Electronic Supplementary Information

Facile preparation of $ZnMn_2O_4$ hollow microspheres as high-capacity anodes for lithium-ion batteries

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Experimental

Materials Synthesis. A typical synthesis of $ZnMn_2O_4$ hollow microspheres was conducted as follows: 3.3 mmol of $Zn(NO_3)_2 \cdot 6H_2O$, 6.7 mmol of $MnSO_4 \cdot H_2O$, and 100 mmol of $(NH_4)_2SO_4$ were dissolved in 700 mL of distilled water to form solution A. 100 mmol of NH_4HCO_3 was dissolved in 700 mL of distilled water to form solution B. 70 mL of ethanol and the solution B were poured into the solution A sequentially under vigorous stirring. Then, the mixture was put into an oven and maintained at 50 ºC for 9 hours. The white precipitates (Zn doped $MnCO_3$) were collected by centrifugation, washed by distilled water and ethanol for three times, and dried at 80 ºC. To convert the carbonate into $ZnMn_2O_4$, the as-synthesized Zn doped $MnCO_3$ was calcined at 600 ºC for 5 hours in air.

Materials Characterization. X-ray diffraction (XRD) patterns were collected on a Bruker D8 Advanced X-Ray Diffractometer with Ni filtered Cu Kα radiation at a voltage of 40 kV and a current of 40 mA. Field-emission scanning electron

microscopy (FESEM) images were obtained on a JEOL JSM 6700F microscope operated at 5 kV. The composition of the samples was analyzed by energy dispersive X-ray spectroscopy (EDX) attached to the FESEM instrument. Transmission electron microscopy (TEM) images were taken on JEOL 2010 and JEOL 2100 microscopes at 200 kV. Thermogravimetric analysis (TGA) was carried out under air flow with a temperature ramp of 10 ºC min^{-1}. Nitrogen adsorption-desorption isotherms were measured at -196 ºC on a nitrogen sorption apparatus (Autosorb 6B, Quantachrome). The Brunauer−Emmett−Teller (BET) surface area of the sample was determined from the adsorption branch of the isotherm in the relative pressure range of 0.05 – 0.30. The pore size distribution of the sample was calculated from the adsorption branch by the Barrett−Joyner−Halenda (BJH) method.

Electrochemical Measurements. The electrochemical measurements were carried out in two-electrode Swagelok-type cells. The working electrodes consisted of 70% active material (that is the $ZnMn_2O_4$ hollow microspheres), 20% conductive carbon black (Super-P-Li), and 10% polymer binder (polyvinylidene fluoride, PVDF). Metallic lithium was used as both the counter electrode and reference electrode. 1M $LiPF_6$ in a mixture of ethylene carbonate and diethyl carbonate (1/1 by weight) was used as the electrolyte. Cell assembly was carried out in an Ar-filled glovebox with moisture and oxygen concentrations below 1.0 ppm. Cyclic voltammetry (0.01 – 3.0 V, 0.2 mV s^{-1}) measurements were performed on a CHI660C electrochemical workstation. The galvanostatic charge-discharge tests were performed on a NEWARE battery tester.

