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 (Li$_{6.55}$Ga$_{0.15}$La$_3$Zr$_2$O$_{12}$)

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

**Deconvolution of 1D $^7$Li spectrum**

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

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

In order to unequivocally demonstrate the correct assignment of the $^1$H resonance at 4 ppm in the $^1$H-$^7$Li 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 $^1$H-$^7$Li HETCOR of the pristine LLZO powder.](image)
Supporting Information

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

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

<table>
<thead>
<tr>
<th>Model</th>
<th>ExpDec1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equation</td>
<td>$y = A_1 \exp(-x/t) + y_0$</td>
</tr>
<tr>
<td>Reduced Chi-Sqr</td>
<td>5.4299E-4</td>
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<tr>
<td>Adj. R-Square</td>
<td>0.98769</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Value</th>
<th>Standard Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>$y_0$</td>
<td>1.00155</td>
<td>0.02067</td>
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<tr>
<td>$A_1$</td>
<td>-0.56144</td>
<td>0.02554</td>
</tr>
<tr>
<td>$t$</td>
<td>0.03557</td>
<td>0.00477</td>
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<tr>
<td>$k$</td>
<td>28.1098</td>
<td>3.7679</td>
</tr>
<tr>
<td>$\tau$</td>
<td>0.02466</td>
<td>0.00331</td>
</tr>
</tbody>
</table>

**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.
Supporting Information

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.