MOFs-derived Hierarchically Porous Mn_2O_3 as High-performance Anode Material for Li-ion Battery

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Experimental section

Mn-LCP was synthesized as follows: an aqueous solution (10 mL) of $Mn(NO_3)_2 \cdot 6H_2O$ (0.70 g, 2.50 mmol) was dropped into an ethanol-water mixture (v:v = 1:1, 10 mL) of 2,3,5,6-tetrabromobenzene-1,4-dicarboxylic acid, H_2(Br4-bdc) (1.20 g, 2.50 mmol), NaOH (0.2 g, 5.0mmol), and 4,4'-bipyridine (0.38 g, 2.50 mmol). Upon stirring the mixture, white powders were obtained. The powders were washed with water and ethanol for several times and dried at 60 °C for 5 h in air (yield 70%).

Synthesis of porous Mn_2O_3: An amount of the synthesized Mn-LCP was put into the crucible. The precursor was heated to 600 °C in air at a heating rate of 10 °C/min and then maintained at 600 °C for 3 h before being air-cooled to room temperature. Then, the black products were collected for structural characterization and the LIBs tests.

Microsized Mn_2O_3: commercial MnO_2 was heated at 600 °C for 5 h in air.

Electrochemical Investigation

The electrodes for electrochemical examinations were prepared with 70 wt% active materials of the fabricated porous Mn_2O_3, 20 wt% conducting acetylene black, and 10 wt% carboxymethyl cellulose (CMC) binder in water. The slurry was pasted on a clean copper foil followed by drying in vacuum at 100 °C for 12 h. The coated foil was then roll-pressed and cut into a disc. The cells were assembled using lithium foil as the counter electrode and the reference electrode, Celgard 2400 as the separator, and a solution of 1M LiPF6 in a mixture of ethylene carbonate (EC)-ethyl methyl carbonate (EMC)-dimethyl carbonate (DMC) (1:1:1 by volume) as the electrolyte. The assembly of the cell was conducted in an argon-filled glove-box. The cells were charged and discharged from 0.01 to 3.0 V at different current densities (Land CT2001A). Cyclic voltammograms (CVs) were carried out on CHI-760 electrochemical workstation over the potential range 0.01–3.0 V at a scan rate of 0.1 mV s^{-1}.

Structural Characterization

The samples were characterized by X-ray powder diffraction (XRD) with a Bruker D8 advanced X-ray diffractometer equipped with graphite-monochromatized Cu Kα radiation (Kα= 1.5418 Å), recorded with the 2θ ranging from 10° to 80°. The scanning electron microscope images were taken with a JEOL JSM-7600F field-emission scanning electron microscope (FESEM). The high-resolution transmission electron microscope (HRTEM) images were recorded on a JEOL-2110 high-resolution transmission electron microscope at an acceleration voltage of 200 kV. The materials were further characterized by transmission electron microscopy (TEM) using JEOL-1011 microscope. Thermal gravimetric analysis (TGA) was carried out on a Mettler Toledo TGA/SDTA851 thermal analyzer apparatus. Nitrogen-sorption measurements were performed on a Tristar II 3020m gas sorptometer. Samples were degassed to 0.003 mmHg for 12 h at 608C. Specific surface areas were calculated by using the Brunauer–Emmett–Teller (BET) method, and pore sizes and volumes were estimated from pore-size distribution curves from the adsorption branches of the isotherms.

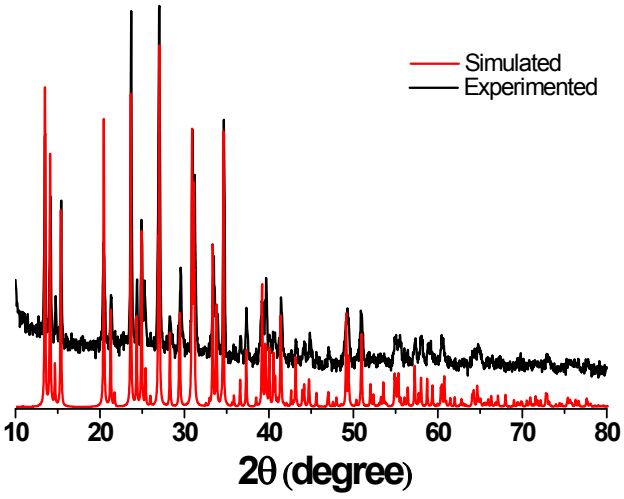

Fig. S1 The XRD pattern of the obtained Mn-LCP sample and the simulated XRD pattern from single crystal data (refcode: SEFNAU).

