Electronic Supplementary Information

Synthesis of a meso-macro hierarchical porous carbon material for improvement of O₂ diffusivity in Li-O₂ batteries

Hongjiao Nie, a,b Yining Zhang, a Jing Li, a,b Wei Zhou, a,b Qinzhi Lai, a Tao Liu a and Huamin Zhang a

a Division of energy storage, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Zhongshan Road 457, Dalian 116023, China

b University of Chinese Academy of Sciences, Beijing 100039, China

Fax: +86-411-84665057

E-mail: zhanghm@dicp.ac.cn, liutao@dicp.ac.cn

Experimental Section:

Synthesis of hierarchical porous carbon (HPC) and mesoporous carbon (MPC): The hierarchical porous carbon (HPC) was synthesized through a dual template method. In brief, melamine (3.15 g) was firstly added into the mixture of formaldehyde solution (5 mL, 37 wt %) and deionized water (12.5 mL). Then, the PH was adjusted to 8.5 with Na₂CO₃ solution. Afterwards, the mixture was stirred to get a clear solution at 85 °C. After cooling down to 40 °C, a mixture of two different diameters colloidal silica, 20-30 nm (5%, 20 mL) and 100-200 nm (5%, 10 mL), was employed as template (the optimal ratio determined through experiments) and mixed with the solution. Then the PH was adjusted to 4.5 by the addition of 2 M HCl to initiate the polymerization. A white melamine-formaldehyde (MF) resin with silicon dioxide
doped was formed after keeping the solution static for 3 h. The resin was dried and cured at 180 °C for 24 h, followed by pyrolyzed under N₂ atmosphere at 950 °C for 2 h. The silica template was removed by 20% HF for 24 h. They were thoroughly washed in deionized water. Finally, the sample was dried at 80 °C. In addition, mesoporous carbon (MPC) with only 20-30 nm (5%, 30 mL) colloidal silica template was also prepared in the same way for comparison.

_Cathode preparation:_ HPC and MPC cathodes were prepared by mixing porous carbon material and PTFE as a binder with a weight ratio of 80/20. After solvent (ethanol) evaporation, the mixture was compressed and punched into disks with a diameter of 15 mm and then dried at 120°C for 12 h. The carbon loading of each electrode was typically 6 mg± 0.1 mg.

_Lithium-oxygen battery construction and performance evaluation:_ Lithium-oxygen battery was constructed in an argon-filled glove box (H₂O<0.1 ppm, O₂<0.1 ppm). The cell consists of a 0.45 mm thick Li foil (16 mm in diameter) as anode, a carbon electrode as cathode and polypropylene fiber (Novatexx 2471 Freudenberg Filtration Technologies KG) soaked with electrolyte (1.0 M bis(trifluoromethane) sulfonamide lithium in TEGDME) as a separator. A stainless steel mesh was used as the current collector. All the cell parts were compressed together to ensure good contact and the cell was completely sealed except for the O₂ entryway. After exposed to flow pure oxygen for 5 h, the Lithium-oxygen battery was discharged galvanostatically at a rate of 30 mA g⁻¹ on a LAND 2100 system (Wuhan, China) with a cutoff voltage of 2 V.

_Material and electrode characterizations:_ The surface morphology of carbon powder and air electrodes were characterized by Scanning electron microscopy (SEM, QUANTA 2000FEG).

N₂ adsorption isotherms were measured at 77.3K using an ASAP2010 system. Surface areas and pore volumes were determined using Brunauer-Emmett-Teller (BET) method. The pore size distribution curves were calculated from the desorption
branches of nitrogen isotherms using the Barrett-Joyner-Halenda (BJH) model.

**Cyclic voltammetry (CV) test:** The cyclic voltammetry (CV) tests were conducted in a traditional three-electrode system with glassy carbon (Φ 4 mm) modified with porous carbon film as working electrode (WE), glass filter protected Li foil as counter electrode (CE), and porous ceramic protected Li foil as reference electrode (RE). Porous carbon (5.0 mg) were dissolved in 2-propanol (5 mL) and PTFE (5 wt%, 25 mg). After ultrasonication for 30 min, 50 μL of the received carbon ink was drop-casted on the glass carbon (GC) electrode and vacuum-drying at room temperature. 1M LITFSI/TEGDME were used as electrolyte. All the measurements were conducted between 2.0 V to 4.3 V using an AFCBP1 bipotentiostat (Pine Research Instrumentation, USA) in an argon-filled glove box (H₂O < 0.1 ppm, O₂ < 0.1 ppm) at room temperature.