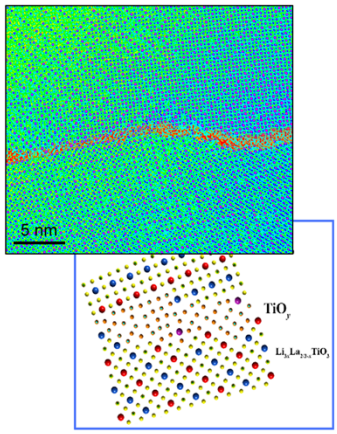
Revealing the Atomistic Origin of Grain-boundary Resistance in Li-ion-conducting Solid Electrolytes



Atomic-scale HAADF-STEM image of a typical GB in LLTO with associated schematic of the intergranular atomic structure and chemistry.

Work performed as a User Project at the Center for Nanophase Materials Sciences and Tsinghua University, China.

Scientific Achievement

The atomic-scale origin of large grain-boundary (GB) resistance, which limits the practical applications of Li-ion-conducting solid electrolytes, was revealed for the first time using advanced analytical STEM.

Significance and Impact

This study elucidates the structural and chemical basis for the large GB resistance in Li superionic conductors. Our discovery paves the way for the search and design of future solid electrolytes with superior performance.

Research Details

- GB atomic and electronic structure investigated in a $(Li_{3x}La_{2/3-x})TiO_3$ (LLTO) prototype solid electrolyte.
- GBs were composed of an intergranular Ti-O binary compound thin film (2-3 unit cells thick) that are not energetically favorable for Li accommodation or transport, resulting in the poor GB conductivity.

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Narrative Highlight:
The solvent-based electrolytes used in conventional lithium-ion batteries can be unsafe and unstable for large-scale applications because of their combustible nature and narrow electrochemical window. Inorganic solid electrolytes, which are non-flammable and often possess much wider electrochemical windows, are being considered as the potential solution. However, the application of these electrolytes remains restricted due to their inherent, high grain-boundary (GB) resistance, which typically lowers the total ionic conductivity by several orders of magnitude. Identifying the ionic transport mechanism(s) at the GBs in solid electrolytes is critical for the revolutionary development of the next-generation of Li-ion batteries. In the present study, we reveal for the first time, the structural and chemical origins of the high GB resistivity in a $(Li_{3x}La_{2/3-x})TiO_3$ (LLTO) prototype solid electrolyte material. Unambiguous evidence acquired via sub-Å-resolution scanning transmission electron microscopy and electron energy loss spectroscopy analysis shows that the LLTO GBs exhibit a severe structural and chemical modification, which is significantly different from the bulk LLTO framework and results in a Ti-O binary compound intergranular thin film with a 2-3 unit cell thickness. Such a GB structure is not energetically favorable for either Li accommodation or transport, giving rise to the poor GB conductivity. The present study elucidates the structural and chemical basis for the large grain-boundary resistance in Li superionic conductors, through direct visualization of the atomic structure and nature of the chemical bonding within the GB thin films. Our study paves the way for the design of future solid electrolytes with superior performance.

Reference

"Atomic-scale Origin of the Large Grain-boundary Resistance in Perovskite Li-ion-conducting Solid Electrolytes"
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