Microstructural Influence on Sodium Filament Growth in All Solid-state Batteries

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Background incl. aims

All solid-state batteries (ASSBs) using metal anode (e.g. lithium and sodium) are projected to possess high energy and power density and avoid the fire risk of liquid electrolyte counterparts. However, few commercial ASSBs working at room temperature are reported due to sluggish kinetics and severe solid-solid interfacial problems. Among various interfacial problems, the dendritic growth potentially leading to cell failure cannot be yet avoided through the high elastic modulus of solid electrolytes (SEs) as initially expected for ASSBs. Apart from the mechanical property of grain boundaries (GBs), their electronic properties are also expected to be responsible for lithium filamentary dendrite growth and penetration in the SEs. Although this intergranular growth mechanism in inorganic SE based lithium ASSBs is well studied, there is still much to be learned for sodium ASSBs. Especially, anisotropic Na+ ion transport presented in grain bulk of the well-known Na superionic conductor (NaSICON) (e.g. Na3Zr2Si2PO14) even with 3D transport path, not to speak of Na-β''-alumina with layered crystal structure and 2D transport path. Its contribution to the overall Na+ ion transport and the sodium filament growth, for instance, at GBs is still unclear.

Methods & Results

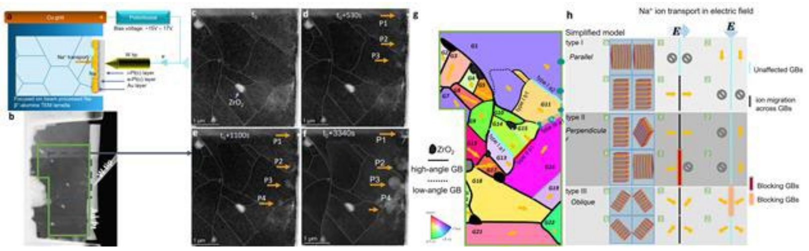
Due to the outstanding stability to Na metal, we used polycrystalline Na-β''-alumina SE (Ionotec. Ltd, UK) as a model material to investigate the microstructural impact on the sodium filament growth. A transmission electron microscopy (TEM) suitable Cu | Na-β''-alumina | Au(Pt) multilayer system was prepared with a focused ion beam (FIB) (FEI Strata 400S) equipment. The electric bias was applied on this system through a scanning tunneling microscopy (STM) nanotip (ZEPtools Technology Company) as schematically illustrated in Figure 1a - b. Na+ ion transport can be prompted by the biasing from the Na-β''-alumina towards the Au/Pt layer and cathodic deposition of sodium occurred at the interface between Na-β''-alumina and the Au/Pt layer in a transmission electron microscope (ThermoFischer Scientific Themis Z). Time-series scanning transmission electron microscopy (STEM) imaging (Figure 1c – f) was used to record the morphological changes e.g. filament growth at the interface between the SE and electrode as well as at the GB. In addition, to build a direct correlation between the filament growth and microstructure, automated crystal orientation mapping (ACOM) by precession electron diffraction-assisted 4D STEM (Figure 1g) was conducted across the polycrystalline Na-β''-alumina specimen. It revealed randomly oriented crystals distributed in the polycrystalline Na-β''-alumina mostly connected by random HAGBs, but hardly any coincidence site lattice boundaries have been observed. Furthermore, since the Na+ ion transport can be different in the grains due to the distinctive orientation of the Na+ ion conduction planes and the external electric field, the GB behavior can also be different as the schematic illustration in Figure 1h for corresponding types. In this case, the filament growth occurred at the GB, which can block the ion transport due to the anisotropic character as shown in Figure 1g.

In addition, significant electron beam effects have been excluded by blank beam reference experiments and sodium filament formation has further been confirmed by post-mortem secondary ion mass spectrometry (SIMS) studies. Moreover, the observed microstructure has been used to simulate the anisotropic Na+ ion transport in the Na-β''-alumina. This helps to understand sodium filament formation and how a critical filament network might form leading to the failure of the battery.

Conclusion

In our study, the relationship between the microstructure and sodium filament growth as well as Na+ ion transport was explored through a crystal orientation analysis. Moreover, sodium filament growth occurred at random HAGBs. The anisotropic ion transport can contribute to the Na+ ion transport blockage of GBs. This blockage at GBs seems to facilitate formation of sodium filaments. Therefore, the microstructure including GB types and orientation should be taken into account for optimizing oxide based SE performance both in terms of sodium filament formation as well as overall ionic conductivity.

Graphic:



Keywords:

solid electrolytes, microstructure, filament growth