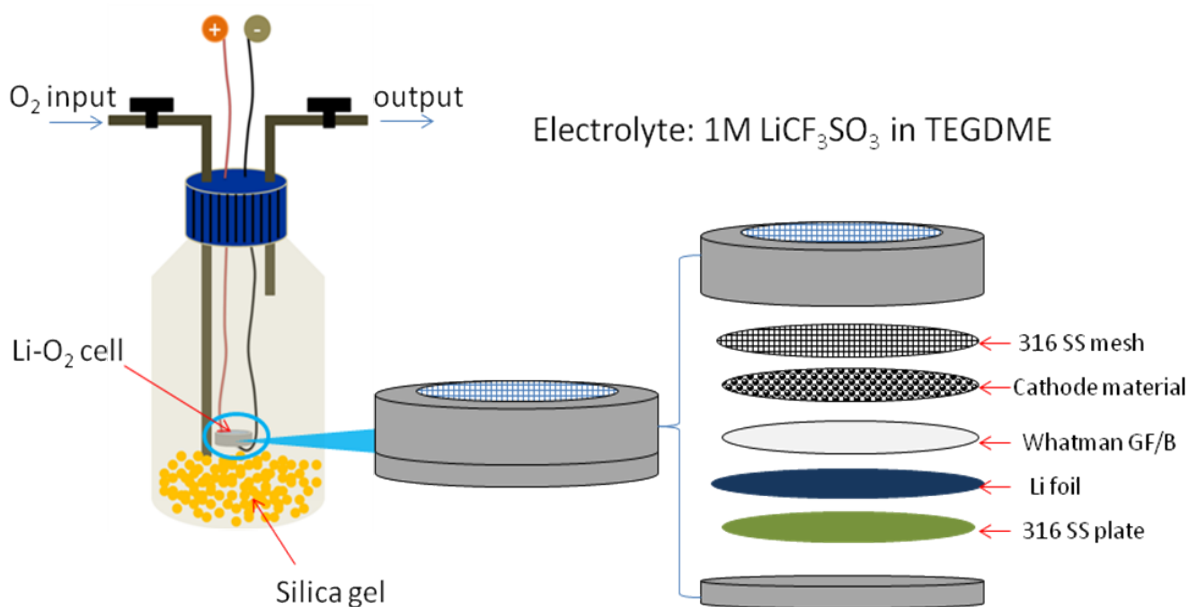


## Electronic Supplementary Information (ESI):

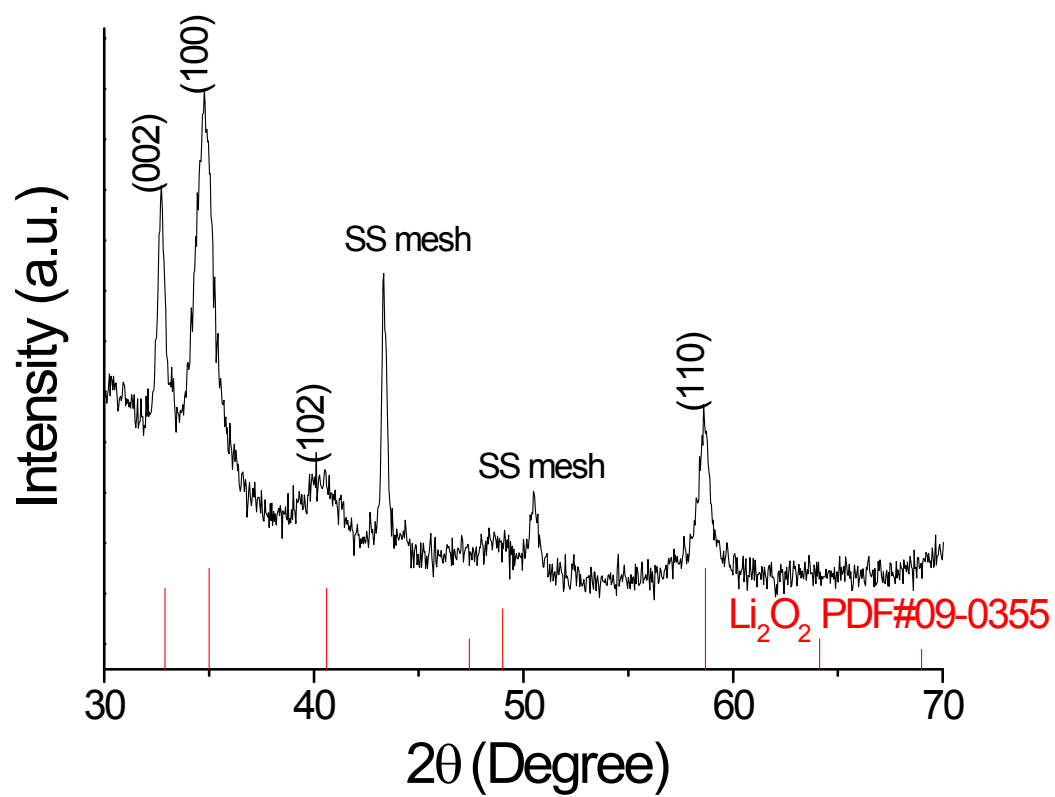
### Influence of carbon pore size on the performance of Li-O<sub>2</sub> batteries