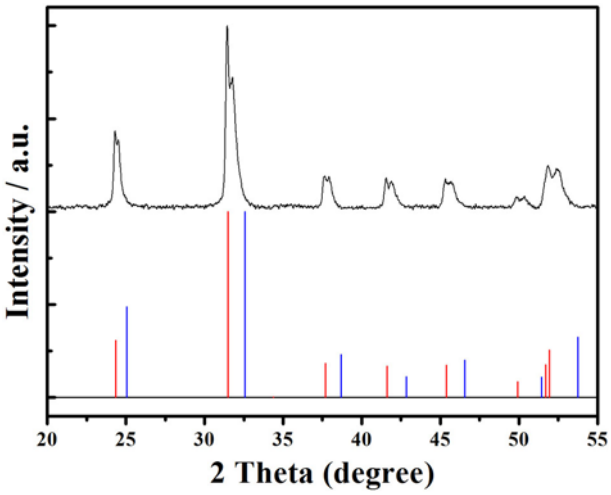

Figure S1. XRD patterns of the $ZnCO_3$−$MnCO_3$ composite. The red lines represent the standard XRD pattern of $MnCO_3$ (JCPDS Card No.: 83-1763, space group: $R\bar{3}c$, $a = b = 4.768$ Å, $c = 15.635$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$), while the blue lines represent the standard XRD pattern of $ZnCO_3$ (JCPDS Card No.: 83-1765, space group: $R\bar{3}c$, $a = b = 4.652$ Å, $c = 15.025$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$).

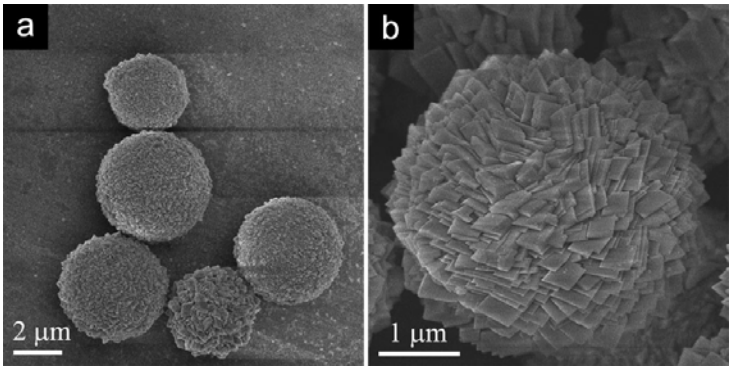

Figure S2. FESEM images of $ZnCO_3$−$MnCO_3$ composite microspheres.

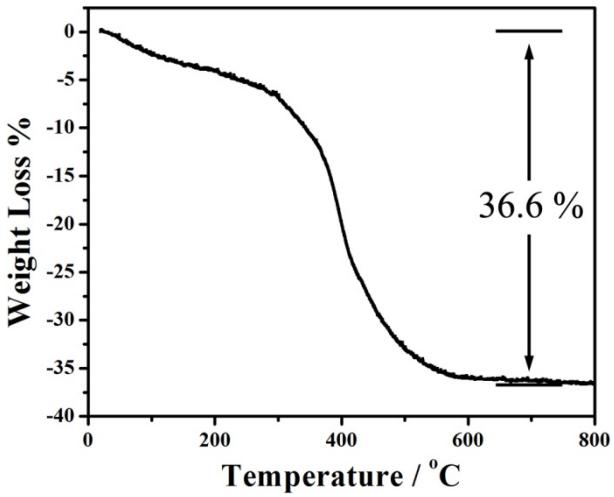

Figure S3. TGA curve of the $ZnCO_3$−$MnCO_3$ composite under air flow with a temperature ramp of 10 ºC min^{-1}.

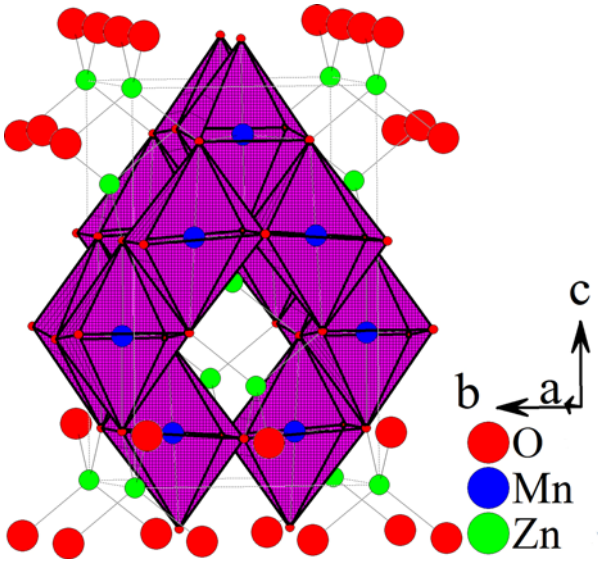

Figure S4. Schematic crystal structure of $ZnMn_2O_4$ spinel.

