Supporting Information

Revealing the Interface Instability between Lithium Metal Anode and Perovskite Solid-State Electrolyte

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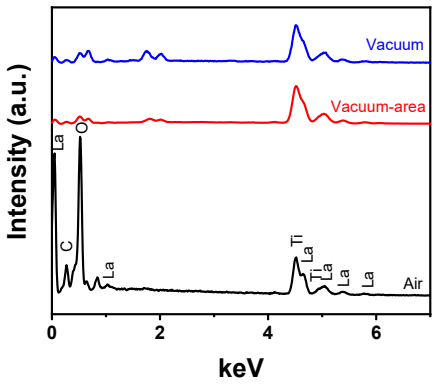

Fig. S1. Vacuum transported EDS spectra of reaction interface after annealing at 75 ℃.

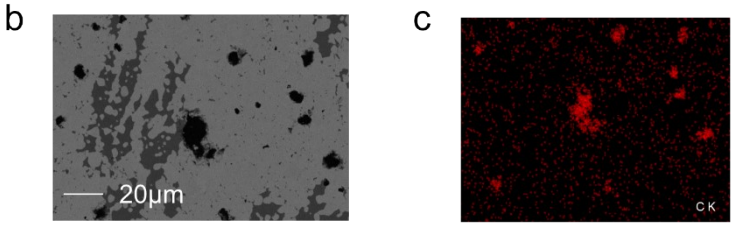

Fig. S2. SEM image and EDS map of sample exposed to air.

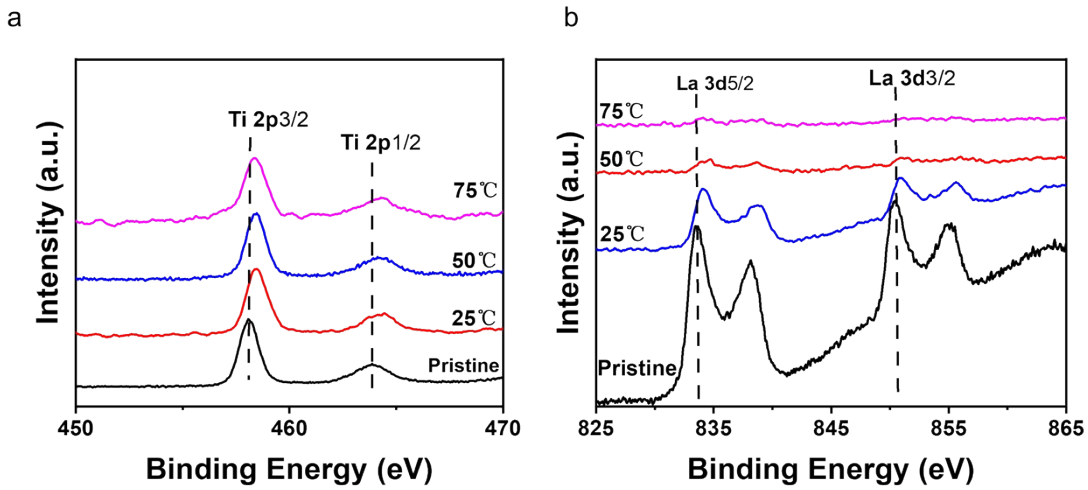

Fig. S3. XPS results of LLTO after different reaction temperatures. (a) Ti 2p. (b) La 3d.

