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Gelatin-pyrolyzed mesoporous carbon as high-performance sodiumstorage material

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Nitrogen-containing mesoporous carbons were obtained by co-pyrolyzing gelatin and magnesium citrate between 600 and 900 $^{\circ}$ C. The presence of magnesium citrate lowers the carbonization temperature and its decomposition product, MgO, works as a template for mesoporous carbon. Fourier-transformed infrared (FTIR) and X-ray photoelectron (XPS) spectroscopic studies indicate that the nitrogen in the material

¹⁰ exists in the form of pyridinic, pyrrolic and oxidized nitrogen. With high specific surface area, homogeneous pore-size distribution and abundant active sites at the edge of the graphene layer, the pyrolysic carbon shows very high reversible sodium (Na) storage capacities up to 360 mAhg⁻¹ and stable cycling stability.

Introduction

- ¹⁵ Carbons have been extensively applied as electrode materials in batteries for their low cost, high chemical stability and high electric conductivity. However, the graphitic carbons that have been successfully applied as anode materials of Li-ion batteries show negligible sodium (Na) storage capacities, probably due to
- ²⁰ the large size of the Na-ions.^{1.4} In contrast, hard carbons with large surface areas show rather high capacities for both Li- and Na-storage. Doeff *et al*⁵ first reported the insertion of Na ions in petroleum-coke carbon with a capacity of 85 mAh g⁻¹. Pore-free carbon black with surface areas of 22-74 cm² g⁻¹ shows a capacity
- ²⁵ of about 120 mAh g^{-1,6} Guo *et al*⁷ used graphene to modify hierarchically porous carbon and obtained a composite with high capacity and an excellent cycling stability. Stevens and Dahn⁸ pyrolyzed glucose at 1000 °C and the obtained porous carbon shows an initial reversible Na-storage capacity of 300 mAh g⁻¹.
- ³⁰ Hard carbons with other precursors such as sucrose⁹ and resorcinol-formaldehyde resin¹⁰ show reversible capacities between 150 and 300 mAh g⁻¹. However, the cycling and rate performances of these porous carbons are usually poor. Introduction of aliovalent elements in the graphene layer of the
- ³⁵ hard carbons enhances their electric conductivity and generates more active sites to adsorb the Na⁺ ions and, therefore, higher Nastorage capacity.¹¹⁻¹⁴.

Designing of nanostructured morphology¹⁵⁻¹⁷ and/or hierarchically porous structure¹⁸ is an effective strategy to

⁴⁰ improve the dynamic performance of the carbon because the electrolyte can enter the mesopores and the diffusion distance of the Na-ions can be decreased. Mesoporous carbon is usually prepared by pyrolyzing the carbon-containing organic precursors nanocast (impregnated) in colloid or mesoporous silica.¹⁹⁻²¹ ⁴⁵ Wenzel *et al*²² prepared hierarchically porous carbon using silica as the template. The rate performance of this carbon is good but its specific capacity is low (130 mAh g⁻¹ at 0.2 C). Replacement of mesoporous silica with MgO^{23, 24} or CaCO₃^{25, 26} nanoparticles as hard templates makes it easy for the template to be remove ⁵⁰ afterwards. However, as the nanoparticles tend to aggregate into larger ones, inhomogeneous pore-size distribution often occurs in the porous carbon. Recently, organic magnesium salts were copyrolyzed with the carbon-precursors to prepare mesoporous carbons²⁷. In such a system, the decomposition product MgO of ⁵⁵ the magnesium salt is small and homogeneous in size, and difficult to aggregate, because they are confined within the carbon matrix.²⁸

Gelatin is usually derived from animal bones and leathers and has high content of nitrogen (~16wt%). We recently prepared ⁶⁰ nitrogen-rich (10.7wt% when pyrolyzed at 750 °C) porous carbon using gelatin as the precursor and nano-CaCO₃ as the hard template.²⁹ It delivers a reversible Li-storage capacity up to 1200 mAh g⁻¹ and high capacity retention. In order to avoid aggregation of the template nanoparticles and to obtain ⁶⁵ mesoporous carbons with higher surface area, we hereby use magnesium citrate as the precursor of MgO template. By copyrolyzing the gelatin and the magnesium citrate and removing the resultant nano-MgO afterwards, we prepared mesoporous carbons with a high surface area and narrow pore-size ⁷⁰ distribution. These nitrogen-containing carbons have a high reversible Na-storage capacity up to 360 mAh g⁻¹.

