Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.
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Halogenation of $Li_7La_3Zr_2O_{12}$ Solid Electrolytes: A Combined Solid-State NMR, Computational and Electrochemical Study - Supporting Information

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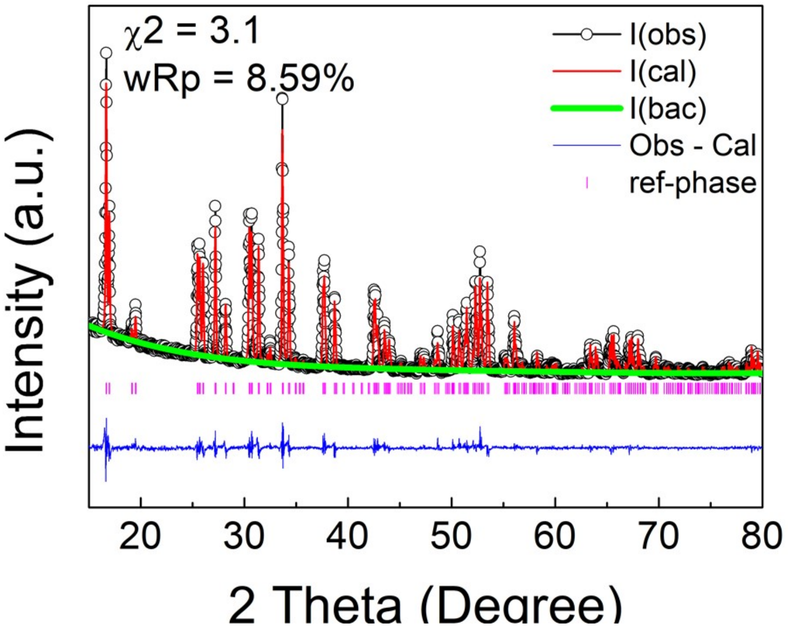

Figure S1. Observed, calculated and difference profiles from refinement of $Li_7La_3Zr_2O_{12}$.

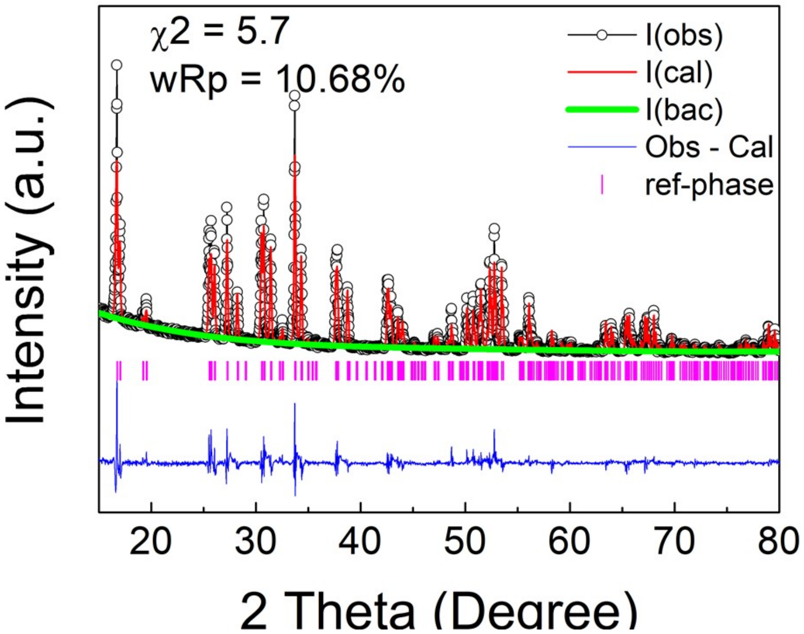

Figure S2. Observed, calculated and difference profiles from refinement of 1PE – LLZO.

