Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Supplementary Information

All Ceramic Cathode Composite Design and Manufacturing towards Low Interfacial Resistance for Garnet-Based Solid-State Batteries

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Figure S1. SEM images of as-calcined LLZO powder.

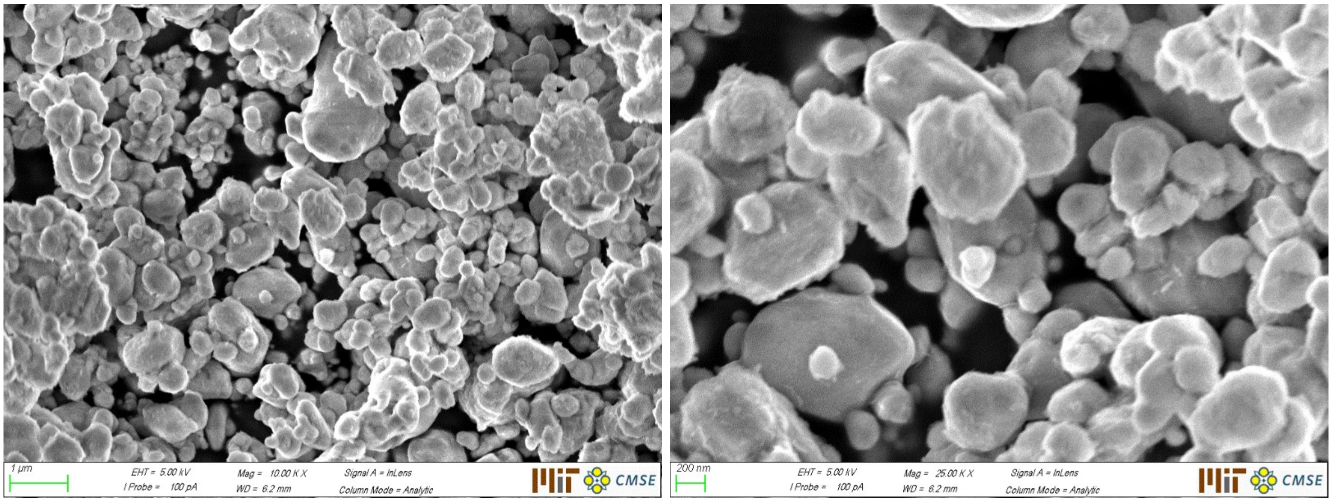


Figure S2. Thickness of $LiFePO_4$-LLZO-Carbon cathode fired at 300 °C.

