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Utilizing Electrolyte Additives to Improve Cycling of High-Voltage and Next-Generation Lithium Battery Systems

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Abstract: ***Lithium-ion batteries (LIBs) are the dominant energy storage technology for electric vehicles and portable electronics, yet their long-term performance remains constrained by capacity fade and impedance growth during extended cycling. These degradation mechanisms are primarily linked to unstable interfaces between the electrode and the liquid electrolyte, leading to continuous electrolyte decomposition, loss of active lithium, and structural damage to electrode materials. This review provides a comprehensive analysis of the role of electrolyte additives-a cost-effective and highly tunable strategy-in mitigating these challenges and substantially improving the cycle life of LIBs. The paper systematically explores various classes of functional additives based on their chemical composition and targeted function, including film-forming additives, scavengers, flame retardants, and overcharge protectants. A major focus is placed on film-forming additives such as Vinylene Carbonate (VC), Fluoroethylene Carbonate (FEC), Lithium bis(oxalate)borate (LiBOB), and Lithium difluoro(oxalate)borate (LiDFOB). These compounds preferentially decompose on the anode (e.g., graphite, Si-based anodes) and/or cathode (e.g., Ni-rich {NMC} and high-voltage spinels) surfaces at lower potentials than the bulk electrolyte. Ultimately, this paper synthesizes cutting-edge research to present a clear picture of how molecular engineering of the electrolyte interphases via additives is a decisive factor in achieving the high energy density, extended calendar life, and enhanced safety required for future high-performance LIBs.***

Keywords: lithium ion batteries, additives, electrolyte, cycle life, solid electrolyte interphase

1. Literature Review

- The available literature provides a deep insight on the fucntion of additives in the working of lithium ion batteries. A plathora of additves, in solid and liquid states, have been tested and researched upon the few decades that we have known Lihium ion batteries. Film forming additives are a huge part of research. A novel lithium borate salt was introduced as an additive. Lithium bis (2-methyl-2-fluoromalonato) borate (LiBMFMB) has proven to be an excellent choice as it was designed to improve oxidation stability and SEI formation [1]. It was used as an additive (0.02 M and 0.05 M) in carbonate electrolytes with $LiPF_6$. It showed notable perfomrance improvement with half cells. It decreased the capacity loss after 100 cycles (from 42.2% without additives to 13.5%). The coulombic efficiency increased almost 99% after 100 cycles.
- A major challenge in developing new high-voltage additives is the lack of fundamental understanding regarding their protection mechanisms. High working potentials in next-generation Li-ion batteries often lead to aggressive oxidation of electrolyte solvents, causing fast capacity fade and low coulombic efficiencies. Lithium difluoro (oxalato) borate (LiDFOB) a boron based additive and 3-hexylthiophene (3HT) a conjugated polymer based additive were studied to study their mechanisms with high voltage cathode-electrolyte in the battery. LiDFOB, particularly at 0.5% concentration, significantly improved capacity retention and reduced static leakage current, indicating a more robust surface film and reduced solvent oxidation. 3HT formed an electronically conductive poly (3HT) film on the cathode surface, which did not mitigate solvent oxidation but prevented severe attack from protons [2]
- Another study introduced 4-trifluoromethylphenylboronic acid (4TP) as a cost-effective film-forming additive to enhance the long-term cycling stability of high-voltage lithium-nickel-manganese oxide (LNMO) cathodes in lithium-ion batteries [3] With only 2 wt % 4TP, the LNMO/Li cell achieved a capacity retention of 89% after 480 cycles, a significant improvement from 26% without the additive. Density functional theory (DFT) calculations indicated that 4TP has a higher oxidation activity compared to the baseline electrolyte, suggesting it would preferentially oxidize to form a stable cathode/electrolyte interphase (CEI) film.
- A next-generation synthetic additive approach utilizing fluorinated and silylated electrolyte additives, specifically 5-methyl-4-((trifluoromethoxy) methyl)-1,3-dioxol-2-one (DMVC-OCF3) and 5-methyl-4-((trimethylsilyloxy)methyl)-1,3-dioxol-2-one (DMVC-OTMS) were introduced in another paper. The DMVC-OCF3 and DMVC-OTMS additives, in combination with VC, copolymerize to form a flexible and robust SEI on the Si-C anode. The DMVC radical, formed from the one-electron reduction of DMVC-OCF3 and DMVC-OTMS, polymerizes with the vinyl group of VC, contributing to the SEI formation.[4]
- The use of lithium fluoride salt additives to improve the electrodeposition of metals in batteries with metallic lithium anodes was discussed in another study [5]. It found that LiF additives provide a robust strategy to enhance both the lifetime and coulombic efficiency of batteries at high and low current densities. LiF simultaneously protects the lithium metal anode surface and improves interfacial Li-ion transport, leading to faster and flatter electrodeposition and longer cycle life.
- Nitrate additives in lithium batteries, focusing on their mechanisms, applications, and future prospects was