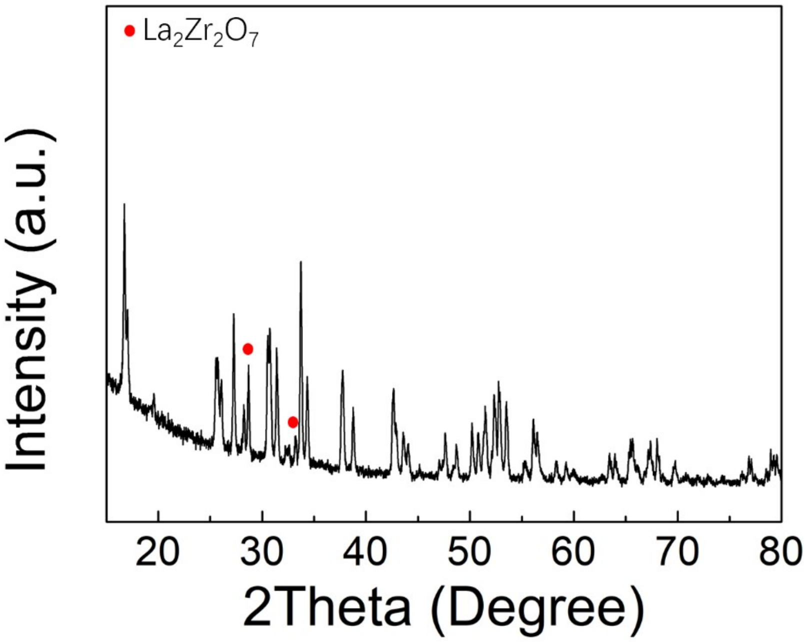

Figure S3. XRD of $Li_{6.5}La_3Zr_2O_{11.5}Cl_{0.5}$ made using LiCl as Cl source via solid state method.

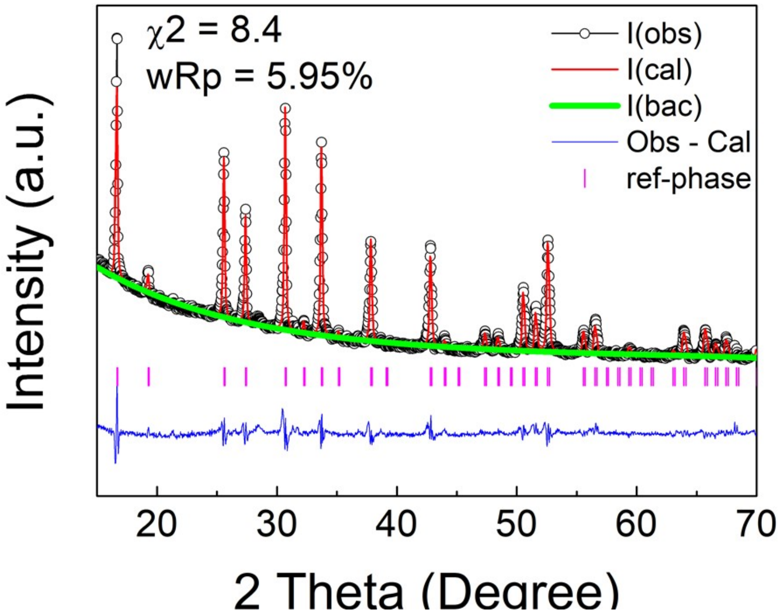

Figure S4. Observed, calculated and difference profiles from refinement of 1PVC – LLZO confirming the successful formation of a cubic garnet.

Variable-Temperature Solid-State NMR Studies

Experimental

Variable-temperature (VT) ^{6}Li and ^{35}Cl MAS NMR spectra were acquired for 1.0PVC:LLZO between 19 and 100 °C. Spectra were acquired using the same experimental details described in the main text. In all cases, temperatures were calibrated using the ^{1}H signal of MeOH and, thus, all temperatures quoted reflect the true temperature of the sample. Additional experiment specific details are given in the relevant figure caption.

Discussion

Variable-temperature NMR studies can provide valuable insight into the dynamics and ion mobility of a system. Variable-temperature ^{6}Li MAS NMR spectra were acquired for the 1.0PVC:LLZO sample, as shown in Figure S5(a). As the temperature is increased from 19 to 100 °C, the broad resonance centred at δ = 1.24 ppm narrows. The corresponding variation in the full width at half maximum (FWHM) is shown in Figure S5(c). Above 35 °C, the onset of narrowing (T_{onset}), the FWHM gradually decreases. This is indicative of Li-ion mobility. Unfortunately, it was not possible to obtain the full motional narrowing curve, as the temperature range that can be explored is limited by hardware requirements. However, using the method reported by Waugh and Fedin, it is possible to estimate the activation energy for motion using T_{onset}.[1,2] In this case, an activation energy of ~0.5 eV is estimated using T_{onset} = 35 °C. It is noted that the values of FWHM at low temperatures contain significant errors due to the overlap of the two resonances. Additionally, as the temperature is increased, changes are observed in the sharp resonance at $\delta = 0.09$ ppm. Firstly, as the temperature is increased, the intensity decreases relative to the broad resonance. Furthermore, a slight change in chemical shift is observed. As it is not possible to acquire variable temperature impedance data for these systems (owing to the instability at high temperatures and the requirement for high temperature sintering in order to prepare a suitably dense pellet) the estimated activation energy provides useful insight into the ion mobility of the system.

