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Nanoparticles-constructed spinel $ZnFe_2O_4$ anode material with superior lithium storage performance boosted by pseudocapacitance

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ABSTRACT

The practical application of $ZnFe_2O_4$ in lithium ion batteries (LIBs) is severely hampered by its fast capacity fading and poor rate performance. To overcome these issues, herein, $ZnFe_2O_4$ powders consist of aggregated nanoparticles (50 ~ 100 nm) with porosity were prepared by a facile co-precipitation method and subsequent thermal decomposition. When used as anode material for LIBs, the $ZnFe_2O_4$ sample delivers capacities of 920, 820, 650, 485, and 421 mA h g^{-1} at current densities of 0.5, 1, 3, 7, and 10 A g^{-1}, respectively. Moreover, the sample can maintain a capacity of 814 mA h g^{-1} even after 300 cycles at the current density of 1 A g^{-1}, implying an excellent rate capability and cycling stability. Cyclic voltammetry analysis reveals that both diffusion-controlled lithium storage and surface pseudocapacitive lithium storage contribute to the total stored charge of $ZnFe_2O_4$, which boosts the high rate capability and superior cycling stability of the $ZnFe_2O_4$.

1. Introduction

Lithium ion batteries (LIBs) have been widely used as the primary power source for portable electronic devices, hybrid electric vehicles (HEVs), full-electric vehicles (EVs), and large-scale renewable energy storage systems [1,2]. To fulfill the ever-increasing demand for high power/energy density, developing new electrode materials with high specific capacity, high rate capability, and superior cycling stability has become an urgent and key task for building the next-generation LIBs [3,4]. Commercial graphite anode for LIBs has a relatively low theoretical capacity (~ 372 mA h g^{-1}) and cannot meet the requirement of high-energy applications. In recent years, mixed transition metal oxides (MTMOs) have been recognized as promising alternative anode materials for LIBs because of their high theoretical capacity based on the conversion reactions [5–8]. In particular, spinel $ZnFe_2O_4$ stands out from the Fe-based MTMOs owning to its particularly high theoretical capacity (1072 mA h g^{-1}), low toxicity, abundant resources, and lower working voltage (~ 1.5 V for lithium extraction) [9,10]. Unfortunately, $ZnFe_2O_4$ suffers from fast capacity decay, low rate capability, and large volume change upon cycling, which severely hamper its practical application in LIBs [11–14]. Fabricating nanostructured $ZnFe_2O_4$ anode materials has been demonstrated an effective strategy to tackle these problems [6,8,15–17]. Various nanostructured $ZnFe_2O_4$, such as nanoparticles [18,19], porous nanospheres/nanosheets [20,21], hollow microspheres [22,23], nanofibers/nanotubes [11,24,25], nano-octahedrons [26], and nanorods [27,28] have been reported. All these materials exhibited improved lithium storage performance compared to the bulk $ZnFe_2O_4$ because of their smaller particle size and larger surface area, which greatly shorten the diffusion pathway of both Li^+ ions and electrons, increase the contact area between active material and electrolyte, and relax the mechanical stress due the huge volume change during lithiation/delithiation process [29–31,32]. In addition to the above mentioned nano-sized effects, another contribution, that of pseudocapacitive behavior, is expected to become increasing important for some metal oxides at nanoscale dimensions [33–35]. However, there are few reports on the contribution of pseudocapacitance effect to the electrochemical properties of $ZnFe_2O_4$ nanomaterials. In the present work, spinel $ZnFe_2O_4$ powders consist of aggregated nanoparticles (50 ~ 100 nm) with porosity were prepared via a facile and scalable co-precipitation approach and subsequent thermal decomposition at 800 °C in air. Particularly, the pseudocapacitive lithium storage behavior is quantitatively analyzed based on cyclic voltammograms (CV). Benefiting from the nanoparticles-constructed structure and significant pseudocapacitive effect, the synthesized $ZnFe_2O_4$ powders exhibit high specific capacity, superior cycling stability, and outstanding high rate capability.

