

Supporting Information for “**Thermally-driven reactivity of $\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$ Solid Electrolyte with LiCoO_2 Cathode**”

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Synthesis of $\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$ (LLTO) electrolyte

$\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$ was synthesized by solid-state reaction following similar procedure described elsewhere ¹ with some modifications. The stoichiometric amount of precursor powders Li_2CO_3 (99 %, Alfa Aesar), La_2O_3 (99.99 %, Sigma Aldrich) and TiO_2 (anatase, 99.8 %, Sigma Aldrich) were mixed in agate mortar pestle for 30 minutes. This followed calcination of the mixed powders at 1000 °C for 12 hours in ambient air with ramp-up and ramp-down rate of 5 °C/min. The calcined powder was homogenised for 30 minutes with the help of agate mortar pestle. The required amount of calcined powder for pelletising was weighed and mixed with 5 weight % of polyvinyl butyral as a binder additive. Ethanol was added to the

mixture in order to help better mixing of calcined powder and binder additive. The mixture was mixed well in mortar pestle till ethanol evaporates and leaves behind fine powder. The obtained precursor-binder mixture (about 0.5 grams for each pellet) was pressed in die of 10 mm diameter at 5 metric tons. The obtained pellet was covered with calcined precursor powder (not with binder additive) and sintered at 1150 °C for 12 hours in ambient air. The ramp-up and ramp-down rate was kept at 5 °C/min for sintering as well.

X-ray diffraction of synthesized $\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$ (LLTO)

Figure S1 shows the XRD pattern obtained from as synthesized LLTO electrolyte using Cu $K\alpha$ radiation source. The XRD peaks (marked red) can be assigned to the tetragonal perovskite LLTO (ICDD: 01-070-6719)². The peak marked with blue corresponds to the Cu $K\beta$ reflection from the strongest line at 32.65 °.

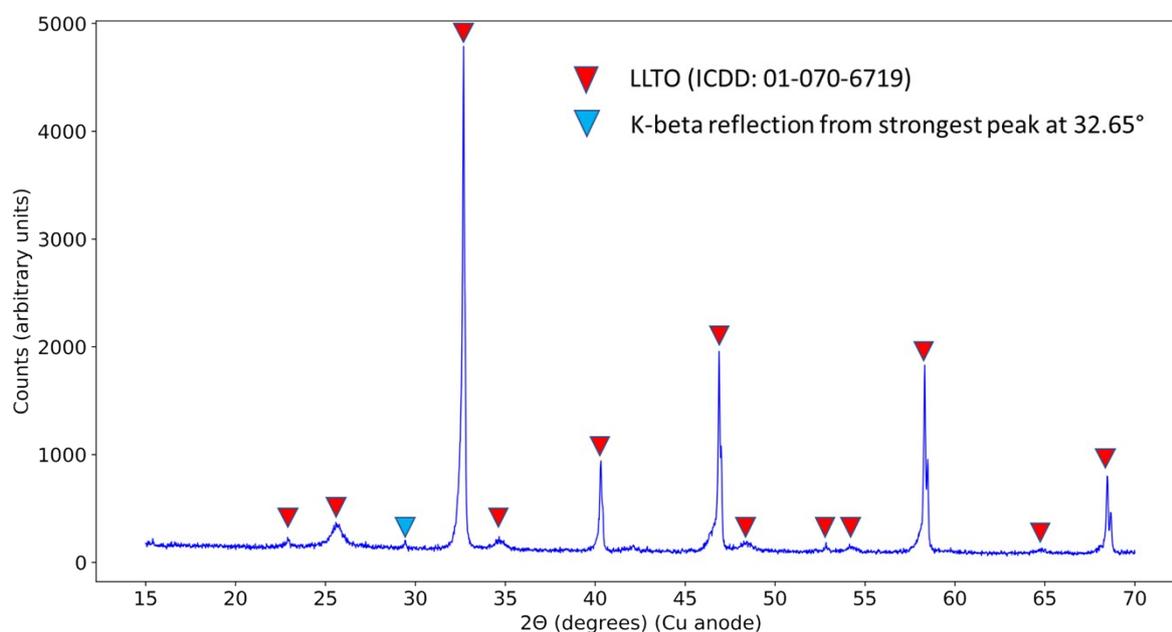


Figure S1: X-ray diffraction pattern obtained from synthesized $\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$ solid electrolyte with Cu $K\alpha$ source.

