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3-Dimensional hierarchically porous $ZnFe_2O_4$/C composites with stable performance as anode materials for Li-ion batteries

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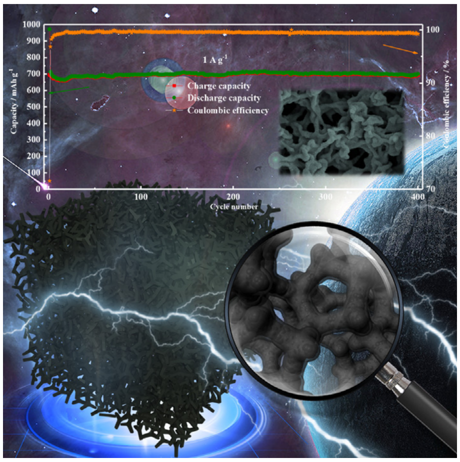
HIGHLIGHTS

- Hierarchically porous $ZnFe_2O_4$ is prepared by sol–gel with phase separation.
- Porous $ZnFe_2O_4$ is coated by N-doped carbon layer.
- $ZnFe_2O_4$/C displays interconnected macropores and co-continuous hollow skeletons.
- Hierarchically porous $ZnFe_2O_4$/C shows excellent cycling and rate performance.

GRAPHICAL ABSTRACT



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ABSTRACT

3-Dimensional hierarchically porous $ZnFe_2O_4$/C composites with interconnected macropores and co-continuous hollow skeletons are facilely synthesized and used as anode materials for Li-ion batteries. The interconnected macropores impede the agglomeration of primary particles and buffer the volumetric variations, hollow mesoporous skeletons not only improve the interfacial contact area between electrode and electrolyte but also facilitate lithium ions transfer rate. Moreover, N-doped carbon layer further enhances the conductivity and mechanical strength of skeletons, as well as accelerates electron transfer during repeated discharge and charge process. The as-prepared 3-dimensional hierarchically porous $ZnFe_2O_4$/C composites possess excellent Li-ion storage properties, delivering a high reversible capacity of 972 mAh g^{-1} at 200 mA g^{-1} after 100 cycles and a decent specific capacity of 711 mAh g^{-1} even at a large current density of 1000 mA g^{-1} after 400 cycles. These values are among the highest reported for $ZnFe_2O_4$-based materials with different morphologies and nanostructures. The resultant $ZnFe_2O_4$/C composites display the potential practical application for high-performance Li-ion batteries.

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1. Introduction

Rechargeable Li-ion batteries are regarded as one of the most promising energy storage devices and exploited for various applications ranging from portable electronic to electronic vehicles owing to their high energy density, long cycle lifetime, safety, no memory effect and environment compatibility [1–5]. Nevertheless, the conventional graphite anode suffers from limitation of safety in operation and a low theoretical capacity (372 mAh g^{-1}) and cannot fulfill the rapid development demands for Li-ion batteries with high power and energy density [6–10]. Therefore, it is crucial to explore other safer anodes alternatives with even larger capacity and stable cyclic performance [11,12].

According to the Li-ion storage mechanism, anode active materials consist of three main categories [13–15]. Carbon based active materials (such as carbon nanotubes, graphene and so on) are classified into intercalation/de-intercalation electrode [16–18]. Si, Sn etc. are a kind of alloy/de-alloy materials [19–22]. Transition metal oxides (TMO), metal sulphides etc. is subject to the mechanism of conversion reaction between lithium ions and anode [13,23–26]. TMO have gained extensive attention for Li-ion batteries owing to their high theoretical capacity (500–1000 mAh g^{-1}) [27–30]. Among the promising TMO candidates, $ZnFe_2O_4$ stands out from the others because of its low cost, low toxicity, environmental friendliness [31–39]. Compared with the other typical TMO, the Li-ion storage mechanism of $ZnFe_2O_4$ is different from that of others because it involves both the conversion and alloying reaction mechanisms. Upon finishing the conversion reaction of $ZnFe_2O_4$ with lithium ions, the reduzate Zn can further react with lithium ions to form Li-Zn alloy contributing to additional capacity [40,41].

Despite these outstanding advantages, the practical application of $ZnFe_2O_4$ is still hindered by fast capacity fading and bad rate capability, which results from huge volume swing during cycling and inherent poor electronic conductivity [34,35]. In addition, its application also suffers from a low Coulombic efficiency at first cycle and a poor energy efficiency due to large voltage hysteresis, and large voltage hysteresis is attributed to inherently different paths of reaction, interfacial thermodynamics derived from surface energy or mobility of the species during phase transformation [11,42,43]. To overcome these critical obstacles, considerable strategies have been developed to improve the electrochemical performance of $ZnFe_2O_4$ in Li-ion batteries, such as (i) designing special morphologies including nanofibers [44], nano-octahedrons [35], nanowires [45], microrods [46], hollow nanospheres [41], hollow fiber and so on [47]; (ii) element doping (such as Mn-$ZnFe_2O_4$ [48], S-$ZnFe_2O_4$ [49] and binary doped $ZnFe_2O_4$ [50,51]); (iii) smart hybridization of bi-hetero component ($ZnO/ZnFe_2O_4$ [52–55] and $ZnFe_2O_4/\alpha\text{-}Fe_2O_3$ [56]); (iv) compounded with carbon-based materials ($ZnFe_2O_4/C$ [45,57–62], $ZnFe_2O_4$/graphene [63–66], and $ZnFe_2O_4$@C/graphene [67–70]). It has been demonstrated that constructing porous nano-morphology and carbon coating are considered to be effective ways to accommodate the volume change as well as enhance the electrical conductivity [57,71]. The porous nano-structure guarantees high electrode/electrolyte contact area and accommodates the volume changes resulting from repeated charge/discharge process [71–73]. Meanwhile small particle size can efficiently shorten the reaction pathway of lithium ions insertion active into electrode. What is more, carbon layer can enhance the electronic conductivity and impede the agglomeration prolonging the cycling life.

