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A novel Fe_3O_4/buckypaper composite as free-standing anode for lithium-ion battery

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ABSTRACT

The octahedral Fe_3O_4 (magnetite) nanoparticles were electrochemically grown on self-supported buckypaper and characterized by XRD, SEM, Raman and TGA. It could be used as a kind of metallic current collector-free anode for lithium ion battery, which would significantly reduce the mass of the whole anode by 66%. The new flexible Fe_3O_4/buckypaper composite anode achieves a higher initial reversible capacity of 1120 mAh g^{-1} and exhibits more stable performance compared with Fe_3O_4 anode coated on Cu foil by traditional electrode-fabrication technique. This is due to that the flexible 3D porous-structured Fe_3O_4/buckypaper composite is light weight and can accommodate the volume change of Fe_3O_4 during the lithiation/delithiation process, and promotes the diffusion and transfer of lithium ion and electron, respectively. Moreover, this buckypaper/Fe_3O_4 composite anode displays excellent rate capability, which maintains a discharge specific capacity of 210 mAh g^{-1} when the applied current rate is 10 °C and still delivers 1150 mAh g^{-1} after returning to 0.2 °C. Our work provides a new way to develop novel electrode structure for light-weighted and flexible lithium-ion battery.

1. Introduction

Lithium-ion battery has become a major power source for portable electronic devices due to their high energy density, long lifespan and environmental friendliness [1,2]. The ever-increasing application demand for electronic devices prompts researchers to develop a new generation lithium ion batteries that has the advantages of less weight, mechanical flexibility, improved durability, high capacity and better safety [3,4]. The anode material of most commercialized lithium ion batteries is graphite which has a low theoretical capacity 372 mAh g^{-1} and limits its practical application [5–7]. Transitional metal oxide materials, which display higher specific capacity over graphite when used as anode for lithium ion batteries, have been widely explored [8–10]. Among these oxides, Fe_3O_4 attract more attentions considering for its high theoretical capacity of 928 mAh g^{-1} [11,12]. Similar to many other anode materials, the formation of Li_2O from the Li^+ oxidation reaction during electrochemical cycling often gives rise to a dramatic change in the volume of Fe_3O_4, and ultimately influences on conventional flat dense electrode configuration. Also, the low conductivity of Fe_3O_4 leads to capacity fading [13]. To resolve these issues, the carbon encapsulated Fe_3O_4 nanoparticles anode materials have been developed, and which delivers stable capacity and high rate capability through shortening diffusion length and reducing damage for anode materials from strain relaxation [14–16]. However, this method tends to involve PVDF, binder and metal collector, which increase total costs and mass of whole anode.

The buckypaper made with carbon nanotubes or carbon nanofibers has large specific surface area, excellent electric/thermal conductivity and mechanical flexibility [17,18]. This nanoporous self-supported structure has already been explored for applications in EMI shielding [19], fuel cell [20], Li ion battery [21] and

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supercapacitor [22]. Moreover, this buckypaper can serve as the anodic supporting material, forming a 3D porous conductive network structure and functioning as the current collector which can largely reduce the total anode mass of the whole device. However, it is few reported about using the buckypaper as the current collector to form the nanocomposite anode for lithium ion batteries.

In this study, we had demonstrated that the Fe_3O_4/buckypaper nanocomposite anode can be used as the anode for the lithium battery with weight is 66% lighter than the traditional Fe_3O_4 on Cu foil anode. The anode was formed by electrochemical synthesize Fe_3O_4 particles on buckypaper. It is found that the flexible buckypaper can effectively relax the structural strain and accommodate the volume change of Fe_3O_4 nanopariticles during lithiation/delithiation, which would prevent the Fe_3O_4 nanopariticles from agglomerating quickly during cycling and keep the capacity stable. Furthermore, the nanoporous self-supported carbon network can improve the electrical conductivity and promote the diffusion of lithium ion in the electrode, which allows a higher rate capability and provides higher areal capacity compared with the traditional flat electrode.

2. Experiment

Electrochemical deposition (constant potential deposition) was carried out in a conventional three-electrode electrochemical cell with a Pt-mesh counter electrode and an Ag/AgCl reference electrode. Buckypaper was used as the working electrode. The buckypaper (Kunming NaTai Energy Co.,Ltd) used in this study contains both carbon nanofibers (CNFs; specification manifests 50–200 nm in diameter) and carbon nanotubes (CNTs; specification manifests 10–50 nm in diameter), whose electrical conductivity is 2000 S/m. The nominal thickness of buckypaper is 90 μm. Prior to electrodeposition, the buckypaper was cleaned by acetone, alcohol and DI water, and then pretreated by the mixed acid (V_{H2SO4} (98%):V_{HNO3} (68%) = 3:1) for 4 h followed by DI water rinse [23]. For Fe_3O_4 deposition, the electrolyte composed of 0.045 M triethanolamine (TEA), 0.1 M $Fe_2(SO_4)_3$ and 2.0 M NaOH with a pH of 12.87. The Fe_3O_4 nanoparticles deposited at −1.05 V (Ag/AgCl) for 1000 s and the 5 °C charge transfer was controlled on buckypaper wafer with 2.00 cm^2 nominal areas. The temperature of electrolyte was kept at 75 °C during electrodeposition.

