

Moisture-Induced Degradation in Garnet Electrolytes for Solid State Batteries and its Impact on Li-Ion Dynamics

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Solid state inorganic electrolytes are important materials for the development of next-generation Li ion batteries based on an all-solid-state framework. One major challenge is to provide an electrolyte with room temperature Li conductivity, $\sigma_{\text{Li}} > 10^{-3} \text{ S cm}^{-1}$ in order to fulfil high power and recharging targets. Ga-doped LLZO garnet ($\text{Li}_{6.55}\text{Ga}_{0.15}\text{La}_3\text{Zr}_2\text{O}_{12}$) is a promising candidate and potentially suitable for the development of high energy density cells if problems with high polarisation resistance and dendritic-driven cell failure can be solved¹. However, high reactivity with moisture leads to proton-lithium exchange in the crystal structure², accompanied by the formation of LiOH and Li_2CO_3 at the surface. The interface properties with Li metal electrodes are affected due to these degradation layers³. In addition, the formation of a proton-rich garnet and drop in Li content in the bulk material is shown here to result in changes to the Li mobility and conduction mechanism. In this work, we reveal the impact of moisture-induced chemical degradation on the Li-ion dynamics in the bulk, the grain boundaries and at the interface with Li metal in garnet electrolytes. Starting with a proton-free $\text{Li}_{6.55}\text{Ga}_{0.15}\text{La}_3\text{Zr}_2\text{O}_{12}$ (Ga0.15-LLZO), degradation studies in a H_2O bath at 100°C were performed to ensure the removal of LiOH at the surface. The local chemical degradation during proton exchange was followed by focussed ion beam - secondary ion mass spectrometry and found to extend as far as $1.35 \mu\text{m}$ into the pellet after 30 minutes. Impedance analysis in symmetrical cells with Li metal electrodes evidenced a greater reactivity in grain boundaries than in grains and a large detrimental effect on the Li transfer kinetics in the Li metal/garnet interface correlated to a threefold decrease in the Li mobility in the protonated garnet. This result evidences that the deterioration of Li charge transfer and diffusion kinetics in proton-containing garnet electrolytes have fundamental implications for the optimisation and integration of these systems into commercial battery devices.

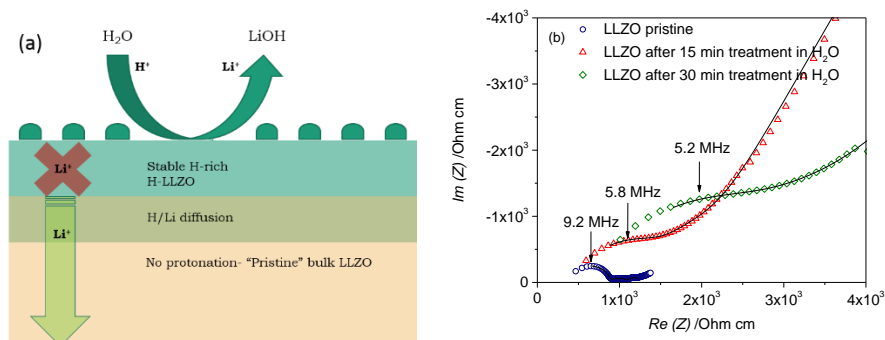


Figure 1. (a) Schematic of possible ionic transport arrangements within the Ga0.15-LLZO grain following H^+/Li^+ exchange; (b) High frequency Nyquist plots taken at 25°C for pristine and H_2O - 100°C Ga0.15-LLZO pellets (15 and 30 minutes), with symmetrical Li electrodes.

References:

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- [2] Orera, A., *et al.* Inorg. Chem. 55, 1324–1332 (2016).
- [3] Cheng, L. *et al.* ACS Appl. Mater. Interfaces 7, 17649–17655 (2015).