Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supporting Information for:

Will the competitive future of solid state Li metal batteries rely on a ceramic or a composite electrolyte?

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The impedance Nyquist plots were analyzed with the Zview software using the following equivalent circuits. For the ceramic electrolyte, the model used for fitting contains two R/CPEs in parallel, one representing the total ionic conductivity of the pellet (bulk + grain) and the other one the resistive interface between the pellet and the two Li electrodes (Fig. S1a). At low temperatures, the Nyquist plot of the composite membrane is composed of a semi-circle followed by a tail, representative of the membrane resistance and the ion blocking (stainless steel) electrodes, respectively (Fig. S1c). In this case, the Nyquist plot can be fitted using the equivalent circuit shown in Fig. S1b. However, the semi-circle representing the membrane resistance is not well resolved at high temperatures (Fig. S1d) due to equipment limitations and the value for the membrane resistance is obtained from the intercept of the Nyquist plot with the x axis. For consistency between low and high temperature data analysis, the membrane resistance was taken as the intercept of the blocking electrodes tail with the x axis for all temperatures.

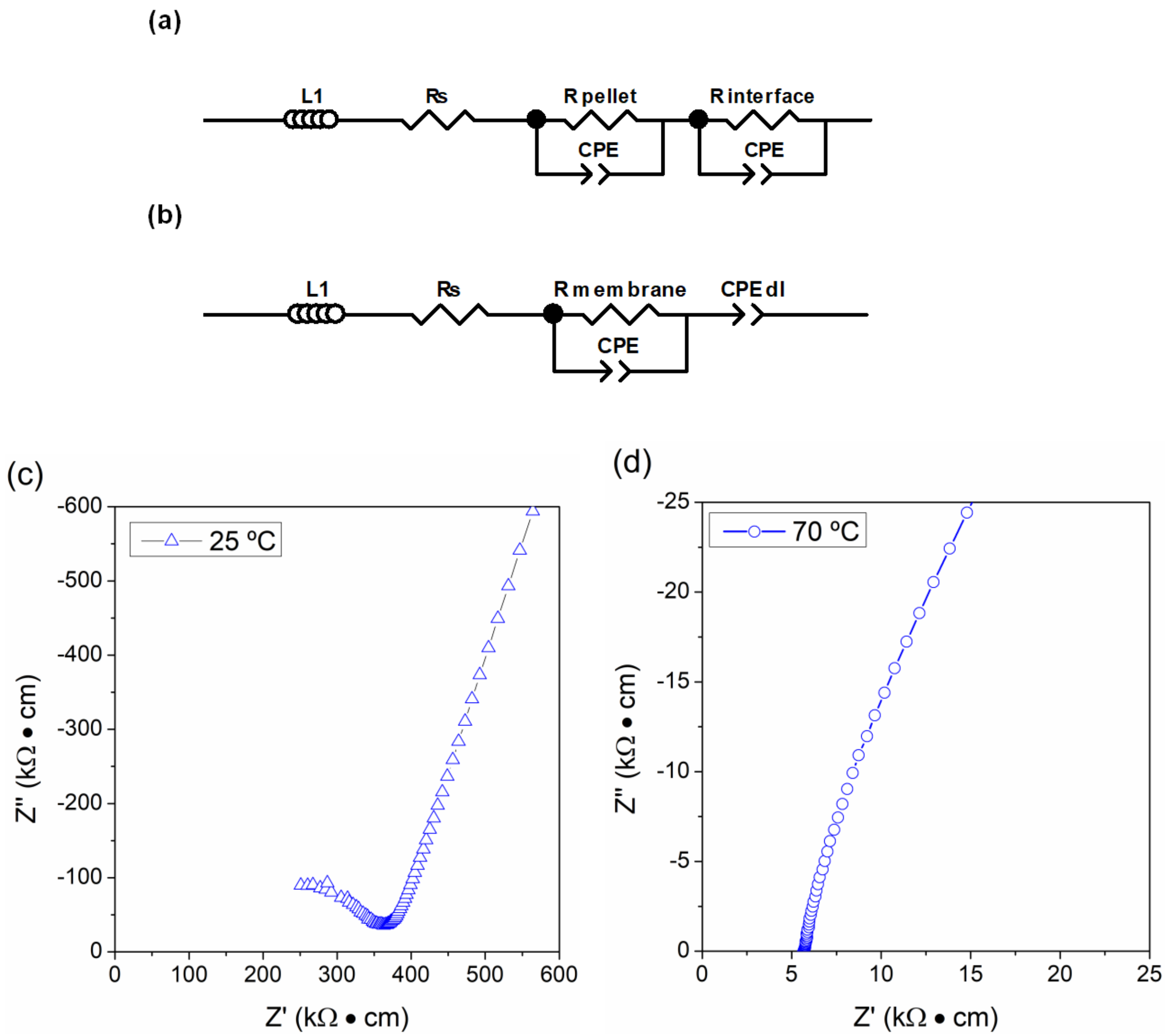

Fig. S1. Equivalent circuit used for fitting the Nyquist plots of (a) the ceramic electrolyte, with R_{Pellet} being the total (bulk + grain) resistance of the garnet and $R_{Interface}$ the resistance between the garnet and the Li electrodes and (b) the composite membrane electrolyte, composed by the resistance of the membrane and the double layer capacitance representing the blocking electrodes. Nyquist impedance plots of the composite membrane at (c) 25 °C and (d) 70 °C, representative of the behavior observed at low and high temperatures, respectively.

