## **Supplementary Information**

Fabrication of three-dimensional ordered macroporous spinel CoFe<sub>2</sub>O<sub>4</sub> as efficient bifunctional catalysts for a positive electrode of lithium-oxygen batteries

By Jong Guk Kim,<sup>a†</sup> Yuseong Noh,<sup>b†</sup> Youngmin Kim,<sup>c</sup> Seonhwa Lee,<sup>d</sup> and Won Bae Kim\*<sup>b</sup>

<sup>a</sup>School of Materials Science and Engineering, Gwangju Institute of Science and Technology (GIST), 261 Cheomdan-gwagiro, Buk-gu, Gwangju 500-712, South Korea

<sup>b</sup>Department of Chemical Engineering, Pohang University of Science and Technology (POSTECH), 77 Cheongam-Ro, Nam-gu, Pohang, Gyeongbuk 37673, South Korea

- °Carbon Resources Institute, Korea Research Institute of Chemical Technology (KRICT), 141 Gajeong-ro, Yuseong-gu, Daejeon 34114, South Korea
  - <sup>d</sup>Department of Physics and Photon Science, Gwangju Institute of Science and Technology (GIST), 261 Cheomdan-gwagiro, Buk-gu, Gwangju 500-712, South Korea

[†] These two authors contributed equally to this work

\* Corresponding Author: Tel: +82-54-279-2397. Fax: +82-54-279-5528, E-mail: kimwb@postech.ac.kr



**Fig. S1** Nitrogen adsorption isotherms of 3DOM CFO@60. Inset shows pore size distribution of 3DOM CFO@60.



Fig. S2 SEM images (a and b) of CFO@60 and CFO@140. TEM images (c and d) of CFO@60 and CFO@140.



Fig. S3 EDX spectrum of the 3DOM CFO@140.



Fig. S4 (a) Coulombic efficiency-cycle number curves for Li-O<sub>2</sub> cells with CFO NPs, 3DOM CFO@60, and CFO@140 catalysts for five cycles. (b) Plots of the differential capacity *versus* the voltage at a current density of 200 mA g<sup>-1</sup>.



Fig. S5 The discharge-charge profiles of  $\text{Li-O}_2$  cells with KB, CFO NPs, 3DOM CFO@60, and CFO@140 at the first cycle. The capacities are normalized by the total mass of electrode (catalyst, carbon, and binder).



**Fig. S6** Discharge-charge curves of Li-O<sub>2</sub> cells with KB, CFO NPs, 3DOM CFO@60, and CFO@140 catalysts at a current rate of 200 mA  $g^{-1}$  with the limited capacity depth of (a) 500 and (b) 1000 mAh  $g^{-1}$ . KB in Fig. S6b was studied in our previous work [5].

The potential-capacity curves of Li-O<sub>2</sub> cells with KB, CFO NPs, 3DOM CFO@60, and CFO@140 catalysts at a current density of 200 mA g<sup>-1</sup> with the restricted capacity of 1000 mAh g<sup>-1</sup> were provided in Fig. S6b. When increasing the restricted capacity from 500 to 1000 mAh g<sup>-1</sup>, the Li-O<sub>2</sub> cell with CFO@140 catalyst also showed the smallest overpotential of 1.31 V as compared to that with KB (1.72 V), CFO NPs (1.62 V), CFO@60 (1.37 V). This result emphasizes again that the CFO@140 catalyst can reduce the potential polarization efficiently at a relatively high restricted capacity of 1000 mAh g<sup>-1</sup>.



**Fig. S7** Magnified potential-capacity curves for (a) initial charging and (b) initial discharging of the Li-O<sub>2</sub> cells with KB, CFO NPs, CFO@60, and CFO@140 at a current density of 200 mA  $g^{-1}$  with the limited capacity depth of 500 mAh  $g^{-1}$ .

For comparison of the potential polarizaion of  $O_2$ -electrode with KB, CFO NPs, CFO@60, and CFO@140 catalysts, the magnified potential-capacity profiles are provided in Fig. S7. The lowest charge potential of CFO@140 means reaction product of Li<sub>2</sub>O<sub>2</sub> are decomposed more easily, while the highest discharge potential means reaction product of Li<sub>2</sub>O<sub>2</sub> are formed more readily. Therefore, the CFO@140 could indicate high catalytic activity in both OER and ORR, as compared with KB, CFO NPs, and CFO@60. Consequently, the enhanced ORR/OER kinetics could lead to improvements in the energy output, the cycling stability, and the round-trip efficiency of the Li-O<sub>2</sub> cells.



**Fig. S8** Potential-time curves of Li-O<sub>2</sub> cells with (a) KB, (b) CFO@60, and (c) CFO@140 catalysts. (d) Terminal voltage-cycle number curves with KB, CFO@60, and CFO@140.



Fig. S9 XRD patterns of the  $O_2$ -electrodes with (a) KB and (b) CFO@140 at different discharge/charge stages. Peaks marked with asterisks are originated from the carbon paper.