Composites Communications 1 (2016) 48–53

Contents lists available at ScienceDirect

Composites Communications

journal homepage: www.elsevier.com/locate/coco

Coating Fe_2O_3 with graphene oxide for high-performance sodium-ion battery anode

Henan Li [a,b], Li Xu [b,c], Hansinee Sitinamaluwa [a], Kimal Wasalathilake [a], Cheng Yan [a,*]

[a] School of Chemistry, Physics and Mechanical Engineering, Queensland University of Technology (QUT), Brisbane, Queensland 4001, Australia
[b] Centre for Clean Environment and Energy, Environmental Futures Research Institute and Griffith School of Environment, Griffith University, Gold Coast Campus, Queensland 4222, Australia
[c] Institute for Energy Research, Jiangsu University, Zhenjiang 212013, PR China

ARTICLE INFO

Article history:
Received 19 June 2016
Received in revised form
4 September 2016
Accepted 5 September 2016

Keywords:
Na-ion batteries
Fe_2O_3 nanoparticles
Graphene oxide
Composite

ABSTRACT

Sodium-ion batteries (SIBs) have recently shown the potential to meet the demands for large scale energy storage needs as an attractive alternative to lithium-ion batteries due to the high abundance of sodium resources around the world. The major hurdle of SIBs resides in developing viable anode materials with a high energy density and an appropriately long cycle life. Here a simple and low-cost method for synthesizing Fe_2O_3/graphene oxide (Fe_2O_3/GO) composites made out of Fe_2O_3 nanoparticles sandwiched between graphene oxide (GO) layers is reported. The unique structure of the Fe_2O_3/GO composites served a synergistic effect to alleviate the stress of Fe_2O_3 nanoparticles, prevent nanoparticles aggregation, maintain the mechanical integrity of the electrode, and facilitate mass transfer of Na ions during batteries operating. Consequently, the Fe_2O_3/GO composites as anode for SIBs attained a reversible specific capacity of ca. 420 mAh g^{-1} after 100 cycles at 0.1 C (1 C=1007 mA g^{-1}) and a good rate capability at various current densities. Moreover, the Coulombic efficiency of the SIBs could rapidly increase in the early cycles. Due to the facile synthesis method and high electrochemical performance, the Fe_2O_3/GO composites would have a significant potential as anode materials for rechargeable SIBs.

1. Introduction

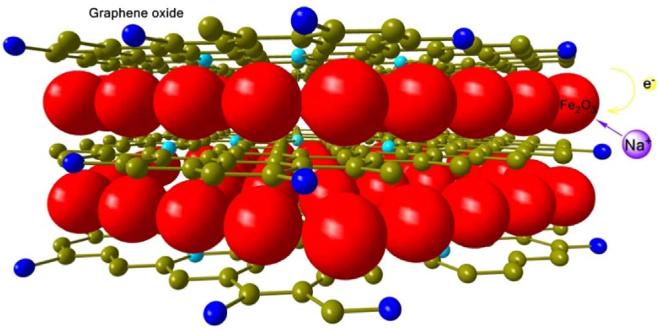
Rechargeable sodium-ion batteries (SIBs) with high energy density have attract a great deal of attention recently as a leading alternative to lithium-ion batteries (LIBs), because the reserves of Na mineral salts are virtually inexhaustible and are widespread around the world [1–4]. One of the major critical challenges for SIBs performance resides in identifying suitable anode materials with a high specific capacity and an appropriately low-cost [2,5]. Graphite as anode material of LIBs cannot be adapted to SIBs, due to its inability to intercalate Na atoms for the large ionic radium Na [6–8]. In this regard, various alternative materials based on metal oxides have been suggested as possible anode materials for SIBs [4,9–12]. Among them, Fe_2O_3 nanomaterials are considered as one of the most promising candidates for SIBs anode materials, because of their nontoxicity, abundance, chemical stability, high theoretical capacity (1007 mAh g^{-1}), and low cost [10,13–16]. Fe_2O_3 nanomaterials have potential advantages for SIBs anode; however, there are some limitations to retard the advancement of SIBs considerably, such as rapid capacity fading during cycling and low Coulombic efficiency resulted from the large volume expansion/contraction, and severe particle aggregation accompanied with alkaline ion insertion and extraction process [17–20]. Thus, developing rationally designed Fe_2O_3 with high Coulombic efficiency, long cycling life and good rate capability is highly desirable.