The Fe_3O_4 nanoparticles were prepared by hydrothermal method. The synthetic procedure is as follows: $FeCl_2$ (2.75 g) and $FeCl_3$ (4.66 g) were added into the deionized water (30 mL) in turn, and then NaOH solution (20 mL, 0.005 mol/L) was added to the foregoing mixture solution with full stirring. The resulting suspension was transferred to the pressure reactor and maintained at 160 °C for 8 h. Finally, the Fe_3O_4 nanoparticles were obtained by washing with deionized water and drying at 60 °C for 12 h.

The crystalline structure of the samples was characterized by a X-ray diffractometer (XRD, Rigaku TTR III) using Cu Kα radiation (λ = 1.5406 Å). The morphology of the composite electrodes was characterized by scanning electron microscopy (SEM, FEI QUANTA 200). Raman spectra were collected by a DXR™ Raman Microscope using an excitation wavelength of 780 nm at the room temperature. Thermogravimetric analysis was carried out in air to determine the ratio of Fe_3O_4 within Fe_3O_4/buckypaper composite. The sample was heated from 50 °C to 800 °C at a ramping rate of 10 °C min^{-1}.

For battery electrochemical performance measurements, the Fe_3O_4/buckypaper composite was used as the electrode of CR2025 coin cell. These cells were assembled by stacking the Fe_3O_4/buckypaper and the Li metal electrode with a porous polypropylene membrane separator and then filled with electrolyte in an Ar-filled glove box, the schematic illustration of a half-cell as shown in Fig. 1.

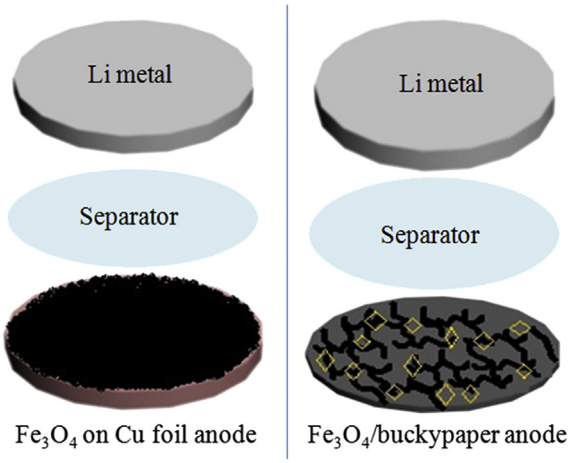

Fig. 1. A schematic illustration of a half-cell for testing of traditional Fe_3O_4 on Cu foil anode and Fe_3O_4/buckypaper composite as anode.

The electrolyte composed of 1 M $LiPF_6$ dissolved in a mixture of ethylene carbonate and dimethyl carbonate. For the purpose of comparison, the traditional adhesive coating technology was used to prepare Fe_3O_4 on Cu foil anode. This anode was fabricated by mixing Fe_3O_4 nanoparticles, polyvinylidene fluoride (PVDF) and acetylene black with a mass ratio of 8:1:1 before adding appropriate amount of N-methyl-2-pyrrolidone (NMP) solvent to form a slurry mixture which was spread uniformly on a copper foil (the thickness of 18 μm) by doctor-blade technique and then dried at 120 °C in a vacuum oven for 12 h. The dried electrode plate was cut into circular anode with a diameter of 16 mm after pressure rolling. The corresponding coin cells were also assembled through the same procedure in an Ar-filled glove box. The cells were tested by galvanostatic charging/discharging at different current density between 0.01 V and 3.0 V (versus Li/Li^+). The Cyclic voltammetry was performed using an electrochemical workstation (CHI660) between 0 V and 3 V at a scan rate of 0.1 mV s^{-1}. The impedance spectra of the cells were measured on the electrochemical workstation (CHI660) for the frequency range of 0.01 Hz–100 kHz.

3. Results and discussion

Fig. 2 shows the XRD patterns of the buckypaper, Fe_3O_4 nanoparticles and Fe_3O_4/buckypaper composite. For buckypaper, a strong diffraction peak around 26.2° can be attributed to (002)

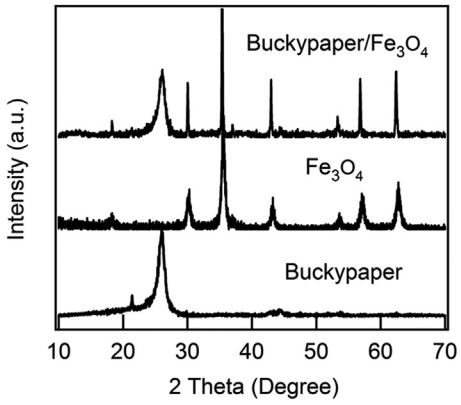

Fig. 2. X-ray diffraction patterns of the buckypaper, Fe_3O_4 and Fe_3O_4/buckypaper composite samples.