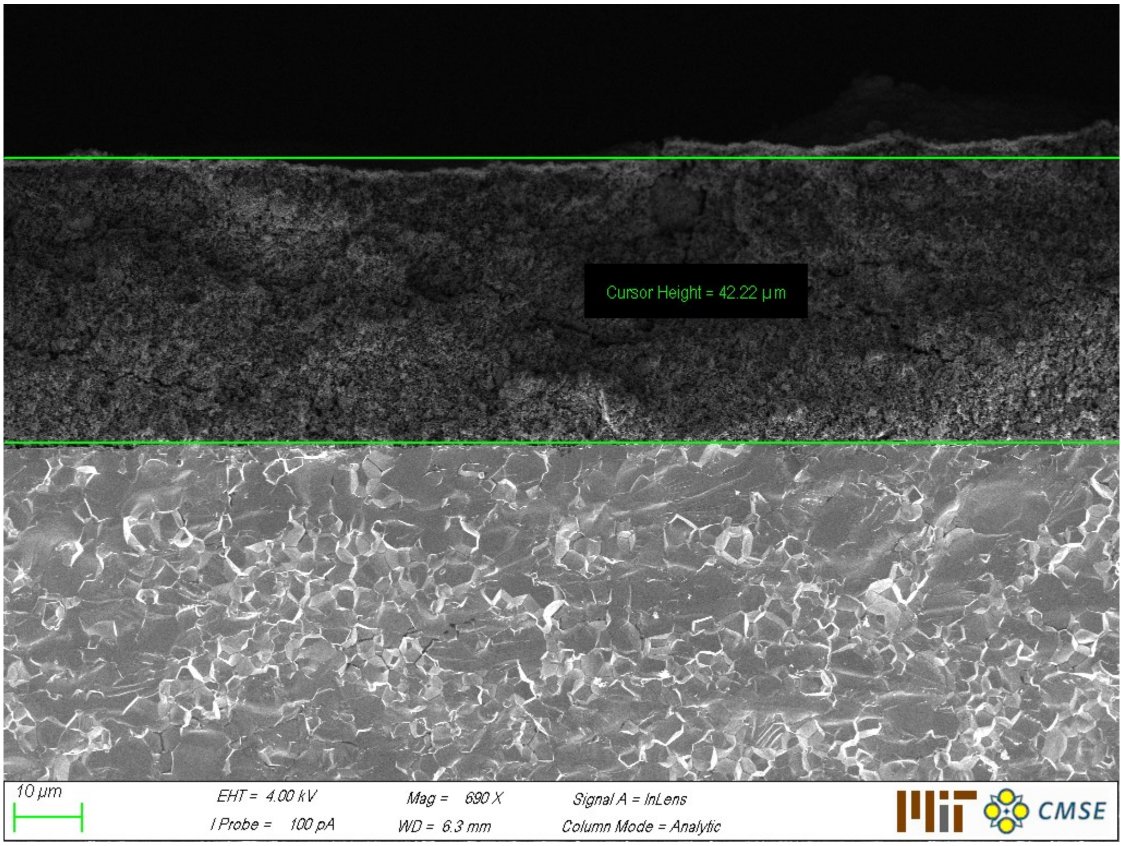


Figure S3. Energy Dispersive X-Ray Spectroscopy (EDS) mapping of LFPO-LLZTO-Carbon composite.

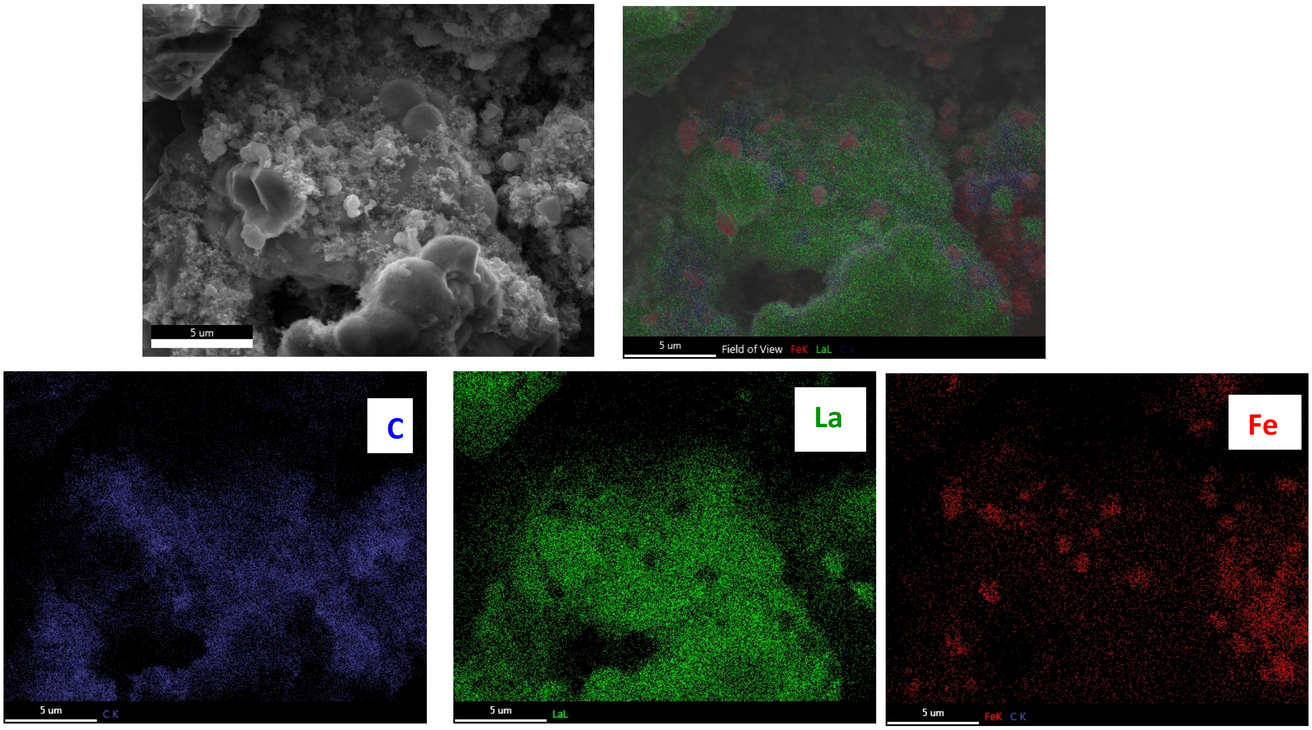
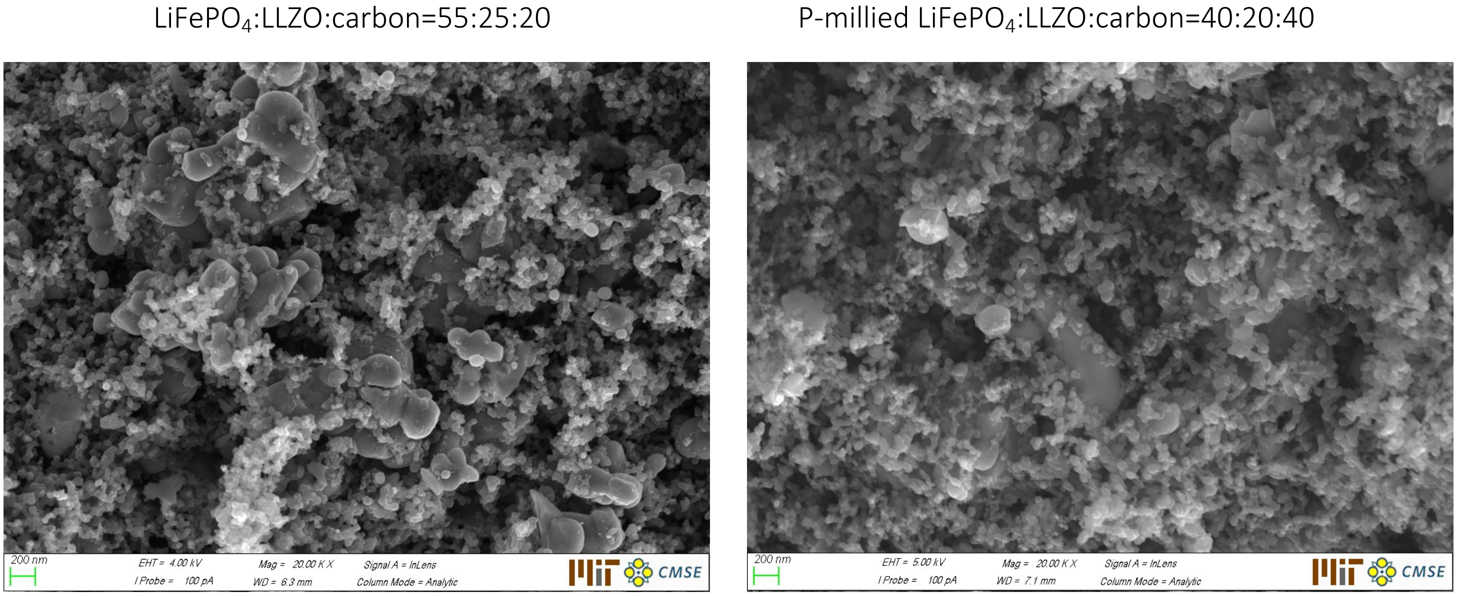


