Materials Science and Engineering Dissertation Defense

Solutions to Interfacial Challenges in Garnet-based Li/S Solid-State Batteries

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Abstract

Garnet-based lithium-sulfur solid-state batteries represent a promising high-energy-density platform, combining the high theoretical capacity of sulfur with the chemical stability of Ta-doped $Li_7La_3Zr_2O_{12}$ (LLZTO) against lithium-metal anode. Nevertheless, the incompressible nature of LLZTO particles hinders intimate interfacial contact with the cathode active material, where the intrinsically low ionic and electronic conductivity of sulfur further limits cathode performance. Three critical challenges were identified at the sulfur-LLZTO (S-LLZTO) interface within the composite cathode.

First, the chemical compatibility of sulfur with LLZTO was systematically investigated. Thermal treatment of S-LLZTO composites at temperatures as low as 200ºC for 10 h was found to degrade the interface through undesirable sulfur oxidation. By contrast, short-duration treatment at 150ºC for 4h preserved interfacial integrity, with properties closely matching those of the untreated sample. These results establish a viable thermal-processing window for sulfur-LLZTO cathode fabrication. In addition, the effect of LLZTO surface contaminants formed during air exposure was evaluated. Sulfur was found to disproportionate readily in the presence of LiOH, forming Li_2S, Li_2SO_3, and H_2O, thereby accelerating interfacial degradation.

Second, a physical vapor deposition method was developed to deposit sulfur onto LLZTO with controlled particle size. Sulfur particle size was shown to exert a pronounced influence on the charge-transfer resistance across the S-LLZTO interface. Reducing the sulfur particle size decreased charge transfer resistance from 400 kOhm.cm2 (for particles >20 um) to 8.8kOhm.cm2 (for 1-4um particles). To decouple particle-size effects from sulfur mass loading, sulfur nanoparticles below 500 nm were also synthesized via a solvent-based route and dispersed onto LLZTO pellet surfaces. These studies demonstrate that sulfur particle size is a key determinant of interfacial kinetics and electrochemical performance.

Third, molten-sulfur wetting-angle measurements on LLZTO pellet revealed the intrinsically poor chemical affinity of sulfur for LLZTO. MoS_2 was therefore introduced as interfacial modifier to improve sulfur wetting and enhance cathode-electrolyte contact. In parallel, a melt electrolyte at the cathode-side interface reduced interfacial resistance by forming intimate contact among sulfur, electrolyte, and electronic conductor. Collectively, these insights provide a rational framework and foundation for engineering high-performance S-LLZTO composite cathodes with improved performance and cycling stability.

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