## Supplementary Materials for

## Highly efficient and stable solid-state Li-O<sub>2</sub> batteries using a

## perovskite solid electrolyte

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Fig. S1. Thermogravimetric (TG) and differential scanning calorimetry (DSC) plots of the CGPE.

As shown in **Fig. S1**, the composite gel polymer electrolyte (CGPE) remained in the solid state up to a temperature of 133 °C. Then, the CGPE was liquidised and thermally stable up to 350 °C before decomposing. Therefore, 133 °C is regarded as the limiting temperature at which the designed Li-O<sub>2</sub> cell using CGPE as an interlayer between the Li metal and A-LLTO solid electrolyte remains in the solid state.



Fig. S2. SEM image of a typical pore in the porous cathode frame.



**Fig. S3**. (a) Electrochemical impedance spectrum measured at 25 °C and (b) direct current polarization curve under the applied voltage of 2 V for the integrated cathode without carbon layer and CoO catalyst. Inset in (a) is the equivalent circuit corresponding to impedance spectrum.



**Fig. S4**. a) SEM image of the porous cathode coated with carbon and CoO catalyst. b–g) Corresponding EDS elemental (C, O, Al, Ti, La, and Co) mapping images. h) EDS spectrum.



Fig. S5. Thermogravimetric analysis (TGA) of the porous cathode following carbon coating.



Fig. S6. Selected discharge-charge curves of of the solid-state Li-O<sub>2</sub> cell, operated at 50 °C in limited capacity mode

of 500 mAh  $g^{\text{-1}}{}_{C^{+}CoO}$  at 0.3 mA cm^-2.



**Fig. S7**. Low and high-magnification SEM images of Li metal electrode (a,c) before and (b,c) after cycling test at the limited capacity mode of 500 mAh  $g^{-1}_{C+CoO}$  under the current density of

 $0.3\ mA\ cm^{-1}$  and the temperature of 50 °C.