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2. Experimental section

2.1. Material preparation

All the reagents are of analytical purity and used without further purification. In a typical procedure, 5 mmol $ZnSO_4·7H_2O$, 10 mmol of $FeSO_4·7H_2O$ were dissolved in 100 mL deionized water. After ultrasonic treatment for 10 min, an aqueous solution of NH_4OH (250 mL, ~0.34 M) was added dropwise into the above sulfate solution under constant vigorous stirring at room temperature. After continuous stirring for 6 h, the deposit was kept in the mother solution at room temperature for 12 h and allowed to settle, then washed with deionized water, filtered, and freeze dried to a constant weight. Finally, the as-prepared precursors were calcinated at 800 °C for 2 h in air to obtain $ZnFe_2O_4$ powders.

2.2. Physical characterization

The crystal structure of the prepared sample was analyzed by X-ray diffraction (XRD) on an PANalytical X'Pert3 Powder using Cu Kα radiation ($\lambda = 0.15405$ nm). The surface morphology of the sample were observed by field-emission scanning electron microscope (FESEM, Hitachi SU5800) and transmission electron microscopy (TEM, JEM-2100F). Thermogravimetric analysis (TGA, TGA-Q600) was performed from 25 to 900 °C at a heating rate of 10 °C min^{-1} in air. The tap density was measured by mechanically taping the dry measuring cylinder containing the product $ZnFe_2O_4$ until the constant volume was observed. The ratio of the mass to tapped volume of the product $ZnFe_2O_4$ powder gives the tap density. The Brunauer-Emmett-Teller (BET) specific surface area of the product $ZnFe_2O_4$ was measured using a Micromeritics Tristar II-3020 nitrogen adsorption apparatus.

2.3. Electrochemical measurements

The electrochemical performances of the prepared sample were tested using coin-type cells (CR2016), which were assembled in an argon-filled glove box. The working electrode was fabricated by mixing the prepared $ZnFe_2O_4$ powders, super P carbon black, and poly (vinylidene fluoride) (PVDF) binder with a weight ratio of 6:3:1 in *n*-methyl-2-pyrrolidone (NMP) solvent to obtain a homogenous slurry. The slurry was pasted onto copper foil current collector and dried in vacuum oven at 80 °C for 12 h. The mass loading of active material in our working electrode was about 1.0 mg cm^2. Lithium metal foils were used as both the counter and reference electrodes. The electrolyte was 1 M $LiPF_6$ dissolved in a mixture of ethylene carbonate(EC), dimethyl carbonate (DMC), and diethyl carbonate(DEC) with a volume of 1:1:1. A polypropylene (PP) membrane (Celgard 2400) was used as the separator.

Cyclic voltammetry (CV) and electrochemical impedance spectra (EIS) measurements were performed on a CHI760E electrochemical workstation. The CVs were recorded within the voltage orange of 0.01 ~ 3.0 V (vs. Li/Li^+) at a series of scanning rates. The EIS were measured in the frequency ranging from 100 mHz to 100 kHz by applying an AC amplitude of 5 mV at a charged state of 3.0 V. Charge-discharge measurement were carried out by a NEWARE battery testing system in the voltage range of 0.01 ~ 3.0 V (vs. Li/Li^+). All the electrochemical tests were performed at room temperature.

3. Results and discussion

Fig. 1a gives the XRD pattern of the $ZnFe_2O_4$ powders obtained by calcinating the precursor at 800 °C in air. All the diffraction peaks of $ZnFe_2O_4$ powders can be indexed to cubic $ZnFe_2O_4$ (JCPDS 22-1012) [14], and no impurity peaks assigned to ZnO and Fe_2O_3 are observed. The narrow and intense diffraction peaks illustrate the good crystallinity of the prepared $ZnFe_2O_4$ powders. The average crystal sizes of the $ZnFe_2O_4$ powders estimated using Scherrer's formula are about 64 nm, which is consistent with the TEM images in Fig. 1d. The morphology of the as-prepared $ZnFe_2O_4$ powders is characterized by SEM and TEM. As shown in Fig. 1b, the material is composed of sphere-like nanoparticles. The nanoparticles agglomerate with each other and there are plenty of void spaces between the interconnected primary nanoparticles. The TEM image in Fig. 1c shows that the particle size of the material is in the range of 50 ~ 100 nm, which is consistent with that calculated from XRD data. HRTEM image (Fig. 1d) shows that primary nanoparticles are singe-crystalline. The lattice fringe spacing of 0.49 nm matches well with the (111) lattice plane of the cubic $ZnFe_2O_4$. The measured tap density of the $ZnFe_2O_4$ powder is ~0.75 g cm^3. This nanoparticles-constructed agglomeration is expected to improve the electrochemical performance in the following aspects: the nano-sized building blocks offer large surface area and short diffusion distances for fast Li^+ ion diffusion. The rigid connections among the primary nanoparticles provide a continuous electronic transfer channel for the $ZnFe_2O_4$ agglomeration. The large amount of void spaces in the agglomeration not only ensure efficient electrolyte penetration, but also confer the ability to accommodate the volume changes upon discharge/charge cycling.

