CARBON 92 (2015) 354–361

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

Pyrolyzed polyaniline and graphene nano sheet composite with improved rate and cycle performance for lithium storage

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ARTICLE INFO

Article history:
Received 14 February 2015
Accepted 17 May 2015
Available online 21 May 2015

ABSTRACT

Pyrolyzed poly-aniline graphene nano sheets (PAGNS) composite was investigated serving as a novel anode material for lithium storage. The composite material with carbon coating and nitrogen doping on graphene were synthesized by heat treatment of polyaniline and graphite oxide precursors under an Ar/H_2 atmosphere at 850 °C. Scanning electron microscopy, transmission electron microscopy, X-ray diffraction, Raman spectroscopy and X-ray photoelectron spectroscopy techniques were employed to characterize the PAGNS composites with various contents of carbon and nitrogen doping on graphene in comparison with pristine graphene nanosheets (GNS). The PAGNS composites show defects resulting from nitrogen doping in graphene lattice, and carbon is coated on graphene surface causing vertical alignment of nanosheets which leads to improved electronic conductivity. Electrochemical tests show that the PAGNS composites exhibit enhanced rate performance and cycle capability. The PAGNS is also examined at a 1.6 A g^{-1} high rate and at 55 °C high temperature, and the material demonstrates 282 mA h g^{-1} capacity after 500 cycles, which is superior over that of GNS. The enhanced Li-ion storage properties could be attributed to the synergetic effect of carbon-coating and nitrogen-doping in graphene nanosheets.

1. Introduction

Graphene was first experimentally prepared in 2004 by Geim et al. [1,2]. Due to the high surface area and electronic conductivity, graphene has been considered to be a good candidate electrode material for supercapacitors (SC) and lithium ion batteries (LIBs) [3,4]. However graphene sheet layers with high surface area are easy to agglomerate, which can lead to decreased electronic conductivity, low efficiency in initial charge/discharge and limited cycling stability [5]. Such an effect can be a disadvantage for graphene as an anode material in lithium storage application. Various types of graphene composite materials, such as conductive polymer/-graphene, metal oxide/graphene, carbon-coated graphene, heteroatom-doped graphene, have been extensively studied as energy storage electrode materials and devices, e.g. LIBs and SCs. There are many studies on graphene with doping of heteroatoms (nitrogen, oxygen, boron, sulfur, etc.) [6], among them, doping of nitrogen was reported through various techniques such as chemical vapor deposition (CVD) [7],

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http://dx.doi.org/10.1016/j.carbon.2015.05.051

solid phase and thermal annealing [8]. In addition, carbon-coated nano-carbon materials, such as carbon-coated graphene [9–11] and graphite [12–14] have shown improved performance in Li-ion storage. The approaches of graphene compositing with heteroatoms can reveal unique physical and chemical properties and improve stability and surface reactivity that are not possible from graphene alone. The composite materials take advantages of synergistic effects and multiple functionalities resulting from interactions between the two compositions [15]. The pyrolysis of polymers such as polypyrrole, polypyrrolidone and polyaniline, used as carbon precursors, has also been investigated extensively [16–19].

In this work, we report on research results of nitrogen-doped and carbon-coated graphene nano sheet composites as anode materials for Li-ion storage. The effects of pyrolyzed polyaniline graphene nano sheets (PAGNS) with various content of carbon coating and nitrogen doping in comparison with that of pristine graphene are investigated. The PSGNS as anode material was synthesized through pyrolysis of polyaniline (PANI) and graphite oxide (PAGO) as precursors by heat treatment at 850 °C in Ar/H_2 atmosphere. The PAGNS composites have demonstrated excellent rate performance and cycling stability, especially at high temperatures.