To address these issues, one of the most effective strategies is to embed Fe_2O_3 nanomaterials into carbon framework for formatting nanocomposites. This carbon matrix as a robust and flexible buffer allow to relate the stress of expansion/contraction, accommodate volume changes, and mitigate the pulverization of nanomaterials during battery operation [21–26]. The unique heterogeneous chemical and electronic structures of graphene oxide (GO) have endowed it as a successfully used carbon matrix to fabricate nanocomposites, aiming to improve the performance of the active materials for LIBs and lithium-sulfur batteries [27–30]. For example, GO has been used to wrap sulfur composites via a solution processing to accommodate the volume expansion [31]. SnO_2/GO/poly(3,4-ethylenedioxythiophene) hybrid was developed as anode materials in LIBs, and GO plays as a scaffold for trap of SnO_2 materials that can prevent their agglomeration during electrochemical cycling [32]. However, reports about Fe_2O_3/GO

---

[*] Corresponding author.
E-mail address: c2.yan@qut.edu.au (C. Yan).

http://dx.doi.org/10.1016/j.coco.2016.09.004
2452-2139/



Scheme 1. Schematic of a sandwiched structure consisting of Fe_2O_3 nanoparticles and GO sheets.

composites used as anode materials in SIBs are hardly viewed.

Herein, we take the advantages of characteristics of GO to construct a unique flexible interleaved structured Fe_2O_3/GO composites via a facile freezing-dry approach towards the anode of SIBs (Scheme 1). GO nanosheets can act as a flexible and mechanically strong buffer to alleviate pulverization of Fe_2O_3 nanoparticles during electrochemical cycling, while the Fe_2O_3 nanoparticles as a building blocks effectively prevent the restacking of GO nanosheets. Therefore, the interleaved network of GO can offer the channel of the mass and electron transport, and stabilize the solid electrolyte interphase (SEI) and superior reversible capacity with a high Coulombic efficiency.

2. Experiment

2.1. Materials and reagents

$NaClO_4$, ethylene carbonate (EC), and dimethyl carbonate (DMC) were purchased from Sigma-Aldrich (USA). All other reagents were of analytical grade and used as received. Ultrapure water was used throughout the study.

2.2. Preparation of Fe_2O_3 nanoparticles

In a typical reaction, ionic liquid $[(C_8H_{17})_2(CH_3)_2N]FeCl_4$ [33] (8 mmol) was added to 80 mL of ultrapure water. Then, CH_3COONa (24 mmol) was added into the above solution with vigorous stirring. The solution was placed into a 100 mL Teflon-lined autoclave, maintained at 140 °C for 24 h. The final product was separated by centrifugation, washed with ultrapure water and absolute ethanol three times, and dried under vacuum at 50 °C for 12 h.

2.3. Synthesis of Fe_2O_3/GO composites

GO was synthesized from graphite by using a modified Hummers method [34]. Fe_2O_3/GO composites were prepared by a simple freezing-dry method. Typically, 20 mg of GO was dispersed in 2 mL of water by ultrasonication for 30 min. To the resulting well-dispersed GO solution was added 180 mg of Fe_2O_3 nanoparticles and mixed well. The resulting solution was freezing dried for overnight, and a homogeneous solid of Fe_2O_3/GO composite was obtained.

