Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A. This journal is © The Royal Society of Chemistry 2015

Supporting Information for

Formation of Stable Carbon Framework in MnO Yolk-Shell Sphere to Achieve Exceptionally Performance for Li-Ion Batteries Anode

Shengbin Wang, Changlei Xiao, Yalan Xing, Huaizhe Xu, Shichao Zhang*

Experimental:

Synthesis of interdispersed MnO-YS spheres:

Solution A: 1.5 g MnSO₄•H₂O and 10 g (NH₄)₂SO₄ are dissolved into 200 mL of deionized water. Solution B: 7.9 g NH₄HCO₃, 20 mL ethanol, and 100 mL deionized water. Then, the solution B poured into the solution A with vigorous stirring. The mixture is kept under stirring for 5 h in the room temperature. The white MnCO₃ spheres are obtained by suction filtration, and dried at 80°C. Finally, the MnO-YS spheres are obtained by heating at 700 °C for 2 h in an inert gas.

Preparation of MnO@CF spheres:

0.2 g MnO-YS spheres and 0.1 g dopamine are dissolved into 100 mL deionized water under stirring for 1 h. Then, Tris-buffer are added to the mixture until pH=8.5. The mixed solution is subjected to continuous magnetic stirring at room temperature for 24 h. Afterwards, the precipitates, *i.e.* MnO@polydopamine, were collected by suction filtration, then washed by a large amount of deionized water, and then dried at 80°C. The resulting sample is heated to 700°C with following N₂, and kept at this temperature for 2 h. The obtained composite was denoted as MnO@CF.

Material Characterization:

The obtained samples were characterized by X-ray diffraction (XRD, Rigaku D/Max-2400, Cu Kα), scanning electron microscope (SEM, Hitachi S-4800), high-resolution transmission electron microscopes (HRTEM, JEOL JEM-2010), Thermogravimetric analysis (TGA, NETZSCH STA 449C),

Raman spectra (labRAM ARAMIS, λ =532 nm) and X-ray photoelectron spectra (XPS, Thermo VG ESCALAB250). The specific surface area determination, pore volume and size analysis are determined by nitrogen adsorption–desorption at 77 K using a Quantachrome Autosorb-1C-VP analyzer. The carbon and nitrogen contents are measured by using a Vario EL cube organic element analyzer.

The electrochemical experiments are examined using Coin-type cells (CR 2032) with lithium foil as the anode. The working electrode is fabricated with 80% MnO@CF or MnO-YS, 10% acetylene black and 10% PVDF binder. The active material loading on copper-foil collector is around 2 mg cm⁻². Cells are assembled in an argon filled glovebox with electrolyte of 1 mol L⁻¹ LiPF₆ in ethylene carbonate-ethyl methyl carbonate-dimethyl carbonate (EC-EMC-DMC = 1:1:1, volume ratio) solution and a separator of Celgard 2400. Electrochemical data are collected using LAND CT2001A test system within the potential range of 0.01-3.0 V (*vs.* Li⁺/Li). A CHI 660E electrochemical workstation is employed for cyclic voltammograms (CV) tests at a scan rate of 0.1 mV s⁻¹ between 0.01 and 3.0 V *vs.* Li⁺/Li. Electrochemical impedance spectra (EIS) are recorded on a Zahner IM6e electrochemical workstation at room temperature, in the frequency range from 1 MHz to 10 mHz.



Fig. S1. (a) SEM and (b) TEM images of MnCO₃; (c) SEM and (d) TEM images of MnO-YS.



Fig. S2. XRD pattern of MnO@CF and MnO-YS.



Fig. S3. SEM-EDS mapping image of MnO@CF.



Fig. S4. The SEM images of the carbon framework.



Fig. S5. The XPS analysis of N1s peak from the MnO@CF.



Fig. S6. The galvanostatic charge/discharge curves of 2nd and 500th cycle.



Fig. S7. Ragone plot showing the position of the MnO@CF material relative to the MnO-YS.



Fig. S8. Equivalent circuit used for simulating the experimental impedance data.

Impedance*	cycles	$R_s(\Omega)$	$R_{SEI}(\Omega)$	$R_{ct}(\Omega)$
MnO@CF	10 th	1.7	18.8	22.3
	100 th	1.6	17.4	21.9
MnO-YS	10 th	6.5	51.7	148.6
	100 th	20.8	192.1	272.9

Table S1. The impedance value of MnO@CF and MnO-YS samples after 10th and100th cycles.

*The EIS measurements are all carried out in the frequency range of 1 MHz to 10 mHz at the discharge state (0.01 V) after 10th and 100th cycles.