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N-doped graphene/graphite composite as a conductive agent-free anode material for lithium ion batteries with greatly enhanced electrochemical performance

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ABSTRACT

Present graphite anode cannot meet the increasing requirement of electronic devices and electric vehicles due to its low specific capacity, poor cycle stability and low rate capability. The study reported a promising N-doped graphene/graphite composite as a conductive agent-free anode material for lithium ion batteries. Herein, graphite oxide and urea were dispersed in ultrapure water and partly reduced by ascorbic acid. Followed by mixing with graphite and hydrothermal treatment to produce graphene oxide/graphite hydrogel. The hydrogel was dried and finally annealed in Ar/H_2 to obtain N-doped graphene/graphite composite. The result shows that all of graphite particles was dispersed in three-dimensional graphene framework with a rich of open pores. The open pore accelerates the electrolyte transport. The graphene framework works as a conductive agent and graphite particle connector and improves the electron transfer. Electrical conductivity of the composite reaches 5912 S m^{-1}, which is much better than that of the pristine graphite (4018 S m^{-1}). The graphene framework also acts as an expansion absorber in the anodes of lithium ion battery to relieve the large strains developed at high discharge rates. As a result, the N-doped G/C electrode provides an excellent electrochemical performance for lithium ion battery, including high specific capacity (781 mA h g^{-1}), outstanding rate capability (351 mA h g^{-1} at 10 C) and intriguing cycling stability (98.1% capacity retention at 10 C after 1000 cycles.

1. Introduction

Lithium ion battery has been widely used since its first commercialization by Sony Corporation in 1990s. It is also considered as an attractive power source for electric vehicle [1–3] and for stationary energy storage of solar and wind power [4,5]. These applications have more demands for lithium ion batteries in all aspect such as specific capacity, performance under high charge/discharge rate, cycling stability, safety and cost. At present, graphite plays a dominating role in field of the anode material in commercial lithium ion batteries owing to desirable charge potential profile, good safety feature and low cost. However, present graphite anodes can not provide high enough specific capacity, cycle stability and rate capability. These greatly limit its further development [6].

Two strategies have been used for the fabrication of graphite anode materials to improve the electrochemical performance. One is to reduce the particle size of graphite, especially nanoscale [7]. The nanostructured carbon is effective for improving lithium ion insertion/extraction by providing large surface area, which is beneficial to the accommodation of additional lithium ions, and a shorter path for lithium ion diffusion [8,9]. However, it also suffer from a large irreversible capacity loss during the initial cycling, in addition to the mass scalability of carbon material being challenging. Another is to modify the surface of graphite particles [10,11]. To date, amorphous carbon [12], carbon nanotube [13] and graphite oxide [14] were used for the above aim. Amorphous carbon has an isotropic feature different from graphite, which enables lithium ions to transport inside randomly and thus exhibits a good rate capability. Besides, amorphous carbon also offers a minor volume change during the charge/discharge process and good cyclic performance [15]. Many investigations have demonstrated that the surface modification by coating amorphous carbon is an effective approach to improve the electrochemical performance. However, a proper coating layer is essential to surface structure and electrochemical properties of the graphite. An incomplete coating layer leads to the exposure of part of the graphite surface, while excessive coating can cause a thick layer.

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This leads to increase the diffusion distance of lithium ions and affect the rate capability. Wang et al. studied the effect of coating amount of glucose on the surface structure and the electrochemical properties [16]. The result shows that the sample coated with 5 wt.% glucose exhibits the highest reversible specific capacity, excellent rate capability, and good cyclic performance. Since the discovery of carbon nanotube, its applications to energy storage devices have been highly issued. Compared with amorphous carbon, carbon nanotube provides a shorter diffusion path for the electron transfer, larger surface area and faster electronic/thermal conductions. Moreover, carbon nanotube can also entangle with particles to form an interconnected network, which is easier for electrons to distribute and transport between particles [17]. Lee et al. used carbon nanotube as a functional additive on the C-rate capabilities of composite anodes [18]. The additive was observed to act as a particle connector or an expansion absorber in the anodes of lithium-ion batteries. By controlling the dispersion process, carbon nanotube bundles were divided and dispersed between host particles. The rounded graphite with 2.0 wt.% of carbon nanotube exhibited a high rate capacity even at high electrode density. In addition, the well-dispersed carbon nanotube bundles enabled to relieve the large strains developed at high discharge rates and to keep the electrical contact between the host particles during repeated intercalation/deintercalation. However, the surface modification of graphite with amorphous carbon or carbon nanotube does not substantially increase the specific capacity of graphite anode materials. Graphene is a single atomic layer of carbon connected by sp^2-hybridized bonds and attracted strong scientific interest since its recent discovery [19]. It has been recognized as the most promising electrode material for lithium ion battery due to superior electrical conductivity, high surface area, and wide electrochemical window [20]. The researches have proved that the specific capacity of graphene anode for lithium ion battery can exceed 1000 $mA\,h\,g^{-1}$, which is about 3-fold that of the graphite electrode [21]. However, the capacity will rapidly decay with the increase of cycle number due to its graphitization. The problems can be effectively solved by the introduction of other particles in the graphene layers. Gu et al. developed a graphite/graphene oxide composite as the anode material of lithium ion battery [22]. The composite has more than 690 $mA\,h\,g^{-1}$ reversible capacity at the rate of 0.5C, simultaneously with excellent cycle performance and rate capability. However, the results of previous researches has proved that graphene oxide is not very suitable to be used as electrode materials for lithium batteries. On the one hand, graphene oxide is an insulating material. Its poor electrical conductivity brings a low high-rate capability. Its use need to add a large amounts of conductive agent to improve the electrical conductivity. This will increase the mass and volume of the electrode material and thus limits its many applications in high powder batteries. On the other hand, graphene oxide contains rich of active groups such as hydroxyl, carboxyl and epoxy groups. The combination of active groups with lithium ions will produce an irreversible capacitance and thus leads to large reversible capacitance loss. Moreover, the decomposition of active groups in graphene oxide inevitable forms some free water during the repeated charge/discharge process. This will bring a decline in electrochemical performance [23,24].