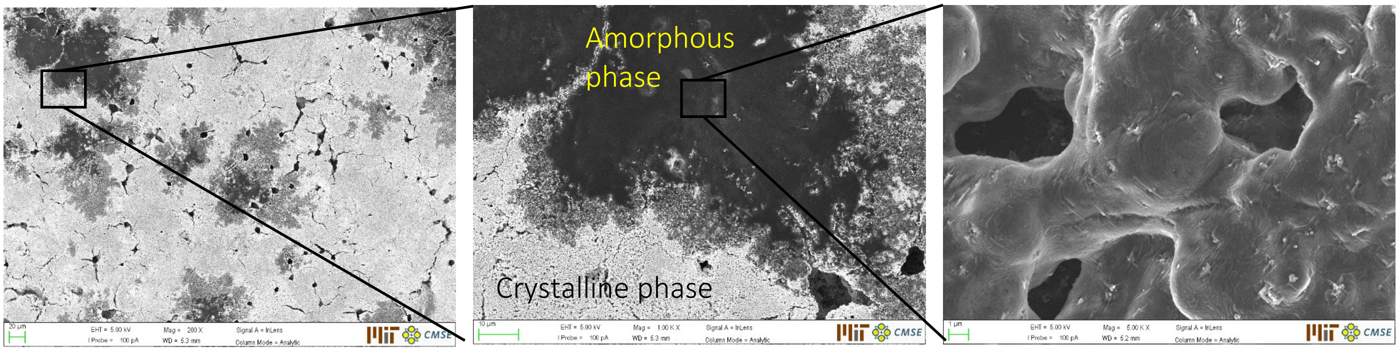
Figure S4. SEM images of different cathode composite.