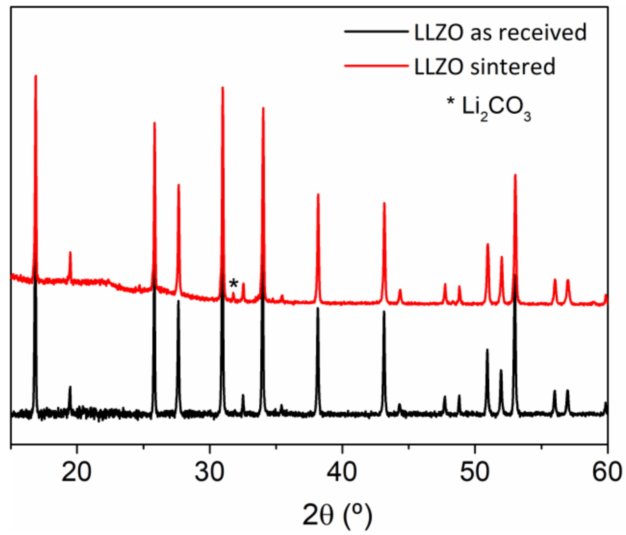

Fig. S2. XRD results of ceramic LLZO before (black) and after (red) the sintered step at 1200 °C in dry O_2, matching the cubic phase of LLZO *[ICSD #261302].*

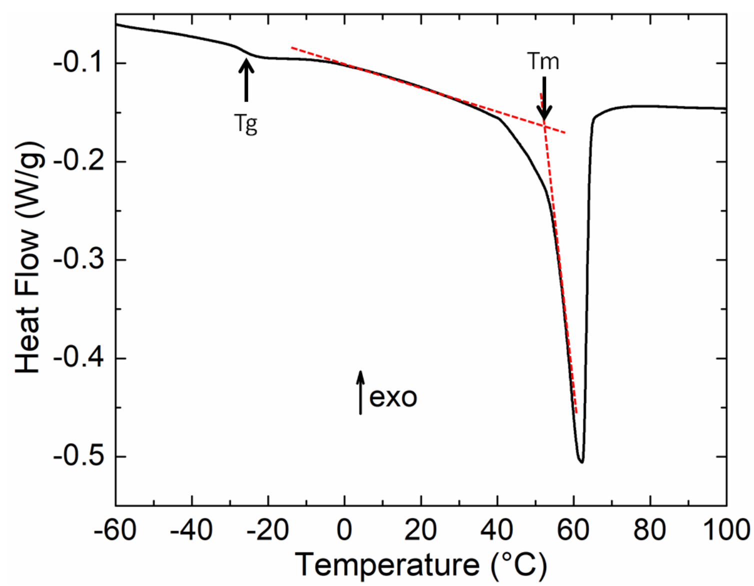

Fig. S3. DSC of the composite membrane highlighting the melting temperature (53 °C) and the glass transition temperature (-27 °C).

