Abstract

The transition to sustainable energy requires safe, efficient, and scalable battery technologies. Metal anode-based batteries, particularly those employing Li and Mg, offer high energy density but face major challenges from unstable interfaces and interphases at the metal electrodes. This thesis addresses these issues through electrolyte engineering, with a focus on fluorinated solvent-based electrolytes. For Li metal batteries, we designed and characterized fluorinated electrolytes, investigated Li^+ transport properties, and studied electrode interfaces using electrochemical and spectroscopic methods assisted by molecular-level simulations. We found that incorporating fluorinated solvents into Li electrolytes stabilizes the performance of high-voltage Li batteries by synergistically improving electrode interfaces and interphases. Building on these findings, we extended the approach to Mg metal batteries, where fluorinated electrolytes improved interfacial stability and enabled higher-voltage operation. *Operando* impedance spectroscopy, combined with microscopy and chemical analyses, provided mechanistic insights into interfacial processes happening on the Mg metallic anodes. Finally, the potential of these electrolytes was evaluated in Mg-S batteries, highlighting key factors for the rational design of next-generation electrolytes. This thesis advances understanding of electrolyte-anode interactions and offers pathways toward safer, high-performance Li and Mg metal batteries.

Keywords: Li metal batteries, Mg metal batteries, electrolyte engineering, electrochemical impedance spectroscopy, interfacial chemistry, electrochemical characterization.