2. Experimental

2.1. *Preparation of pyrolyzed polyaniline–graphene nano sheets*

Aniline and ammonium persulfate (APS) were acquired from Sinopharm Chemical Reagent Co. Ltd. (China). Graphite oxide (GO) was prepared by a modified Hummers and Offeman method [20] using commercial artificial graphite powder (Aldrich, powder size <20 μm). The GO was then dried at 60 °C for 12 h in a vacuum oven. The synthetic process is depicted in Fig. 1. Typically, 0.5 g of GO was dispersed in 100 ml of 1 M HCl solution with the assistance of 30 min ultra-sonication. After that, 1 ml of the aniline monomer was added to the stable GO solution with constant stirring. 100 ml of the APS (0.46 g) solution was dropped into the above solution and kept at 0–5 °C for 4 h for polymerization. Finally, the product was washed with methanol and ethanol alternately, dried in a vacuum oven at 60 °C for 12 h. The pyrolysis of the PANI–GO composite was carried out in a tube furnace in an Ar/H_2 (8%) atmosphere at 850 °C for 2 h with the heating rate of 5 °C min^{-1}, resulting in PAGNS product. Following the same procedure, two samples were prepared and referred to as PAGNS0.5 and PAGNS1, which correspond to the mass ratios of GO to aniline at 1:0.5 and 1:1, respectively, while PAGO0.5 and PAGO1 represent PANI–graphite oxides prior to pyrolysis. For comparison, graphene nanosheets, designed as GNS, were also prepared by the same procedure without the addition of aniline and APS.

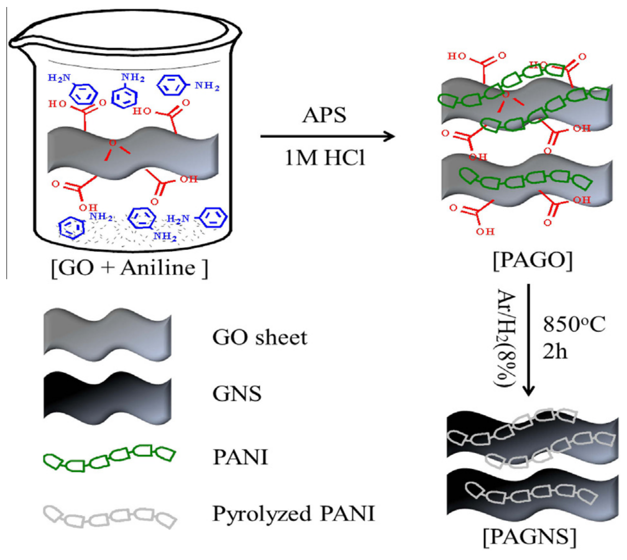

Fig. 1 – Illustration of synthesis process of PAGNS from GO. (A colour version of this figure can be viewed online.)

2.2. *Characterization*

Morphological and structural information was obtained from field emission scanning electron microscopy (SEM, Hitachi S–4700) and transmission electron microscopy (TEM, FEI TecnaiG220). X-ray diffraction (XRD) patterns were recorded in a Rigaku D-MAX diffractometer with Cu-K_α radiation (λ = 0.15406 nm). Raman spectra were recorded on a confocal microscopic laser Raman spectrometer (JY HR–800, France) with 632.8 nm He-Ne ion laser excitation. X-ray photoelectron spectroscopy (XPS) data was obtained with an Amicus electron spectrometer from Kratos Analytical equipped with an Al K_α radiation. Curve fitting was performed by using the XPSPEAK41 software.

2.3. *Electrochemical measurements*

Electrochemical performance of GNS and PAGNS as anode materials of LIBs was evaluated by galvanostatic charge/discharge technique. The working electrodes were prepared by mixing active materials (with a mass around 2 mg), conductive carbon black (super P of Timcal) as a conductive agent and poly(vinylidene fluoride) (PVDF) dissolved in N-methyl-2-pyrrolidone (NMP) as binder in a weight ratio of 85:5:10 for PAGNS, and 80:5:15 for GNS to form a slurry, which were then pasted on a copper foil, roll-pressed and dried under vacuum at 110 °C for 12 h. Coin cells were assembled in an argon-filled glovebox (Mbraun), with metallic lithium as the counter/reference electrode, and 1 M $LiPF_6$ in ethylene carbonate (EC) and dimethyl carbonate (DMC) (EC/DMC, 1:1 vol) as electrolyte, and Celgard 2320 membrane as separator. The cells were charged and discharged over a voltage range of 0.05–3.2 V (vs. Li^+/Li) at various current densities using a LAND battery testing system.

Cyclic voltammograms (CV) were measured using Autolab Electrochemical Workstation (PGSTAT302 N, Metrohm) at a scanning rate of 0.5 mV s^{-1} between 0.01 and 3.0 V (vs. Li^+/Li). Electrochemical impedance spectroscopy (EIS) measurements were also performed using Autolab Electrochemical Workstation by applying an AC voltage of 5 mV amplitude in the frequency range of 10 mHz–100 kHz.