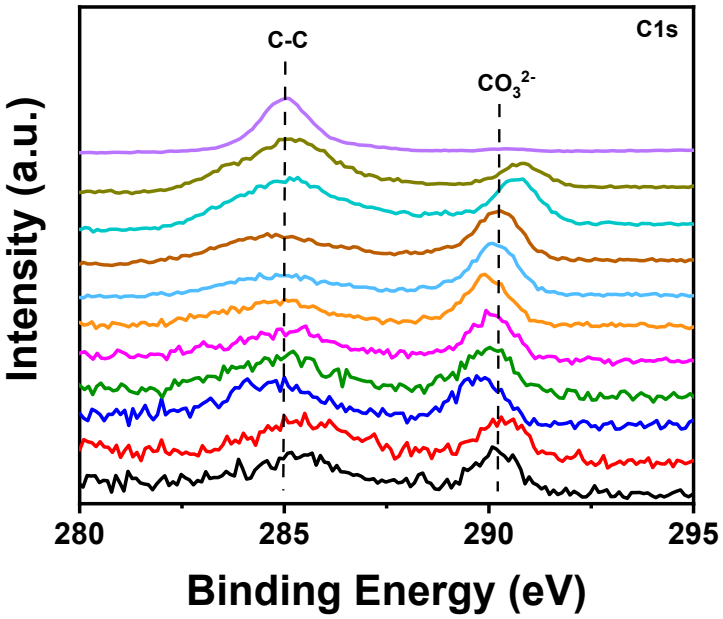

Fig. S4. Etching XPS C 1s spectra of LLTO interface sample at 75 ℃.

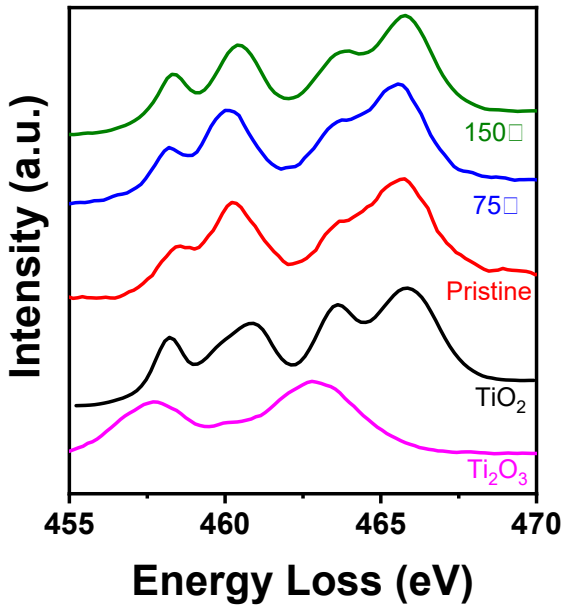

Fig. S5. EELS spectra of Ti 2p of Ti_2O_3, TiO_2 and LLTO at different reaction temperatures.

Samples	Pristine	75 ℃	150 ℃
14 nm	11.05 eV	10.07 eV	9.27 eV
7 nm	10.05 eV	9.57 eV	8.88 eV
1 nm	9.62 eV	7.90 eV	7.22 eV

Table. S1. The corresponding energy position difference (ΔE) values.

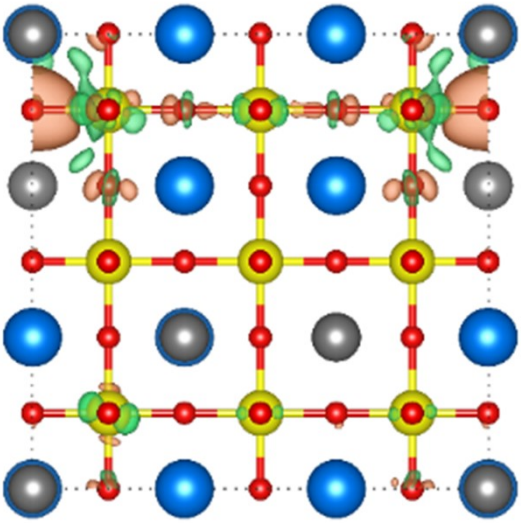

Fig. S6. Differential charge density distribution of LLTO with O vacancy.

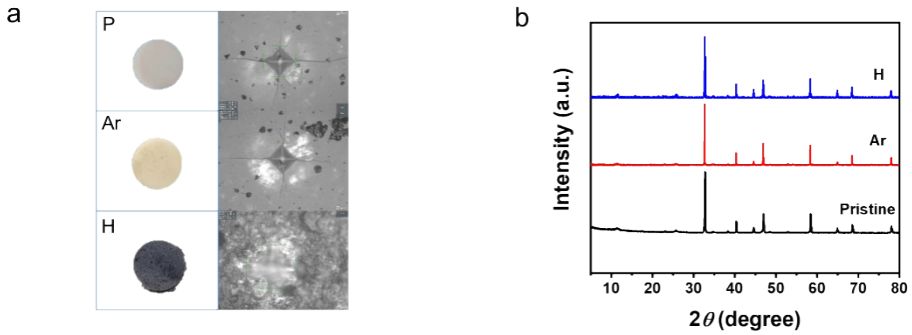

Fig. S7. The optical microscope images of the annealed LLTO samples under different atmosphere conditions and the corresponding XRD patterns.