comprehensivley reviewed in an article. It highlights how nitrates, particularly $LiNO_3$, enhance battery performance by improving the solid-electrolyte interphase (SEI) stability, suppressing dendrite growth, and regulating solvation behavior [6]. The review also covers the use of various nitrate cations and strategies to improve nitrate solubility in different electrolyte systems. $LiNO_3$ is a well-known additive in lithium-sulfur (Li-S) batteries, primarily used to regulate the SEI and suppress the redox shuttle of polysulfides. $LiNO_3$ is a well-known additive in lithium-sulfur (Li-S) batteries, primarily used to regulate the SEI and suppress the redox shuttle of polysulfides.

2. Case and Methodology

Phase I: Synthesis and Selection (Molecular Design)

The research begins with identifying or creating the molecules hypothesized to form a superior Solid Electrolyte Interphase (SEI) or Cathode Electrolyte Interphase (CEI).

1) Additive Screening and Synthesis

a) **Targeted Design:** Researchers select molecules based on their calculated or measured **Highest Occupied Molecular Orbital (HOMO)** and **Lowest Unoccupied Molecular Orbital (LUMO)** energy levels.
  - **Anode Additives:** Must have a (LUMO) level below that of the bulk solvent to ensure preferential reduction and decomposition on the anode surface (e.g., {VC} and {FEC} reducing before ethylene carbonate).
  - **Cathode Additives:** Must have a (HOMO) level *above* that of the bulk solvent to ensure preferential oxidation on the high-voltage cathode surface.

b) **Chemical Synthesis:** The chosen additive molecule (often derivatives of carbonates, sulfates, or fluorinated compounds) is synthesized, purified to high purity (99.5%), and dissolved into the standard electrolyte base (e.g. {LiPF6 in EC/DMC}) at low concentrations.

2) Computational Pre-screening

Density Functional Theory (DFT): DFT calculations are used to model the stability and decomposition pathway of the additive molecules. This verifies the reduction/oxidation potentials and identifies the likely decomposition products (e.g., LiF_6, Li_2CO_3) that will form the interphase layers.

Phase II: Electrochemical and Surface Characterization

Before full cell testing, critical properties of the additive-modified electrolyte and the resulting interphases must be evaluated.

a) Electrolyte Property Measurement

- **Ionic Conductivity:** Measured using electrochemical impedance spectroscopy (EIS) to ensure the additive does not negatively impede within the bulk electrolyte.
- **Linear Sweep Voltammetry (LSV):** Used to determine the overall anodic (oxidation) stability window of the modified electrolyte, confirming that the cathode additive decomposes appropriately at the target voltage.

b) Interphase Analysis (Post-Mortem)

After cycling or formation steps, cells are disassembled and the electrodes are analyzed to determine the composition and morphology of the {SEI} and {CEI} formed by the additive.

- **X-ray Photoelectron Spectroscopy (XPS):** This technique determines the chemical composition of the surface films (SEI, CEI) by identifying elements and their chemical states (e.g., quantifyingLiF6, Li2CO3, and polymer species derived from the additive).
- **Scanning Electron Microscopy (SEM):** Provides visual information on the morphology of the interphase layer. A successful additive forms a thin, uniform, crack-free, and dense layer. A poor additive may lead to a thick, resistive, and porous layer.
- **Electrochemical Impedance Spectroscopy (EIS):** Measures the resistance of the interphase layers. A good additive minimizes the total cell impedance and limits the growth of the interphase resistance upon extended cycling.