Fig. 2 shows the nitrogen adsorption/desorption isotherms of the $ZnFe_2O_4$ powders. The sample shows type IV sorption isotherms (IUPAC classification) with a distinct H3-type hysteresis loop at the relative pressure (P/P_0) range of 0.1–0.95, which is a characteristic of mesoporous materials. The BET specific surface area of the $ZnFe_2O_4$ powders is calculated to be 7.5 $m^2 g^{-1}$, and the average pore size is 3.6 nm. In addition, the pore volume was measured to be 0.0132 $cm^3 g^{-1}$. The large specific surface area and mesoporous structure would benefit electrochemical reaction and electrolyte penetration in the $ZnFe_2O_4$ electrode.

Fig. 3a illustrates the CV curves of the $ZnFe_2O_4$ sample for the first four consecutive cycles at a scan rate of 0.1 mV s^{-1}. There is a notable difference between the first cycle and subsequent cycles. In the first cathodic sweep, the intense reduction peak at 0.64 V can be assigned to the electrochemical reduction of Fe^{3+}/Zn^{2+} to Fe° /Zn°, the further lithiation of Zn° to a Li-Zn alloy, and the formation of solid electrolyte interface (SEI) film during the lithiation step [12,19]. This reduction peak shifts to 0.84 V and become weak in the subsequent cycles, which can be due to the drastic lithium-driven structural and/or textural modifications on the electrode during the first lithiation process [36]. In the first anodic sweep, the strong oxidation peak at 1.58 V can be assigned to the reversible oxidation of metallic zinc and iron to Zn^{2+} and Fe^{3+} during the delithiation step [37,38]. This oxidation peak slightly shifts from 1.58 V to 1.67 V during the subsequent cycles, which is likely due to structure rearrangement [26,39]. The well-overlapped CV profiles of the third and the fourth cycle indicate the good electrochemical reaction reversibility and retention property of the electrode. Fig. 3b presents the galvanostatic discharge/charge profiles of the $ZnFe_2O_4$ in the 1st, 2nd, 10th, 50th, 100th cycles at a current density of 500 mA g^{-1}. The first discharge profile displays a long voltage plateau at about 0.8 V and at last gradually declines to the cutoff voltage of 0.01 V, which is related to the reduction of $ZnFe_2O_4$ and the formation of SEI film on the surface of the electroactive material [24]. The discharge plateau shifts to about 1.0 V in the subsequent cycles, which agree well with the CV analysis. A sloping plateau at 1.5 ~ 2.0 V is observed for all the charge process, which is due to the oxidation conversion from Zn°/Fe° to Zn^{2+}/Fe^{3+} during delithiation [40]. Fig. 3c displays the cyclability of the $ZnFe_2O_4$ electrode at a current density of 500 mA g^{-1}. The $ZnFe_2O_4$ electrode delivers an initial discharge capacity of 1690 mA h g^{-1} and a charge capacity of 1154 mA h g^{-1}, corresponding to a coulombic efficiency of 68.3%. The large irreversible capacity loss during the first cycle is mainly caused by the formation of SEI film on the surface of the electroactive materials [41]. After the prominent capacity loss in the first cycle, the capacity declines very slowly until 25th cycle (975 mA h g^{-1}), from which the capacity begins to climb up to 1259 mA h g^{-1} at 100th cycle, indicating the excellent cycling stability and capacity retention performance. The