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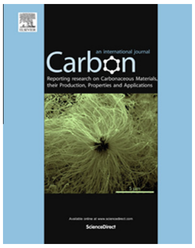

Mesoporous zinc ferrite/graphene composites: Towards ultra-fast and stable anode for lithium-ion batteries

Xiayin Yao, Junhua Kong, Dan Zhou, Chenyang Zhao, Rui Zhou, Xuehong Lu *

School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore

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ABSTRACT

Mesoporous zinc ferrite ($ZnFe_2O_4$)/graphene composites are synthesized using a facile ambient-pressure method, i.e., co-precipitation of metal cations onto graphene oxide followed by solid state reaction to yield $ZnFe_2O_4$ nanoparticles anchored on reduced graphene oxide. The resultant $ZnFe_2O_4$/graphene composites have large specific surface area with mesopores, and the size of the $ZnFe_2O_4$ nanoparticles is less than 20 nm. When the composites are employed as an anode material for lithium-ion batteries, it exhibits superior electrochemical performances in term of high reversible capacity, good cyclic performance and excellent rate capability. Its reversible discharge capacities can be maintained at 870 mAh/g at 1.0 A/g for 100 cycles and consecutively 713 mAh/g at 2.0 A/g for another 100 cycles. Moreover, other graphene-based composites containing ferrites, such as cobalt ferrite and nickel ferrite, are also synthesized with this generic strategy which is promising for large-scale production of lithium-ion battery anode materials.

1. Introduction

Rechargeable lithium-ion batteries (LIBs) have been widely used as power sources for portable electronic products and are regarded as one of the leading candidates for powering hybrid electric or all-electric vehicles [1]. The major limitation of the currently used graphite anode in LIBs is that its theoretical capacity is only 372 mAh/g. In order to meet the increasing demand for higher energy and power density batteries, great efforts have been made to develop new anode materials, such as transitional metal oxides [2], oxysalts [3] and silicon [4–6]. Among these newly developed anode materials, zinc ferrite ($ZnFe_2O_4$) has been considered to be a promising candidate for LIB anodes because of its non-toxicity, being environmentally friendly, good structural stability and low cost [7]. It has been reported that each formula unit of $ZnFe_2O_4$ can react with nine Li ions, giving a theoretical specific capacity of about 1000.5 mAh/g [8,9]. However, $ZnFe_2O_4$ anode materials usually suffer from low rate capability resulting from poor electrical conductivity as well as kinetic limitations and poor cycling performance owing to large volume changes induced by electrode pulverization during repeated lithiation/delithiation processes. Generally, these problems could be alleviated by preparation of nano-structured electrodes with carbonaceous materials [10–13], which can buffer the volume expansion as well as increase the electrical conductivity.

Recently, graphene, a type of two-dimensional carbon nanomaterial with excellent conductivity and structural flexibility, has been used by researchers as the carbonaceous materials in LIB electrodes to improve their cycling stability

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* *Corresponding author*: Fax: +65 6790 9081.
E-mail address: ASXHLu@ntu.edu.sg (X. Lu).
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and rate capability [14–16]. There is already some reported work on $ZnFe_2O_4$/graphene composites for LIBs [17–19] and photocatalysis applications [20–22]. A $ZnFe_2O_4$/graphene nanohybrid synthesized via a solvothermal route exhibits enhanced electrochemical properties when employed as anodes of LIBs [17]. Similarly, Fu and Wang [20] prepared $ZnFe_2O_4$/graphene composites via a hydrothermal method and investigated their photocatalytic activity for degradation of methylene blue under visible light. The results show that the photoactivity is significantly improved by combination of graphene and $ZnFe_2O_4$. However, so far the reported synthesis strategies for $ZnFe_2O_4$/graphene composites all involve high-pressure processes, which are not ideal for mass production of the composites for practical applications.

Very recently, metal oxide electrodes with mesoporous morphologies have been demonstrated to be beneficial to electrochemical performance of lithium-ion batteries as the nanometer-scale porosity allows easy electrolyte access to the electrode surfaces, facilitating charge transfer across the electrode/electrolyte interface, as well as accommodates the volume changes during Li-ion insertion/extraction [23,24]. Porous $ZnFe_2O_4$ nanostructures could be synthesized by thermal decomposition of oxalate precursor [25] or double hydroxide precursor at ambient pressure [26,27]. It is anticipated that the combination of mesoporous $ZnFe_2O_4$ with conductive graphene nanosheets would enhance electrical conductivity of the active material while ensuring good access of the electrolyte to the material surface, leading to significantly improved electrochemical performance.