Electrochemical impedance spectroscopy (EIS) of $\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$

Gold 60 nm was deposited using RF sputtering on LLTO pellet (diameter \approx 10 mm, height \approx 1mm) to construct Au|LLTO|Au symmetric cell. Figure S2 shows the EIS spectra obtained from the sample. The equivalent circuit shown in figure S2 (a) inset was used to model the spectra composed of bulk Li-ion conductivity, domain boundary Li-ion conductivity and Au Li-blocking electrode. The bulk conductivity determined from spectra was found to be 1.28 mS/cm

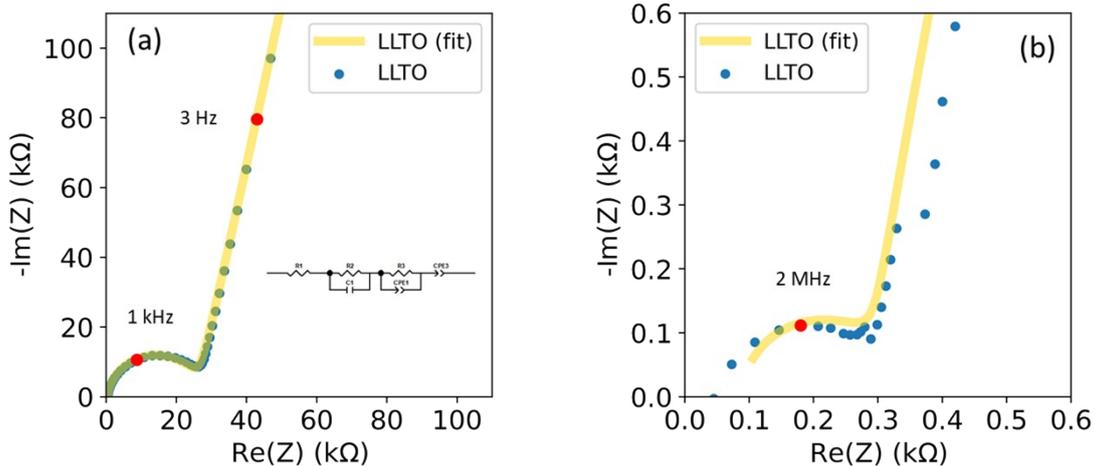


Figure S2: EIS spectra from Au|LLTO|Au symmetric cell. (a) full EIS spectra, (b) magnified EIS spectra in high frequency region. The inset in (a) shows the equivalent circuit used to model the spectra.

Electrochemical impedance spectroscopy (EIS) of Au|LCO|LLTO|LCO|Au

Figure S4 (a-d) shows the magnified EIS spectra from Au|LCO|LLTO|LCO|Au symmetric cells for different thermally treated samples. Gold was deposited after the thermal treatment by RF sputtering.

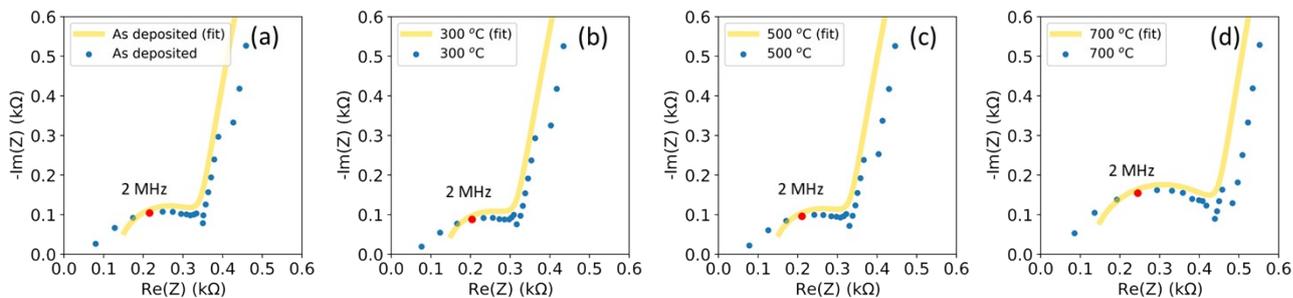


Figure S3: Magnified spectra in high-frequency range from the (e) as deposited sample and samples annealed at (f) 300 °C, (g) 500 °C and (h) 700 °C respectively.