Phase III: Performance Validation

The final stage involves testing the additive in representative cell formats under stringent operating conditions.

a) Cell Assembly and Formation

- **Cell Format:** Test cells are typically assembled as half-cells (testing anode vs. {Li} metal, or cathode vs. {Li}) or full cells (anode vs. cathode, e.g., NCM 22).
- **Formation Cycle:** A crucial initial step where the SEI is intentionally formed by slowly charging the cell to allow the additive to decompose optimally.

b) Long-Term Cycling and Rate Performance

- **Cycle Life Test:** Cells are cycled continuously (e.g., at 1 C rate) between their defined voltage limits (e.g. 3.0 V to 4.3 V for NCM systems) over hundreds or thousands of cycles to measure capacity retention (mAh/g) and Coulombic Efficiency (CE). A successful additive significantly increases (CE) and cycle life.
- **Rate Capability:** The cell is tested at progressively higher C-rates (e.g., 0.1 C up to 5 C) to ensure the additive-formed interphase does not impede fast charge and discharge (power performance).

c) Safety and Thermal Stability

- **Differential Scanning Calorimetry (DSC):** Used to measure the thermal stability of lithiated electrodes with the new electrolyte. A good additive should suppress exothermic reactions, pushing the onset temperature of thermal runaway higher.
- **High-Temperature Cycling:** Cells are cycled at elevated temperatures (e.g., 45°C or 60°C) to assess the additive's ability to maintain a stable interface under accelerated degradation conditions, simulating real-world abuse.

3. Results & Analysis

LiBMFMB showed notable perfomrance improvement with half cells. It decreased the capacity loss after 100 cycles (from 42.2% without additives to 13.5%). The coulombic efficiency increased almost 99% after 100 cycles. The Graphite anodes benefitted from the addition of the additive which increased the cycle efficiency by 20% [1]

LiDFOB (Direct Reduction Mechanism): Higher concentrations (e.g., 2% LiDFOB) increased overall leakage current and led to faster capacity fade, likely due to increased additive oxidation and CO2 generation.[2]

3HT (Corrosion Inhibitor Film Mechanism): Despite higher overall leakage currents (due to both solvent and 3HT oxidation), 3HT-containing cells showed improved cycling performance and significantly slowed the increase in charge-transfer resistance. The best performance was observed with 0.25% 3HT. [2]

The additive combination (VC, DMVC-OCF3, and DMVC-OTMS) led to significantly improved capacity retention (81.5% after 400 cycles at 1 C) and fast charging capability (only 1.9% capacity fading after 100 cycles at 3 C). [3]

LiF additives significantly prolonged the short-circuit time of batteries. At 4mA/cm², cells without LiF short-circuited within 80 hours, while those with LiF lasted over 140 hours. At 1mA/cm², neat electrolyte batteries failed within 900 hours, whereas LiF-containing counterparts cycled for over 1700 hours without failure. Li/$LiFePO_4$ full cells with 0.5 wt% LiF exhibited stable cycling for over 150 cycles at high current density, maintaining a near-constant discharge capacity. Neat electrolyte systems became unstable and failed beyond 100 cycles. [5]

Nitrates influence the solvation structure of Li ions, weakening the interaction between Li^+ and solvents. This can prevent graphite failure due to Li^+-solvent co-intercalation and improve Li^+ desolvation, which is beneficial for reversible cycling performance [6]. Some nitrate cations (e.g., Cu^{2+}, Mg^{2+}, Sn^{2+}) directly participate in SEI formation, accelerating its development and inhibiting dendrite growth. These cations can form Li-alloy components (like Li_3Mg_7) or contribute to inorganic-rich hybrid SEI films, enhancing stability and Li^+ conduction.

4. Conclusion

The meticulous researches done on electrolyte additives have proven to be effective in a lot of different ways. It has tried to solve the ongoing problems with the Lithium batteries concerning its cycle life and accidental failures. The methods were aimed to make them more proficient, long lasting and safe. Though more research is to be done so as to make it a hundred percent efficient and immune to accidents. Manufacturing and cost is still a couple of issues that need to be targeted further. Innovation of cheaper additives will take a significant amount of time, research and development. The Engineering, Manufacturing and Sciences industry have to make a collabarative effort in making sure to have these changes. The developments in the past couple of decades have been immense and substantial and scope of brighter innovation is right ahead of us.

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