

Supporting Information

Characterization of the interfacial Li-ion exchange process in a ceramic-polymer composite by solid state NMR

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X-ray diffraction of Ga-substituted LLZO ($\text{Li}_{6.55}\text{Ga}_{0.15}\text{La}_3\text{Zr}_2\text{O}_{12}$)

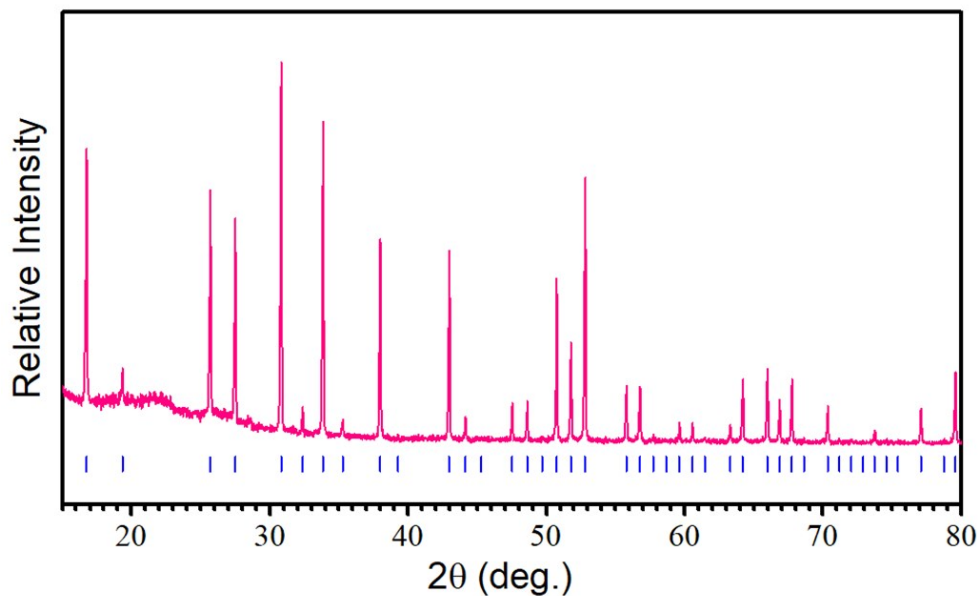


Fig. S1 XRD of the pure cubic Ga-substituted LLZO ($\text{Li}_{6.55}\text{Ga}_{0.15}\text{La}_3\text{Zr}_2\text{O}_{12}$) powder.

Deconvolution of 1D ^7Li spectrum

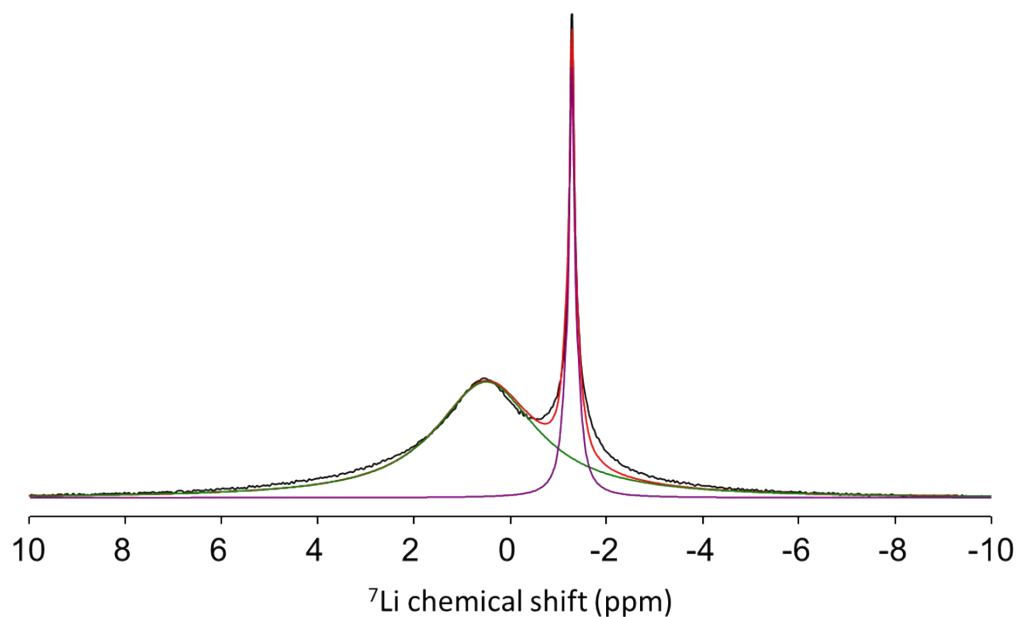


Fig. S2 Deconvolution of ^7Li 1D spectrum. More than two components are necessary to fit the LLZO peak.

^1H - ^7Li HETCOR of the pristine LLZO powder

In order to unequivocally demonstrate the correct assignment of the ^1H resonance at 4 ppm in the ^1H - ^7Li HETCOR correlation shown in Fig. 2b, a similar experiment was performed in a sample containing pure LLZO (no PEO:LiTFSI). The result of such experiment is shown in Fig. S3. This spectrum clearly shows the presence of two main resonances that are assigned to H at LiOH and to protons inside the LLZO structure coexisting with Li-ion. The presence of this signal in a sample without PEO clearly excludes the possibility of this correlation being originated from PEO to LLZO coupling. This result is also in agreement with the NMR characterization of a partially hydrated LLZO sample by Bernuy-Lopez *et al.*, Chem. Mater. **2014**, 26 (12), 3610-3617.

