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Directly growth of flower-like 3D MnO_2 on carbon paper as efficient oxygen electrode catalyst for rechargeable Li-O_2 batteries†

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Detailed synthesis process of MnO_2/CP cathode materials

Synthesis of MnO_2/CP composite

The manganese oxide was deposited on the CP substrate, which was treated by HNO_3 about 1h. The electrochemical deposition was carried out in a 0.1 mol/L $Mn(CH_3COO)_2$ + 0.1 mol/L Na_2SO_4 at a current density about 0.5mA/cm^2 for 5min. After deposition, the as-produced samples were washed with distilled water for 3 times and dried at 353 K for 4 h. The resultant composite is noted as MnO_2/CP. The loading mass of the oxide is calculated from the mass difference between samples before and after electrochemical deposition.

Characterization

Morphologies of the as-prepared samples were analyzed via Field Emission Scanning Electron Microscope (FE-SEM, FEI Quanta 200 FEG, Holland) and transmission electron microscope (TEM, FEI TECNAI G2 12, Holland). The chemical composition of the obtained products was determined using energy-dispersive X-ray spectroscopy analysis attached to the SEM (EDS). X-ray photoelectron spectroscopy (XPS) was carried out on a Physical Electronics 5400 ESCA.The Brunauer-Emmett-Teller (BET) specific surface areas were obtained from nitrogen adsorption measurements at about 77 K performed in a SA3100 instrument. Before the measurements, the samples (about 0.2 g) were evacuated at 473 K for 2h.

Electrochemical measurement

The LOB cells were assembled for electrochemical characterization with MnO2/CP composite (diameter of 14mm) as the working electrodes, lithium foils as the reference and counter electrodes, a separator (a piece of Whatman GF/D glass microfiber filter paper and a piece of Celgard 2400) and 1M LiCF3SO3 in tetra(ethylene) glycol dimethyl ether (TEGDME) as the electrolytes. All cells were assembled in a glove box system filled with argon and in glove overnight before testing. Afterwards, the cell was purged with tetraglyme-saturated oxygen for 2h. Galvanostatic discharge – charge measurements were performed on a battery test system (LAND CT2001A) between 2.0 and 4.3 V (vs. Li+/Li) at different rates the at room temperature.The specific capacity was calculated based on the mass of MnO2 if not specified. Electrochemical impedance spectroscopy (EIS) was performed on a IM6 (Germany) in a frequency range of 100 kHz to 10 mHz with an AC voltage amplitude of 5 mV.