## **Electronic Supplementary Information for**

3D Ordered Macroporous LaFeO<sub>3</sub> as Efficient Electrocatalyst for Li-O<sub>2</sub> Batteries with Enhanced Rate Capability and Cyclic Performance

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## 1. Chemicals and materials

Styrene (C<sub>6</sub>H<sub>5</sub>CH=CH<sub>2</sub>, AR), Sodium dodecyl sulfate (C<sub>12</sub>H<sub>25</sub>-OSO<sub>3</sub>Na, AR), Potassium persulfate (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, AR), Anhydrous alcohol (C<sub>2</sub>H<sub>5</sub>-OH, AR), Methanol (CH<sub>3</sub>-OH, AR), Ethylene glycol [(HOCH<sub>2</sub>)<sub>2</sub>, AR], Lanthanum nitrate (La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, AR), Manganous nitrate (Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, AR) ware all purdchased from Sinopharm Chemical Reagent Co. Ltd. Lithium bis (trifluoromethanesulfonyl) imide (TFSI, Aladdin, SR); N-methyl-2- pyrrolidinone (NMP, Aladdin Reagent, AR); Tretraethylene glycol dimethyl ether (TEGDME, Aladdin Reagent, AR).

## 2. Instrumentation

XRD measurements were performed on a Bruker D8 Focus power X-ray diffractometer with Cu  $K\alpha$  irradiation. SEM was performed on a field emission Hitachi S-4800 instrument, operating at an accelerating voltage of 10 kV. TEM was performed using a FEI Tecnai G2 S-Twin instrument with a field emission gun operating at 200 kV. Nitrogen adsorption measurements were performed on a Micromeritics ASAP 2020 adsorption analyzer. Specific surface areas were calculated by the Brunaure-Emmert-Teller (BET) method. Li-O<sub>2</sub> cell measurements were cycled on a LAND CT2001A multi-channel battery testing system. Electrochemical impedance spectroscopy was performed on BioLogic VMP3 electrochemical workstation. FTIR tests were performed on a Nicolet 6700 spectrometer. <sup>1</sup>H NMR spectra were examined on a Bruker Avance II 400 spectrometer.



**Fig. S1** SEM images of edges of (a) the PS colloidal crystals and (b) 3DOM-LFO after heat treatment at 600 °C for 3 h.



**Fig. S2** SEM images of 3DOM-LFO after heat treatment at (a) 500 °C, (b) 600 °C, (c) 700 °C, and (d) 800 °C for 3 h.



Fig. S3 X-ray diffraction patterns of 3DOM-LFO after heat treatment at different temperatures.



Fig. S4 Voltage profile on charge for  $Li-O_2$  cells with  $Li_2O_2$ -loaded 3DOM-LFO/KB, NP-LFO/KB, or KB electrodes at a current density of 0.05 mA cm<sup>-2</sup>.



Fig. S5 Discharge/charge profiles of Li– $O_2$  cells with pure KB, NP-LFO/KB, and 3DOM-LFO/KB electrodes at current densities of (a) 0.025, (b) 0.05, (c) 0.10, and (d) 0.20 mA cm<sup>-2</sup>.



**Fig. S6** The discharge curves of the Ar-filled cells based on (a) pure KB, (b) NP-LFO/KB, and (c) 3DOM-LFO/KB electrodes at a current density of 0.10 mA cm<sup>-2</sup>.



Fig. S7 The discharge/charge profiles of Li– $O_2$  cells based on  $O_2$  electrodes with 3DOM-LFO/SP catalyst loading of 10%, 30%, and 50% at at a current density of 0.05 mA cm<sup>-2</sup>.



Fig. S8 FTIR spectra of the 3DOM-LFO/SP electrodes at the end of discharge and charge.

**Table S1** The ratio in moles of the each discharge product in total products obtained from both the FTIR spectra of the discharged electrodes on different cycles (Fig. S8) and FTIR calibration curves.

Cycle Number	3DOM-LFO/SP electrode			
-	Li <sub>2</sub> O <sub>2</sub>	CH <sub>3</sub> CO <sub>2</sub> Li	HCO <sub>2</sub> Li	Li <sub>2</sub> CO <sub>3</sub>
1 <sup>st</sup> discharge	0.952	0.008	0.016	0.024
10 <sup>th</sup> discharge	0.891	0.010	0.025	0.074
20 <sup>th</sup> discharge	0.791	0.018	0.065	0.126
40 <sup>th</sup> discharge	0.677	0.068	0.108	0.147



**Fig. S9** The discharge/charge profiles of Li– $O_2$  cells in DMA with (a) Super P carbon (SP) and (b) 3DOM-LFO/SP electrodes under specific capacity limit of 1000 mA h  $g_{carbon}^{-1}$ . The Current density: 300 mA g<sup>-1</sup>.



**Fig. S10** <sup>1</sup>H NMR (400 MHz,  $D_2O$ , TMS) spectra of solution extracted by washing the conventional 3DOM-LFO/SP electrode with  $D_2O$  after indicated number of cycles.