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Fabrication and characterization of double protective carbon aerogel (CA)/α-Fe_2O_3@Polypyrrole (PPy) composites as an anode material for high performance lithium ion batteries

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ABSTRACT

Carbon aerogel (CA)/α-Fe_2O_3@Polypyrrole (PPy) composites with double protective structure are synthesized via a solvothermal method with further in-situ polymerization of polypyrrole. The structure, morphology, loading content of α-Fe_2O_3 in composite and electrochemical properties are investigated by X-ray diffraction, Fourier transform infrared spectroscopy, scanning electron microscopy, high resolution transmission electron microscopy, thermogravimetry, constant current charge/discharge tests, cyclic voltammetry tests and electrochemical impedance spectroscopy. The results show α-Fe_2O_3 directional grows on the inner carbon aerogel while embeds in the outer PPy layer. As an anode material of lithium ion batteries, the CA/α-Fe_2O_3@PPy composite electrode exhibits more excellent cycling stability and rate capability than that of the bare α-Fe_2O_3 and CA/α-Fe_2O_3. The unique structure is responsible for the excellent electrochemical performance, which not only provides double protection against the aggregation and volume changes of α-Fe_2O_3 particles, but also ensures favorable transport kinetics for both electron and lithium ion.

1. Introduction

Li-ion batteries (LIBs) have been developed rapidly in the past decades, and show great applications in portable electronic devices and electric vehicles owing to their high energy density and long cycling stability [1–3]. In general, Li-ions batteries are composed of the three main components: anode, cathode and electrolyte [4–6]. As the graphite anode cannot reach a capacity higher than 372 $mAh{\cdot}g^{-1}$ and this capacity limit is almost achieved in some currently used commercial graphite electrodes, therefore, there is a large number of publications where the new potential anode materials are shown as the alternative anodes for LIBs. Among the existing anode technologies, Silicon-based materials [7–10], Tin-based materials [11–13], and transition metal oxides (TMOs) [14–17] are considered as promising anode candidates because of their higher electrochemical capacities than that of graphite anode. Of the attractive TMOs anode materials, α-Fe_2O_3 is a promising candidate anode materials for LIBs as its higher specific capacity (1007 $mAh{\cdot}g^{-1}$) than commercial graphite, environmental friendless, low cost and lower potential for lithiation/delithiation reactions [18–22].

However, the poor electronic conductivity of α-Fe_2O_3 and huge volume expansion lead to a large irreversible capacity loss during cycling process [23,24]. Up to now, a variety of effective strategies have been utilized to overcome these obstacles. One of the successful solutions is to design and fabricate α-Fe_2O_3 with different morphologies, such as nanoparticles [25], porous nanotubes [26], nano-rings [27], nanorods [28], and microspheres [29], which is consideration of shorten migration path for Li^+ and electron and accommodate the volume variations via additional void space during cycling. Another effective strategy is integrated with carbon materials, including biomass carbon [30], graphene [31], carbon nanotube [32], porous carbon [33], carbon fiber, nanorods [34] and carbon aerogel [35,36], which inhibits the aggregation and pulverization of the electrode material and accelerates the kinetics of the electrochemical conversion reaction [37].

In our previous work [35], we reported a composite material consisting of the anoporous carbon aerogel coated with α-Fe_2O_3, owing to the macroporous architecture of three-dimensional CA/α-Fe_2O_3 can facilitate good contact of the internal active materials with the electrolyte and effectively alleviate the volume variation during the lithium ions insertion and extraction, it exhibits enhanced electrochemical properties of CA/α-Fe_2O_3 when used as an anode. However, the alleviation the volume variation of α-Fe_2O_3 is only effective in a single direction from the inner side.