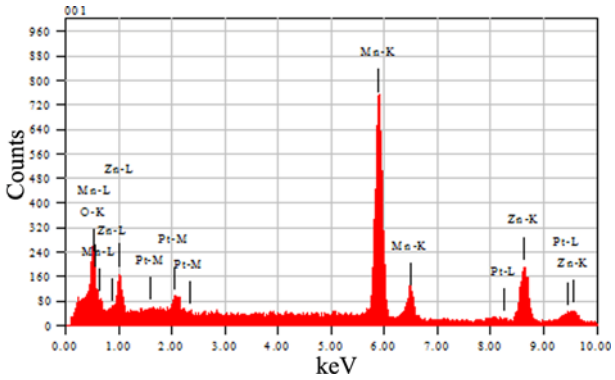

Figure S5. EDX spectrum of the $ZnMn_2O_4$ hollow microspheres.

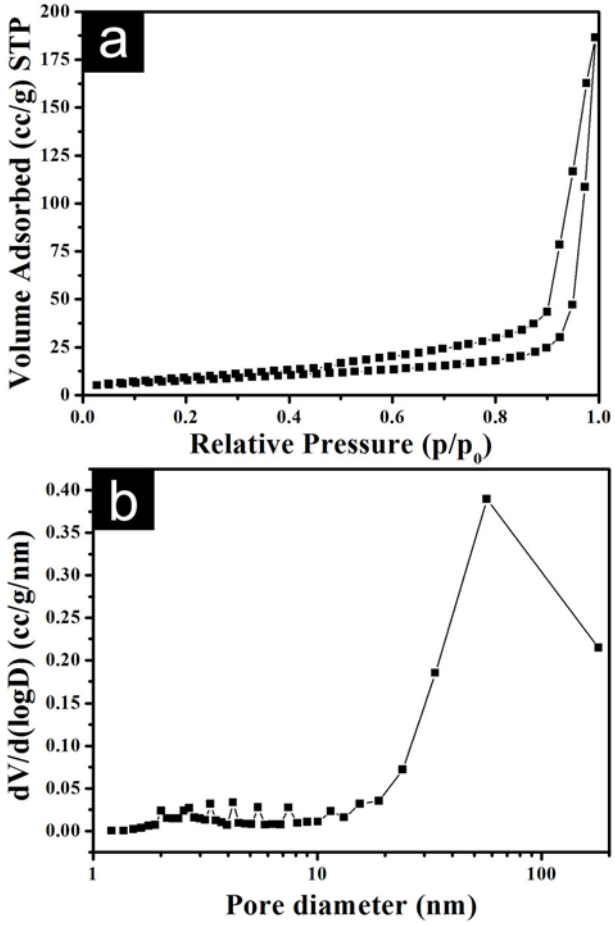

Figure S6. N_2 adsorption-desorption isotherm (a) and pore size distribution (b) of the $ZnMn_2O_4$ hollow microspheres.

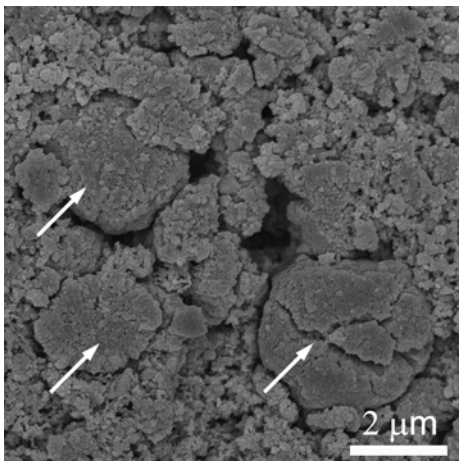

Figure S7. FESEM images of the electrode made of $ZnMn_2O_4$ hollow spheres after 100 cycles at 400 mA g^{-1}.