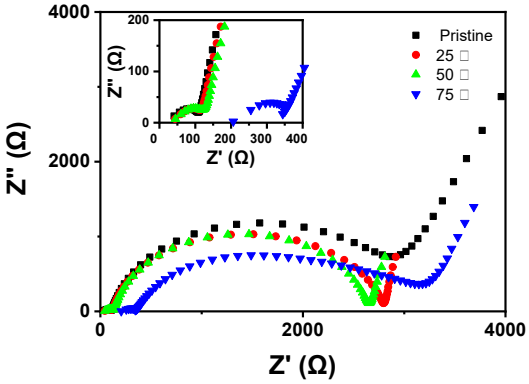

Fig. S8 Electrochemical impedance spectroscopy (EIS).

Samples	**Measured density** ($g\ cm^{-3}$)	**Theoretical density** ($g\ cm^{-3}$)	**Relative Density** (%)
Pristine	4.796	5.021	95.5

Table. S2. Densities of pristine LLTO ceramic sample.

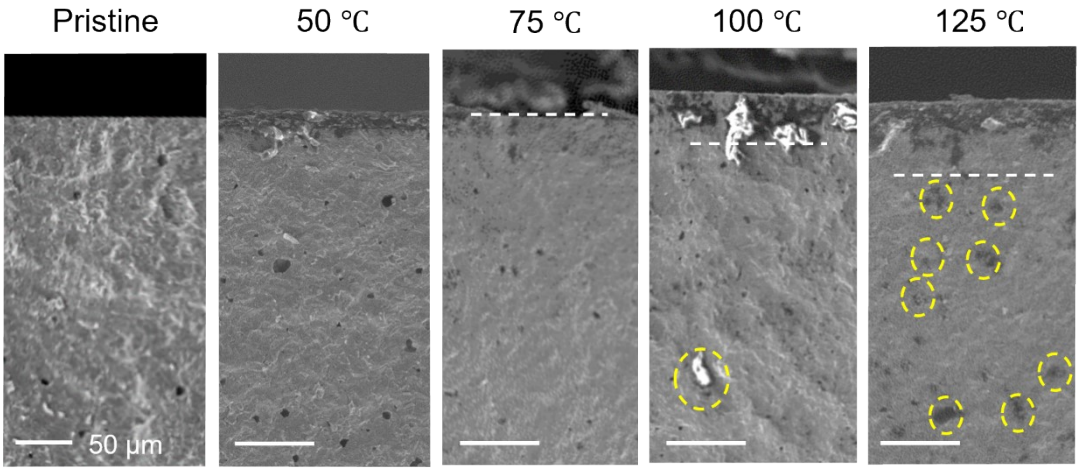

Fig. S9. Cross-sectional SEM results of LLTO under different reaction temperatures.

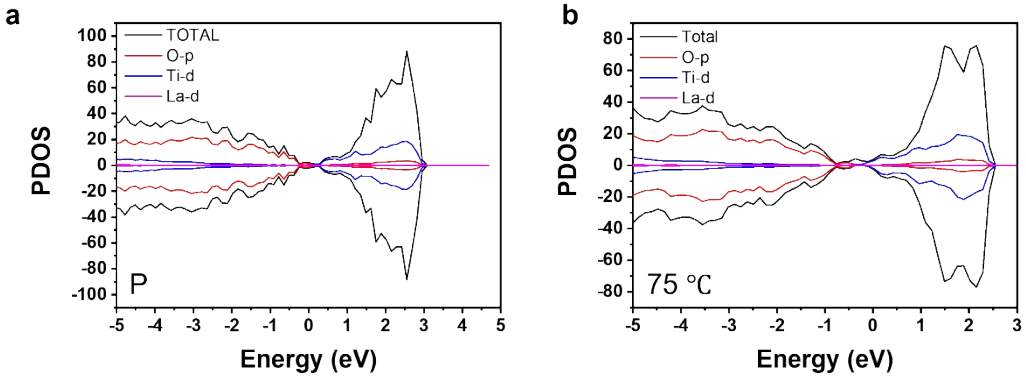

Fig. S10. The projected density of states (PDOS) diagrams for both the pristine sample and the sample after the reaction at 75 °C.