Herein, we report on the fabrication of CA/α-Fe_2O_3@PPy composite

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by using a simple low solvothermal method combined with subsequent in-situ polymerization of polypyrrole (PPy). Polypyrrole is a novel form of conducting polymers, which has been explored recently in nanostructured electrodes for electrochemical capacitors and Li-ion batteries as its superior electrical conductivity, environmental stability, flexible surface and ease of preparation [38]. The final composite with internally connected three dimensional network structure consists of the carbon aerogel substrate, ball-like α-Fe_2O_3 nanoparticles and the outer PPy layer, which is designed as double protection structure and can avoid the direct exposure of α-Fe_2O_3 to the electrolyte, improve conductivity, and significantly inhibit pulverization of active materials during the repeated lithium insertion/extraction. Remarkably, compared with α-Fe_2O_3 and CA/α-Fe_2O_3, the CA/α-Fe_2O_3@PPy composite exhibits improved electrochemical cycling stability and excellent rate capability when they are used as anode materials for LIBs.

2. Experimental

2.1. Materials

All chemicals were analytical grade and used without further purification. Formaldehyde, resorcinol, $FeCl_3{\cdot}6H_2O$, glycol, polyvinylpyrrolidone (PVP), pyrrole monomer (98% reagent grade) were obtained from the Sinopharm Chemical Reagent Corporation (BeiJing China).

2.2. Preparation of CA/α-Fe_2O_3@PPy composite

The CA/α-Fe_2O_3@PPy composite was prepared via a simple, three step approach which consists of synthesis of carbon aerogel by supercritical drying firstly, and subsequent loading α-Fe_2O_3 particles on CA via solvothermal method in glycol solution, finally, coating of polypyrrole via in-situ chemical polymerization. Prior to the preparation of CA/α-Fe_2O_3@PPy, CA/α-Fe_2O_3 composite was fabricated as previously reported by our group [35,39]. In a typical synthesis process of CA/α-Fe_2O_3@PPy, the as-prepared CA/α-Fe_2O_3 powder was immersed deionized water, and sodium dodecyl sulfate (SDS) was added under continuous stirring. After that, 50 μL of pyrrole monomer and 0.2 g $FeCl_3{\cdot}6H_2O$ were added under strong magnetic stirring, which was continued for 4 h. The resultant suspension was separated by vacuum filtration and rinsed several times by deionized water and acetone. Finally, the black precipitate was dried under vacuum at room temperature for 8 h.

For comparison, bare α-Fe_2O_3 and CA/α-Fe_2O_3 samples were also fabricated under the same conditions.

2.3. Characterization

The morphologies of these samples were characterized by scanning electron microscope (SEM, HITACHI SU-70, Japan) and transmission electron microscopy (TEM, JEOL 2100F) at an acceleration voltage of 200 kV. Structure characteristics were collected using X-ray diffraction (XRD, Rigaku D/MAX-2550, Japan) at a scanning rate of $1^{\circ}min^{-1}$ in the range of 20–55° and Fourier transform infrared spectroscopy (FTIR, MAGNAIR750) in the wave-numbers range of 500–4000 cm^{-1}. The thermogravimetric (TG) analysis was performed on a PerkinElmer TA-SDTQ 600 Thermo Analyzer under air flow at a rate of 10 °C·min^{-1} in the range of 30–750 °C. The surface area of the as obtained samples was evaluated by N_2 adsorption/desorption isotherm at 77 K (V-sorb 2800TP), and the pore size distribution was determined from the adsorption branch of isotherms based on the Barrett-Joyner-Halenda (BJH) model.

