Nitrogen-doped carbon/graphene hybrid anode material for sodium-ion batteries with excellent rate capability

Huan Liu ^a, Mengqiu Jia ^{a,*}, Bin Cao ^a, Renjie Chen ^b, Xinying Lv ^a, Renjie Tang ^a,
Feng Wu ^b and Bin Xu ^{a,*}

^a State Key Laboratory of Organic-Inorganic Composites, Beijing Key Laboratory of Electrochemical Process and Technology for Materials, Beijing University of Chemical Technology, Beijing 100029, China.

^b School of Materials Science & Engineering, Beijing Key Laboratory of Environmental Science and Engineering, Beijing Institute of Technology, Beijing 100081, China

* Corresponding authors. Tel/Fax: 86-10-64434907. E-mail: binxumail@163.com (B. Xu); jiamq@mail.buct.edu.cn (M. Jia)

Abstract

Nitrogen-doped carbon/graphene (NCG) hybrid materials were prepared by an *in-situ* polymerization and followed pyrolysis for sodium-ion batteries. The NCG has a large interlayer distance (0.360 nm) and a high nitrogen content of 7.54 at%, resulting in a high reversible sodium storage capacity of 336 mAh g⁻¹ at 30 mA g⁻¹. The NCG shows a sandwich-like structure, i.e. nitrogen-doped carbon nanosheets closely coated on both sides of graphene. The carbon nanosheets shorten the ion

diffusion distance, while the sandwiched graphene with high electronic conductivity guarantees fast electron transport, making the NCG exhibit excellent rate capability (94 mAh g⁻¹ at 5 A g⁻¹). It also exhibits good cycle stability with a capacity retention of 89 % after 200 cycles at 50 mA g⁻¹.

Keywords: Nitrogen-doped carbon; Graphene; Hybrid material; Anode; Sodium ion battery; Electrochemical performance

1. Introduction

Sodium-ion batteries (SIBs) have attracted increasing attention for applications in large-scale grid energy storage because of the natural abundance and low cost of sodium resources [1-4]. Current researches in SIBs mainly focus on electrode materials, especially cathode materials [3, 5]. However, one of the most serious problems in realizing SIBs is the absence of the suitable negative electrodes [6, 7]. Carbonaceous materials, *e.g.*, graphite and disordered carbon have been commercially utilized as anode materials for Li-ion batteries (LIBs). Unfortunately, the larger ionic radius of Na⁺ ion (1.02 Å, 55% larger than Li⁺ ion) makes it more difficult to be reversibly inserted into and extracted from the host materials. As a result, graphite cannot be utilized as an insertion host of Na⁺ ion due to its small interlayer distance [6]. Disordered carbon appears to be the most suitable anode materials for sodium-ion storage as its large interlayer distance and amorphous structure can facilitate Na⁺ ion insertion-extraction [8-11]. Various precursors, such as sucrose [12], polymer resin [13] and biomass [14, 15] have been used to prepare hard carbons for SIBs. The

specific capacities of the hard carbons are generally in the range of 100-300 mAh g⁻¹. However, their capacity and high-rate capability still require improvement because of their intrinsically low graphitization [16]. In addition, their cycle stabilities are insufficient for practical application.

Nitrogen-doping has been proved to be an effective strategy for improving the electrochemical performances of carbons for both SIBs and LIBs [17-19]. The doped nitrogen atoms can introduce some active sites for energy storage, resulting in enhanced specific capacities. Moreover, the incorporation of nitrogen atoms into graphitic networks can increase the conductivity of the carbons, which facilitates the rate performances. Fu et al prepared nitrogen doped porous carbon fibers derived from polypyrrole (Ppy) for SIBs, which presented good electrochemical capacity and excellent rate performance [20]. Our group have reported nitrogen-doped mesoporous carbons with a high reversible sodium storage capacity up to 360 mAh g⁻¹ and good rate capability [19].

As a unique 2D carbon materials with large surface area, good chemical stability and excellent electronic conductivity, graphene has been widely used in conducting networks for LIBs and supercapacitors because its high electronic conductivity can guarantee a high rate capability of the electrodes [21-24]. Recently, Yan and co-workers [25] have prepared a hierarchically porous carbon/graphene composite with high sodium storage performance, indicating the advantages of designing a hybrid nanostructure with graphene for carbon anode materials of SIBs.

