La^{3+}) into the LFP crystal lattice to modify its structure. These dopants can create lattice vacancies or widen the lithium-ion diffusion channels, thereby enhancing bulk ion transport. For example, doping with F^- (which replaces O^{2-} in the lattice) increases the interlayer spacing of the olivine structure, reducing the activation energy for lithium-ion diffusion. Wu et al. found that LFP doped with 1% F^- exhibited a lithium-ion diffusion coefficient 1.5 times higher than undoped LFP at -20°C, leading to 15% higher capacity retention [2]. When combined with surface coating, these strategies work synergistically: the coating improves interface stability, while doping enhances bulk ion transport, collectively mitigating low-temperature polarization and capacity fade.

3.2. Electrolyte innovations

The electrolyte is a critical determinant of low-temperature performance, as its viscosity and ionic conductivity directly affect ion transport. Recent innovations in electrolyte formulation, including low-freezing-point solvents and bio-inspired designs, have shown significant potential for improving LFP battery performance under cold conditions.

3.2.1. Low-freezing-point solvents

Traditional carbonate solvents (e.g., EC, DMC) suffer from high melting points and sharp viscosity increases at low temperatures. To address this, researchers have explored low-freezing-point solvents that maintain low viscosity and high ionic conductivity in cold environments. Ethyl acetate (EA) is one such solvent: with a melting point of -83 °C, EA remains liquid even at -60 °C, and its low viscosity (2.4 cP at 25°C) ensures minimal viscosity increase at low temperatures.

Smart et al. demonstrated the utility of EA-based electrolytes: at -30°C, an electrolyte composed of EA, $LiPF_6$ (1M), and 5% vinylene carbonate (VC) exhibited a viscosity of ~25 cP—far lower than the ~480 cP of conventional EC/DMC electrolytes under the same conditions [3,4]. This low viscosity translated to high ionic conductivity (0.2 mS/cm at -30°C), enabling efficient ion transport. In $LiMn_2O_4$ batteries using this electrolyte, the capacity retention at -60°C (C/20 discharge) was ~80%, compared to 0% for EC/DMC-based batteries [5]. While this study focused on $LiMn_2O_4$, the principle applies to LFP batteries: Zhang Binbin et al. later confirmed that LFP batteries using EA-based electrolytes retained 65% of their room-temperature capacity at -30°C, compared to 10% for conventional electrolytes.

3.2.2. Bio-inspired electrolytes

In recent years, bio-inspired electrolytes have emerged as a novel approach to balancing low-temperature performance and safety. These electrolytes leverage the unique structures of natural materials to enhance ion transport and stability. For example, researchers at Northwest Normal University developed a bacterial cellulose (BC)/lignin-based electrolyte (BC/Li-FR), where lignin microspheres act as flame retardants, and BC forms a three-dimensional network of ion channels.

The BC network provides a continuous pathway for lithium ions, reducing diffusion resistance at low temperatures. Wei Hu et al. reported that this electrolyte exhibited an ionic conductivity of 0.162 mS/cm at -20°C—significantly higher than that of conventional electrolytes (0.05–0.08 mS/cm under the same conditions). Moreover, the lignin microspheres improved safety by suppressing flame propagation: the electrolyte's limiting oxygen index (LOI) was 32, compared to 18 for conventional electrolytes. In LFP batteries using BC/Li-FR, the capacity retention after 800 cycles at -20°C (0.5C) was 85%, demonstrating excellent long-term stability.

3.3. System-level optimization

Beyond material-level improvements, system-level optimization—including electrode engineering and thermal management—plays a crucial role in enhancing low-temperature performance. These strategies focus on optimizing the battery's structure and operating conditions to minimize the impact of cold temperatures.

3.3.1. Electrode engineering

Low temperatures exacerbate the limitations of electrode design, as slowed ion diffusion and increased interfacial impedance become more pronounced. For LFP cathodes, the solid-phase lithium-ion diffusion coefficient decreases by 1–2 orders of magnitude at -20°C compared to room temperature, leading to severe polarization.

One effective solution is to reduce electrode areal density (the capacity per unit area), which shortens the ion transport distance within the electrode. Li Meng et al. found that reducing the cathode areal density from 3.5 mAh/cm^2 to 2.2 mAh/cm^2 shortened the average ion transport distance by 37%. This reduction in distance enables more efficient ion diffusion, even at low temperatures: at -20°C, the discharge capacity of the low-density electrode was 72% of the room-temperature value, compared to 58% for the high-density electrode [6]. Additionally, using linear polymer binders (e.g., polyacrylic acid) instead of conventional PVDF can improve electrode flexibility and reduce interfacial impedance—Zeng Lingjie demonstrated that LFP electrodes with PAA binders exhibited 10% lower resistance at -20°C than those with PVDF [7]. These engineering strategies, while seemingly simple, effectively mitigate ion transport limitations at the system level.

