Carbon 122 (2017) 82–91

Contents lists available at ScienceDirect

Carbon

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

Graphene oxide templated nitrogen-doped carbon nanosheets with superior rate capability for sodium ion batteries

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ARTICLE INFO

Article history:
Received 17 March 2017
Received in revised form
6 June 2017
Accepted 14 June 2017
Available online 18 June 2017

ABSTRACT

Doping of N atoms into the carbonacous materials can generate extrinsic defects and more active sites, improve electrode wettability and also broaden the interlayer distance of carbon, hence promote Na storage capacity and high rate capability. Herein, we report the nitrogen-doped carbon nanosheets materials (PPyCs) obtained from pyrolysis of Polypyrrole coated graphene oxides. The pyrolysis temperature plays an important role on the electrochemical performance of PPyCs. With thermal treatment at 400, 600 and 800 °C, PPyCs have different content of N doping, and the doped N shows different existential forms. The PPyCs thermal treated at 600 °C (PPyC-600) exhibit a reversible capacity of 388.8 mA h g^{-1} at a current density of 100 mA g^{-1}, and even at a high current density of 10 A g^{-1}, high capacity of 198.6 mA h g^{-1} is maintained after 10,000 cycles, demonstrating outstanding cyclic stability, and high-rate capability. Furthermore, the assembled NVP/PPyC-600 full-cell demonstrates a high capacity of 122.2 mA h g^{-1} at a current density of 100 mA g^{-1} after 100 cycles, indicating the practical application of PPyCs nanosheets anode in sodium ion batteries.

1. Introduction

How to store energy has become a challenge as important as how to produce it. A variety of renewable and clean energy source technology, such as wind and solar energy, are developing rapidly [1,2]. As the typical energy storage system (ESS), the high energy density lithium-ion batteries (LIBs) has dominated the power source for portable electronic devices, and even the electric vehicles and adjustor of the supply and demand of renewable energy [3–7]. Li atom has a very small ionic size, which facilitates the diffusion of Li^+ into the electrode material [8–10]. Moreover, lithium is the lightest metallic element and has the lowest redox potential, which enables batteries with high voltage and high energy density [11]. However, lithium has a major drawback that the reserve is fairly rare on our planet. The exploding market of portable electronic devices powered by lithium batteries is raising the cost of lithium raw materials, and thus, the providers of large-scale grid energy storage system are looking for other battery solutions [4,12].

Sodium ion batteries (SIBs) have been considered as a potential intriguing alternative to LIBs due to their potential cost advantage stemming from the natural abundance of sodium (Na) resource. Na has a relatively low redox potential (E^0 (Na/Na^+) = −2.71 V *vs.* Standard Hydrogen Electrode), which is only 0.3 V higher than that of Li [13]. Although the concept of rechargeable SIBs for energy storage dates back to the 1980s, the research of Na-ion batteries was significantly decreased after the success of the commercial application of LIBs in the 1990s [14,15]. The development of SIBs has been stalled by the need of high-demanded energy/power density, lengthen the cycle life. Electrode materials which are successfully applied in LIBs should theoretically showing a similar electrochemistry to their counterparts in SIBs. However, electrochemical storage performance of some electrode materials that have been introduced for SIBs differs remarkably from that in Li-ion batteries [16–19]. In fact, very few anode materials have been reported as viable as used in LIBs. Graphite [20], as the most common anode for

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http://dx.doi.org/10.1016/j.carbon.2017.06.038
0008-6223/

commercial LIBs, has been reported to display a very low capacity when used as a SIBs anode [15,21]. Since Na ions cannot be inserted into the graphite layer easily, a large amount of non-graphitizable carbonaceous materials, e.g. hard carbon, has garnered significant attention in SIBs [22–27]. Hard carbon derived from sucrose by Clement et al. [28] exhibited an initial reversible capacity as high as 335 mA h g^{-1} at 40 mA g^{-1}, but cycling stability is unsatisfactory. Liu et al. [24] reported a nitrogen-rich porous carbon via a template method showing an excellent cycling durability, but the rate capability should be further improved. Thus, identifying an anode with a proper Na^+ storage voltage, large reversible capacity and high structural stability is urgently needed for the development of SIBs.