Variable-temperature ^{35}Cl MAS NMR spectra were also acquired for 1.0PVC:LLZO between 19 and 100 °C. As shown in Figure S5(b), as the temperature is increased a decrease in chemical shift is observed from $\delta = 1.84$ to -7.33 ppm. In addition to this, the lineshape narrows with increasing temperature. However, it is noted that, above 84 °C, a slight shouldering is observed towards lower frequency. This could suggest the presence of additional, unresolved sites at high temperatures and/or the presence of disordering.

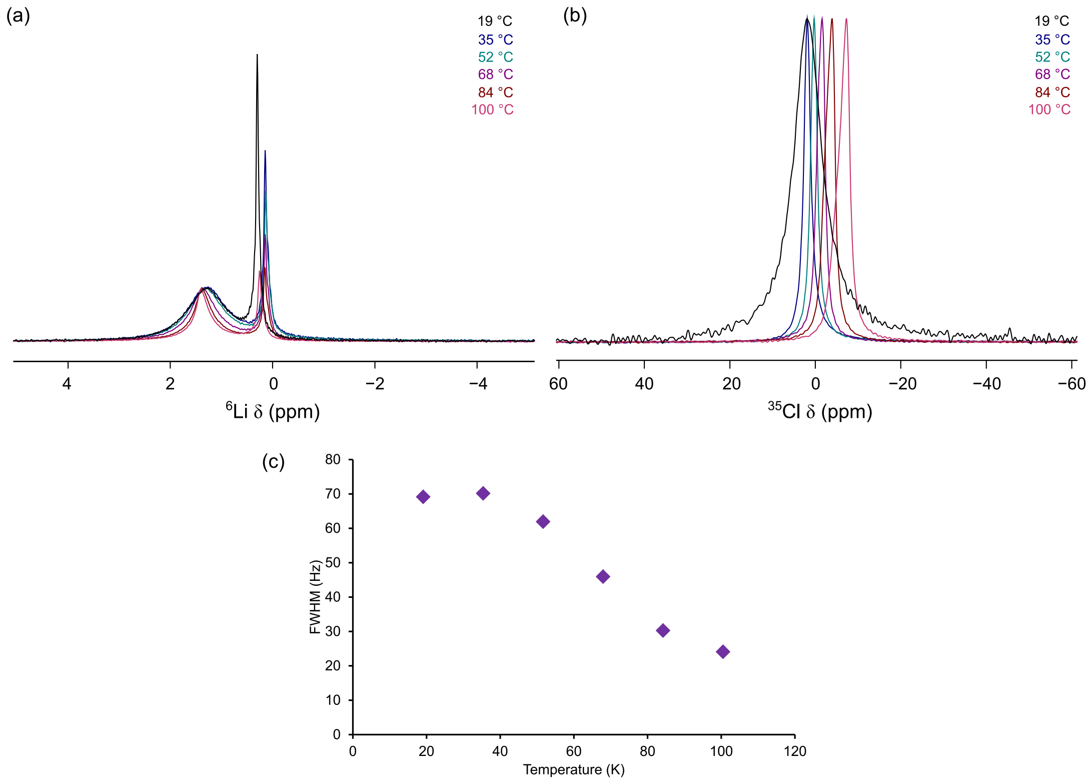

Figure S5. Variable-temperature (a) ^{6}Li and (b) ^{35}Cl MAS NMR spectra for 1.0PVC:LLZO. Each spectrum is the result of averaging (a) 200 and (b) 1600 transients with a recycle interval of (a) 8 and (b) 0.4 s. A MAS rate of 10 kHz was used. In (a), spectra are normalised to the intensity of the resonance at δ = 1.24 ppm. In (c) the variation in FWHM with temperature for the resonance at δ = 1.24 ppm in the VT ^{6}Li MAS NMR data is shown.