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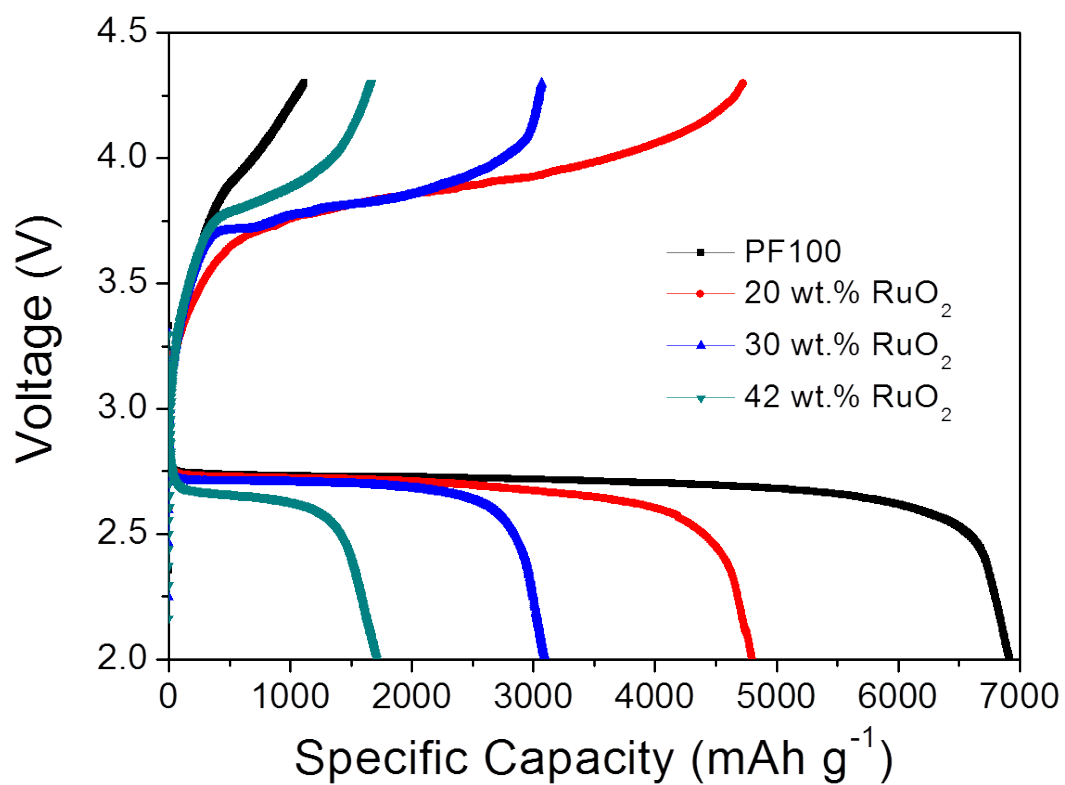
**Method of synthesis of RuO<sub>2</sub>/PC100:** In a typical synthesis of RuO<sub>2</sub>/PC catalyst, ruthenium(III)-2,4-pentanedionate and PC100 were mixed in a weight ratio of 1:1 in acetone (10 ml), followed by vacuum drying at room temperature. The composite was then transferred in a tube furnace and sintered at 400 °C under Ar atmosphere for 3 h. The obtained sample was treated at 120 °C in oven for 24 h before electrode preparation.