Experimental

Synthesis and physical characterization

In a typical process, the powder of commercial gelatin and

magnesium citrate was first mixed (1:1 w/w) by planetary ballmilling. The mixture was then pyrolyzed between 600 and 900 °C for 1 h under flowing nitrogen at a ramping rate of 10 °C min⁻¹. Mesoporous carbon was obtained by washing the pyrolysis 5 product with diluted HCl and distilled water. The samples were

denoted as Mxxx (xxx for pyrolysis temperature). The morphology of the carbons was characterized on a S4800 field-emission scanning electron microscope. The powder X-ray diffraction (XRD) was performed on an X' Pert-Pro MPD

- ¹⁰ diffractometer with monochromatic Cu K α radiation (λ =0.1541 nm). Nitrogen adsorption/desorption measurements were performed on Micromeritics ASAP 2020 to obtain pore properties such as the specific surface area (S_{BET}), total pore volume (V_{Total}) and pore-size distribution. The S_{BET} value was calculated by the
- ¹⁵ conventional Brunauer-Emmett-Teller method, the V_t value was calculated from the adsorbed N₂ amount at a relative pressure of 0.99, and the pore-size distribution was determined by the density function theory (DFT) method using a carbon slit pore equilibrium model. Fourier-transformed infrared (FTIR) spectra
- ²⁰ of the pyrolytic carbon and the discharged/recharged electrodes were recorded on a Bruker VERTEX 70 V spectrometer. The Raman spectrum was recorded on Renishaw 1000 Raman spectrometer (514 nm). X-ray photoelectron spectroscopy (XPS) was performed on a Sigma Probe spectrometer with a high-
- ²⁵ performance Al monochromatic source operated at 15 kV. The XPS spectra were calibrated using the C_{1s} spectrum of neutral carbon peak at 284.8 eV. The content of the carbon, nitrogen and oxygen in the as-prepared carbons was determined by inductively coupled plasma (ICP) method.

30 Electrochemical measurements

For Na-storage performance evaluation, the pyrolysic carbon (80wt%) and polyvinylidene fluoride (20wt%) were mixed in NMP to form a slurry. Electrode was prepared by spreading the slurry onto a Cu foil and then getting dried at 110 °C in vacuum

- ³⁵ for 8 h. Coin cells were assembled in an argon-filled glove box (MBraun Lab Master 130) with the prepared electrode as the working electrode, fresh Na foil as the counter electrode, 1 mol L⁻¹ NaClO₄ dissolved in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 v/v) as the electrolyte, and glass
- ⁴⁰ fiber as the separator. The electrochemical performances of the pyrolytic carbons were evaluated by galvanostatic cycling and cyclic voltammetry (CV) between 0.0 and 3.0 V *vs.* Na⁺/Na. The cycling was carried out on a Land BT2000 battery tester (Wuhan, China) at 50 mA g⁻¹ while the CV traces were recorded on a
- ⁴⁵ CHI600D electrochemical workstation (Shanghai, China) at a scan rate of 0.05 mV s⁻¹. After the galvanostatic discharge/recharge treatments, the cells were dissembled in the glove box. The working electrode sheets were rinsed with dimethyl carbonate (DMC) and dried in the mini-chamber of the ⁵⁰ glove box for FTIR analysis.

Results and discussion

The typical morphology of the gelatin-based carbons was shown in Fig.1a. Well-developed interconnected mesopores and some macropores are observed on the pyrolysic carbons. Such ⁵⁵ porous structure permits the organic electrolyte to enter the "bulk" of the material and decreases the diffusion distance of the Na-ions,



Fig. 1 Typical morphology of the pyrolysic carbon (M700) (a) and XRD patterns (b), the nitrogen (77 K) adsorption/desorption isotherms (c) and DFT pore-size distribution (d) of the mesoporous carbons prepared at various temperatures.

beneficial for enhancing the dynamic performance of the material.

⁶⁵ The XRD patterns of the mesoporous carbons are shown in Fig.1b. The carbons obtained at different pyrolysis temperatures share similar diffraction features. Two broaden diffraction peak is observed at around 23.5° and 44° (2θ), corresponding to the graphite (002) and (101) plane, demonstrating the amorphous ⁷⁰ feature of these carbons. Its position has no obvious change with the pyrolysis temperature except for M600.