In this work, we report a facile two-step strategy for synthesis of mesoporous $ZnFe_2O_4$/graphene composites as high-performance anode materials for LIBs. By this route, $ZnFe_2O_4$ nanoparticles with sizes of less than 20 nm can be simultaneously formed and anchored on the graphene nanosheets. Compared with the $ZnFe_2O_4$/graphene composites reported in literatures, the $ZnFe_2O_4$/graphene composites prepared in this work show a mesoporous structure with pore size of less than 10 nm and exhibit superior electrochemical performances in term of high reversible capacity, good cyclic performance and excellent rate capability. Moreover, this synthesis strategy contributes a generic route for large-scale production of binary transitional metal oxide/graphene composites that may be used for LIBs and many other applications.

2. Experimental

2.1. Synthesis of the mesoporous $ZnFe_2O_4$/graphene composites

All of the chemicals were analytical grade and used without further purification. The composites were synthesized through a two-step procedure, including the co-precipitation of metallic cations onto graphene oxide (GO) and solid state reaction in order to form mesoporous $ZnFe_2O_4$ as well as reduce GO to graphene. GO was synthesized from graphite powder (natural, −10 mesh, Alfa Aesar, 99.9%) according to a modified Hummers' method [28,29]. The concentration of the obtained homogeneous GO colloid suspension in water is about 2.5 mg/ml. To synthesize the composites, in a typical synthesis, 60 g of 2.5 mg/ml GO aqueous suspension was further diluted with 340 g deionized water, and then 10 ml ammonium hydroxide solution (Aldrich, 28.0–30.0%) was added with stirring in order to adjust the pH of the system to 10. After that, 180 ml aqueous solution containing 0.4 mmol of zinc sulfate heptahydrate (Aldrich, ⩾99.0%) and 0.8 mmol of iron sulfate heptahydrate (Aldrich, ⩾99.0%) were dropwise added to the above suspension at room temperature and further stirred for 6 h. The precipitate was collected by centrifuge and repeatedly washed with deionized water, and then freeze dried. Finally, the obtained precursor was calcinated by heating it to 600 °C at the rate of 5 °C min^{-1} and keeping at 600 °C for 2 h in argon atmosphere. $ZnFe_2O_4$ nanoparticles were also prepared under the same reaction conditions except in the absence of GO. Graphene nanosheets were obtained by carbonization of freeze-dried GO under 600 °C for 2 h in argon atmosphere.

2.2. Characterization

X-ray diffraction (XRD) patterns were obtained on a D8 Discover GADDS (Bruker AXS, Germany) powder diffractometer. Scanning electron microscopy (SEM) images were acquired with a JEOL-7600 field emission scanning electron microscope. Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) experiments were performed on a JEOL 2100 transmission electron microscopy at an accelerating voltage of 200 kV. Thermogravimetric analyses (TGA) were performed with a TGA Q500 at 700 °C with a heating rate of 10 °C min^{-1} in air. The Brunauer–Emmett–Teller (BET) test was determined via a Micromeritics Tristar II-3020 nitrogen adsorption apparatus. Pore size distribution plot was obtained by the Barrett–Joyner–Halenda (BJH) method.

2.3. Electrochemical measurements

To characterize electrochemical properties of the composites, a working electrode containing 60 wt.% active materials, 30 wt.% Super P, and 10 wt.% polyvinylidene fluoride was prepared. The electrochemical properties were measured with a standard CR2032 coin cell with lithium metal as the counter electrode, Celgard 2600 as the separator, and a solution of 1.0 M $LiPF_6$ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 by volume) as the electrolyte. The cells were assembled in an argon-filled glove box and tested in the voltage range of 0.005 and 3.0 V (*vs.* Li^+/Li) with a Neware-CT3008 battery test system (Neware Technology Limited, Shenzhen, China). Cyclic voltammetry (CV) measurements were performed using an Autolab PGSTAT302N electrochemical workstation (Metrohm, Switzerland) at 0.1 mV/s in the voltage range of 0.005–3.0 V.

3. Results and discussion

Fig. 1 illustrates the synthesis route for the $ZnFe_2O_4$/graphene composites. In the first step, the two types of metal cations, i.e. Zn^{2+} and Fe^{2+}, in the precursor are hydrolyzed in the GO colloid suspension with the addition of ammonium