Discovering the influence of lithium loss on Garnet Li$_7$La$_3$Zr$_2$O$_{12}$ Electrolyte Phase Stability

Andrea Paolella$^a$, Wen Zhu$^a$, Giovanni Bertoni$^{b,c}$, Sylvio Savoie$^a$, Zimin Feng$^a$, Hendrix Demers$^a$, Vincent Gariepy$^a$, Gabriel Girard$^a$, Etienne Rivard$^a$, Nicolas Delaporte$^a$, Abdelbast Guerfi$^a$, Henning Lorrmann$^d$, Chandramohan George$^e$ and Karim Zaghib$^{a,*}$

$^a$ Hydro-Québec, Center of Excellence in Transportation Electrification and Energy Storage, Varennes, Québec J0L 1N0, Canada

$^b$ IMEM – CNR, Istituto dei Materiali per l’Elettronica e il Magnetismo, Parco Area delle Scienze 37/A, I-43124 Parma, Italy

$^c$ CNR – Istituto Nanoscienze, Via Campi 213/A, I-41125 Modena, Italy

$^d$ Fraunhofer-Institut für Silicatforschung ISC, Neunerplatz 2, 97082 Würzburg, Germany

$^e$ Dyson School of Design Engineering, Imperial College London, SW7 2AZ, London, UK

Corresponding author: Zaghib.karim@ireq.ca

SUPPORTING INFORMATION
METHODS SECTION

Si Synthesis

**Undoped cubic LLZO synthesis**

In a general undoped LLZO cubic synthesis 6, 77 g of Li$_2$CO$_3$, 11.64 g of La$_2$O$_3$ and 5.87 g of ZrO$_2$ are mixed in planetary mill with ZrO$_2$ balls under air atmosphere and then annealed in tubular furnace on graphite boat. The flow was kept at 2 L/min from room temperature to 700 °C and then it was stopped when the synthesis temperature was increased up to 950 °C and kept for 2 hours. 1 g of powder was annealed in static conditions and cooled down. On the contrary when 4 g of precursors are used tetragonal LLZO phase is obtained. It’s important to underline that the graphite boat must not be porous. After each synthesis graphite become more and more porous and only tetragonal LLZO may be obtained instead of cubic LLZO.

**Undoped tetragonal LLZO synthesis**

In a general undoped LLZO tetragonal synthesis 6, 77 g of Li$_2$CO$_3$, 11.64 g of La$_2$O$_3$ and 5.87 g of ZrO$_2$ are mixed in planetary mill with ZrO$_2$ balls under air atmosphere and then annealed in tubular furnace on graphite (or zirconia or alumina) boat. The flow was kept at 2 L/min from room temperature to 700 °C and then the synthesis temperature was increased up to 950 °C and kept for 2 hours keeping N$_2$ gas flowing. Finally, the powder was cooled down.

**Ga-doped cubic LLZO synthesis**

In a general doped LLZO cubic synthesis 5, 9.2 g of Li$_2$CO$_3$, 11.39 g of La$_2$O$_3$, 5.77 g of ZrO$_2$ and 0.56 g of Ga$_2$O$_3$ are mixed in planetary mill with ZrO$_2$ balls under air atmosphere and then annealed in tubular furnace on graphite (or zirconia or alumina) boat. The temperature was increased from room temperature to 700 °C and then the synthesis temperature was increased up to 950 °C and kept for 2 hours keeping N$_2$ gas flowing. Finally, the powder was cooled down.

**In situ X-rays diffraction measurements**

High temperature in situ X-ray (HTXRD) measurement was performed on a SmartLab diffractometer (Rigaku) with Co-Kα radiation. The spectra were collected
every ~5 minutes with scan-step size 0.04°. The precursor powder was packed on a graphite sample holder and heated/cooled at a ramp rate of 30-40 °C/min and holding at 850 – 950 °C for desired time periods in nitrogen atmosphere with constant flow or cut off flow at certain temperatures.

