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Molecular Engineering Approaches for Electrolyte Design towards Stable Lithium Metal Batteries

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As conventional lithium-ion batteries (LIBs) are approaching their limits in terms of their theoretical energy density, replacing the graphite anode by metallic Li to develop Li metal batteries (LMBs) could meet the demands for high energy storage. However, the problems on Li metal anode (LMA) such as dendrites formation and low Coulombic efficiency (CE) hindered its application. This thesis contains the progress on LMA protection and three new electrolyte chemistries to stabilize LMA surface and realize stable cycling of LMBs.

Owing to the narrow electrochemical windows of ether-based electrolytes and nonsolvating ability of fluorinated ethers, a new solvent, 2,2-dimethoxy-4-(trifluoromethyl)-1,3-dioxolane (DTDL), combining a cyclic fluorinated ether with a linear ether segment was developed to achieve a high voltage stability up to 5.5 V, tune Li^+ solvation power and realize stable CE of 99.2% after 500 cycles.

By mimicking the successful electrolyte system of the mixture of 1,3-dioxolane (DOL) and DME, a new fluorinated dioxolane molecule, 2-(2,2,2-trifluoroethoxy)-4-(trifluoromethyl)-1,3-dioxolane (TTD), was first developed as co-solvent in high-voltage LMBs through the introduction of electron-withdrawing group (CF_3) to extend decomposition voltage. After pairing with 1.5 M lithium bis(fluorosulfonyl)imide (LiFSI) by TTD and DME by the volume ratio of 8:2, the new electrolyte exhibited anti-oxidation2 up to 6 V and reached a high CE value of 99.4% within 210 cycles at 3 mA cm^{-2} current density with the capacity of 3 mAh cm^{-2}.

Although the localized high concentration electrolytes (LHCEs) outperformed state of the art electrolytes, the direct correlation between solvation structure in LHCEs and the SEI composition is not well-understood. A new class electrolyte based on bis(2,2,2-trifluoroethoxy)methane (BTFM) and 1,2-dimethoxyethane (DME) was introduced to regulate anion decomposition to achieve an ultra-high Li_2O content (63%) in the SEI along with a highly uniform phase distribution, which realized a record-high CE of 99.72% and proved the impact of homogeneously distributed high Li_2O ratio.

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