The nitrogen adsorption/desorption isotherms of the gelatinbased carbons prepared at different pyrolysis temperatures are shown in Fig. 1c. According to the classification of IUPAC, all 75 these carbons present Type IV adsorption/desorption isotherms, *i.e.* continuous adsorption increase over the whole relative pressure and typical hysteresis loops at medium to high relative pressure $(p/p_0=0.45-0.9)$, characteristic of mesoporous carbons. Increasing the pyrolysis temperature leads to significant increase 80 of the BET surface area and pore volume of the carbons. The BET surface area and the pore volume increase from 851 m² g⁻¹ and 0.72 cm³ g⁻¹ for M600 to 1384 m² g⁻¹ and 1.55 cm³ g⁻¹ for M750. Further increase of the pyrolysis temperature leads to slight decrease of both the BET surface area and the pore volume, 85 meaning that the micropores begin to be melted into larger ones above 750 °C. This is different from the pyrolysis of gelatin with nano-CaCO₃ as the hard template²⁹, where both the BET surface area and pore volume monotonically increase with pyrolysis temperature until 900 °C.

⁹⁰ The well-developed mesoporous structure of the carbons is confirmed with the pore-size distribution curves (Fig.1d). In addition to some micropores of 1 to 2 nm, most of the pores in all samples range between 3 and 10 nm with a unimodal at 5 nm. The micropores originate from the pyrolysis of the gelatin, while ⁹⁵ the mesopores are vacancies that the *in situ* formed MgO nanoparticles occupy. Clearly, using magnesium citrate as the precursor of nano-MgO significantly increases the BET surface area and decreases the pore size of the pyrolysic carbons, compared with that using nano-CaCO₃ template²⁹. 5

The Raman spectrum of the mesoporous carbons (Fig. 2a) indicates that the pyrolysis temperature does not influence the position of the *D*- (*ca.* 1345 cm⁻¹) and the *G*-bands (*ca.* 1590 cm⁻¹)



Fig. 2 Raman (a) and FTIR (b) spectra of the mesoporous carbons prepared at various temperatures

Table 1 Porosity parameters and nitrogen content in the pyrolysic carbons

Sample	S_{BET} $(m^2 \cdot g^{-1})$	V_{Total} $(m^3 \cdot g^{-1})$	Nitrogen (at%)	Oxygen (at%)
M600	851	0.72	4.37	21.24
M650	1137	0.98	4.51	27.42
M700	1319	1.33	3.30	17.35
M750	1384	1.55	3.54	16.74
M800	1100	1.35	3.32	20.58
M900	1026	1.16	3.01	19.34

- ¹⁰ though the nitrogen content in the carbons decreases with increasing pyrolysis temperature (Table 1). In addition, the intensity ratio of the *D*- to the *G*-band (I_D/I_G) is independent of the pyrolysis temperature except for sample M600. This is consistent with the above XRD results. It means that 600 °C is
- ¹⁵ too low for the effective carbonization of the gelatin and that temperatures between 700 and 750 °C are sufficiently high for forming the pyrolysic carbon. These are also different from the pyrolysic carbon using nano-CaCO₃ template.²⁹
- FTIR spectroscopic characterization (Fig. 2b) indicates that ²⁰ residential organic species can still be detected and are similar in different samples though the gelatin was pyrolyzed at high and different temperatures. All the samples contain absorption peaks for the C=N and N-H bonds. Oxygen-containing groups, such as –OH stretching and C=O stretching, can be detected even in
- ²⁵ M900. With the temperature increasing, the peak for the C=N bond shifts to lower frequencies, illustrating the weakening of the C-N bonding.

XPS analysis was conducted to determine the elements and their chemical states in the pyrolysic carbons. The survey

³⁰ spectrum (Fig.3a) of M700 possesses three peaks centered at 284.8 eV, 400.0 eV and 533.6 eV, corresponding to C_{1s} , N_{1s} and O_{1s} , respectively. The C_{1s} spectrum (Fig. 3b) can be deconvoluted into three components. The strong peak at 284.8 eV is attributed to the graphitic (*sp*² hybridized) carbon, the weak peak at 285.8