LiFePO$_4$:LLZO:carbon=55:25:20

P-millied LiFePO$_4$:LLZO:carbon=40:20:40

Figure S5. SEM images of LCO infiltrated solution followed by firing at 600 and 700 ^{o}C for 1h. 600 ^{o}C annealed infiltrated LCO contains amorphous LCO and crystalline-like LCO.

600 ^{o}C/ 1h



700 ^{o}C/ 1h

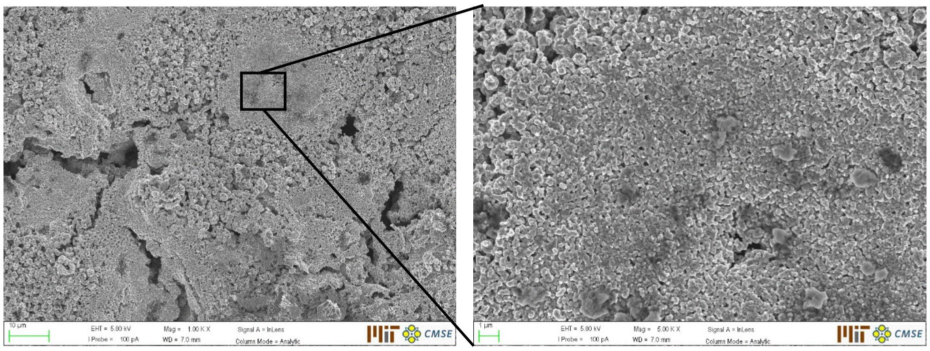


Figure S6. SEM images of $LiCoO_2$–LLZO interface prepared at 700 °C.

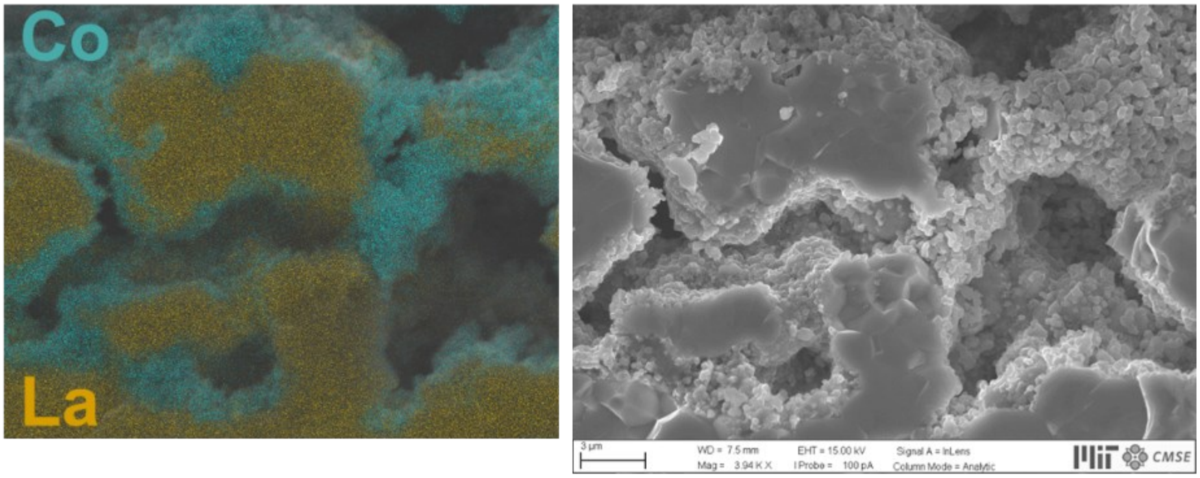


Figure S7. Impedance spectra of the full cell before charging (**a**) and comparison of impedance spectra before and after 1st charging (**b**)