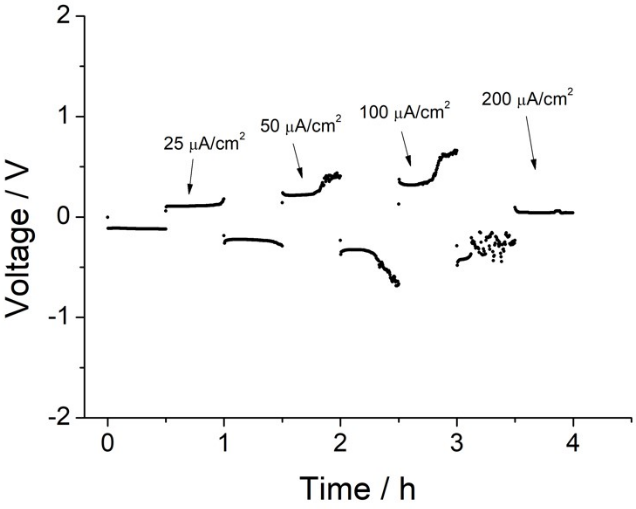

Figure S6. Constant current cycling testing of Li/LLAZO/Li cell from 0.025 mA/cm^2 to 0.2 mA/cm^2.

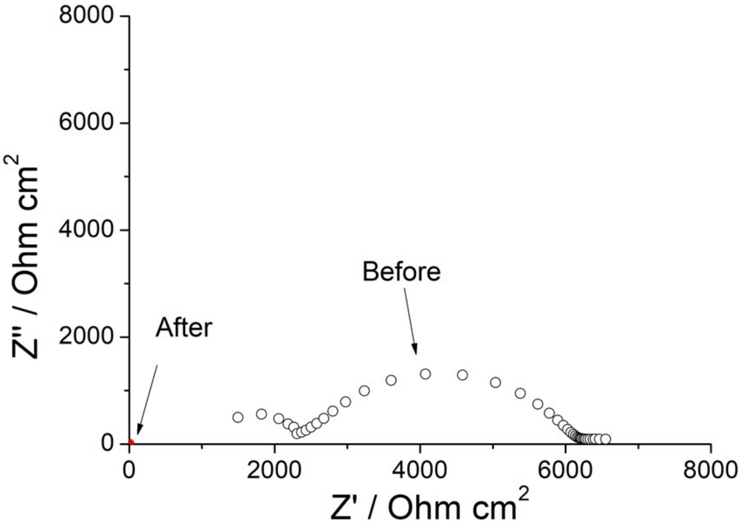

Figure S7. EIS of the cell before and after cycling of Li/LLAZO/Li cell.

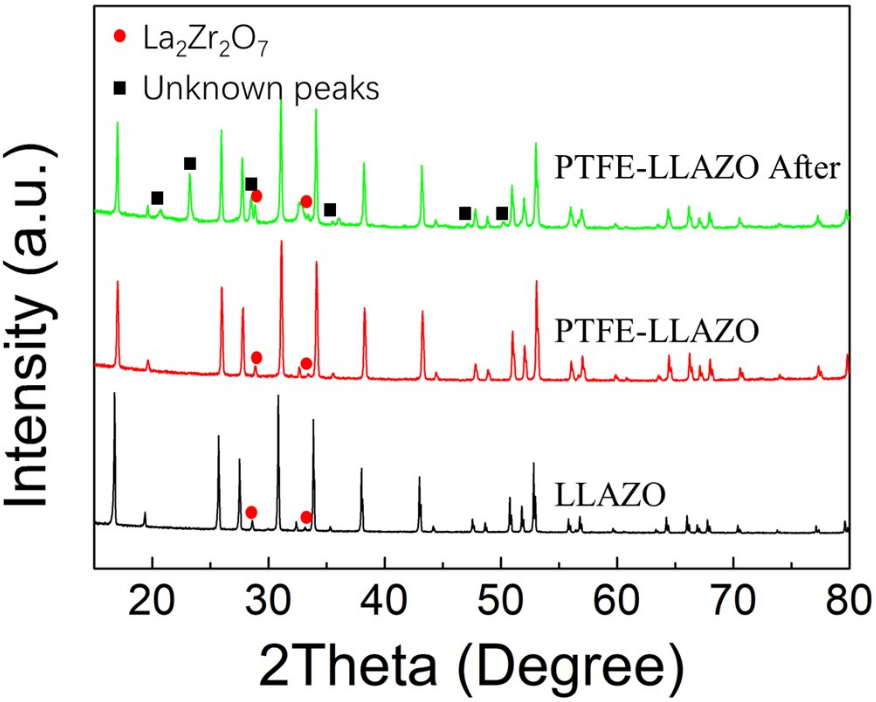

Figure S8. XRD patterns of LLAZO, LLAZO(PTFE) pellet, and LLAZO(PTFE) pellet after the cycling test.