Herein, we fabricated a sandwich-like nitrogen-doped carbon/graphene (NCG)

hybrid material by *in-situ* polymerization reaction and followed pyrolysis of the polyaniline/graphene oxide composites. Benefiting from its unique nanostructure and the doped nitrogen, the obtained NCGs exhibit high reversible capacity, good cycling stability and excellent rate capability, indicating a promising anode material for SIBs.

2. Experimental

2.1 Synthesis and characterization

Graphene oxide (GO) was prepared through a modified Hummers method. Typically, GO (200 mg) was dispersed in 1 M HCl solution (100 mL) with the assistance of ultrasonication for 1 h. Then, 1 M HCl (100 mL) with aniline monomer (2.3 g) was added into the above suspension and sonicated for 30 min. Afterwards, 100 mL of 0.25 M ammonium persulfate (APS, solvent: 1 M HCl) was rapidly added into the above mixture and stirred for 8 h at 0-5 °C to obtain PANI-GO composites. Finally, the composite was washed repeatedly and dried in a vacuum oven at 90 °C for 12 h, then pyrolyzed at 700-900 °C for 2 h under flowing nitrogen at a ramping rate of 10 °C min⁻¹. The samples prepared at the pyrolysis temperatures of 700, 800, and 900 °C were denoted as NCG700, NCG800 and NCG900, respectively. For comparison, pure nitrogen-doped carbon derived from polyaniline were prepared by the same procedure at the pyrolysis temperature of 700 °C (designed as NC) without addition of graphene oxide.

The morphology of the samples was observed by scanning electron microscopy (SEM, SUPRA 55) and transmission electron microscopy (TEM, JEOL-2100). The composition and crystalline structure of the samples were characterized by powder

X-ray diffraction (XRD, Bruker D8 with Cu K α radiation), and X-ray photoelectron spectroscopy (XPS, ESCALAB 250). Raman spectra were obtained with a Renishaw 1000 Raman spectrometer (514 nm). Nitrogen adsorption/desorption measurement was performed on Micromeritics ASAP 2460 to obtain the porosity parameters of the samples. The specific surface area (S_{BET}) was calculated by the conventional Brunauer-Emmett-Teller method, the total pore volume (V_{total}) was calculated from the adsorbed N₂ amount at a relative pressure of 0.99.

2.2 Electrochemical measurements

For electrode preparation, a slurry of 80 wt% active materials, 10 wt% carbon black (Super-p), and 10 wt% PVDF (binder) in NMP was coated onto Cu foil and then dried at 120 °C for 12 h in a vacuum oven. Button cells (2025-type) were assembled using the as-prepared electrodes as working electrodes, glass fiber as separator, a Na foil as counter electrode and 1 M NaClO₄ in the mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 by volume) as electrolytes in an Ar-filled glovebox (Mikrouna, H₂O, O₂ < 0.1 ppm). The electrochemical performance of the cells was evaluated by galvanostatic charge-discharge cycle and cyclic voltammetry (CV) between 0.01 and 3.0 V vs. Na⁺/Na. The galvanostatic charge-discharge was carried out on a Land BT2000 battery tester and the CV traces were recorded on a CS350 electrochemical workstation.

3. Results and discussion

Fig. 1a shows the schematic diagram for the preparation of NCG samples. Firstly, PANI/GO composites were prepared by an *in-situ* polymerization reaction. The

aniline monomer was polymerized on the surface of GO nanosheets using ammonium persulfate as the catalyst. Then the PANI/GO composites were thermal treated at high temperatures under nitrogen flowing. During this process, the GO were thermally reduced to graphene nanosheets, while the surface coated PANI were pyrolyzed to carbon with some residual nitrogen atoms attached, resulting in a sandwich-like, nitrogen-doped carbon/graphene **hybrid nanocomposite**. The nitrogen atoms are expected to attached in the carbon sheets, forming four types of nitrogen configurations (Fig. 1b) [26, 27]: (i) pyridinic-like N (N-6) connecting with two carbon atoms and donating one p electron to the aromatic system, (ii) pyrrolic-like N (N-5) connecting with two carbon atoms and contributing two electrons to the system, (iii) quaternary-like N (N-Q) substituting one carbon atom within the carbon lattice, (iv) nitrogen oxide (N-oxide).

