

Electronic Supplementary Information

Hybrid porous bamboo-like CNTs embedding ultrasmall LiCrTiO₄ nanoparticles as high rate and long life anode materials for lithium ion batteries

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Experimental

Materials

Divinyl benzene (80%) (DVB) and boron trifluoride diethyletherate complex were purchased from Aladdin Reagent Company, and 4-vinylbenzylchlorid (90%) (VBC) was purchased from J&K Chemical Reagent Company. All other reagents were AR grade and provided by commercial suppliers and used without further purification. The polymer nanotubes (PNTs) and sulfonated polymer nanotubes (SPNTs) were prepared according to our methods previously reported.^{1,2}

Synthesis of ultrasmall LiCrTiO₄ nanoparticles embedded in bamboo-like porous carbon nanotubes

Firstly, 70 mg of SPNTs were dispersed in 4 mL of ethanol under ultrasonication for 30 min. Secondly, 1.7 g of tetrabutyltitanate (TBT) was added to the mixture, which was stirred for 12 h at ambient temperature to allow a saturated adsorption of TBT into the walls of the SPNTs. Thirdly, 8 mL of ethanol solution (0.414 g LiNO₃ and 1.92 g Cr(NO₃)₃·9H₂O) was added into the above system and stirred for 6 h at 60°C. After centrifugation, the residue was carefully taken out and wiped with tissue paper to remove excess liquid. The obtained solid materials were dried in air at 80°C for 12 h. Finally, the as-synthesized precursor was calcined at 850°C for 3 h in N₂ atmosphere (heating rate: 5°C min⁻¹) to obtain ultrasmall LiCrTiO₄ nanoparticles (6±2 nm) homogeneously embedded in bamboo-like porous carbon nanotubes. The obtained nanocomposites were denoted as LCT.

Characterization

The morphology, microstructure and composition of the samples were investigated by using a field emission scanning electron microscope (FESEM Hitachi S-4800) and high resolution transmission electron microscope (HRTEM JEOLJEM-2010F). X-ray diffraction (XRD) measurements were carried out with a Bruker D8 using filtered Cu K α radiation. Thermogravimetric analysis (TGA) was carried out with a Netzsch STA 449C in air at a heating rate of 10°C min⁻¹ from 30 to 800°C. Nitrogen adsorption-desorption isotherms were obtained using an Autosorb-iQ Pressure Sorption Analyzer (Quantachrome Instruments U. S.) at 77 K. The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method, and the pore size distribution was calculated by the Density Functional Theory (DFT) method.

Electrochemical characterization

The electrodes were fabricated by a conventional coating method. A slurry consisting of the as-synthesized active material (70 wt%), acetylene black (20 wt%) and polyvinylidene fluoride (10 wt%) in N-methyl-2-pyrrolidone was uniformly spread onto a Cu foil. The electrodes were dried at 110°C for 12 h in a vacuum oven. In an argon-filled glove box, coin cells were fabricated using lithium metal as the counter electrode, a Celgard 2400 membrane as the separator and LiPF₆ (1 M) in ethylene carbonate/diethyl carbonate/dimethyl carbonate (1:1:1 vol) as the electrolyte. The cyclic voltammograms (CVs) were collected on an electrochemical workstation (CHI660D, Chenhua, China) at a scan rate of 0.1 mV s⁻¹. The galvanostatic charge-discharge tests were performed on a Land (CT2001A China) between 0.01 and 3.0 V (versus Li⁺/Li). The specific capacities were calculated based on the total mass of the

composite materials and the typical loading of the active material on the Cu foil is about 0.54 mg cm⁻².

References

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- 2 Y. K. Tang, L. Liu, H. Y. Zhao, D. Z. Jia and W. Liu, *J. Mater. Chem. A*, 2016, **4**, 2089-2095.