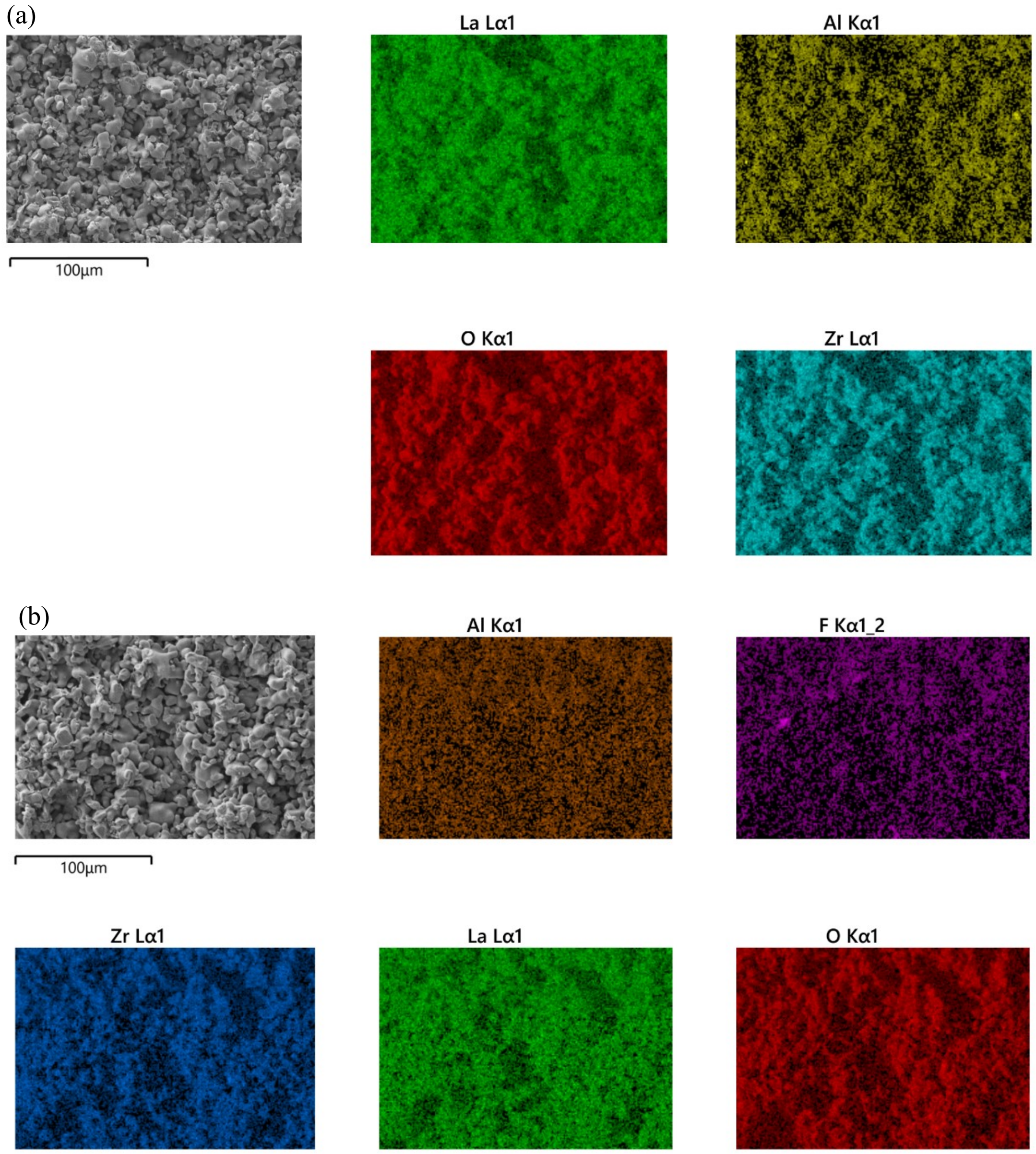

Figure S9. SEM and EDX of (a) LLAZO; (b) PTFE-LLAZO pellet.

References

1. J. Waugh and E. I. Fedin, *Sov. Phys. Solid State*, 1963, **4**, 1633–1636.
2. A. Kuhn, S. Narayanan, L. Spencer, G. Goward, V. Thangadurai and M. Wilkening, *Phys. Rev. B*, 2011, **83**, 094302.