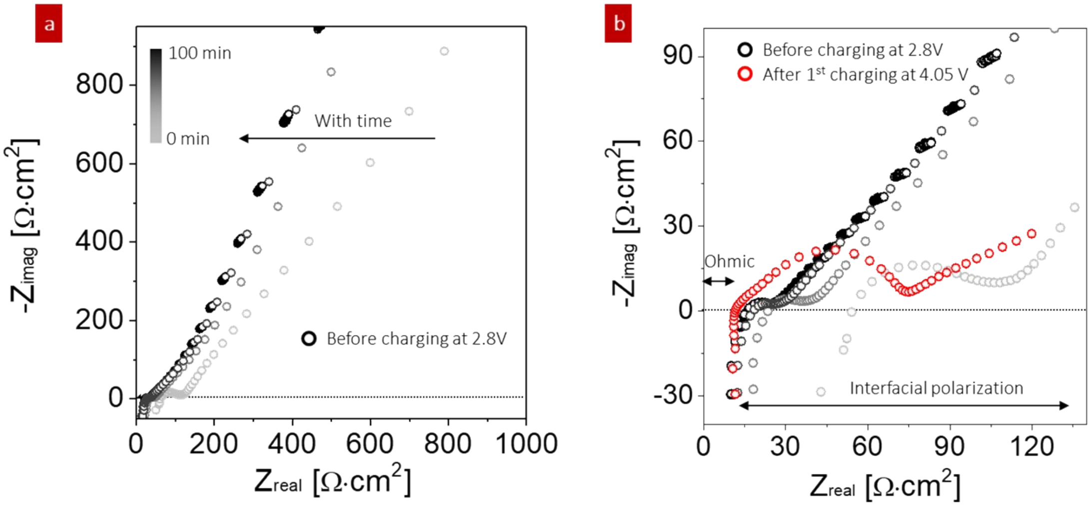


Fig. S7 presents impedance spectra of the as-prepared full cell. The as-assembled battery was introduced to a chamber heated to 80 °C, and impedance spectra were measured every 10 min, with the intention of stabilization of the spectra due to thermal equilibrium. In 100 min, the entire spectra (ohmic and polarization) were stabilized (**Fig. S7a, Fig. S7b** magnified view), and the impedance spectra after charging (**Fig. 4g** in the main text) were added for comparison. After the 1st charging, the total resistances decreased from > 500 $\Omega\cdot cm^2$ to 120 $\Omega\cdot cm^2$ while the ohmic resistance of the cell remained very similar, indicating that the change is responsible for the resistive compounds at the electrolyte/electrode interface or inside the electrode composite. The interfacial impedance can be reduced by either both removal of impurities or enhanced electronic conductivity of Li_xCoO_2 ($x < 1$) during charging. The former is possible based on the observed irreversible long plateau at 3.75 V; however, we believe that the best way to demonstrate the scenario was to examine the impedance spectra of the LCO–LLZO cathode composite after introducing a conductive phase. The introduction of a conductive phase in an oxide-based cathode composite is challenging because of the difficulty of finding co-sinterable oxide conductors that are compatible enough for high-temperature processes[1,2]. We believe that these additional measures could improve our understanding of the observed behavior.

Table S1. Equivalent circuit parameters used for fitting of EIS spectra in **Fig. 4g**.

L1+R1+R2/Q2+R3/Q3 +R4/Q4		After 1st cycle	After 14 cycle
	L1 [H]	1.178e-6	1.194e-6
	R1	17.89 Ω	14.66 Ω
		10.01 Ω·cm^2	8.209 Ω·cm^2
(RQ)2	R2	20.98 Ω	42.91 Ω
		11.74 Ω·cm^2	24.02 Ω·cm^2
	Q2 [F.s$^{(a-1)}$]	33.25e-6	7e-6
	a2	0.6589	0.7769
(RQ)3	R3	74.13 Ω	398.9 Ω
		41.51 Ω·cm^2	223.3 Ω·cm^2
	Q3 [F.s$^{(a-1)}$]	6.62e-6	5.523e-6
	a3	0.911	0.8222
(RQ)4	R4	25.27 Ω	29.01 Ω
		14.15 Ω·cm^2	16.25 Ω·cm^2
	Q4 [F.s$^{(a-1)}$]	1.877e-3	0.0127
	a4	0.3778	0.1415

Figure S8 Bode plots after 1st charge (black) and after 14th cycle (red)