S2. Ionic conductivity measurements

Densification process of LLZO pellets (undoped cubic, undoped tetragonal, cubic Ga doped) were all performed by annealing 1 mm thick pellet (13 mm diameter) at 1100 °C in air muffle furnace for 16 hours in alumina crucible surrounded by 1 gram of mother sacrificial powder. The final pellets were polished in glove box and a silver paste was deposited in both sides. The pellets were tested between two stainless steel spacers in coin-cells. Electrochemical impedance spectroscopy measurements were performed at 20, 40, 60 and 80 °C with an AC amplitude of 5 mV and a frequency range of 250 kHz to 10 mHz at 0.0 V versus open circuit voltage (OCV). The temperature dependence of the total ionic conductivity (Arrhenius plot) for each LLZO pellet can be expressed by the following Arrhenius equation, eq.1:

$$\sigma = \frac{A}{T} \exp\left(-\frac{E_a}{k_B T}\right)$$

where $\sigma$ is the ionic conductivity, $T$ the absolute temperature, $A$ the pre exponential constant, $k_B$ the Boltzmann constant and $E_a$ is the activation energy for the ionic conductivity. $E_a$ was determined from the slope of the log($\sigma T$) versus $1/T$ plot.

S3 Morphology and elemental composition analysis

LLZO surfaces were analyzed using scanning electron microscope (SEM) Lyra 3 by TESCAN and elemental composition obtained using windowless energy dispersive spectrometer (EDXS) Extreme by Oxford instruments. Samples were cooled at -45 °C using a Deben peltier coolstage stage to prevent damage and heating of the LLZO during the observation. The micrograph and X-ray map were acquired at an accelerating voltage of 5 kV, a probe current of 500 pA, and a working distance of 10 mm.

S4 Transmission electron microscopy and chemical mapping

High resolution transmission electron microscopy images (HRTEM) and bright-field images in scanning mode (BF-STEM) were acquired on a JEOL JEM-2200FS
transmission electron microscope operated at 80 kV or 200 kV (point resolution 0.19 nm at 200 kV). Chemical mapping was performed using an energy dispersive X-ray spectrometer in scanning mode (STEM-EDXS) by measuring Ga-K and La-L X-ray lines. For the Li content, we used electron energy loss spectroscopy (STEM-EELS) from Li-K (~55 eV) and La-N (~115 eV) lines. The LLZO powder samples were grinded in toluene solution and deposited on holey-carbon support grids. The parameters of STEM-EELS acquisition were convergence semi-angle $\alpha = 11$ mrad and collection semi-angle $\beta = 8$ mrad. Conventional quantification techniques were applied as implemented in Gatan Digital Micrograph™ (Gatan, Inc.), consisting in pre-edge background extrapolation and subtraction using a power-law function, and modelling the ionization edges with atomic Hartree-Slater models (Egerton, 2011). We limited the analysis to crystals with a thickness $t/\lambda < 1.5$ ($\lambda$ the inelastic mean free path), to keep a reliable quantification from the ionization edges. At higher thickness, the multiple scattering of plasmons severely reduces the accuracy in the extraction of the edges. At the condition of measurements, $\lambda = 115$ nm as calculated according to Malis et al. and Everton et al. Figure S12 illustrates the Li-K and La-N\textsubscript{4,5} quantification procedure from the spectrum image, considering the profile of Figure 4c of the manuscript as example. Due to the presence of the other low-loss edges in the pre-edge region of Li-K, complicating the extrapolation, and the low accuracy expected by using Hartree-Slater models for N\textsubscript{4,5} edges, we assume a relative error in the quantification of Li/La of 20%. We did not quantify the Zr-N\textsubscript{2,3} edge due to its overlapping with the plasmon peak from double scattering and the absence of a reliable model for N\textsubscript{2,3} edges.

S5. Li$_2$CO$_3$ decomposition

Like almost all syntheses, side reactions can have an impact on the overall effect of the product. In this subsection, we discuss the premature decomposition of Li$_2$CO$_3$, which by producing Li$_2$O reduces the accessibility of part of the lithium. We believe that it is the relative reaction rate of Li$_2$CO$_3$ decomposition and its reaction with other solid precursors that controls the lithium loss. This relative rate is in turn controlled by the CO$_2$ concentration with the N$_2$ gas flow.