Fig. 1 (a) Schematic diagram for the preparation of NCGs; (b) the bonding configurations of nitrogen functionalities in NCGs.

The morphology of the as-prepared NC and NCGs was characterized by scanning

electron microscopy (SEM) and transmission electron microscopy (TEM). As shown in Fig. 2a, the nitrogen-doped carbon (NC) derived from pure polyaniline shows agglomeration state of irregular particles. After the addition of GO with nanosheet morphology (Fig. 2b) in aniline polymerization, the PANI/GO-derived NCGs show crumpled lamellar morphology similar to graphene but larger thickness of tens of nanometers and rough surface (Fig. 2c and d). HRTEM image (Fig. 2e) indicates amorphous carbon layers coated on both sides of the graphene nanosheets, revealing the sandwich-like structure of the nitrogen-doped carbon/graphene composites. The sandwiched graphene can enhance the conductivity of the hard carbon, and hence guarantee fast electron transport and good rate capability. Moreover, the interface between graphene and nitrogen-doped carbon can give rise to a large number of defects such as edges (as pointed by the round), which may be active sites for sodium ion storage.

Fig. 2 SEM image of NC (a) and graphene oxide (b); SEM (c, d) and HRTEM (e) images of NCG700.

Fig. 3a shows the XRD patterns of NC and NCGs prepared at different carbonization temperatures. The XRD patterns of all the samples exhibit two broad peaks indexed to (002) and (101) planes, respectively, indicating typical amorphous carbon. The (002) diffraction in NC locates at $2\theta = \sim 24.6^\circ$, and the interlayer spacing (d_{002}) is calculated to be 0.379 nm. For NCG700, the d_{002} is calculated to be 0.36 nm. With pyrolysis temperature increases, the d_{002} of NCGs shows a little decrease (Table 1) but all are significantly larger than that of graphite (0.335 nm), which is essential for the reversible storage of sodium ions. The amorphous crystalline structure of the samples is further confirmed by the two broad peaks of D- and G-bands in the Raman spectra (Fig. 3b). The G peak of the NC appears at 1578 cm^{-1} , and it upshifts to $\sim 1590\text{ cm}^{-1}$ for NCGs, which can be attributed to the restoration of the conjugated structure during pyrolysis process after the addition of graphene [28]. The I_D/I_G ratio in the Raman spectra is usually used to evaluate the disordered degree of the carbon materials. The I_D/I_G ratio of NC is 0.92, which increases to 0.98 for NCG700, implying a more disordered structure. It is supposed some defects and edge planes were introduced by the addition of graphene. N_2 sorption (77K) were employed to characterize the porous structure of the carbons. As shown in Fig. 3c, all the samples display type IV adsorption/desorption isotherms. The BET surface area of NC is $220\text{ m}^2\text{ g}^{-1}$. The NCGs exhibit lower BET surface areas of $35.1\text{-}94.1\text{ m}^2\text{ g}^{-1}$, and shows decreasing tendency with the pyrolysis temperature. XPS are performed to analyze the elemental composition (Fig. 3d), proving the existence of nitrogen in all the NCGs.

Fig. 3 XRD patterns (a), Raman spectrum (b), nitrogen adsorption/desorption isotherms (c) and XPS spectra (d) of the NC and NCGs prepared at different pyrolysis temperatures.

XPS spectra reveals the NCGs obtained at different pyrolysis temperatures are all rich in nitrogen. As listed in Table 1, NCG700 has similar atomic percentages of nitrogen (7.54 at%) to NC (8.32 at%). As the pyrolysis temperature increases to 900 °C, the nitrogen content remains 5.68 at%. As shown in Fig. 4, the nitrogen attached on the carbon can be distinguished into four components by deconvolute the XPS spectra: the pyridine nitrogen (N-6) at 398.7 ± 0.3 eV, pyrrolic nitrogen (N-5) at 400.3 ± 0.3 eV, quaternary nitrogen (N-Q) at 401.4 ± 0.5 eV, and oxidized nitrogen (N-oxide) between 402 and 405 eV [27]. N-Q atoms will increase the electric conductivity of the graphene layer because it brings extra free electrons, while the N-6

and N-5 atoms located at the edge of the graphene layer are more effective in adsorbing exotic atoms and enhancing the Na-ion storage capacity [26]. With the pyrolysis temperature increases, the total amount of N-6 + N-5 shows a decreasing tendency but the amount of N-Q increases.