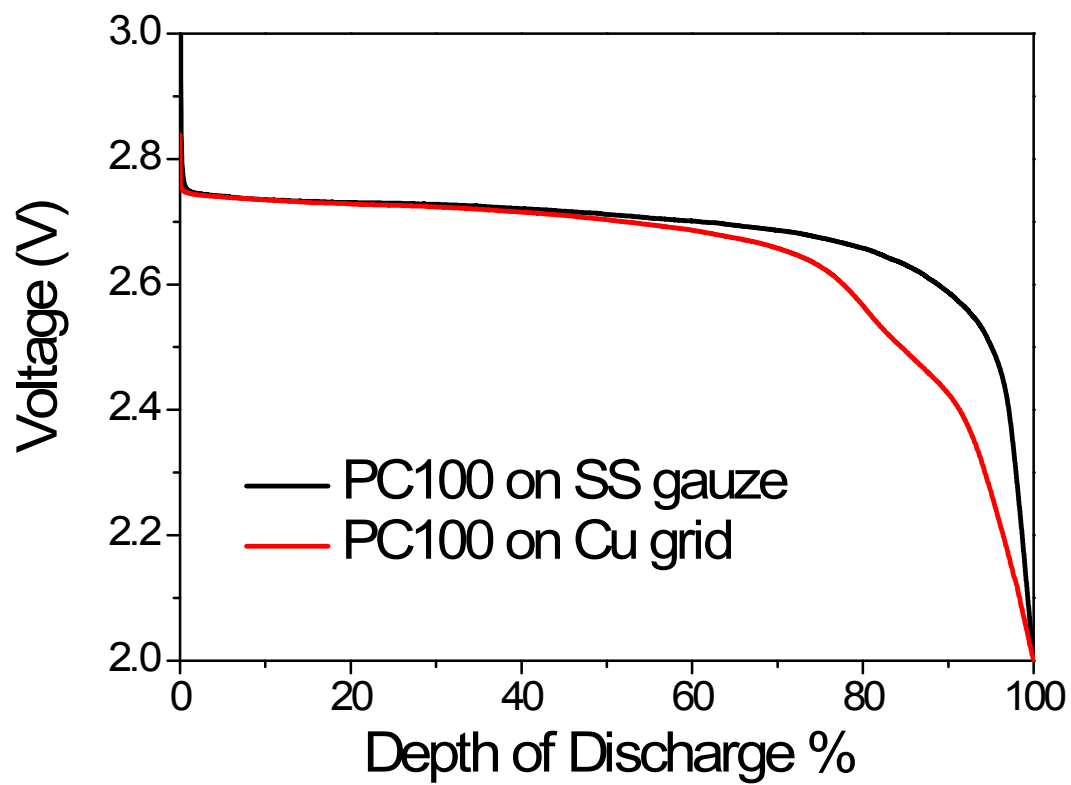
**Fig. S1** Schematic drawing of the testing system of Li-O<sub>2</sub> battery.



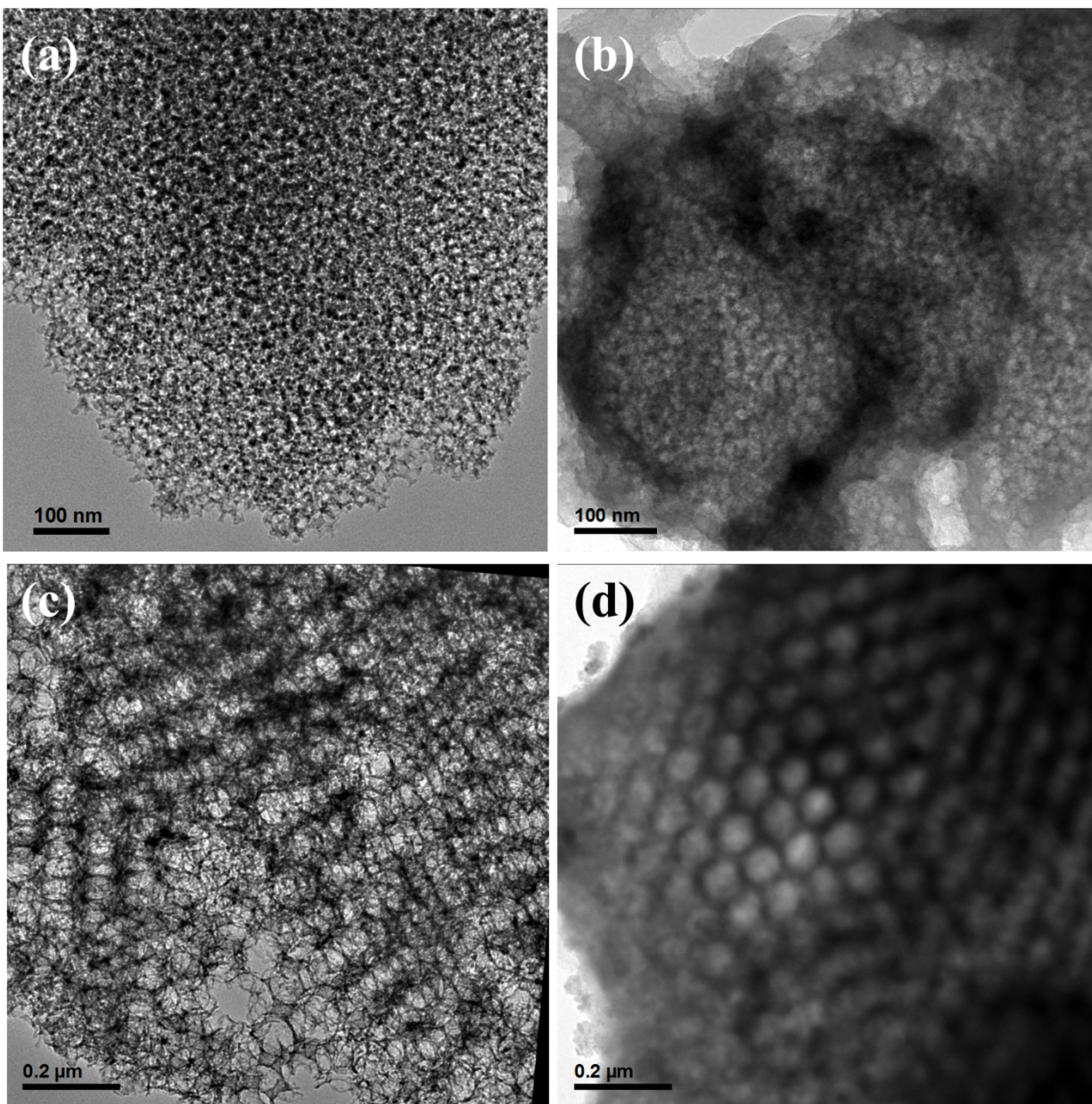
**Fig. S2** XRD pattern of the carbon substrate (PC100) discharged to 2 V in 1 M LiTFS-TEGDME electrolyte.