When the partial pressure of CO$_2$ approaches or reaches the equilibrium partial pressure of CO$_2$ for the reaction,

\begin{equation}
\text{Li}_2\text{CO}_3 \rightarrow \text{Li}_2\text{O} + \text{CO}_2,
\end{equation}
the decomposition of Li$_2$CO$_3$ significantly slows down or stops completely. For the readers’ convenience, we adopt from the literature$^{3-5}$ the equilibrium CO$_2$ pressures at atmospheric pressure as a function of temperature in Table S1, where the units are changed to SI. Since at these temperatures the gas is well described by the ideal gas model, the partial pressures of CO$_2$ can be safely represented by the CO$_2$ concentration, as presented in the 3$^{rd}$ row of Table S1.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>883</th>
<th>996</th>
<th>1083</th>
<th>1161</th>
<th>1238</th>
</tr>
</thead>
<tbody>
<tr>
<td>P (Pa)</td>
<td>133</td>
<td>533</td>
<td>2000</td>
<td>4266</td>
<td>8398</td>
</tr>
<tr>
<td>Ratio (%)</td>
<td>0.13</td>
<td>0.53</td>
<td>1.97</td>
<td>4.21</td>
<td>8.29</td>
</tr>
</tbody>
</table>

**Table S1:** Equilibrium CO$_2$ pressure of Li$_2$CO$_3$ decomposition. Adopted from (cite report 3). The melting point of Li$_2$CO$_3$ at ambient pressure is 996 K.

During the synthesis of LLZO, this side reaction of Li$_2$CO$_3$ decomposition creates Li$_2$O pellets, which are quite stable at our synthesis temperature, and it is difficult to incorporate them into the desired final product LLZO. The best scenario for us is that Li$_2$CO$_3$ melts and mixes well with LZO without CO$_2$ emission and then emits CO$_2$ to finish the final step (eq. 3).

\[
eq 3 \quad 7\text{Li}_2\text{CO}_3 + \text{La}_2\text{O}_3 + 2\text{La}_2\text{Zr}_2\text{O}_7 \rightarrow 2\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12} + 7\text{CO}_2
\]

However, it is evidently impossible to completely prevent the premature decomposition of Li$_2$CO$_3$. On the other hand, the reaction between Li$_2$CO$_3$ and La$_2$Zr$_2$O$_7$ and La$_2$O$_3$ takes place simultaneously, but because of the incorporation of Li$_2$O into LZO; i.e., the formation of LLZO is exothermic, the equilibrium partial pressure of reaction (3) will be higher than that of reaction (2). While the presence of CO$_2$ tends to suppress both reactions, its suppression of reaction (3) is more stringent. It is commonly accepted that reactions between solids are slower than reactions involving only liquid and gas. In our case, above 750 °C, we have liquid Li$_2$CO$_3$, gaseous CO$_2$, solid LZO and, from the decomposition of Li$_2$CO$_3$, solid Li$_2$O. Therefore, without environmental CO$_2$, Li$_2$CO$_3$ will decompose the fastest,
producing Li$_2$O, whose reaction with LZO to form LLZO is the slowest. Suppressing Li$_2$CO$_3$ decomposition reduces premature CO$_2$ emission but leaves solid LZO to react with liquid Li$_2$CO$_3$ faster and, due to the closer contact of solid-liquid than solid-solid interfaces, more reliably than with solid Li$_2$O.

To this end, we enclosed the reactants in a chamber with the N$_2$ gas flow shut off to create a CO$_2$-rich environment, where CO$_2$ comes from inevitable Li$_2$CO$_3$ decomposition.

The effect of this decomposition suppression is quite phenomenal, as impurities due to the loss of lithium are drastically reduced. From a theoretical point of view, we calculated gas diffusion by solving the CO$_2$ concentration inside the chamber during the hour of the synthesis. We refer the readers to the Methods section for the details of this calculation. Briefly, we wished to see how CO$_2$ emission (from the Li$_2$CO$_3$ decomposition) affects the CO$_2$ partial pressure around the sample, which in turn affects the rate of Li$_2$CO$_3$ decomposition. If, in the end, we find a CO$_2$ concentration close to or higher than that at equilibrium, we can conclude that the decomposition of Li$_2$CO$_3$ will be suppressed; if it is far less than that, the decomposition shall not be affected significantly.

