Studies on Advanced Solid Electrolytes for Solid-State Metal Batteries

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Abstract

Deploying electric vehicles (EVs) is now becoming essential rather than a choice due to reducing environmental pollution and a smaller carbon footprint. EV batteries demand high energy and powder densities for long-range drive, high acceleration, quick charging operation, and better user safety. Conventional lithium-ion batteries are inadequate to fulfil these requirements due to the presence of flammable liquid electrolytes and poor compatibility with lithium metal. Solid-state lithium metal batteries (SSLMBs) emerged as promising candidates comprising solid electrolytes (SEs) with the potential to offer higher energy/power density and safety. Among various SEs, garnet-based $Li_7La_3Zr_2O_{12}$ (LLZO) has been the most researched SE across the globe due to its excellent ionic conductivity, wide electrochemical window, and chemical stability with Li metal. Yet, its practical deployment is restricted by the large grain boundary (GB) resistance, poor interfacial stability, and uncontrolled dendrite growth. My doctoral research addresses these challenges through a systematic and multi-scale engineering method. This includes developing a scalable synthesis, interface design, microstructural tailoring, dual-therapy introduction, and composite integration. An aqueous combustion synthesis route using alanine fuel was optimized to produce pristine cubic LLZO with a neck-fused structure. Interfacial instability was mitigated via surface fluorination (NH_4F) and a solvated ionic liquid infusion into the pristine LLZO matrix. This approach suppressed interfacial resistance, increased the critical current density up to 1.45 $mA \cdot cm^{-2}$ and delivered stable Li plating/stripping beyond 1200h with minimal overpotential (65 mV vs. 290 mV). Microstructural engineering via bio-templating derived plate-like and 3D interconnected LLZO architectures that reduced GB resistance, delayed dendrite growth and delivered excellent performance for more than 500 cycles in $Li/LiMn_2O_4$ full cell configuration. An innovative dual-therapy approach was introduced with NiO as a sintering aid (solid therapy) and SIL (liquid therapy) in doped LLZO. This synergistically enhanced densification up to 90%, minimized liquid uptake, and impeded the dendrite growth via forming a K_2NiF_4-type lithiated impurity at the GBs. To offer the scalable integration of garnet electrolyte, LLZO fillers were incorporated into the cellulose matrix, dual-polymer composites, and hybrid paper-polymer scaffolds to improve conductivity, flexibility, and mechanical durability. Finally, exploratory extensions showed the adaptability of liquid therapy to $Na_3Zr_2Si_2PO_{12}$ (NZSP) solid electrolyte for sodium metal batteries and probed unconventional Al/S co-doping in LLZO for structural tuning. Together, the overall work develops a comprehensive roadmap for garnet electrolytes to address the various challenges and advance the practical realization of SSLMBs.

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