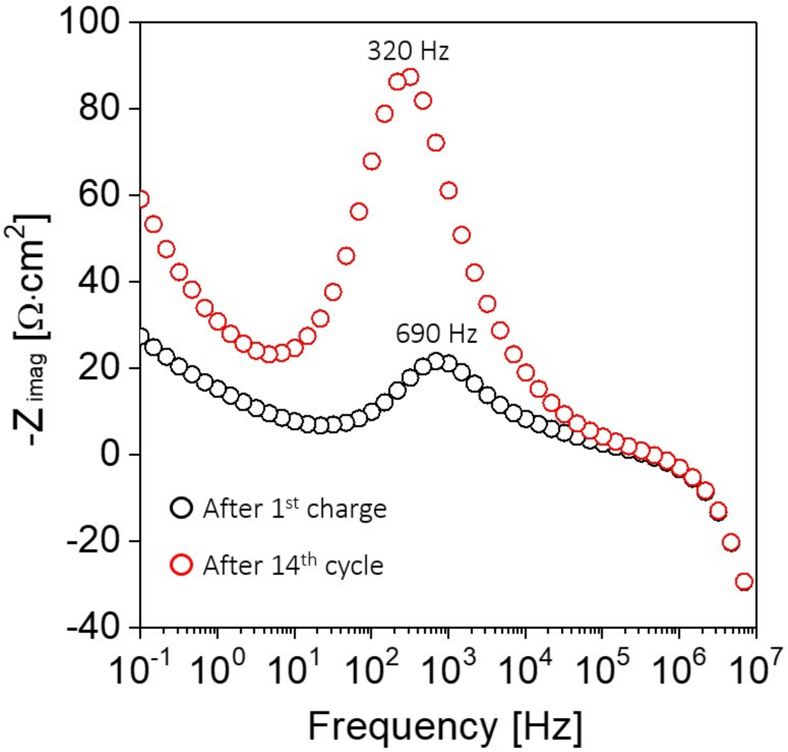


Figure S9. Impedance spectra of Li metal symmetrical cell before and after 100 cycles at current density of 0.1 mA/cm^2 at 80 °C.

