

# Garnet–Polymer Composite Electrolytes: New Insights on Local Li-Ion Dynamics and Electrodeposition Stability with Li Metal Anodes

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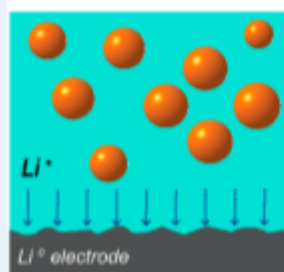
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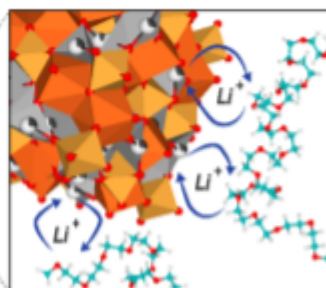
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Homogeneous Li electrodeposition  
through a Garnet-PEO solid electrolyte



Role of local Li+ exchange at the  
ceramic-polymer interface



**ABSTRACT:** Ceramic–polymer solid electrolytes, combined with Li metal anodes, hold the promise for safer and more energetically dense battery technologies, as long as key interfacial challenges are fully understood and solved. Here, we investigate a garnet–PEO(LiTFSI) composite electrolyte system, the garnet filler being  $\text{Li}_{6.55}\text{Ga}_{0.15}\text{La}_3\text{Zr}_2\text{O}_{12}$  (LLZO) microparticles. A “soft” mechanical milling process ensures good miscibility between the garnet and polymer phases over a wide range of volume fraction (up to 70 vol % garnet). Excellent degree of structural and chemical homogeneity is achieved without degradation nor segregation, even at the local level, as confirmed by solid-state NMR spectroscopy, electron microscopy and gel permeation chromatography. The total Li-ion conductivity of the composites is governed by the polymer matrix, as a consequence of the high interfacial resistance ( $\sim 10^4 \Omega \text{ cm}^2$ ) between the garnet particles and the PEO(LiTFSI) matrix. However, by using  $^7\text{Li}$  NMR 2D exchange spectroscopy (ESXY) in the solid state, it is shown that Li ions can locally exchange between the garnet surfaces to the surrounding polymer chains. This dynamic transfer phenomenon, occurring within the composite, seems to play a key role in kinetically stabilizing the interface with Li metal electrode, as observed from galvanostatic cycling and EIS experiments. Comparison of a garnet-free PEO electrolyte with a PEO–garnet (10 vol %) composite shows key performance improvements in the latter: although the Li-ion conductivity at 70 °C slightly decreases from  $7.0 \times 10^{-4} \text{ S cm}^{-1}$ , for PEO–LiTFSI, to  $4.5 \times 10^{-4} \text{ S cm}^{-1}$  for 10 vol % LLZO, the composite shows up to 1 order of magnitude lower interfacial resistance with Li metal electrode (33 vs 300  $\Omega \text{ cm}^2$ ), stable Li electrodeposition, and no dendrite formation. In contrast to previously believed, it is demonstrated that these improvements are not related to a change of the mechanical behavior but rather to a structural reorganization in the composite followed by local ion dynamics effects at the vicinity of the Li metal interface.

**KEYWORDS:** composite electrolyte, garnet, PEO, lithium metal, solid electrolyte, interface, lithium dendrite, solid-state NMR, elastic modulus, solid-state battery