Generally speaking, several methods have been proposed for the synthesis of $ZnFe_2O_4$, including urea combustion [40], electrospinning [47,51,60], electrophoretic deposition [64], high-temperature decomposition [57], hydrothermal [63,65,70], solvothermal [69,74], microwave irradiation [67] and co-precipitation [31]. Preparation methods mentioned above involve sophisticated equipment, rigorous experimental condition, toxic substance, product inhomogeneity, prohibitively high fabrication costs or poor reproducibility. Compared with other preparation methods, sol–gel method is characteristic of simple procedures and resultant homogeneity [62], and the size and distribution of pores can be easily controlled in this method. Some hierarchically porous electrodes prepared by sol–gel have been reported [75]. Hasegawa has synthesized the hierarchically porous $LiFePO_4/C$ composites and applied it as cathode material, delivering excellent performance with discharge capacity of 137 mAh g^{-1} at 0.1 C and 104 mAh g^{-1} at 1 C. In our previous work, hierarchically porous TiO_2/C composite was prepared as anode material for Li-ion batteries with excellent discharge/charge performance [42]. The references confirm that in the hierarchical porous structure, the presence of micropores provides high specific surface area and increases the interfacial area between electrode and electrolyte, while meso- and macropores allow the efficient mass transport of the electrolyte through the electrode. In conclusion, hierarchically micro-, meso- and macroporous materials meet the requirement of high active anode.

In this work, we have successfully developed a facile sol–gel accompanied by phase separation route to prepare Zn-Fe hydroxide xerogel monolith for the first time, followed by calcination to produce 3-dimensional (3D) hierarchically porous $ZnFe_2O_4$, and then N-doped carbon coating porous $ZnFe_2O_4$ to form $ZnFe_2O_4/C$ composites. The preparation and characterization of $ZnFe_2O_4/C$ composites are examined in detail, and the discharge/charge performance and the Li-ion storage mechanism are also discussed.

2. Experimental

2.1. Materials

Zinc chloride anhydrous ($ZnCl_2$, Sigma-Aldrich, ≥98%) and iron chloride tetrahydrate ($FeCl_2{\cdot}4H_2O$, Sigma-Aldrich, 98%) were utilized as zinc and iron sources, respectively. Glycerol ($C_3H_8O_3$, Sinopharm Chemical Reagent Co., Ltd, AR) was used as starting solvent to synthesize Zn-Fe hydroxide binary composite monolith. Poly (acrylic acid) (PAA, Sigma-Aldrich, 35 wt% in water, average molecular weight of 100,000) was used as a phase separation inducer as well as a network former. Propylene oxide (PO, Sinopharm Chemical Reagent Co., Ltd, AR) was added as a proton scavenger to initiate the gelation of the system. Tris(hydroxymethyl) aminomethane ($C_4H_{11}NO_3$, Aladdin, ≥99.8%) and hydrochloric acid (HCl, Sinopharm Chemical Reagent Co., Ltd, 37 wt% in water) were prepared for Tis-buffer solution. Dopamine hydrochloride ($(HO)_2C_6H_3CH_2CH_2NH_2{\cdot}HCl$, Sigma-Aldrich, ≥99%) was used as N-doped carbon precursors. Ethanol absolute (C_2H_6O, Sinopharm Chemical Reagent Co., Ltd, AR) and distilled water were as a washing solvent and starting composite solvent, respectively.

2.2. Synthesis

2.2.1. Preparation of Zn-Fe hydroxide and $ZnFe_2O_4$ monoliths

In a typical experimental procedure, firstly, 4 g of PAA and 1.2 mL of distilled water were mixed in a glass tube, and then 2.4 mL of glycerol was added. 0.408 g $ZnCl_2$ and 1.192 g $FeCl_2{\cdot}4H_2O$ with the molar ratio of 2:1 were added in sequence under stirring, and the mixture was continuously stirred for 1 h to form homogeneous sol. Then, 1.76 mL of PO was dropwise added into the above homogeneous sol under stirring. The glass tube with homogeneous sol was degassed by ultrasonication for 10 s, and was sealed and kept 60 °C for gelation and aging. The obtained wet gel was immersed in ethanol absolute for three times to exchange ring-opening reaction product, and then was dried by evaporation at 60 °C for 48 h. Some of the dried gels were then heat-treated up to 550 °C for 5 h with a heating rate of 2 °C min^{-1} in air atmosphere, and the crystalline $ZnFe_2O_4$ monoliths could be obtained after heat treatment.

2.2.2. Carbon coating to prepare $ZnFe_2O_4/C$ composites

175 mg of $ZnFe_2O_4$ active material was dispersed in 30 mL of Tis-buffer with a pH of 8.5 with stirring. Then 45 mg of dopamine was