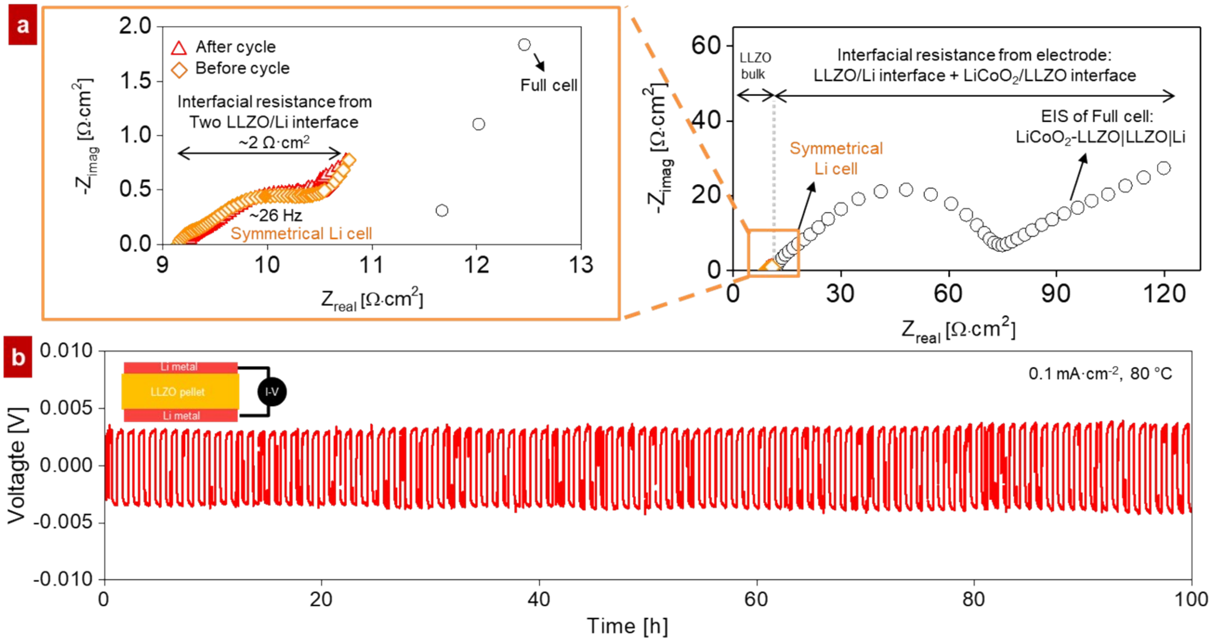
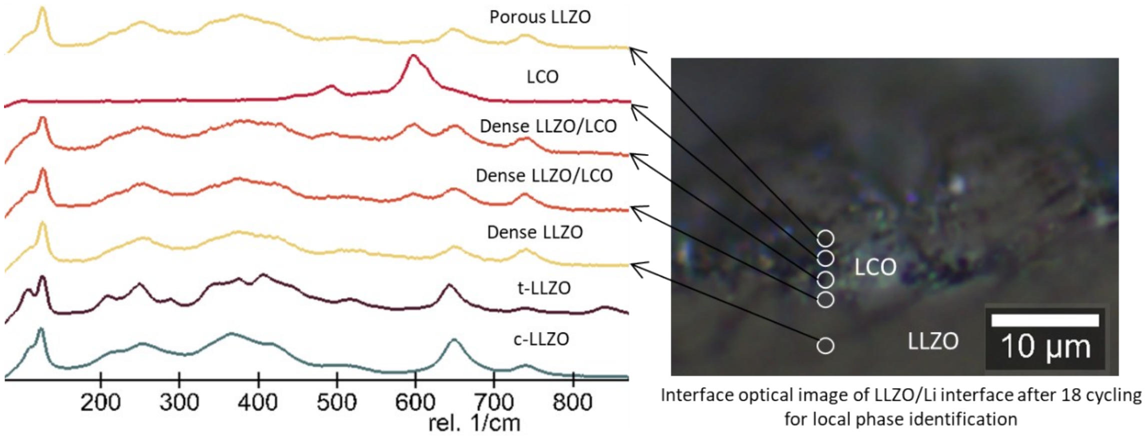
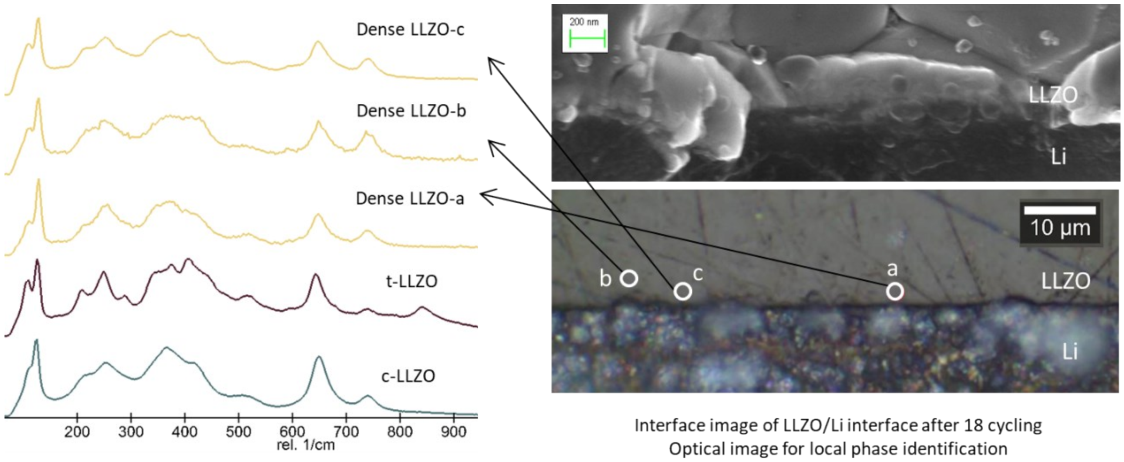


Figure S10 Raman spectra at LCO/LLO interface after cycling



Interface optical image of LLZO/Li interface after 18 cycling
for local phase identification

Figure S11 Raman spectra at Li/LLO interface after cycling



Interface image of LLZO/Li interface after 18 cycling
Optical image for local phase identification

Figure S12 SEM image of LCO/LLZO interface after cycling

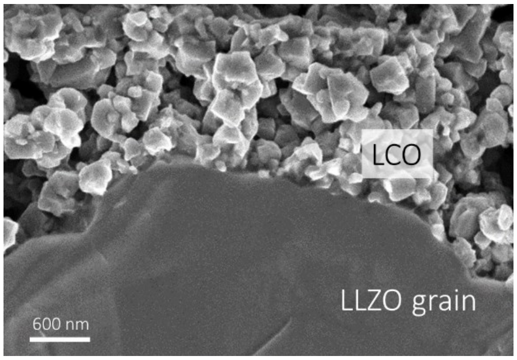


Figure S13 The open-circuit voltage decays in the 2-h rest of the full cell ($LiCoO_2$-LLZO|LLZO|Li) at 80 °C after the fully charged state of 4.05 V at 0.05C. The self-discharge % was evaluated using ΔV/1.05 V (4.05−3.00) *100.

