

Interfacial Redox Stabilization in High-Entropy Garnet Electrolytes

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Interfacial reduction limits the stability of garnet electrolytes in lithium-metal batteries. Here, we examine how multication substitution regulates redox evolution at the lithium-garnet interface during electrochemical cycling. We compare the high-entropy garnet $\text{Li}_6\text{La}_3\text{Zr}_{0.5}\text{Nb}_{0.5}\text{Ta}_{0.5}\text{Hf}_{0.5}\text{O}_{12}$ (LLZNTH) with conventional Ta-doped $\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{O}_{12}$ (Ta-LLZO), which exhibit comparable room-temperature ionic conductivities.

Despite similar initial interfacial resistances, LLZNTH reaches a critical current density of 0.8 mA cm^{-2} , twice that of Ta-LLZO. After critical-current testing, its interfacial area-specific resistance increases from 16 to $20 \Omega \text{ cm}^2$, compared with 14 to $75 \Omega \text{ cm}^2$ for Ta-LLZO. LLZNTH also sustains stable lithium plating and stripping for 500 h at 0.1 mA cm^{-2} (Fig. 1).

X-ray photoelectron spectroscopy reveals progressive Ta and Zr reduction in Ta-LLZO during cycling, while reduced Ta, Zr, and Nb components show little further evolution in LLZNTH. Raman spectra indicate better preservation of the LLZNTH garnet framework. Molecular dynamics simulations suggest that cation mixing and surface lithium enrichment limit reactive Li(metal)-O contacts on the modeled (001) interface. These findings support self-limiting reduction in LLZNTH and show that Nb incorporation need not cause progressive degradation. They highlight the local cation environment as a design variable for stabilizing lithium-garnet interfaces.

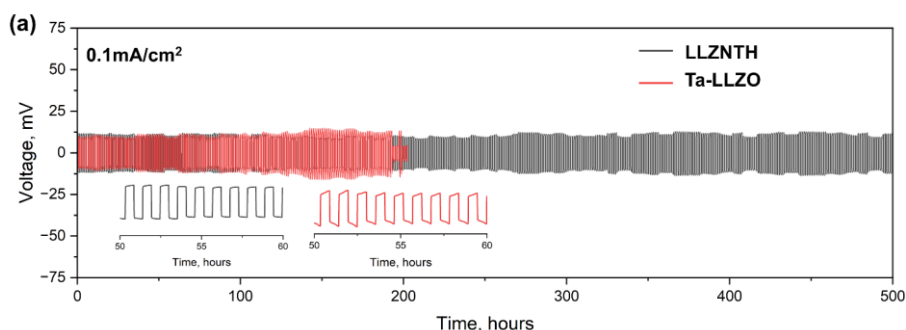


Figure 1. Lithium plating and stripping at 0.1 mA cm^{-2} in symmetric cells.

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