

## Electronic Supplementary Information

### **A hierarchical porous electrode using micron-sized honeycomb-like carbon material for high capacity lithium-oxygen batteries**

**Jing Li,<sup>a,b</sup> Huamin Zhang,\*<sup>a</sup> Yining Zhang,\*<sup>a</sup> Meiri Wang,<sup>a</sup> Fengxiang Zhang<sup>a</sup> and Hongjiao Nie<sup>a,b</sup>**

<sup>a</sup>Division of energy storage, Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Zhongshan Road 457, Dalian, 116023, China.

<sup>b</sup>University of Chinese Academy of Sciences, Beijing, 100039, China

Fax: +86-411-84665057

E-mail: zhanghm@dicp.ac.cn  
zhangyn@dicp.ac.cn

#### **Experimental Section:**

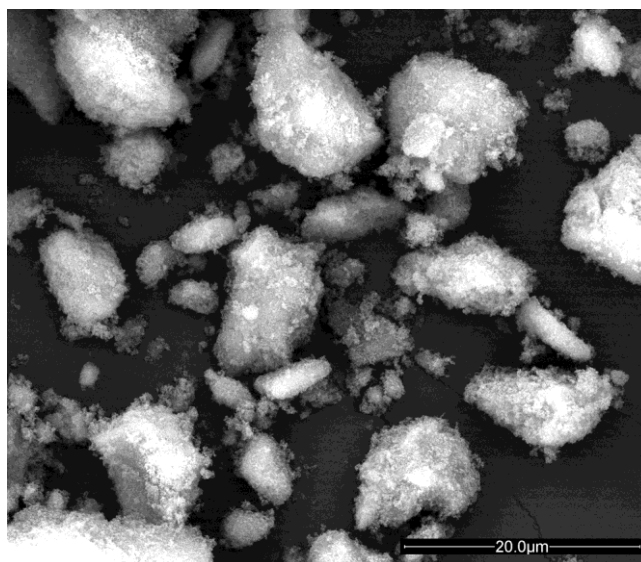
*Synthesis of micron-sized honeycomb-like carbon (MHC) Material:* The commercial hydrophobic CaCO<sub>3</sub> nanoparticles (*ca.*30~50 nm, Henan Keli New Material Co. Ltd) and sucrose (Tianjin Fuchen) were used as template and carbon precursor, respectively. Firstly, sucrose (2 g) was dissolved in deionized water (15 ml), in which CaCO<sub>3</sub> nanoparticles (4 g) were dispersed at 60 °C under vigorous stirring until a slurry mixture was obtained. Then, the mixture was vacuum dried at 60 °C for 24 h, and the carbonization was carried out in a furnace under argon atmosphere with temperature ramping from 25 to 500 °C at 5 °C min<sup>-1</sup>, 500 to 900 °C at 2 °C min<sup>-1</sup>, and then kept at 900 °C for 5 h. Lastly, the template was removed by washing with 2 M HCl aqueous solution under stirring for 5 h, and filtered with deionized water. After

vacuum drying at 80 °C for 24 h, the MHC material was obtained.

*Cathode Preparations:* Cathodes with a composition of 80 wt.% carbon material and 20 wt.% polytetrafluoroethylene (PTFE) were fabricated by mixing MHC and PTFE emulsion (Teflon®, solid content = 61.5%, DuPont). The resulting PTFE-bonded carbon jelly blend was rolled into a thin film. After dried at 80 °C under vacuum for over 24 h, the film was punched with a diameter of 15 mm and the cathode with a carbon loading of  $6.3 \pm 0.4$  mg was obtained. Commercial carbon material-Ketjen black EC-600JD (KB) (Akzo Nobel Corp.) cathode was also fabricated in the same way as above for comparison.

*Material Characterizations:* The pyrolysis of CaCO<sub>3</sub>-sucrose composite was investigated by thermogravimetry (TG) on a Setaram Setsys 16/18 thermoanalyzer with a heating rate of 10 °C min<sup>-1</sup> to 880 °C in Ar flow. The pore size distributions (PSDs) of MHC material and MHC electrodes were analyzed by nitrogen adsorption/desorption isotherms at 77 K on a Micromeritics Accelerated Surface Area and Porosimetry System (ASAP 2010). KB material and prepared KB cathodes were also analyzed for comparison. The pore volume of macropores for both electrodes was obtained on a mercury porosimeter (Autopore 9520). The morphologies of carbon materials, the CaCO<sub>3</sub>-sucrose composite and the prepared electrodes were characterized by a QUANTA 200F scanning electronic microscope (SEM), operating at an acceleration voltage of 20 kV. The morphology of discharged electrodes were also characterized by SEM. Prior to SEM analysis of the discharged electrodes, the

electrodes were carefully extracted from the cells and cleaned with tetraethylene glycol dimethyl ether (TEGDME) for three times in a glove-box with H<sub>2</sub>O and O<sub>2</sub> below 1 ppm, followed further drying in vacuum for 24 hours.



**Figure S1.** SEM image of the CaCO<sub>3</sub>-sucrose composite before carbonization.

*Assembly of Li-O<sub>2</sub> Battery Cells and Performance Evaluation:* In order to evaluate the discharge capacity of the materials, single cells were fabricated in an argon-filled glove box (H<sub>2</sub>O < 0.1 ppm, O<sub>2</sub> < 0.1 ppm). The cells were assembled using a porous cathode together with a lithium anode (16 mm in diameter, 0.45 mm thick) and polypropylene fiber separator (Novatexx 2471, Freudenberg Filtration Technologies KG). To minimize the electrolyte decomposition as observed in Li-O<sub>2</sub> batteries, ether-based electrolyte (1.0 M bis(trifluoromethane)sulfonamide lithium (LITFSI) in TEGDME) was used in this work. The water content of TEGDME solvent was strictly controlled under 10 ppm determined by Karl-Fischer titration. After exposed to pure O<sub>2</sub> (99.995%) for 4 h, the battery test was carried out at 1.2 atm pure O<sub>2</sub> and room

temperature (25 °C). All Li-O<sub>2</sub> cells were discharged galvanostatically (Arbin BT-2000) at a rate of 30 mA g<sup>-1</sup> of carbon with a cut-off voltage of 2.0 V. The specific capacity of the cell was normalized by the mass of the carbon materials in the cathode.