Without further knowledge, we assumed a constant temperature of 750 °C, i.e., the temperature when Li$_2$CO$_3$ starts to decompose, and a 2-dimensional model. The rate of CO$_2$ emission was also assumed to be uniform over the hour, which translates to a constant CO$_2$ injection rate of 0.05 g/hour through the surface of the sample. The dimension of the chamber was Ø7 mm*1476 mm, where the gas flow can be controlled. The sample is placed near the middle of the chamber. The CO$_2$ injection rate is proportionally adjusted to provide a realistic concentration. Since we are most interested in the concentration profile in the longitudinal section of the chamber, we believe this simplified 2-dimensional model suffices.

**S6-Numerical Methods**

The numerical simulation of CO$_2$ emissions in a still nitrogen atmosphere was carried-out using Ansys Fluent. A 2D geometry was used to model the tubular oven. One end of the oven is modeled with a “velocity inlet” where velocity is set to 0 (see label C of Figure 5). The other end where a check valve is present is modeled using an “outlet vent” boundary conditions that basically acts as a restriction (see label A of Figure 5). All other surfaces are walls where net diffusive and heat transfer fluxes do not occur. CO$_2$ is introduced at a rate of 0.1 g/h in the simulation domain by
means of source terms within the species model (see area labeled B in Figure 5). Figure 5a shows the CO$_2$ concentration gradient after 1 hour. The CO$_2$ concentration at the surface of the sample reaches 12%.

![XRD spectra of Ga-LLZO (red) and un-doped LLZO (blue) cooled to RT.](image)

**Figure S1** XRD spectra of Ga-LLZO (red) and un-doped LLZO (blue) cooled to RT.
Figure S2. *in situ* XRD patterns of undoped LLZO from 26 °C to 826° C with N₂ constant gas flow.
Figure S3. In situ XRD patterns of undoped LLZO from 26 °C to 804 °C with stop gas flow.
Figure S4. In-situ XRD patterns of undoped LLZO from 26 °C to 804 °C with stop gas flow.
Figure S5. In-situ XRD patterns of undoped LLZO under vacuum.
Figure S6: tetragonal LLZO obtained annealing 4 gr instead of 1 gram in tubular furnace with gas flow.
Figure S7. Schematic representation of tubular furnace.
Figure S8. SEM backscattered electron image of Ga:LLZO after synthesis and EDS mapping.
Figure S9. a) XRD pattern, b) SEM image and c) EDS spectrum of scale up Ga:LLZO synthesized with no gas flow.
Figure S10. Thermogravimetric analysis of Li$_2$CO$_3$ and Li$_2$CO$_3$ + Ga$_2$O$_3$. 
Figure S11. XRD pattern of a) undoped LLZO after synthesis, b) undoped LLZO after sintering under N₂ flow and c) undoped LLZO after sintering with no gas flow.
Figure S12. a) Annular dark field (ADF-STEM) survey image for the particle from Figure 4c of the manuscript. The spectrum image for the EELS profile is in green. The red cross indicates the beam parking position in vacuum before the spectrum image acquisition. b) The extracted
spectrum from the inner point of the spectrum image. From the intensity of the elastic peak with respect to the total area of the spectrum (log-ratio method) we estimated a thickness \( t/\lambda = 0.99 \), which corresponds to \( t \approx 113 \) nm. c) Enlarged view of the spectrum from a). A plasmon at 15 eV is indicated, together with the Zr-N\(_{2,3}\) edge, the Li-K edge, and La-N\(_{4,5}\) edge. For better reading, the La-N\(_{4,5}\) edge is shifted by +15 eV to accounts for the delayed offset as expected for high-shell electrons. The Li-K edge onset is broadened by multiple scattering at the present thickness. We opted for extrapolating the conventional power-law background (BG) in the pre-edge region for Li-K while keeping a low but positive residual intensity in the pre-edge region of La-N\(_{4,5}\) (see the full red line in the spectrum).

References


