



Growth of Highly Nitrogen-Doped Amorphous Carbon for Lithium-ion Battery Anode



Wei Guo^a, Xiu Li^b, Jiantie Xu^{c,*}, Hua Kun Liu^c, Jianmin Ma^{b,c,*}, Shi Xue Dou^c

^a College of Chemistry and Chemical Engineering, Anyang Normal University, Anyang 455002, PR China

^b Key Laboratory for Micro-/Nano-Optoelectronic Devices of the Ministry of Education, School of Physics and Electronics, Hunan University, Changsha 410082, PR China

^c Institute for Superconducting and Electronic Materials, University of Wollongong, Wollongong 2500, Australia

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ABSTRACT

Amorphous nitrogen-doped carbon nanosheets was synthesized through thermal decomposition of ethylenediaminetetraacetic acid manganese disodium salt hydrate ($C_{10}H_{12}N_2O_8MnNa_2 \cdot 2H_2O$). The as-synthesized nitrogen-doped carbon nanosheets were characterized by X-ray diffraction, scanning electron microscopy, transition electron microscopy and X-ray photoelectron spectroscopy. The N content of the as-synthesized carbon nanosheets could reach as high as 11.77 at.%, with an especially high total of 7.94 at.% pyridinic N plus pyrrolic N. When tested as anode material for lithium ion batteries, the optimized carbon nanosheets exhibited high capacity, excellent rate capability, and stable cyclability over 600 cycles. The specific capacity was still as high as 465.8 mAh g^{-1} at 0.5 C after 600 cycles, with a capacity decay from the 2nd cycle of 0.05% per cycle over 599 cycles. The excellent performance of C-600 is attributed to a synergistic effect of high surface area, numerous nanopores, high thermal stability, and low charge transfer resistance.

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1. Introduction

Lithium-ion batteries (LIBs) have attracted increasing attention for application in electric and hybrid-electric vehicles (EVs and HEVs) owing to their high energy and power densities, as well as their long cycle life and environmental benignity [1,2]. To further increase the energy density and rate capability of LIBs, much effort has been devoted to developing high-performance electrode materials [3]. Carbon-based materials have their dominant position in anodes for LIBs because of their low cost, abundant natural resources, and easy availability compared to other promising anode materials, including Si, metal oxides, $Li_4Ti_5O_{12}$, and tin [4,5]. Among the carbon-based materials, graphite is the current commercial material in LIBs. Graphite suffers, however, from its low theoretical capacity (372 mAh g^{-1}) and poor rate capability, restricting its application in high-energy LIBs in the future. Consequently, various carbonaceous materials have been widely identified as anode materials with higher capacity than graphite, including carbon nanotubes, graphene, porous carbon, and amorphous carbon [6–8]. In order to further improve their

capacity, as well as their excellent rate capability, many efforts have been made, including the synthesis of carbon in various structures, and/or with heteroatoms doped into the carbon networks. For instance, carbonaceous materials with various structures, such as macro- and mesoporous carbon, hollow carbon nanospheres, and holey graphene, show attractive anode performance in LIBs due to their structural merits such as large surface area, high pore volume, and numerous holes, providing short transport lengths for lithium ions and large electrode/electrolyte interfaces for the charge-transfer reaction [9–25]. On the other hand, the anode performance of carbonaceous materials was also significantly improved by doping with heteroatoms in the carbon networks, including nitrogen, boron, phosphorus, sulfur, and their mixtures [8,11,15,18,20–25]. Doping with nitrogen has been intensively proven to be an enabling strategy to enhance both the capacity and the rate capability of carbonaceous materials. This is mainly due to the net positive charge stemming from the higher electronegativity of N ($\chi = 3.04$) than carbon ($\chi = 2.55$) and the stronger interactions between the N-doped carbon structure and the Li ions.

It is well known that there are four types of nitrogen that can be incorporated with carbon in two-dimensional (2D) graphitic networks [26–28], including pyridinic N, pyrrolic N, graphitic N, and oxidized N, as shown in Scheme S1 in supporting information.

* Corresponding authors.

E-mail addresses: jx307@uowmail.edu.au (J. Xu), nanoelechem@hnu.edu.cn (J. Ma).

By generating excess electrons, the incorporation of N-C (especially, graphitic N) increases the electronic conductivity of carbonaceous materials. In addition, pyridinic N and pyrrolic N can also promote the formation of large amounts of nanopores, in which nitrogen-doped active sites from pyridinic N and pyrrolic N in the 2D graphene lattice are located along the nanopore openings (Scheme 1). As expected, large amounts of nanopores provide more active sites for the fast transportation and storage of lithium ions, leading to enhanced electrochemical performance [28]. Therefore, it is highly desirable to fabricate carbon materials with a high nitrogen doping level, especially pyridinic N and pyrrolic N.

Herein, we present a simple way to fabricate nitrogen-doped carbon nanosheets with high nitrogen doping levels of 9.16–11.77 at.% by annealing ethylenediaminetriacetic acid manganese disodium salt ($C_{10}H_{12}N_2O_8MnNa_2 \cdot 2H_2O$) in argon atmosphere. The growth formation of carbon nanosheets was followed by the characteristics of the two-dimensional (2D) growth, according to the reported literature [29]. According to the thermal decomposition of the raw material at various temperature stages in Ar (Fig. S1a in the Supporting Information), we sintered it at various temperatures: 500, 600 and 700 °C. The as-obtained samples sintered at 500, 600, and 700 °C are denoted as C-500, C-600 and C-700, respectively. Due to the presence of high N content in the precursor, the as-synthesized C-500, C-600, and C-700 exhibited a high nitrogen doping level of 11.77, 9.80, and 9.16 at.%, respectively. For C-600, the total combined content of pyridinic N and pyrrolic N is 7.94 at.%, which is higher than for C-500 (6.85 at.%) or C-600 (5.37 at.%). As an anode material for lithium ion batteries, C-600 shows high capacity, excellent rate capability, and stable cyclability over 600 cycles. Areversible capacity 465.8 mAh g⁻¹ at 0.5C can be maintained after 600 cycles, with a capacity decay from the 2nd cycle of 0.05% per cycle over 599 cycles.