**Fig. S3** Initial charge-discharge voltage profiles of PC100 decorated with different amount of RuO<sub>2</sub> at a constant current of 0.1 mA (100 mA g<sup>-1</sup>).



**Fig. S4** Discharge voltage profiles (vs. depth of discharge, DOD) of PC100 loaded on SS gauze and on Cu grid.



**Fig. S5** TEM images of the porous carbons: (a) pristine PC20, (b) discharged PC20, (c) pristine PC100 and (d) discharged PC100. The cells were discharged to 2 V at a constant current of 2.0  $\mu\text{A}$ .

# Theoretical calculation of cell capacity of Li-O<sub>2</sub> batteries

The carbon yield from PF resin is 30%, thus the carbonized silica/carbon composite consists of 5 g silica and 0.165 g carbon (1.1 ml of PF resin solution with a concentration of 0.5 g mL<sup>-1</sup>).

Weight of silica ( $W_{\text{silica}}$ ) is 5 g.

Weight of carbon ( $W_{\text{carbon}}$ ) is 0.165 g.

Density of silica ( $\rho_{\text{silica}}$ ) is 2.648 g cm<sup>-3</sup>.

Density of Li<sub>2</sub>O<sub>2</sub> ( $\rho_{\text{Li}_2\text{O}_2}$ ) is 1.2063 g cm<sup>-3</sup>.

Molar mass of Li<sub>2</sub>O<sub>2</sub> ( $M_{\text{Li}_2\text{O}_2}$ ) is 45.88 g mol<sup>-1</sup>.

$N_A$ : Avogadro constant

$\Delta$ : constant value to convert the unit of A·s to mAh

D: Carbon pore size

**Model A:** all voids left by silica in porous carbon were occupied by Li<sub>2</sub>O<sub>2</sub> during discharge

Weight of Li<sub>2</sub>O<sub>2</sub>:  $W_{\text{Li}_2\text{O}_2}^{\text{A}} = (W_{\text{silica}}/\rho_{\text{silica}}) \times \rho_{\text{Li}_2\text{O}_2}$

Theoretical capacity ( $Q_{\text{T}}^{\text{A}}$ ) =  $(W_{\text{Li}_2\text{O}_2}^{\text{A}}/M_{\text{Li}_2\text{O}_2} \times N_A \times 2) \times \Delta / W_{\text{carbon}} = 16128 \text{ (mAh g}^{-1}\text{)}$ , which is irrelevant to carbon pore size.

**Model B:** A monolayer of Li<sub>2</sub>O<sub>2</sub> with a thickness of 7.8 nm forms inside carbon pores.

Weight of Li<sub>2</sub>O<sub>2</sub>:  $W_{\text{Li}_2\text{O}_2}^{\text{B}} = (W_{\text{silica}}/\rho_{\text{silica}}) \times \rho_{\text{Li}_2\text{O}_2} \times [1 - (1 - 7.8 \times 2/D)^3]$

Theoretical capacity ( $Q_{\text{T}}^{\text{B}}$ ) =  $(W_{\text{Li}_2\text{O}_2}^{\text{B}}/M_{\text{Li}_2\text{O}_2} \times N_A) \times \Delta / W_{\text{carbon}} = 16128 \times [1 - (1 - 7.8 \times 2/D)^3] \text{ (mAh g}^{-1}\text{)}$ , which decreases with the increase of carbon pores.