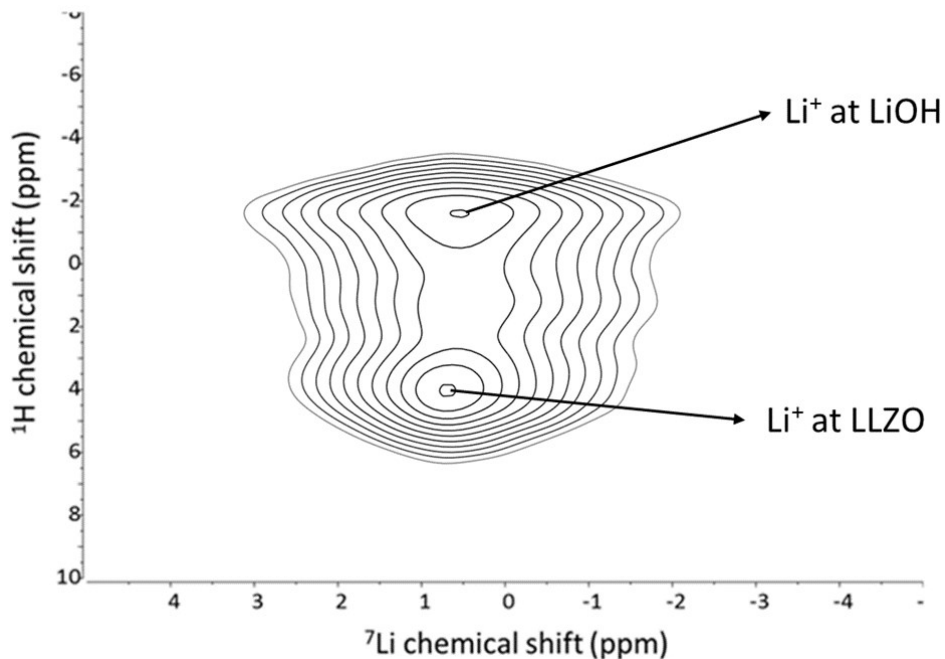


Fig. S3 ^1H - ^7Li HETCOR of the pristine LLZO powder.

Curve fitting results of cross-peaks intensities vs. mixing time from ^7Li - ^7Li EXSY (1.3 mm rotor)

Table S1 1.3 mm rotor ^7Li - ^7Li EXSY fitting results.

Model	ExpDec1		
Equation	$y = A_1 \exp(-x/t) + y_0$		
Reduced Chi-Sqr	5.4299E-4		
Adj. R-Square	0.98769		
		Value	Standard Error
B	y0	1.00155	0.02067
	A₁	-0.56144	0.02554
	t	0.03557	0.00477
	k	28.1098	3.7679
	tau	0.02466	0.00331

Estimation of the time necessary to have an efficient Li-ion mobility within the composite electrolyte via EIS

The bulk conductivity of the composite electrolyte (*i.e.* the resistance-capacitance semi-circle visible at high frequencies) is observed between 1 MHz and 5000 Hz in our EIS measurements, as shown Fig. S4. From these frequency values, it is possible to estimate the time necessary to have an efficient Li-ion mobility within the composite. In this case, at room temperature, we calculated the time taken to participate in the bulk conductivity of the composite as 0.2 ms ($1/5000 = 0.0002$), which is more rapid than the time taken for the spontaneous exchange at the interface (150 ms), as obtained from NMR studies.

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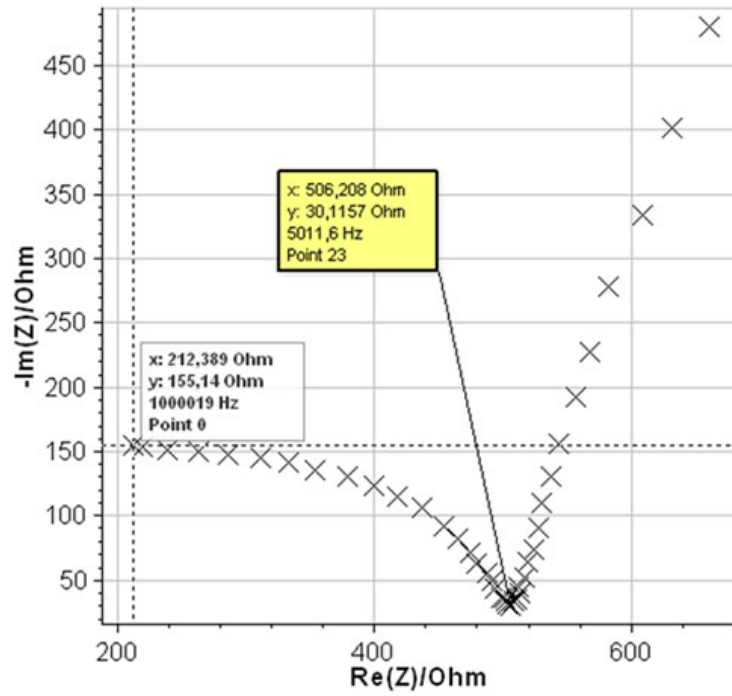


Fig. S4 EIS spectrum of a PEO:LiTFSI + 10 vol% LLZO composite membrane at room temperature. The bulk conductivity is observed at frequencies above 5000 Hz.