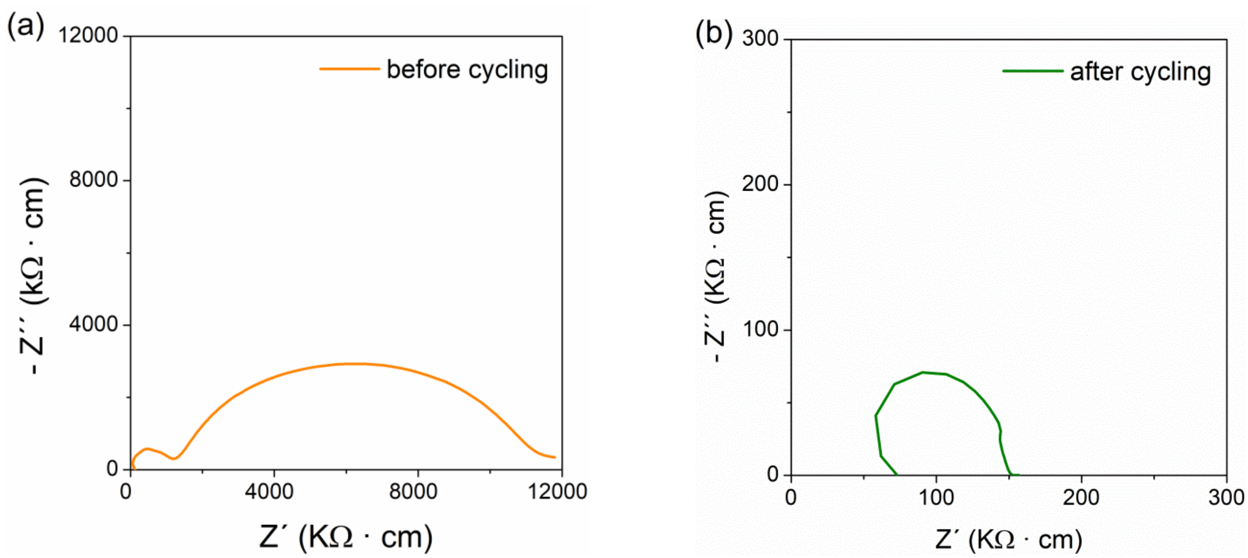

Fig. S4. Nyquist impedance plots of the Li/ceramic electrolyte/Li system (a) before and (b) after stripping plating test, measured at room temperature.

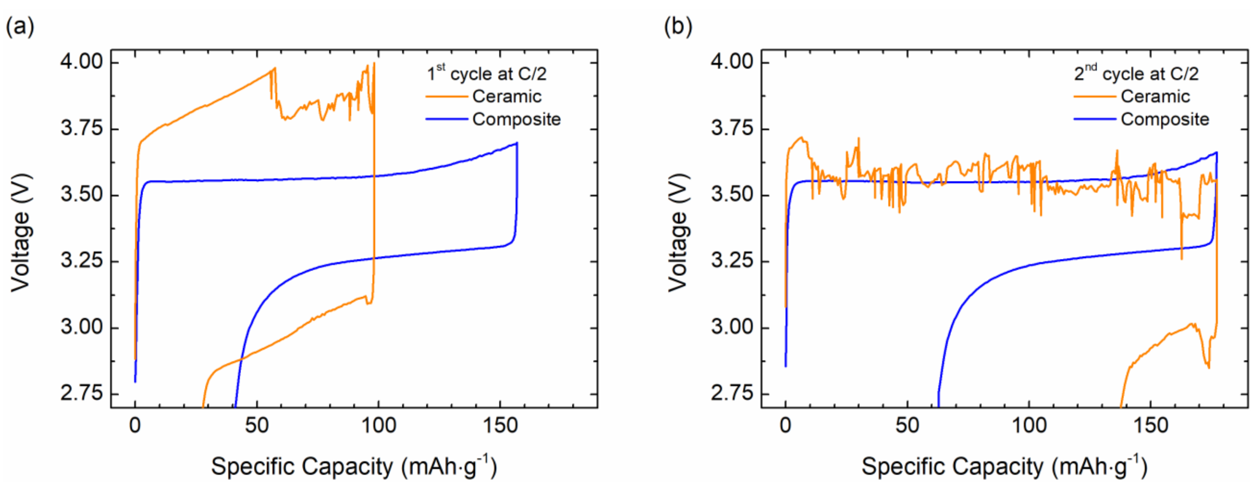

Fig. S5. Voltage profiles of the (a) first and (b) second cycle at C/2 for the two solid state batteries showing the voltage instability of the cell with the ceramic electrolyte above 3.7 V.

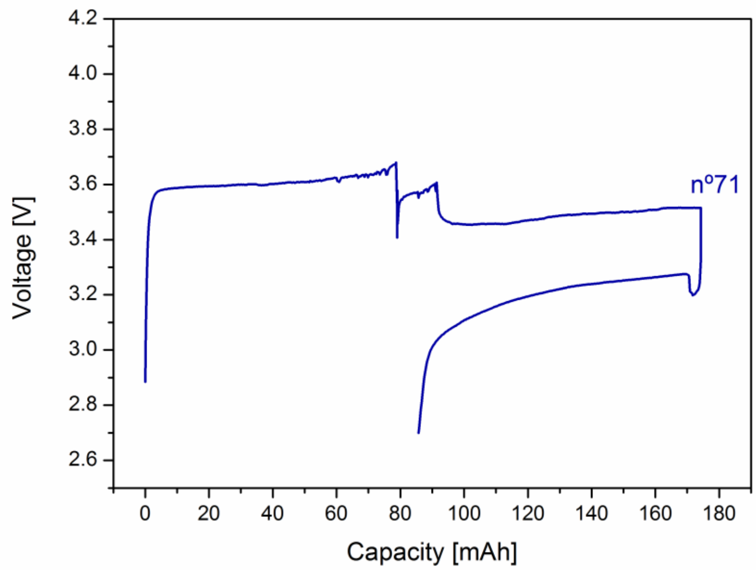

Fig. S6. Voltage profile of cycle nº 71 of the SSB based on the composite membrane showing a sudden drop in polarization, indicating a drop in the cell resistance.