Hard X-ray photoelectron spectroscopy (HAXPES) sample configuration

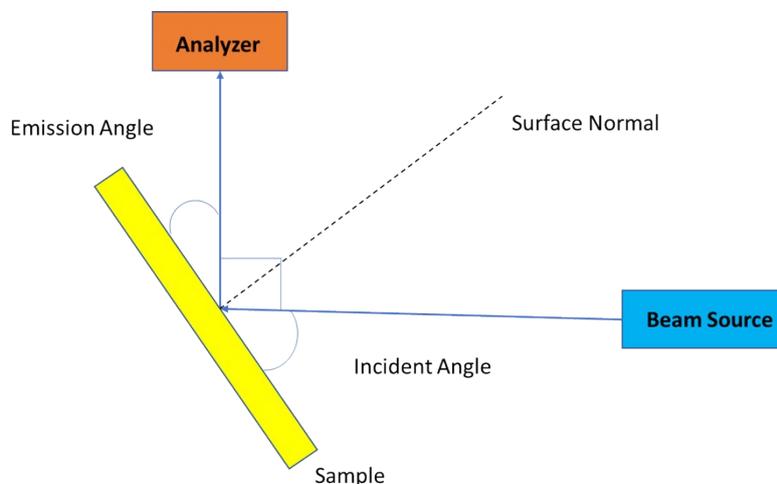


Figure S4: HAXPES experiment sample configuration

C 1s spectra from X-ray photoelectron spectroscopy (XPS) depth profile

Figure S5 shows the C 1s spectra from XPS depth profile with soft X-ray ($Al\ K\alpha$) coupled with Ar-ion sputtering. The C 1s spectra were collected after every 3 minutes of sputtering time for samples undergone different annealing treatment. The spectra of C 1s are shown for those sputtering times that are near the interface of LCO|LLTO as discussed in Section 3 (III).

The C 1s signal remained very low for all LCO|LLTO samples irrespective of annealing condition. This observation rules out the formation of Li_2CO_3 at the LCO|LLTO interface.

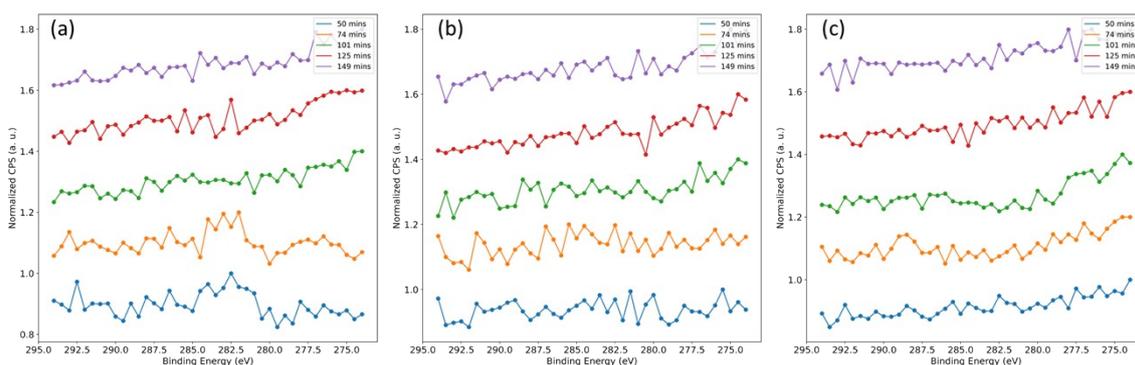


Figure S5: X-ray photoelectron spectroscopy (XPS) for C 1s for LCO|LLTO for (a) as deposited sample, (b) 500 °C annealed and (c) 700 °C annealed sample. The C 1s spectra are shown after selected Ar-ion sputtering time to decipher information near the LCO|LLTO.

References

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- 2 J. Ibarra, A. Várez, C. León, J. Santamaría, L. M. Torres-Martínez and J. Sanz, *Solid State Ionics*, 2000, **134**, 219–228.