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Interconnected porous carbon with tunable pore size as a model substrate to confine $LiFePO_4$ cathode material for energy storage

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ABSTRACT

$LiFePO_4$/C composites with tunable particle size and loading content have been prepared using the porous carbon with large pore volume and controllable pore size as an interconnected conductive framework and rigid nano-confinement matrix. The large pore volume of carbon provides sufficient space for $LiFePO_4$ hosting and the controllable pore size of carbon restricts the growth of $LiFePO_4$ crystals to further improve the rate performance. When used as the cathode materials for lithium-ion batteries, they exhibit a stable and high reversible capacity of 161 mA h g^{-1} at 0.1 C, 106 mA h g^{-1} at 20 C and 50 mA h g^{-1} at 50 C. The cell retains 94% of its initial capacity at 20 C over 200 cycles with an ultrahigh specific power of 10,446 W kg^{-1}. The high rate performance and good cycle stability can be ascribed to the small nanosized $LiFePO_4$ confined in the nanopores of the carbon matrix with suitable loading content and good contact between $LiFePO_4$ and the continuous conductive carbon framework, thus allowing fast lithium-ion diffusion and electrons transfer. This structure model may be valid for better understanding the rate performance and might be extended for fabrication of other high power electrode materials.

1. Introduction

In recent years, lithium-ion batteries (LIBs) have captured a large share of the rechargeable battery market for their great potential being used as power sources for electric vehicles (EVs) and hybrid electric vehicles (HEVs) [1,2]. The exploration of high-performance electrode materials is of vital importance to promote the electrochemical performance of LIBs [3,4]. Lithium iron phosphate ($LiFePO_4$), as a promising cathode material, has received substantial attentions, due to its high specific capacity, excellent structural stability, environmental benignity, and abundance of Fe element [5]. However, the charge/discharge capacity falls off rapidly with an increased rate, especially at a high current density, which seriously retards its wide applications in energy storage systems. The reason is attributed to its kinetic problems with low electronic conductivity and ion diffusion coefficient [6,7]. The key to address the problems lies in designing advanced materials including surface coating or admixing with electronically conductive materials [8–20], doping with ions [21,22], and creating sufficient porosity [23–28].

Among various approaches, carbon coating is regarded as an efficient way to surmount the electrochemical conductivity limitation. Besides improving the conductivity of $LiFePO_4$, carbon acts additionally as a functional dispersing agent to decrease the particle size of $LiFePO_4$, which greatly shortens the diffusion length of lithium ions and ameliorates the rate capacity. Different porous carbons were used to combine with $LiFePO_4$ [29–33]. For example, Doherty et al. prepared 50 wt% loading of $LiFePO_4$ inside hierarchically porous carbon synthesized from a porous silica hard template, which delivered a specific capacity of 140 mA h g^{-1} at 0.1 C and 100 mA h g^{-1} at a discharge rate of 5 C [29]. Wang et al. prepared a $LiFePO_4$/C composite with 87 wt% $LiFePO_4$ loading using mesoporous carbon CMK-3 as the support, which showed a high capacity of 118 mA h g^{-1} at 10 C [31]. Hill et al. made a high surface area $LiFePO_4$ cathode material using mesoporous carbon templated from cubic KIT-6 silica, showing a high power and rate capacity of 128 mA h g^{-1} at 23 C [33]. However, the loading of $LiFePO_4$ is quite low, only 34.4 wt%, which certainly leads to a low tap density. It should be noted that to achieve a continuous, uniform and thin carbon coating is often very difficult. A high amount of carbon content in the composites would seriously decrease the energy density, thus restricting practical applications.

Concerning the aforementioned main factors, we considered using highly interconnected carbon framework with abundant pores to synthesize $LiFePO_4$ cathodes, of which the morphology and dimension can be fine tailored through varying the pore sizes of the carbon matrix. In our previous work, we have synthesized advanced nitrogen-doped porous carbon materials based on

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poly(benzoxazine-co-resol) system [34–36], which offers a high degree of flexibility in the molecular design of monomers using amines as the nitrogen source. Nitrogen-containing carbon framework is practically more desirable in applications of electrochemistry [37,38]. Based on this system, we have prepared a high loading $LiFePO_4$/C composite, which delivers a high capacity of 155 mA h g^{-1} at 0.1 C and 85 mA h g^{-1} at 20 C [39].

For fundamentally understanding the correlation between the particle size of $LiFePO_4$ and their electrochemical performance, it is better to use control samples that are derived from the same precursors and are structurally tailorable. In this paper, we have purposively designed a synthesis of interconnected carbon framework with tunable pore size by adding colloidal silica nanospheres as the hard templates. By changing the size of the silica template, the mesopore size of the carbon is precisely controlled to be 7, 14 and 22 nm. As a consequence, the obtained porous carbons possess a large pore volume in the range of 4.27–4.68 cm^3 g^{-1} as well as uniform mesopores, into which $LiFePO_4$ can be infiltrated. The synthesized $LiFePO_4$ cathodes are structurally tailorable due to the confinement effect of the porous carbon, which results in faster lithium-ion diffusion and higher rate performance. The obtained composite containing 86 wt% of $LiFePO_4$ with particle size of 14 nm achieves an improved capacity of 161 mA h g^{-1} at 0.1 C and 106 mA h g^{-1} at 20 C and the lithium-ion diffusion coefficient is increased by one order of magnitude compared with the bigger $LiFePO_4$ particles of 22 nm in size. Although the carbon content is still high compared with the commercial products (carbon content is less than 5 wt%), the large pore volume of carbon can promise a relatively higher content of $LiFePO_4$ than that of the samples by using this porous carbon template method. This proposed structure may be acted as a model substrate to be extended for the fabrication of other high power electrode materials.