2. Experiments

2.1. Synthesis of N-doped Carbon

Commercial $C_{10}H_{12}N_2O_8MnNa_2 \cdot 2H_2O$ was annealed at 500, 600, and 700 °C for 2 h with temperature rate of 3 °C min⁻¹ under flowing argon to achieve high-N-content nitrogen doped carbon (C-500, C-600, and C-700), respectively. The resultant products were then immersed in a certain concentration of hydrochloric acid solution (37 wt%) to remove possible insoluble inorganic compounds, and further dried at 80 °C in vacuum overnight.

2.2. Characterization

The scanning electron microscope (SEM) images were collected with a JEOLJSM-6700F field emission scanning electron microscope (15 kV). The transmission electron microscope (HR-TEM) images were collected on a JEOL 2010 high-resolution transmission electron microscope operated at 200 kV. The X-ray diffraction (XRD) patterns of the products were collected with a Rigaku D/max diffraction system using a Cu K α source ($\lambda = 0.15406$ nm). The Raman spectra were collected on a Raman spectrometer (Labram-010) using a 632 nm laser. Thermogravimetric analysis was also carried out on a STA449C instrument with a heating rate of 5 °C in Ar (for heating the $C_{10}H_{12}N_2O_8MnNa_2 \cdot 2H_2O$ precursor), and with a heating rate of 10 °C in air (for heating the obtained samples of C-500, C-600, and C-700). X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250Xi using a monochromic Al X-ray source (200 W, 20 eV). Raman spectra were collected using a Raman spectrometer (Lab533 RAM HR, Horiba Jobin Yvon SAS). Nitrogen adsorption–desorption measurements were performed on a Gemini VII 2390 Analyzer at 77 K using the volumetric method. The specific surface area was obtained from

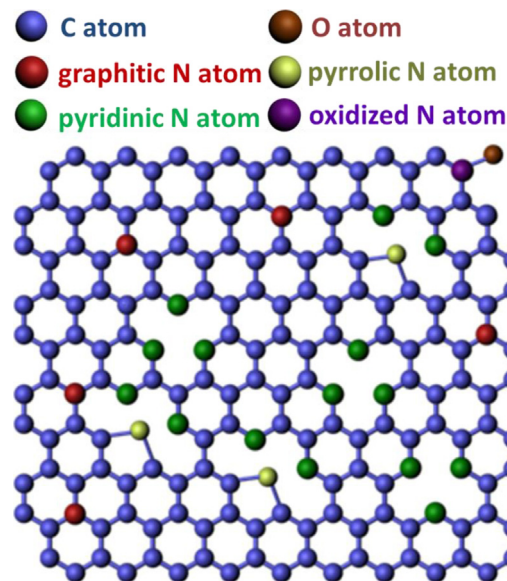
the N₂ adsorption–desorption isotherms and was calculated by the Brunauer–Emmett–Teller (BET) method.

2.3. Electrochemical measurements

The electrochemical characterization of C-500, C-600, and C-700 was carried out using 2032 type coin cells. The electrodes were fabricated by blending the active material, C-500, C-600, or C-700, with acetylene black and polyvinylidene fluoride (PVDF) binder in a weight ratio of 8:1:1. N-methyl-2-pyrrolidone (NMP) was used as the blending solvent for the mixture. The electrode loading was approximately 3 mg cm⁻². CR 2032 coin-type cells were assembled in an Ar-filled glove box with lithium foil as the counter electrode and reference electrode, a porous polypropylene film as separator, and 1 M LiPF₆ in a 1:1:1 (v/v/v) mixture of ethylene carbonate (EC), diethyl carbonate (DEC), and dimethyl carbonate (DMC) as the electrolyte. The cells were galvanostatically charged and discharged using an automatic battery tester system (Land[®], China) at various C-rates from 0.2 to 20 C in the voltage range of 0.02–2.5 V at room temperature. It should be noted that the normalized current density (C) in 1 h for all carbon is assumed to be 500 mA g⁻¹ in terms of various theoretical capacity of N doped carbon for simple description. Electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) measurements were performed on a Biologic MVP3 electrochemical workstation, in which EIS measurements were conducted over the frequency range of 1 MHz to 10 mHz and CV measurements were performed at a scan rate of 0.2 mV s⁻¹.

3. Results and discussion

Fig. 1a displays the X-ray diffraction (XRD) patterns of the as-prepared C-500, C-600, and C-700, and shows broad peaks centered at around 25.8° and 42.5°, which can be indexed to the (002) and (100) diffraction of graphitic carbon, indicating amorphous features for the as-prepared samples. As shown in Fig. 1b, all the Raman spectra of the three samples show two remarkable peaks centered at around 1340 and 1589 cm⁻¹, assigned to the defects or disorder (D band) and the E_{2g} mode (G band), respectively [30]. The presence of D band confirms the disordered structures of the samples, in agreement with the XRD observations. C-600 displays a lower intensity ratio of the D to the



Scheme 1. Scheme of four types of nitrogen in carbon nanosheet.

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