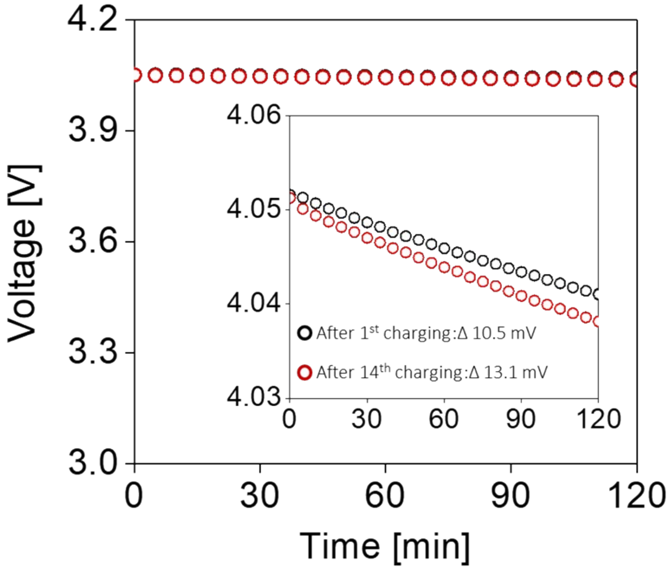
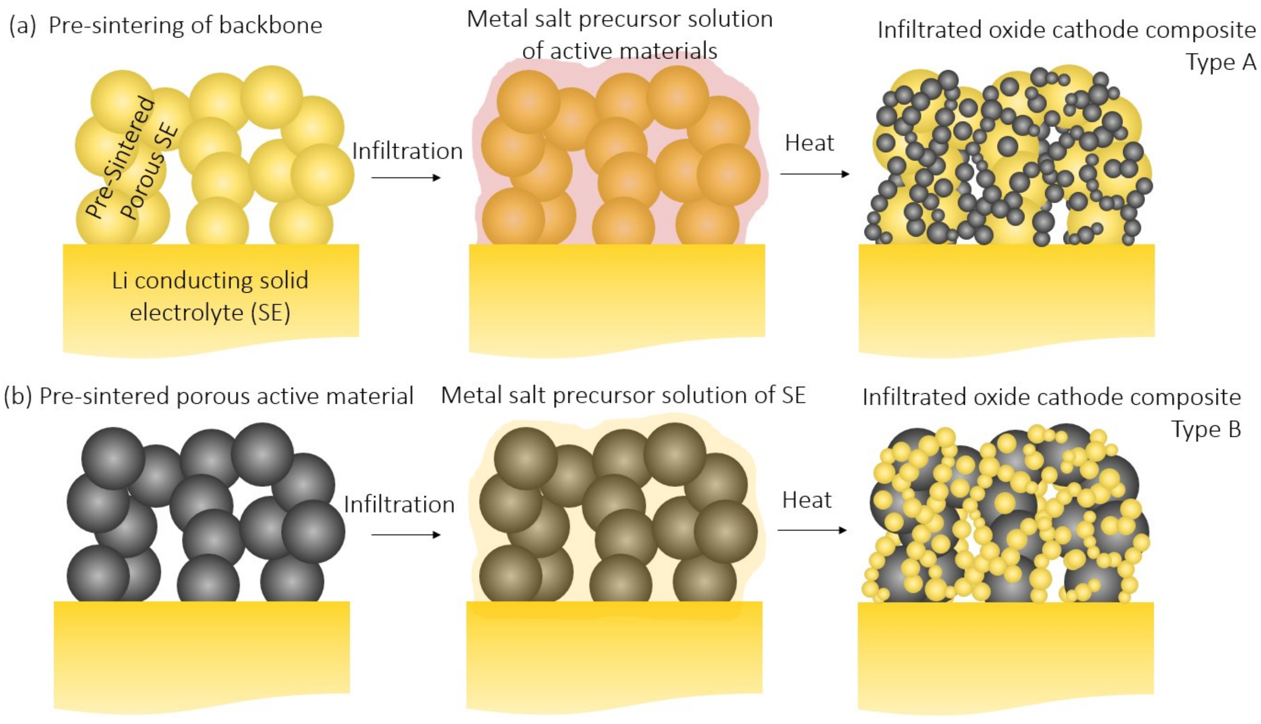


Figure. S14. Two types of suggested cell designs: infiltration of LCO into porous LLZO backbone and infiltration of LLZO into porous LCO backbone and subsequent low-temperature sintering.



References

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2 T. Liu, Y. Ren, Y. Shen, S.-X. X. Zhao, Y. Lin and C.-W. W. Nan, *J. Power Sources*, 2016, **324**, 349–357.