- $_{35}$ eV is assigned to the carbons on the C-N and C-O bonds, and the weakest peak at 289.1 eV corresponds to carbon on the C=O bonds. The N_{1s} spectrum (Fig.3c) can be fit into peaks at 398.4, 400.4 and 404.1 eV, corresponding to pyridinic, pyrrolic and oxidized nitrogen atoms (Scheme 1a), respectively, according to
- ⁴⁰ Kapteijn's assignments.³⁰ Table 2 summarizes relative integral intensities of component for various nitrogen atoms in the N_{1s} spectrum. It shows that, with pyrolysis temperature increasing,

the content of the pyridinic nitrogen decreases while those of the pyrrolic and oxidized nitrogen increase. However, no graphitic ⁴⁵ nitrogen can be recognized. Nitrogen atoms at different positions on the graphene layer of the hard carbon play different roles and affect the electrochemical behavior of the pyrolysic carbon in



Scheme 1 The thermal cross-linking and the pyrolysis of the gelatin molecules (a) and the possible nitrogen species in the gelatin-pyrolyzed carbon (b).

different ways³¹. Introduction of graphitic nitrogen atoms will increase the electric conductivity of the graphene layer because it brings extra free electrons. The pyrrolic, pyridinic and oxidized ⁵⁵ nitrogen atoms, as they are located at the edge of the graphene layer, are more effective in adsorbing exotic atoms and enhancing the Na-ion storage capacity here. We tried to find component for the graphitic nitrogen in the N_{1s} spectrum but failed. Therefore, these nitrogen species are expected to provide extra sites for Na-⁶⁰ ion storage rather than help to enhance the electric conductivity of the carbon. The conductivity of the carbons increases via continuous loss of hydrogen and oxygen during pyrolysis.

We have noticed that the pyrolysis of gelatin with nano-CaCO3 as the hard template and that with MgO template from 65 thermally decomposed magnesium citrate is significantly different in BET surface area, pore volume, pore size, nitrogen content and species, the structure of the pyrolysic carbons, and their dependence on pyrolysis temperature. We assume that these differences originate from the crossing-linking of the 70 gelatin molecules. The gelatin molecules tend to be crosslinked with each other at ca. 80 °C during nano-casting of nano-CaCO₃ template²⁹ (Scheme 1b). Thermal crosslinking makes the gelatin molecules more stable and more difficult to be pyrolyzed. Therefore, the carbonization of ⁷⁵ gelatin occurs at higher temperature, more nitrogen can be left in the pyrolysis product, and graphitic nitrogen can be formed in the graphene layer. In the mixture of gelatin and magnesium citrate, however, the magnesium citrate molecules separate the gelatin molecules and suppress their ⁸⁰ cross-linking. As a result, the carbonization of the gelatin occurs at lower temperature and more nitrogen will be lost at the same pyrolysis duration and temperature. In addition, it is difficult to form graphitic nitrogen.

The mesoporous carbons prepared at different temperatures show similar voltage profiles between 0.0 and 3.0 V (Figs. 4a to 4e), all characteristic of the behavior of the hard carbon anode materials. Due to the incomplete carbonization and low electric conductivity, M600 shows a capacity of only 160 mAh g⁻¹ and its initial coulombic efficiency is as low as 24%. In contrast, all the other 4 samples display reversible capacities around 330 mAh g⁻¹ (360 mAh g⁻¹ for M700 in the 1st cycle). These are the highest Na-storage capacities in literature, to our knowledge. However, the coulombic efficiencies of all these 4 samples are still low, 5 36% for M700 and 39% for M750. The low initial coulombic efficiency is attributed to the severe electrolyte decomposition



Fig. 3 XPS survey spectrum (a), C_{1s} (b) and N_{1s} (c) spectra of the carbon prepared at 700 °C and the N_{1s} spectra of the carbons pyrolyzed at different temperatures (d).

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Table 2 Relative integral intensities (%) of nitrogen at different chemical states (positions) in the graphene layer of the pyrolysic carbons

Sample	Pyrrolic N (%)	Pyridinic N (%)	Oxidized N (%)
M600	53.08	35.79	11.13
M700	54.43	31.18	14.39
M750	57.31	27.88	14.81
M800	61.58	22.72	15.70
M900	64.31	19.13	16.57

due to interactions between electrolyte and the surface species on ¹⁵ the carbons (Fig. 4h). Once a stable SEI layer is constructed during the initial discharge, the coulombic efficiency quickly increases to *ca*. 100% in the second and subsequent cycles. In addition, almost no part of the discharge profile is parallel to the capacity axis, implying that the number of the Na-ions stored ²⁰ within the graphene layers is negligible above 0.0 V.