3.3.2. Thermal management

Thermal management systems are critical for maintaining LFP batteries within their optimal operating temperature range (20–40°C) in cold environments. Two primary approaches have been developed: external heating and internal pulse heating.

External heating involves using devices such as self-regulating heating tapes or PTC (positive temperature coefficient) heaters to warm the battery from the outside. These systems are simple to implement but suffer from slow heating rates and uneven temperature distribution—for example, a 50 Ah LFP battery may require 30–40 minutes to warm from -20°C to 25°C using external heating tapes.

Internal pulse heating, by contrast, uses the battery’s own resistance to generate heat. This method involves applying short, high-current AC pulses to the battery, causing joule heating within the electrodes and electrolyte. Shuai Xiaofeng et al. showed that applying 10-second AC pulses (10C current) to a -20°C LFP battery could raise its temperature to 15°C in just 5 minutes, with a temperature uniformity of ±2°C. This rapid, uniform heating not only improves low-temperature discharge performance but also reduces lithium plating during charging: Luo Baoquan et al. reported that pulse-heated LFP batteries retained 90% of their room-temperature charging capacity at -15°C, compared to 60% for unheated batteries.

4. Challenges and future outlook

While significant progress has been made in improving the low-temperature performance of LFP batteries, several challenges remain. Addressing these will be key to enabling their widespread adoption in cold climates.

4.1. Current limitations

4.1.1. Energy density penalty

Nanostructuring and carbon coating—effective for improving low-temperature performance—often reduce volumetric energy density. For example, nanostructured LFP with 5% carbon coating has a volumetric energy density of ~405 Wh/L, compared to ~450 Wh/L for micron-sized LFP. This 10% reduction is a significant drawback for EVs, where high energy density is critical for long driving ranges.

4.1.2. Electrolyte durability

Low-freezing-point solvents like EA improve low-temperature performance but suffer from poor chemical stability. Smart et al. found that EA-based electrolytes decompose by 38% after 200 cycles at -20°C, leading to gas evolution and battery swelling [5]. This decomposition not only reduces capacity but also increases internal pressure, posing safety risks.

4.2. Emerging solutions

To overcome these limitations, researchers are exploring innovative approaches across material science, chemistry, and engineering.

Multi-Scale Structured Materials: Xu Bin’s team developed hierarchical porous LFP microspheres (5 μm diameter) with 50–100 nm surface pores. This structure combines the high energy density of microscale particles with the fast ion transport of nanoscale pores. At -20°C, these microspheres retained 81% of their room-temperature capacity, with only a 3% reduction in volumetric energy density (436 Wh/L vs. 450 Wh/L for conventional LFP).

Bio-Inspired Electrolyte 2.0: Building on earlier bio-inspired designs, Li Feng reported a novel electrolyte additive: pentafluoro(phenoxy)cyclotriphosphazene. These additive forms a dual-layer SEI film on the anode—composed of NaF (from additive decomposition) and fluorocarbons (from electrolyte reduction)—that enhances ion transport and suppresses lithium plating [8].

5. Conclusion

This review systematically analyzes the mechanisms of low-temperature performance degradation in LFP batteries and summarizes four key enhancement strategies: material modification, electrolyte optimization, electrode design, and thermal management. Key findings include: Material innovations: Cathode nanostructuring (100–200 nm particles), combined with carbon coating and ion doping (e.g., La^{3+}, Mg^{2+}), enhances interfacial conductivity and ion diffusion, enabling 94% capacity retention at -20°C. These modifications address both ion transport and electronic conductivity limitations. Electrolyte advances: Low-freezing-point solvents (e.g., EA) reduce viscosity to 25 cP at -30°C, while bio-inspired electrolytes (e.g., BC/Li-FR) improve ionic conductivity to 0.162 mS/cm at -20°C. These formulations enhance ion mobility while maintaining safety and stability. System improvements: Thin electrodes shorten ion transport paths by 37%, and pulsed heating systems enable operation down to -40°C. These system-level optimizations complement material improvements, ensuring practical performance in cold environments.

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