Pyrolysing nitrogen-containing polymers is widely used to obtain nitrogen (N) doped carbon materials [26,29–32], some researches pay attention to the temperature effect on the existential form of doped N in carbonaceous materials [33]. Typically, the existential form of doped N can be turned by the annealing temperature, and manifested high catalytic activities for both oxygen reduction and hydrogen evolution [34]. It is also reported that the existential form of doped N have an effect on the wettability on the pyrolysis carbonaceous materials, which boosts the supercapacitive performance [35]. Importantly, previous works have identified that the electrochemical performance of the carbon-based materials as anode for LIBs and SIBs can be highly improved by doping different existential form of nitrogen into the carbon [36–38]. Zhang et al. [39] synthesized a 2D porous nitrogen-doped carbon sheets by chemical activation of PPy-functionalized graphene with KOH, demonstrating enhanced SIBs performance. During the carbonization process, nitrogen atoms within the pentagonal ring of polypyrrole are converted into pyridinic-N and graphitic-N. Recently, Xu and co-workers [40] prepared a sandwich-like nitrogen-doped carbon/graphene hybrid material with good sodium storage performance, and discussed the influence of the content of N atoms on the electrochemical performance. Wang et al. [41] reported a carbon nanosheet derived from PPy-functionalized graphene, according to their results, the nitrogen content decreased as the temperature increased, while the highest content of N doping sample showed the best electrochemical performance. Introduction of N atoms can generate extrinsic defects and more active sites, improving electrode wettability and also broaden the interlayer distance of carbon, hence promote Li/Na storage capacity and high rate capability [42]. There are also evidences showing that after N doping, a pseudo-capacitance can be generated due to the interaction between the electrolyte and N species on the surface [43,44]. However, the electrochemical performance of carbonaceous materials may not only be related to the nitrogen-doped content and functionality, but also be associated with the pore textures and conductivity of electrode [45]. Additionally, the exploration of full cell configuration for carbon electrodes derived from nitrogen-containing polymers is rare reported. Herein, we report the nitrogen-doped carbon nanosheets materials obtained by pyrolysis PPy coated GO nanosheets at different temperatures under argon (Ar) atmosphere. We analyzed the existential form of doped N in carbon nanosheets under different annealing temperature and the influence of the content of different N species on the electrochemical performance of carbon anodes for SIBs. Furtherly, we discussed the differences of specific surface area, pore size distribution and conductivity of doped N in carbon nanosheets under different annealing temperature. The electrochemical results reveal that the carbon nanosheets demonstrate superior electrochemical properties including high specific capacity and excellent long-term cycling performance when used as the anode materials for SIBs.

2. Experimental section

2.1. Materials synthesis

2.1.1. Synthesis of GO

GO was synthesized using modified Hummer's method [10]. Briefly, 0.6 g graphite and 3.0 g $KMnO_4$ dissolved in 30 mL concentrated sulfuric acid, the mixture was transferred into a 50 mL Teflon lined stainless steel autoclave, the reaction was carried out in ice bath for 2 h and subsequently sealed and heated at 80 °C for another 2 h in an oven. After cooling, diluting and centrifuging, the obtained GO was dispersed in deionized water and continuously sonicated for 1 h to gain GO solution with a concentration of 0.25 mg mL^{-1}.

2.1.2. Synthesis of PPyCs

0.1 mmol hexadecy ltrimethyl ammonium bromide (CTAB) was dissolved in 20 mL the as-prepared GO solution under stirring. A flocculent precipitate appeared, then, the pH value was adjusted to 2 by the titration of concentrated hydrochloric acid. The mixture was cooled to 0 °C by using an ice bath, and then 100 μL of pyrrole monomer was added. At the same time, 1 mmol $(NH_4)_2S_2O_8$ (APS) was dissolved in 5 mL of distilled water and dropwised into the above suspension. After vigorously stirring for 24 h, the as-obtained black flocculent precipitate was collected by filtration and dried at 50 °C for 24 h, and then annealed at different temperature for 4 h under argon atmosphere to obtain the final products. The samples thermally annealed with the temperature of 400, 600 and 800 °C were denoted as PPyC-400, PPyC-600 and PPyC-800, respectively.

2.1.3. Synthesis of NVP

Vanadium pentoxide (V_2O_5, ≧99.0%), Oxalic acid dehydrate ($H_2C_2O_4·2H_2O$, ≧99.5%), Ammonium dihydrogen phosphate ($NH_4H_2PO_4$, ≧99.0%), sodium acetate dehydrate ($CH_3COONa·2H_2O$, ≧99.0%) and Oleic acid ($C_{18}H_{34}O_2$, ≧98.0%) were used as raw materials. Firstly, V_2O_5 and $H_2C_2O_4·2H_2O$ in a molar ratio of 1:3 were dissolved in deionized water under vigorous stirring at 70 °C until a transparent blue solution was formed, which indicates the formation of VO^{2+}. After evaporating the water for several hours with vigorous stirring, the $VOC_2O_4·nH_2O$ was obtained for further use. $NH_4H_2PO_4$ was milled initially with oleic acid for 1 h using a QM-3B high-energy milling machine. Then, $VOC_2O_4·nH_2O$, and $CH_3COONa·2H_2O$ were added and further milled for 1 h. The overall molar ratio of the milling mixture is Na: V: P: oleic acid = 3: 2: 3: 3 in the milling mixture. The precursor paste was dried in oven at 100 °C for 1 h, followed by annealing in tube furnace at 700 °C for 10 h under a gas flow composed of 95% Ar and 5% H_2 to yield the NVP.

2.2. Materials characterization

X-ray power diffraction (XRD, Rigaku D/max 2500) and FT-IR spectrometer (Nicolet 6700) were performed to investigate the structure and crystallographic phase of the as-synthesized N-doped Carbon Nanosheets. Raman spectra of powder samples were recorded on Lab RAM HR Raman microscope with a laser excitation wavelength of 532 nm. The morphologies and sizes of the as-prepared products were characterized by scanning electron microscopy (SEM, Quanta FEG 250) and transmission electron microscope (TEM, JEOL JEM-2100F). TG trace of PPy was obtained using a combined DSC/TGA instrument (TGA, NETZSCH STA 449C thermobalance). The temperature and heat flow were calibrated using standard materials (indium and zinc) in Ar at a heating rates of 10 °C min^{-1}. The X-ray photoelectron spectroscopy (XPS) analysis was performed on an AXIS-ULTRA DLD-600W system. A