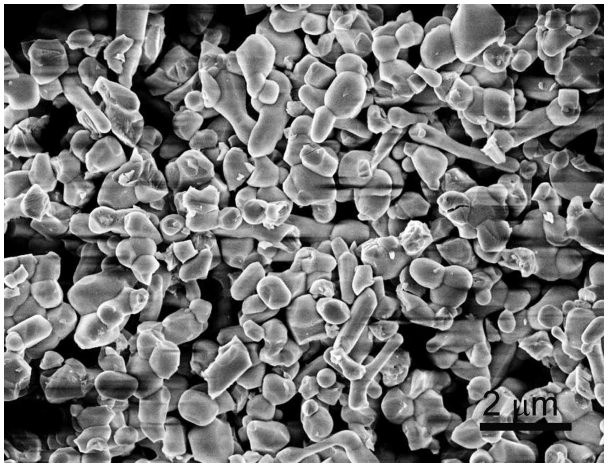

Fig. S2 The SEM image of the synthesized microsized Mn_2O_3.

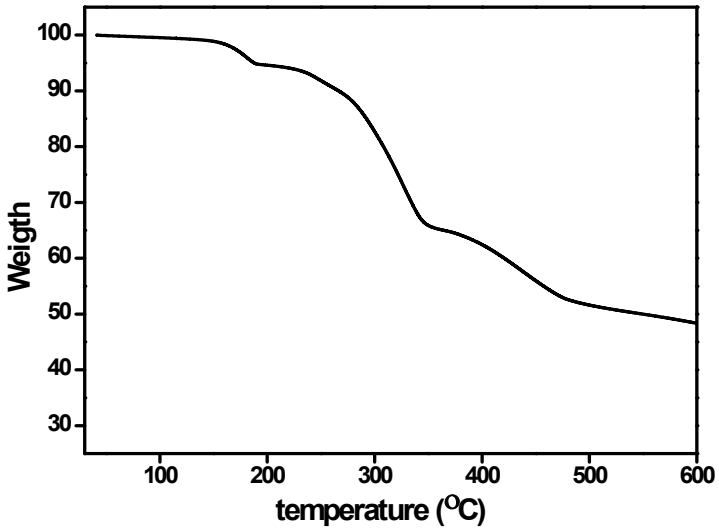

Fig. S3 the TGA curve of the Mn-LCP (in air 10 °C/min).

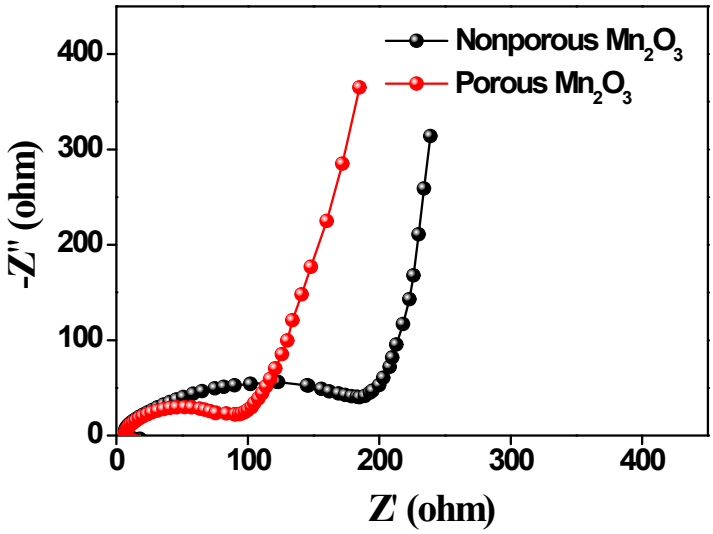

Fig. S4 Nyquist plots for the electrodes based on the porous porous Mn_2O_3 and microsized Mn_2O_3.