

Electronic Supplementary Information

A Porous LiFePO₄ and Carbon Nanotube Composite

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Experimental Section

Multiwalled carbon nanotubes (CNT) were purchased from Chengdu Alpha Nano Technology Co. Ltd, purified and functionalized by the mixed acid method to achieve better water dispersion. LiFePO₄-CNT composite materials were prepared by using an *in situ* sol-gel method as follows: first, 0.03 mol of lithium dihydrogen phosphate (LiH₂PO₄) was dissolved in 200 mL of water and stirred at 70 °C for 1 h. Separately, 0.03 mol of iron (III) citrate and 0.2365 g of CNTs were dissolved in 300 mL of water via ultrasonic agitation for 30 min, followed by mechanical agitation (magnetic stir-bar) at 65 °C for 1 h. The two solutions were mixed together and dried at 60 °C for 24 h. After thorough grinding with a mortar and pestle, the obtained material was fired in an inert (argon) atmosphere at 700 °C for 10 h with a heating rate of 10 °C min⁻¹. For the synthesis of pristine porous LiFePO₄, the procedure was similar but CNTs were not added.

XRD measurements were carried out with an ARL X'TRA advance diffractometer using filtered CuKa radiation, and the experimental diffraction patterns were collected at room temperature by step scanning in the range of 10-80°. The morphology of the composites was investigated on a field-emission scanning electron microscope (FESEM, Hitachi S-4800). TEM measurements were performed with a JEOL

JEM-200CX transmission electron microscope. The charge and discharge experiments were carried out using a NEWARE BTS (5V, 50mA) computer-controlled battery test station with coin-shape cells (1.54 cm^2) between 2.2 and 4.0 V at different rates. Electrochemical cyclic voltammetry tests were performed using a Princeton Applied Research PARSTAT 2273 advanced electrochemical system with lithium film as both the counter and reference electrode over the potential range of 2.2-4.0 V at the scanning rate of 0.1 mV s^{-1} . Electrochemical complex impedance measurements were also carried out using a Princeton 2273 electrochemical system with an applied perturbation signal of 10 mV over the frequency range of 1 MHz to 100 mHz. Working electrodes were prepared by mixing appropriate amounts of the LiFePO₄ (or LiFePO₄-CNT), Super P, and poly(vinyl difluoride) (PVDF) in the ratio of 80:15:5 by weight, which were then pasted onto pure Al foil. Microporous polypropylene film (Celgard 2400) was used as the separator. The liquid electrolyte consisted of a solution of 1M LiPF₆ in ethylene carbonate (EC)-dimethyl carbonate (DMC) (1:1, v/v). The cells were assembled in an argon-filled glove-box and all the electrochemical measurements were conducted at room temperature.

XRD patterns

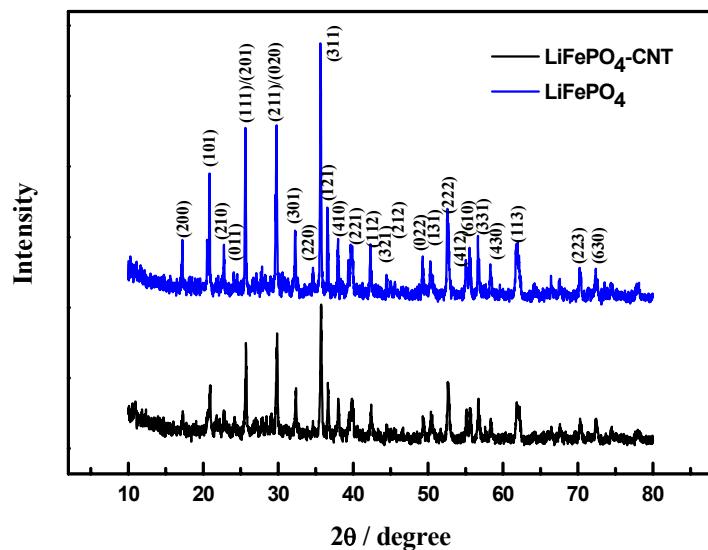


Fig. S1 XRD patterns of porous LiFePO₄ (blue) and LiFePO₄-CNT composite (black).

Impedance spectra

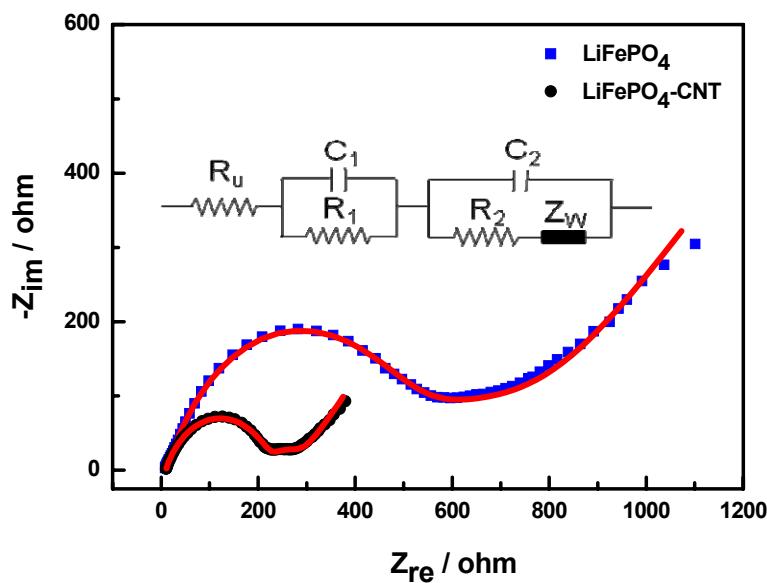


Fig. S2 Impedance spectra of porous LiFePO₄ (blue) and LiFePO₄-CNT composite (black), red solid lines are the fitting curves by using the inset equivalent circuit.

References

- S1 L. Laffont, C. Delacourt, P. Gibot, M. Y. Wu, P. Kooyman, C. Masquelier and J. M. Tarascon, *Chem. Mater.*, 2006, **18**, 5520.
- S2 D. Burch and M. Z. Bazant, *Nano Lett.*, 2009, **9**, 3795.
- S3 C. Delmas, M. Maccario, L. Croguennec, F. Le Cras and F. Weill, *Nat. Mater.*, 2008, **7**, 665.