ELECTROLYTE DESIGN FOR INTERFACIAL STABILITY IN LITHIUM-ION AND ZINC-ION BATTERIES

ABSTRACT

Within secondary batteries, device lifespan is predicated upon the reversibility of a particular set of electrochemical reactions at the interfaces. Deviations from this redox reaction represent inefficiencies that divert reversible charge storage into parasitic reactions, degrade the material properties of active materials, consume cell components, inactivate the inventory of available reagents, and promote a cascade of heat-mediated thermal runaway reactions. This thesis aims to provide fundamental understanding of electrolyte design which promotes interfacial stability for building next-generation secondary batteries that offer high energy density, long cycling lifespans, and resilience against thermal runaway.

Lithium-ion battery safety has driven the design of nonflammable electrolytes in both liquid- and solid-state systems. However, bulk nonflammability alone does not ensure intrinsic cell-level thermal safety in lithium metal batteries (LMBs), particularly under extreme thermal runaway (TR) conditions where interfacial reactions dominate heat generation. In this work, a nonflammable polymer-salt-solvent electrolyte matrix showcases a confinement effect for multiscale correlation of intra-electrolyte transport properties to cycling stability at room temperature and cell-level thermochemical characteristics under thermal stress. Through combined electrochemical characterization, spectroscopy, and diffusometry, it is demonstrated that intra-electrolyte associations, driven by charge-carrier coordination and hydrogen-bonding interactions, suppress detrimental solvent diffusion toward reactive electrode interfaces. These results provide new mechanistic insights into the thermokinetic effects of electrolyte confinement on interfacial reactivity. The advantageous electrochemical stability and bulk transport properties of the electrolyte design improve the safety characteristics retaining high ionic conductivity and cycling stability with a lithium metal anode as well as graphite and hard carbon (HC) anodes.

In tandem with the established field of lithium-ion batteries, rechargeable zinc-ion battery development has experienced a surge of literature interest. The use of nonaqueous molecules opens up a new horizon of electrolyte design space that has shown promise in overcoming the traditional limitations of aqueous zinc systems. The underlying principles of zinc-ion solvation in solely

nonaqueous and aqueous-nonaqueous hybrids enable the correlation of coordination environments, anion selection, and solvent polarity to key performance criteria including deposition morphology, Coulombic efficiency, and electrochemical stability window. Although a variety of strategies and methods have been employed to develop aqueous electrolytes in ZIBs, the primary problems of the large hydration shell result in manifold challenges. The desolvation and release of free water, water electrolysis and changes in pH create a system with limited electrochemical reversibility that arises in the form of corrosion, dendrite growth, and undesirable side products with free water supplied at the cathode and anode. We introduce ligand substitution to demonstrate an electrolyte design framework which provides opportunity to stabilize the interface and prevent parasitic reactions.