2.4. Electrochemical evaluation

A slurry was prepared by mixing 80 wt% Fe_2O_3/GO composites or Fe_2O_3 as anode material, 10 wt% acetylene black as conducting agent, and 10 wt% polyvinylidene fluoride (PVDF) as binder and a certain amount of N-methylpyrrolidinone (NMP) as solvent. The mixed slurry was coated uniformly onto a thin copper foil, dried in air and subsequently dried in vacuum at 120 °C for overnight. Pure Na metal foil and glass fiber were used as counter electrode and separator, respectively. The electrolyte consisted of 1 M $NaClO_4$ in a 1:1 (w/w) mixture of EC and DMC. Coin cell batteries assembled procedures were performed in the inert atmosphere of an Ar-filled dry glove box. The electrochemical behavior of coin cells in terms of galvanostatic discharge-charge cycling tests at ambient temperature using a LAND-CT2001A battery tester (China). For the cyclic voltammetry (CV) test was performed over a voltage range 0.01–2.5 V vs Na/Na^+ at $0.02\ mV\ s^{-1}$ using a CHI660D electrochemical workstation (CH Instrument, China).

2.5. Materials characterization

The structures of the as-prepared Fe_2O_3/GO composites were investigated by X-ray diffraction (XRD) analysis (Bruker D8 diffractometer with high-intensity Cu_{Ka} radiation (l=1.54 Å)) and confocal Raman microscope (DXR, Thermo-Fisher Scientific, 532 nm excitation). SEM measurements were carried out with a field-emission scanning electron microscope (JEOL JSM-7001F) equipped with an energy-dispersive X-ray spectrometer operated at an acceleration voltage of 10 kV. Nitrogen (N_2) adsorption/desorption isotherms were determined using Micromeritics ASAP 2010 M.

3. Results and discussion

The phase and composition information on the as-prepared Fe_2O_3/GO composites and Fe_2O_3 nanoparticles were studied by powder XRD (Fig. 1A). The XRD pattern of the as-prepared Fe_2O_3 nanoparticles can be indexed to the hexagonal structure of α-Fe_2O_3 with cell constants of a=5.036, b=5.036, c=13.749 Å (JCPDS no. 33-0664). No impurity peaks could be observed, indicating that the Fe_2O_3 nanoparticles are of high purity and single-phase. Meanwhile, XRD pattern of the Fe_2O_3/GO composites was almost agree to that of pristine Fe_2O_3 nanoparticles. The characteristic Raman spectrum of the Fe_2O_3/GO composites was mostly reminiscent of that of the GO, both having two prominent peak at 1351 and 1591 cm^{-1}, corresponding to D and G bands, respectively (Fig. 1B). The measured I_D/I_G ratio for GO was around 0.98. When Fe_2O_3 nanoparticles were wrapped into GO to form the Fe_2O_3/GO composites, the I_D/I_G ratio was around 0.94. The decreased I_D/I_G ratio indicates a partial recovery of the ordering degrees of carbon, which is contribute to enhance electronic conductivity [32,35]. Besides, the Raman spectrum of the Fe_2O_3/GO composites exhibited additional peaks at 220, 401, and 601 cm^{-1}, respectively, corresponding to the A_{1g} and E_g vibration modes of α-Fe_2O_3 [13]. Furthermore, the porosity of the Fe_2O_3/GO composites was investigated by the N_2 absorption-desorption isotherms. The Brunauer-Emmett-Teller (BET) specific surface area of Fe_2O_3/GO composites was $44\ m^2\ g^{-1}$, much higher that of Fe_2O_3 nanoparticles ($19\ m^2\ g^{-1}$). The Barrett-Joyner-Halenda (BJH) average pore width of Fe_2O_3 nanoparticles was distribute of 5.5 nm. Such porous structure could greatly benefit electrolyte ion diffusion to active sites and accommodate volume changes of nanoparticles during cycling [36,37], indicating that the Fe_2O_3/GO composites may possess better performance than that of Fe_2O_3 nanoparticles.

SEM images in Fig. 2 showed that Fe_2O_3 nanoparticles with ith an average diameter of about 240 nm were well encapsulated by the GO layers structure. The crumpled and rough morphology of Fe_2O_3/GO composites could be attributed to the flexible and corrugated nature of GO layer. The elemental maps of C, O, and Fe taken for the image showed a uniform distribution of Fe and C across all the regions of the composites indicating that Fe_2O_3