Fig. 4 N 1s spectra of the NC and NCG samples, (a) NC, (b) NCG700, (c) NCG800, (d) NCG900.

The NC and the NCGs prepared at different temperatures show similar charge-discharge profiles between 0.01 and 3.0 V (Fig. 5), all characteristic of the behavior of the hard carbon anode materials [29, 30]. Thanks to the large interlayer spacing and the numerous defects introduced by nitrogen-doping, all the NC and NCG samples display high reversible capacities above 290 mAh g⁻¹. However, the

initial coulombic efficiencies of all the sample are around 50 %, which is a common phenomenon for hard carbon and is attributed to the severe electrolyte decomposition due to interactions between the electrolyte and the surface species on the carbons [31]. Once a stable solid electrolyte interphase (SEI) layer is constructed during the initial discharge, the coulombic efficiency quickly increases to ca. 100% in the second and subsequent cycles. NCG700 delivers a reversible capacity of 336 mAh g⁻¹, higher than 297.8 mAh g⁻¹ of NC. The enhanced capacity may be attributed to the more disordered structure of NCG700 as proved by the higher I_D/I_G ratio in the Raman spectrum (Fig. 3b). With the pyrolysis temperature increases, the decreased d₀₀₂ and nitrogen content (especially N-6+N-5) make the reversible capacities of NCGs have a little decrease.

Fig. 5 Charge-discharge and CV (inset; scanning rate of 0.1 mV s⁻¹) curves between

0.01 and 3.0 V at scan rate of 30 mA g⁻¹, (a) NC, (b) NCG700, (c) NCG800, (d) NCG900.

The CV curves of the first three cycles are shown in the inset of Fig. 5a-d. The large irreversible reduction peaks at 0.4 V in the first cathodic scan can be ascribed to the formation of the solid electrolyte interphase (SEI) film. After the second cycle, the CV curves almost overlap with each other, indicating good cycle performance of NCGs during sodium ion insertion and extraction. The pair of peaks in the potential range of 0.01-0.2 V can be assigned to sodium insertion in the interlayer of the graphitic nanocrystallinities, and the pair of broad peaks between 0.2 and 1.5 V correspond to the charge transfer on the surface of [small graphitic clusters](#) [32-36]. Additionally, a rectangular shape region can be observed in the potential range of 1.5-3 V, correspond to the capacitive sodium storage behavior, which is helpful to improve the high rate performance. Although NCGs prepared at different pyrolysis temperatures show similar CV curves, some small differences can be observed. With the pyrolysis temperature increases, the peaks in 0.01-0.2 V become sharp while the wide peaks in 0.2-1.2 V gradually weaken. This phenomenon may be explained by the more ordered domains with the increase of pyrolysis temperature, agreeing with XRD analysis (Fig. 3a). As the specific surface area decreases with the pyrolysis temperature, the rectangular region characteristic capacitive behavior become weaker and weaker.

Fig. 6a shows the cycle performance of NC and all NCGs at 50 mA g⁻¹. The NCG700 exhibits highest reversible capacity and best cycling performance compared

with NC and other samples. After 200 charge-discharge cycles, NCG700 retains a reversible capacity of 270 mAh g⁻¹, corresponding 89 % of its initial reversible capacity (303 mAh g⁻¹) at 50 mA g⁻¹. In contrast, the reversible charge capacity of the NC fades quickly, from the initial 289 mAh g⁻¹ to only 85 mAh g⁻¹ after 200 cycles, i.e. the capacity retention is only 29%. These results indicate that the addition of graphene sheets is an effective strategy to improve the cycling durability and reversibility of carbon anode materials. Compared the cycling performance of NCGs, it is found that increasing pyrolysis temperatures has a negative effect on the cycling performance and NCG900 shows an obvious capacity fading with prolonged cycling. The better cycling performance of NCG 700 than that of NCG800 and NCG900 may be related to its larger interlayer distance, which facilitates the free insertion/extraction of Na⁺ and can endure volume changes during charge-discharge.

