

## Abstract

This thesis focuses on advancing the performance, stability, and safety of room-temperature sodium-sulfur (RT Na-S) batteries, addressing critical challenges related to the sodium metal anode, particularly dendrite formation, volume expansion during cycling, and the instability of the solid electrolyte interphase (SEI). The research employs a multi-faceted approach involving innovative material design, electrolyte optimization, and advanced characterization techniques to achieve significant improvements in battery performance.

The first objective aims to mitigate dendrite formation and manage volume changes in sodium metal anodes by developing a robust 3D host structure. A micro-architecture carbon nanotube (MACNT) framework is designed and integrated into the sodium metal anode to serve as a scaffold for sodium plating and stripping. This MACNT@SS anode demonstrates a substantial enhancement in cycling stability, achieving a Coulombic efficiency of over 98% across 300 cycles at a current density of  $1 \text{ mA cm}^{-2}$ . The 3D structure effectively accommodates the large volume changes associated with sodium metal, preventing the formation of harmful dendrites, which are a major cause of short circuits and capacity degradation in sodium metal batteries.

The second objective focuses on further stabilizing the sodium metal anode by enhancing the uniformity of sodium deposition. To achieve this, a patterned polypropylene interlayer (PPIL) is introduced between the sodium metal anode and the separator. The PPIL features alternating dense and sparse fiber regions that effectively regulate sodium ion flux during cycling. This innovative interlayer design results in a significant improvement in the uniformity of sodium deposition, suppressing dendrite growth and thereby enhancing the battery's cycling stability. Symmetric cells with the PPIL demonstrate stable operation for over 1000 hours at a high current density of  $5 \text{ mA cm}^{-2}$ , with no evidence of short-circuiting, indicating the interlayer's effectiveness in preventing dendrite penetration and ensuring consistent anode performance.

The third objective targets improving the SEI's mechanical integrity and ionic conductivity, which are critical for the long-term stability of sodium metal anodes. To address this, a novel organic molecule, 9F, is employed as an electrolyte additive. The 9F additive facilitates the formation of a stable and robust SEI, composed of a mixture of organic and inorganic species, that effectively protects the sodium metal surface. Electrochemical tests reveal that cells with the 9F-modified electrolyte exhibit a Coulombic efficiency of approximately 99% and

maintained stable cycling performance for over 400 cycles at a current density of  $1 \text{ mA cm}^{-2}$ . The enhanced SEI suppresses dendrite formation and reduces the interfacial resistance, contributing to improved battery efficiency and longevity.

The fourth objective aims at controlling dendrite growth by altering the sodium-ion solvation environment within the electrolyte. This is achieved by introducing a  $\text{BiI}_3$  additive, which modifies the solvation structure of sodium ions, thereby reducing the occurrence of side reactions and promoting a more uniform sodium deposition. The introduction of  $\text{BiI}_3$  into the electrolyte significantly improved the homogeneity of the SEI and reduced the likelihood of dendrite formation. Cells utilizing the  $\text{BiI}_3$  additive demonstrate a Coulombic efficiency of 98.5% and stable cycling for over 500 hours at a current density of  $3 \text{ mA cm}^{-2}$ . This result highlights the effectiveness of solvation environment manipulation in enhancing the electrochemical stability of sodium metal anodes.

The final objective focuses on developing a multiphasic SEI that could provide both high mechanical stiffness and a low ionic diffusion barrier, ensuring long-term stability for RT NaS batteries. Methylammonium iodide ( $\text{CH}_3\text{NH}_3\text{I}$ ) introduces a novel electrolyte additive, resulting in the formation of an SEI composed of NaF, NaI, and  $\text{NaNH}_2$ . The multiphasic nature of this SEI allows for a unique combination of properties: NaF provides high mechanical stiffness ( $\sim 75 \text{ GPa}$ ), NaI contributes to enhance ionic conductivity, and  $\text{NaNH}_2$  offers the necessary ductility to accommodate volume changes. The SEI exhibits a remarkably low sodium ion diffusion barrier of  $9.37 \text{ kJ mol}^{-1}$ , facilitating efficient and reversible sodium plating and stripping. Symmetric cells equipped with this SEI maintain stability for over 3200 hours at a current density of  $1 \text{ mA cm}^{-2}$ . Additionally, in full-cell Na-S batteries, this SEI enables consistent operation over 500 cycles, with an initial discharge capacity of approximately  $700 \text{ mA h g}^{-1}$ , demonstrating its effectiveness in improving both capacity retention and cycling stability.

Throughout the thesis, advanced characterization techniques such as Field Emission Scanning Electron Microscopy (FESEM), X-ray Photoelectron Spectroscopy (XPS), Raman spectroscopy, and X-ray Diffraction (XRD) are extensively utilized to analyze the morphological, compositional, and structural changes in the SEI and electrode materials. These techniques provided critical insights into the mechanisms underpinning the improved

performance, including the uniformity of sodium deposition, the chemical stability of the SEI, and the interaction between the electrolyte and electrode materials.

In conclusion, this thesis successfully meets its objectives by addressing the key challenges in RT Na-S battery technology. The development of innovative 3D host structures, patterned interlayers, electrolyte additives, and multiphase SEI layers has led to significant advancements in cycling stability, Coulombic efficiency, and the safety of sodium-based batteries. These findings contribute valuable knowledge to the field of energy storage and offer promising pathways for the development of more efficient, reliable, and commercially viable RT Na-S batteries.