2.4. Electrochemical measurement

Electrochemical lithium-storage properties of the synthesized products were measured by CR2032 coin-type test cells assembled in a dry argon-filled glove box. The electrodes were fabricated by casting a slurry of 80 wt% active material, 10 wt% acetylene black, and 10 wt% polyvinylidene fluoride (PVDF) in *N*-methyl pyrrolidinone (NMP) solvent onto Cu foil substrates. After coating, the electrodes were dried at 120 °C under vacuum for 12 h. Li metal foil was utilized as the counter electrode, 1 mol·L^{-1} $LiPF_6$ in ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 by volume) was used as the electrolyte, Celgard 2400 was used as the separator, and the synthesized samples as a working electrode. The assembled cells were tested (discharging, charging, and cycling) by a CT2001A LAND battery system at room temperature within a voltage range of 0.01–3.0 V (vs. Li/Li^+). Cyclic voltammograms (CVs) were measured with an electrochemical workstation (PCI4-750) at a scan rate of 0.1 mV·s^{-1} between 0.01 and 3.0 V (vs. Li/Li^+). The Electrochemical impedance spectroscopy (EIS) performance was measured by half coin cell on a CHI 660E (Shanghai China) in the frequency of 0.01 Hz to 1 M Hz.

3. Results and discussion

3.1. Structure characterization

Fig. 1(a) shows the XRD patterns of bare α-Fe_2O_3, CA/α-Fe_2O_3 and CA/α-Fe_2O_3@PPy. The samples are well crystallized, all the diffraction peaks are found to have no significant difference and can be indexed to (012), (104), (110), (113), (024) and (116) hexegonal hematite α-Fe_2O_3 (JCPDS NO. 33-0664). In contrast to CA/α-Fe_2O_3, the pattern of CA/α-Fe_2O_3@PPy is inclined to baseline, which indicates that the CA/α-Fe_2O_3@PPy composite is layered by amorphous PPy polymer. There are no additional diffraction peaks appear in CA/α-Fe_2O_3@PPy composite, suggesting that the coating of PPy does not change the phase of α-Fe_2O_3.

To further confirm the presence of PPy, both the CA/α-Fe_2O_3 and CA/α-Fe_2O_3@PPy are detected by FTIR spectroscopy. As can be seen in Fig. 1(b), three obvious new peaks can be found in the CA/α-Fe_2O_3@PPy spectrum compared with CA/α-Fe_2O_3. The peak located at 1550 cm^{-1} can be attributed to the fundamental vibration of C═C and C—C in the pyrrole ring [40], the one at 1180 cm^{-1} matches with the stretching vibration of C—N [41,42], and the wave number at 1040 cm^{-1} is ascribed to the C—H in-plane vibration.

As shown in Fig. 1(c), the TG analyses of CA/α-Fe_2O_3 and CA/α-Fe_2O_3@PPy were performed to check the exact weight content of each component in the CA/α-Fe_2O_3@PPy composite. The first part of the weight loss appeared around 200 °C attributed to the elimination of the moisture and unreacted monomers. It's not difficult to deduce that the CA content in the CA/α-Fe_2O_3 is 4.2%. TG curve of CA/α-Fe_2O_3@PPy shows a continuous weight loss between 200 and 750 °C, which could be attributed to the combustion of CA and PPy, implying that the amount of PPy and α-Fe_2O_3 active material in composite are about 13.3% and 82.5%, respectively.

The fabrication process for CA/α-Fe_2O_3@PPy composites prepared though the CA is illustrated in Fig. 2, and the morphologies of as-prepared CA, CA/α-Fe_2O_3 CA/α-Fe_2O_3@PPy composite were also observed using SEM and TEM images. The SEM images shown in Fig. 2(a) and (b) indicate that the synthesized CA samples are uniform three-dimensional network porous structure with the particle diameter of about 200 nm. As shown in Fig. 2(c), α-Fe_2O_3 particles were anchored uniformly on the surface of CA, Fig. 2(d) presents the magnified SEM of CA/α-Fe_2O_3 sample, which shows that the as-prepared α-Fe_2O_3 is ball-like particles with the average diameter of 100 nm. Fig. 2(e) shows the typical morphology of the CA/α-Fe_2O_3@PPy composite, the interconnected network structure is well preserved without any agglomerations, but the regular α-Fe_2O_3 particles were not observed any more. A close SEM observation in Fig. 2(f) clearly demonstrates the ball-like particles vertically anchoring around the surface of CA, EDS analysis showed N is detected. By comparing Fig. 2(d) and (f), we can conclude that α-Fe_2O_3