2. Experimental

2.1. Chemicals

Resorcinol (99.5%) was purchased from Tianjin Kermel Chemical Reagent Co., Ltd. Ludox AS-40, Ludox HS-40 and Ludox SM-30 were purchased from Sigma–Aldrich. Formalin (37 wt%), 1,6-diaminohexane (DAH, 99.0%), phosphoric acid (85%), iron (III) nitrate nonahydrate (98.5%) and lithium acetate dehydrate (99%) were supplied by Sinopharm Chemical Reagent Co., Ltd. All chemicals were used as received.

2.2. Preparation of mesoporous $LiFePO_4$/C composites

2.2.1. Synthesis of porous carbons

The commercially available, aqueous suspension of silica colloids (Ludox AS-40, Ludox HS-40, Ludox SM-30), containing 40 wt%, 40 wt%, 30 wt% silica and with an average colloid size of 24 nm, 12 nm and 7 nm were used directly in the synthesis. Typically, 2 mmol resorcinol was first dissolved in deionized water with vigorous stirring at 24 °C and then 4 mmol formaldehyde were added to form a clear solution. Subsequently, a certain amount of Ludox was added into the clear solution. After addition of 0.5 mmol DAH, the clear solution turns white immediately. The resultant solution was further heated to 80 °C accompanied with vigorous stirring for 18 h. The precipitated compounds were obtained by filtration and then purified with water and ethanol. The as-prepared Si/polymer composites were pyrolyzed at 800 °C for 2 h under nitrogen atmosphere. The pyrolyzed product was treated with aqueous NaOH solution (2.5 M) to remove the silica and further recovered by filtration, washed with water and ethanol. The molar ratio of SiO_2 and resorcinol was fixed at 5:1, the obtained carbon materials synthesized using different silica template were accordingly denoted as C7, C14, and C22.

2.2.2. Synthesis of $LiFePO_4$/C composites

$LiFePO_4$/C composites were fabricated using the synthesized porous carbon as the matrix. A lithium iron phosphate precursor solution was prepared using water as the solvent. In a typical procedure, 10 mmol of $Fe(NO_3)_3{\cdot}9H_2O$, 10 mmol of $C_2H_3O_2Li{\cdot}2H_2O$, and 10 mmol of H_3PO_4 were dissolved in a minimal amount of water with stirring to ensure the total solution to 5 mL. Then, the transparent solution was added dropwise to 0.1 g of carbon with stirring, followed by drying at 90 °C in a vacuum oven. The amount of the impregnating solution was calibrated based on the pore volume of the porous carbon. To fully utilize the pore volume, the same impregnation procedure was repeated once more, followed by drying at 90 °C overnight. Finally, the powder was heated under a flowing atmosphere of H_2 (5 vol%)/N_2 (95 vol%) at 3 °C min^{-1} to 750 °C and maintained there for 6 h to yield a black powder. The $LiFePO_4$/C composite with $LiFePO_4$ loading of 86% using carbon C14 as support was denoted as LFP/C14-86%. In the same manner, $LiFePO_4$/C composites were sequentially named LFP/C22-86%, LFP/C7-86% and LFP/C7-80%.

2.3. Characterization

The X-ray diffraction (XRD) measurements were taken on a Rigaku D/Max 2400 diffractometer using Cu-Ka radiation (40 kV, 100 mA, $\lambda = 1.5406$ Å). The experimental line broadening has been considered during the calculation of grain sizes and the size calculation method of all the samples was same by using the software Jade. Scanning electron microscope (SEM) investigations were carried out with a Hitachi S-4800I instrument at 10 kV. Transmission electron microscopy (TEM) images were obtained with a FEI Tecnai F30 or a Hitachi HF2000 transmission electron microscope, equipped with a cold field emission gun. Nitrogen sorption isotherms were measured with a Micromeritics tristar 3000 instrument at liquid nitrogen temperature. Samples were degassed at 200 °C for at least 4 h prior to determination of the isotherms. The Brunauer–Emmett–Teller (BET) method was utilized to calculate the specific surface areas (SBET). Pore size distributions (PSDs) were derived from the adsorption branches of the isotherms using the Barrett–Joyner–Halenda (BJH) model. Thermogravimetric analysis was measured from room temperature to 800 °C in air with a heating rate of 10 °C min^{-1} using a STA449 F3 Jupiter thermogravimetric analyzer (NETZSCH).

2.4. Electrochemical analysis

The electrodes were fabricated using a mixture of active material (80 wt%), conductive carbon black (15 wt%), and polyvinylidene fluoride (PVDF 5 wt% Aldrich) in N-methyl-2-pyrrolidone (NMP) to form a slurry. The slurry was spread onto Al foil and dried in a vacuum oven at 100 °C overnight. The electrode area is 1.13 cm^2 and the loading of active material is 2.0 ± 0.5 mg cm^{-2}. Electrochemical experiments were performed via CR2025 cointype test cells assembled in an argon-filled glove box, using Li metal as the negative electrode and Celgard 2400 membrane as the separator. The electrolyte consists of a solution of 1 M $LiPF_6$ in dimethyl carbonate (DMC), ethyl methyl carbonate (EMC) and ethylene carbonate (EC) (1:1:1, v/v/v). The galvanostatic charge and discharge experiment was performed in the range of 2.5–4.2 V at room temperature on a Land CT2001A battery test system. Cyclic voltammetry (CV) measurement was carried out on an electrochemical workstation (CH Instruments Inc., Shanghai, China, CHI660D). The electrochemical impedance spectroscopy (EIS) was performed by using EG&G model 273 Galvanostat/Potentiostat equipped with