Summary

The growing demand for energy storage, driven by advancements in renewable energy and electric vehicles (EVs), has led to the exploration of safer, more efficient, and sustainable alternatives to conventional lithium-ion batteries (LIBs). Solid-state lithium metal batteries (LMBs) have emerged as promising candidates, offering enhanced safety and higher energy density. However, critical challenges persist, particularly in the development of suitable, advanced electrolytes that can achieve high ionic conductivity and stability at ambient temperatures.

In such scenario, this thesis focuses on the design and development of advanced solid polymer electrolytes (SPEs) based on poly(ethylene oxide) (PEO) and highly concentrated ionic liquids (HCIL) for all-solid-state LMBs. Three major objectives are pursued: (1) the development of high-performance crosslinked PEO-based SPEs using UV-induced crosslinking strategies, (2) the study of the phase behaviour, ionic conductivity, and electrochemical performance of SPEs with varying ratios of PEO, N-propyl-N-methylpyrrolidinium bis(fluorosulfonyl) imide (C_3mpyrFSI) ionic liquid (IL) and lithium bis(fluorosulfonyl)imide (LiFSI) salt, and (3) the development of polymer-in-highly-concentrated ionic liquid (PiHCIL) SPEs with enhanced ion transport and electrochemical stability.

Key findings from this research include the achievement of combing UV-induced crosslinking and highly concentrated ionic liquids to synergistically reduce PEO crystallinity and improve electrochemical stability, and therefore leading to enhanced battery cell performance. Particularly, the crosslinked SPE achieved a promisingly high oxidative stability of 4.9 V vs. Li^+/Li and high ambient temperature ionic conductivity of 4×10^{-4} S cm^{-1}. Stable and reversible lithium plating/stripping was demonstrated over hundreds of hours. Laboratory-scale solid-state cells in which the crosslinked SPE was assembled with high loading lithium iron phosphate (LFP) or high loading, high voltage lithium manganese oxide (LMO) cathodes showed remarkable cycling performance. Another important finding is the successful preparation of SPEs with a wide range of EO:Li:IL ratios, and the identification of an optimal ratio of 8:1:1 that achieved high ionic conductivity (5.6×10^{-4} S cm^{-1}) and a remarkable oxidative stability of 5.1 V vs. Li^+/Li. This novel electrolyte design enabled stable Li metal cell cycling over 100 cycles, suppressed dendrite formation, and supported all-solid-state LFP cell performance with over 99% capacity retention at C/5 rate for long-term cycling.

Advanced characterization techniques, including Fourier transform infrared (FTIR) spectroscopy, Raman spectroscopy, solid-state magic angle spinning (MAS) nuclear magnetic resonance (NMR), and electrochemical impedance spectroscopy (EIS), were employed to probe the ion mobility, ion interactions and the effect of ion coordination environment onto ion dynamics within the SPEs. Results reveal that crosslinking enhanced Li^+ solvation and more uniformly distributed ion clusters, thus accounting for the high ionic conductivity and the potential high electrochemical stability. In addition, increased HCIL content disrupted the crystallinity of PEO, enhanced chain mobility, and created interconnected ion-conducting networks that facilitated fast ion transport. Solid-state NMR further confirmed that the disordered ion environment in the PiHCIL-SPEs promoted superior ionic conductivity, which is key to the improved electrochemical performance of the LMBs.

Overall, this work contributes to the growing body of knowledge on solid-state batteries by proposing a novel approach to SPE design, addressing key challenges in achieving high-performance and safe all-solid-state LMBs. The findings open new pathways for future development of SPEs, bringing solid-state LMBs closer to commercialization for high-energy-density applications in EVs and beyond.