- Furthermore, it seems that the impact of the nitrogen content is not significant on the Na-storage capacity, probably due to two contrary factors. On the one hand, the active sites provided with the doped nitrogen atoms decrease with pyrolysis temperature. ²⁵ On the other hand, the conductivity of the carbons increases with
- the pyrolysis temperature.

Figs. 4f and 4g show that M700 has the best cycling stability and the best rate performance among these mesoporous carbons. This is attributed to the combined effect of the nitrogen content

- ³⁰ and the structure of the carbon materials. Nitrogen doping introduces a large number of defects. Meanwhile, the mesoporous structure of the carbon materials shortens the diffusion distance of the Na⁺ ions and offers large electrode-electrolyte interface for the charge transference, beneficial for improving the rate ³⁵ performance of the material. On the other hand, the nitrogen-
- induced defects and the large surface area mean more active

positions for the electrolyte decomposition and nucleation sites for the solid electrolyte interphase (SEI) layer. Therefore the dependence of the electrochemical properties of the carbons is not 40 monotonic on the pyrolysis temperature.

The CV profiles of the first three cycles are shown in the inset of Figs. 4a to 4e. No obvious redox peaks are observed except for



Fig. 4 The voltage and CV (inset; scanning rate of 0.05 mV s⁻¹) profiles of 45 the pyrolytic carbon materials between 0.0 and 3.0 V at a current density of 0.1 mA g⁻¹ (a to e) in the first three cycles, their cycling performances (f), and the rate performance (g) and FTIR spectra of M700 discharged to 0.0 V and recharged to 3.0 V in the first cycle (h)

the strong reduction peak below 1.0 V in the first cycle. This peak so is attributed to the electrolyte decomposition and formation of the SEI layer because it disappears in the 2nd cycle and does not have a corresponding oxidation peak. The rectangular shape of all the CV curves at high potentials actually implies the substantial contribution of the capacitive Na-storage behavior to the total Nass storage capacity.³² This means that Na-storage within the graphene layer of the pyrolysic carbons is still negligible. The majority of the Na⁺ ions might be adsorbed on the edge of the graphene layer and the inner surface of the mesopores, a capacitive behavior distinct from the conventional intercalation 60 (like that of Li-ion in graphite³³).

The FTIR spectra of M700 discharged to 0.0 V and recharged to 3.0 V in the first cycle are compared in Fig. 4h. The obvious absorption peaks in the discharged sample confirm the decomposition of the electrolyte. The main components in the ⁶⁵ SEI layer can be recognized as ROCO₂Na (1650 cm⁻¹ for C=O,

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85

1073 cm⁻¹ for C-O and 824 cm⁻¹ for C-H), Na₂CO₃ (peaks at 1445 cm⁻¹, 1411 cm⁻¹ and 877 cm⁻¹ for CO₃²⁻) and RONa (peak at 1303 cm⁻¹ for C-O), similar to the species observed on the hard carbon anode for Li storage.²⁹ Roughly all the absorption peaks in the ⁵ discharged sample can find their counterparts in the recharged sample, implying the similarity of the species in the SEI layer of

these two samples and the stability of the SEI layers. This agrees with the characteristics of the CV profiles (Fig. 4) and explains the high coulombic efficiency in the 2^{nd} and subsequent cycles.

10 Conclusions

In summary, a series of nitrogen-containing mesoporous carbons were obtained by co-pyrolyzing gelatin and magnesium citrate between 600 and 900 °C in flowing nitrogen. Thanks to the presence of magnesium citrate, mesosporous carbons were

- ¹⁵ formed at lower pyrolysis temperature with higher specific surface area, smaller pore volume, and more homogeneous poresize distribution than those using nanocast precursors. These pyrolysic carbons show reversible capacities up to 360 mAh g⁻¹ as well as outstanding cycling and rate performances between 0.0
- ²⁰ and 3.0 V vs. Na⁺/Na. These indicate that nitrogen-containing mesoporous carbons can be promising candidates of anode materials for Na-ion batteries and that magnesium citrate is a good precursor of nano-MgO template for mesoporous carbons. Furthermore, considering the abundance and high activity of the
- ²⁵ nitrogen atoms at the edge of the graphene layers, these nitrogencontaining mesoporous carbons are expected to find broad applications in catalysis and exotic-atom adsorption in other energy conversion and storage devices as well.

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