Fig. 6 Cycle performance at a current density of 50 mA g⁻¹ (a) and rate performance (b) of NCGs.

As displayed in Fig. 6b, the nitrogen-doped carbon/graphene has superior rate capability to the nitrogen-doped carbon. As the current density increases to 0.5 A g⁻¹, the capacity of NC decays to only 40.8 mAh g⁻¹. However, with graphene nanosheets sandwiched in, the NCG samples exhibit much enhanced rate capacities. For example, the NCG700 can deliver reversible capacities of 336, 274, 249, 207, 177 and 139 mAh g⁻¹ at the current density of 0.03, 0.1, 0.2, 0.5, 1 and 2 A g⁻¹, respectively. Even when the current density increases up to 5 A g⁻¹, a capacity as high as 94 mAh g⁻¹ can be remained. When the current density is finally reduced back to 30 mA g⁻¹, the average capacity can recover to 294 mAh g⁻¹. The rate performance of NCG700 is very attractive, much superior to some precious reported carboneous anode materials, such as reduced graphene oxide (95.6 mAh g⁻¹ at 1 A g⁻¹) [31], electrospun carbon nanofibers (82 mAh g⁻¹ at 2 A g⁻¹) [37] and hollow carbon sphere (75 mAh g⁻¹ at 5 A g⁻¹) [38]. The excellent rate performance of the nitrogen-doped carbon/graphene can be attributed to its unique sandwich-like structure. The carbon nanosheets on both sides of graphene shorten sodium ion diffusion distance, while the sandwiched graphene with high electronic conductivity guarantees fast electron transport.

The nitrogen-doped carbon/graphene hybrid anode material exhibit excellent sodium storage performances, which can be ascribed to the amorphous crystallites and nitrogen doping of the carbon, as well as graphene sandwiched structure. Amorphous

crystallites with a large interlayer spacing are accessible for Na⁺ insertion, and the defects arisen from both nitrogen heteroatoms and the carbon/graphene interface provide some active sites for Na⁺ storage as well, resulting in high reversible capacity. The sandwiched graphene stabilized the structure of amorphous carbon, and the large interlayer spacing facilitates free insertion/extraction of Na⁺ and can endure volume changes during charge-discharge, which are all beneficial for getting good cycling performances. The carbon nanosheets on both sides of graphene shorten sodium ion diffusion distance, while the sandwiched graphene with high electronic conductivity guarantees fast electron transport, making the NCGs have excellent rate capability.

4 Conclusion

Nitrogen-doped carbon/graphene hybrid materials prepared by an *in-situ* polymerization and followed pyrolysis were used as anode materials for sodium-ion batteries. The NCG has large interlayer spacing, high nitrogen content, and a sandwich-like morphology, i.e. nitrogen-doped carbon sheets coated on both sides of conductive graphene. The unique composition and nanostructure of the NCG enable it exhibit high reversible sodium storage capacity, good cycle durability and excellent rate capability. Therefore, a hybrid nanostructure of nitrogen-doped carbon and graphene is one of the most promising candidates as anode materials for high-performance sodium ion batteries.

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Table 1 Microstructure parameters and composition of the carbons.

Samples	d_{002} (nm)	S_{BET} ($m^2 g^{-1}$)	V ($m^3 g^{-1}$)	C (at %)	O (at %)	N (atom %)				
						Total	N-6	N-5	N-Q	N-oxide
NC	0.379	220	0.20	84.31	7.37	8.32	2.57	2.08	2.56	1.10
NCG700	0.360	94.1	0.12	86.56	5.91	7.54	2.43	2.28	2.31	0.43
NCG800	0.358	32.8	0.10	88.32	4.87	6.81	2.10	1.18	2.79	0.74
NCG900	0.351	35.1	0.12	89.96	4.45	5.68	1.82	0.23	2.92	0.71