In the study, we reported a new strategy for the synthesis of N-doped graphene/graphite composite (termed as N-doped G/C). The result shows that all of graphite particles was dispersed in three-dimensional graphene framework with rich of open pores. The unique structure creates ultrafast electron transfer and electrolyte transport, and stable structure of the anode material. The as-prepared N-doped G/C as conductive agent-free anode material exhibits a greatly enhanced electrochemical performance for lithium ion batteries.

2. Experimental

2.1. Synthesis of N-doped G/C

Graphite oxide (GO) (1.0 g) and urea (2.0 g) were dispersed in ultra pure water (200 mL) by the ultrasonication. Followed by the adding ascorbic acid (2.0 g) and the heating (90 °C) for 1 h to form a uniform and viscous solution. The solution was mixed with graphite (6.7 g) by the mechanical stirring for 1 h and subsequently treated by the hydrothermal reaction for 10 h under 160 °C to produce a graphene oxide/graphite gel. The gel was dried at 105 °C for 2 h and finally annealed at 400 °C for 6 h in Ar/H_2 atmosphere ($Ar{:}H_2 = 95{:}5$) to obtain the N-doped G/C composite. To determine the amounts of graphene in the composite, two control samples, including single graphite and single graphite oxide, were treated by using the same procedure. According to the mass changes of graphite and graphene oxide before and after treated, we can calculate the content of graphene in the composite. The result shows that the content of graphene in the as-prepared N-doped G/C is 10.7%. To study on the effect of nitrogen doping and thermal annealing on the electrochemical performance, the graphene/graphite (G/C) and the N-doped graphene oxide/graphite (N-doped GO/C) were also fabricated by using above method unless no addition of urea or no use of the thermal annealing.

2.2. General characterization

Scanning electron microscope (SEM) was performed using HITACHI S4800 with a X-ray Energy Dispersive Spectrometer (EDS) (INCA Energy, Oxford Instruments). X-ray diffraction (XRD) was measured on the D8 Advance with a Cu Kα radiation. Raman measurements were carried out using InVia laser micro-Raman spectrometer. X-ray photoelectron spectroscopy (XPS) was performed by PHI 5700 using Al KR radiation. N_2 adsorption and desorption isotherms were measured at 77 K on a Quantachrome Nova 2000 and the CO_2 isotherms were recorded at 273 K with a Micromeritics TriStar 3000. Prior to the gas sorption measurements, all samples were outgassed in a vacuum at 120 °C for 24 h. The specific surface area and the pore size distribution were calculated using the Braunauer–Emmett–Teller (BET) method, and the relative pressure range of p/p^0 from 0.1 to 0.3 was used for multipoint BET calculations. Non-local density functional theory (NLDFT) assuming the pores are slit/cylinder shaped was used to determine the pore size distribution and mesopore volume. Electrical conductivity measurement was carried out in a ST-2258C multifunction digital four-probe tester, which equipped with a SZT-D semiconductor powder resistivity tester (Suzhou Jingge Electronic Co., Ltd. China). The powder sample was directly placed in a round hole with the diameter of 5 mm on the SZT-D semiconductor powder resistivity tester. Then, the powder was slowly compressed to 100 atmospheres by the piston on the system. At the same time, the electrical conductivity values under different pressures were recorded.

2.3. Electrochemical measurement

Electrochemical properties of N-doped G/C, G/C and graphite electrodes were evaluated using 2016 coin cells. The active material was mixed with polyvinylidene fluoride (PVDF, Sigma–Aldrich) at weight ratio of 9:1 in N-methylpyrrolidone (NMP, Sigma–Aldrich) solvent to form uniform slurries, which were then coated on copper foils. The loading density of active materials was about 3.0 $mg\,cm^{-2}$. Subsequently dried in a vacuum oven at 120 °C overnight and rolled by using a rolling machine. The copper foil was placed on the specialized slicing machine to prepare the working electrode. These working electrodes were incorporated