Abstract

The growing demand for high-energy-density, intrinsically safe energy-storage systems has intensified research into sodium metal batteries (SMBs) as promising post-lithium-ion technologies, owing to the natural abundance and low cost of sodium. However, the commercialization of SMBs is severely constrained by the safety hazards, unstable sodium metal interfaces, and dendritic growth associated with conventional liquid electrolytes. Solid and quasi-solid polymer electrolytes (SPEs and QSPEs) have emerged as viable alternatives; nevertheless, their widespread adoption remains limited by low room-temperature ionic conductivity, poor Na^+ transference numbers, narrow electrochemical stability windows (ESW), sluggish solvation–desolvation kinetics, and persistent electrode–electrolyte interfacial instability. This thesis aims to develop advanced polymer electrolyte systems that transition systematically from QSPEs to room-temperature-operable SPEs while simultaneously enhancing interfacial stability, widening the ESW, and improving ion-transport behavior. The central strategy relies on molecular-level engineering of polymer crystallinity, solvation structures, and Na^+ coordination environments, combined with the integration of functional active fillers to introduce flame retardancy, mechanical reinforcement, and homogeneous ion flux.

Following the scientific motivation outlined in Chapter 1 and a critical assessment of the research landscape in Chapter 2, Chapter 3 establishes a comprehensive experimental–computational workflow integrating physicochemical, electrochemical, spectroscopic, mechanical, and surface-sensitive characterization. This framework enables systematic correlation of structure, solvation chemistry, and interfacial behavior with electrochemical performance. Chapters 4 and 5 focus on QSPE development through polymer blending and solvation engineering. Blended QSPE achieves high room-temperature ionic conductivity, elevated Na^+ transference number, thermal and mechanical stability with stable sodium plating/stripping over extended durations, and excellent full-cell rate capability. Subsequent solvation analysis reveals how tailored polymer chemistry regulates ion coordination, interphase chemistry, and dendrite suppression. In Chapter 6, multifunctional active fillers are introduced, with boron nitride serving as a chemically active, bifunctional filler that enhances ionic mobility, thermal and mechanical stability, flame retardancy, and long-term cycling stability, including pouch-cell validation. With the learnings from QSPE formulations, Chapter 7 demonstrates a controlled transition from QSPEs to SPEs through the incorporation of

NASICON-type ceramic fillers into optimized polymer blends. This strategy establishes continuous ion-conductive pathways, improves interfacial charge-transfer kinetics, suppresses dendritic behavior, and enables stable room-temperature solid-state SMB operation with high-rate capability. Finally, Chapter 8 summarizes the key findings and outlines future research directions, highlighting the extension of solvation-engineered polymer–filler electrolytes toward high-energy room-temperature sodium–sulfur batteries through polysulfide-confining architectures.

Overall, this thesis establishes polymer blending, solvation tuning, and functional filler integration as synergistic and scalable design principles for next-generation polymer electrolytes, providing both fundamental insight and practical pathways toward safe, high-energy, and commercially viable solid-state sodium energy-storage systems.