

Short communication

Electrochemical capacitor performance of N-doped mesoporous carbons prepared by ammoxidation

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Abstract

The electrochemical double-layer capacitive properties of mesoporous carbon (MC) materials with a moderate amount of nitrogen functionality are reported. Ordered mesoporous carbon is prepared using mesoporous silica (MS) as a template and sucrose as a carbon source. Two types of N-doped MCs are prepared by ammoxidation performed at different stages of the MC preparation process—ammoxidation before (NC) and after (CN) carbonization. Irrespective of the ammoxidation sequence, N-doped MCs maintain mesoporous properties such as a high surface area with narrow pore-size distribution. However, the amounts and chemical states of incorporated nitrogen are highly dependent on the sequence of ammoxidation. In a cyclic voltammetry test, N-doped MCs, compared with MC, exhibit higher capacitance in addition to fast charge/discharge characteristics, which results from their mesoporosity and the pseudo-capacitive effect of incorporated nitrogen. In particular, the NC-type MCs show the best capacitive properties among the materials studied due to the large amount of pyridinic species that modifies the electron donor/acceptor properties of the surface and thereby results in an enhanced, fast and reversible faradaic redox reaction.

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1. Introduction

Electrochemical double-layer capacitors (EDLCs) have attracted considerable attention due to their high power density, high energy density, excellent reversibility, and long cycle life [1–4]. Various carbonaceous materials, including carbon aerogels [5–7], activated carbon [8–12] and mesoporous carbon (MC) [13–15], have been studied for use as electrodes of EDLCs.

Among these carbonaceous materials, MCs are highly suitable for use as EDLC electrodes because of their large surface area and regularly interconnected mesopore structures [16]. The

large surface area is beneficial for accumulating a large amount of charges corresponding to high energy density. The ordered mesoporous structure can contribute to the enhancement of the diffusion rate of the charge carrier in the pore network, resulting in better capability in high drain-rate operations [13,16].

Further improvement in capacitance can be achieved by a fast and reversible faradaic redox reaction, known as pseudo-capacitance [17–20]. Functional groups or heteroatoms such as nitrogen, which are present on the surface of the carbon electrode material, can improve the charge-exchange characteristics of carbon, thus leading to an enhancement of electrochemical capacitance [21,22]. It has been assumed that nitrogen groups change the electron donor/acceptor characteristics of carbon depending on their chemical states.

Several groups have reported on the preparation of nitrogen-doped carbon material for the electrodes of electrochemical

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capacitors [23–25]. Hulicova et al. [23] prepared such materials using melamine and fluorine mica as a carbon precursor and template, respectively. Jurewicz et al. [24,25] found an improvement in electrochemical capacitance when activated carbon was subjected to ammoxidation. The investigators claimed that the incorporation of nitrogen after ammoxidation changed the acidic-basic properties of the activated carbon that resulted in an increased level of total specific capacitance.

In this work, MC materials with nitrogen functionality are prepared through ammoxidation for use as an electrode of an electrochemical capacitor. The effect of the ammoxidation sequence is investigated in terms of the capacitive properties of the resultant N-doped MC materials. The main purpose is to investigate the promoting effects of the mesoporous structure and the pseudo-capacitance of nitrogen, both of which are beneficial to the performance of electrochemical capacitors.

2. Experimental

2.1. Preparation and characterization of carbon electrodes

The 2-D hexagonal mesoporous silica (MS) SBA-15 was used as a template for mesoporous carbon. The MS was prepared using Pluronic P123 (non-ionic triblock copolymer, EO₂₀PO₇₀EO₂₀, BASF) as surfactant and TEOS (98%, Fluka) as a silica source [26]. The MC was prepared as described by Lee et al. [27], and as follows. In brief, 0.0037 mol of sucrose was dissolved in 0.0014 mol of H₂SO₄ and 0.28 mol of H₂O, after which, 1 g of MS was added. The resultant mixture was initially dried at 100 °C for 6 h, followed by further drying at 160 °C for another 6 h. The partially carbonized sucrose/silica composite was again impregnated with an aqueous solution consisting of 0.0023 mol of sucrose, 0.0009 mol of H₂SO₄, and 0.28 mol

of H₂O. The resultant mixture was dried at 100 °C and 160 °C for 6 h each. The samples were carbonized at 850 °C for 4 h in a nitrogen environment. The carbonized black powder was treated with aqueous HF solution at 80 °C for 6 h to remove the silica template, and was then washed with distilled water to yield MC.

To functionalize MC with nitrogen, ammoxidation was carried out at 300 °C for 5 h in a horizontal-flow reactor under a stream of ammonia and air at a volume ratio of 1:1. Depending on the sequence of ammoxidation, two types of N-doped MC (NC and CN) were obtained. In the case of NC, ammoxidation was carried out just before the carbonization step at 850 °C, whereas ammoxidation was conducted after carbonization for CN.

Nitrogen sorption isotherms and textural properties of the materials were determined by an ASAP 2010 Micrometrics sorptometer. Nitrogen contents were determined by elemental analysis with a LECO, CHNS 932 instrument. X-ray photoelectron spectroscopy (XPS) was carried out with a ThermoVG, SIGMA PROBE.

2.2. Measurement of capacitance

To investigate the electrochemical capacitance of carbon materials, cyclic voltammetry was conducted using a conventional three-electrode system with a saturated calomel electrode (SCE) as a counter electrode and a platinum gauze as a counter electrode. All potentials are reported with respect to the SCE. The working electrode was prepared by coating a small amount of carbon ink that contained carbon material, isopropyl alcohol, and polytetrafluoroethylene (PTFE) as a binder. Cyclic voltammograms were obtained between 0 and 0.7 V at room temperature and a scan rate of 10 mV s⁻¹ in 1 M H₂SO₄ solution.

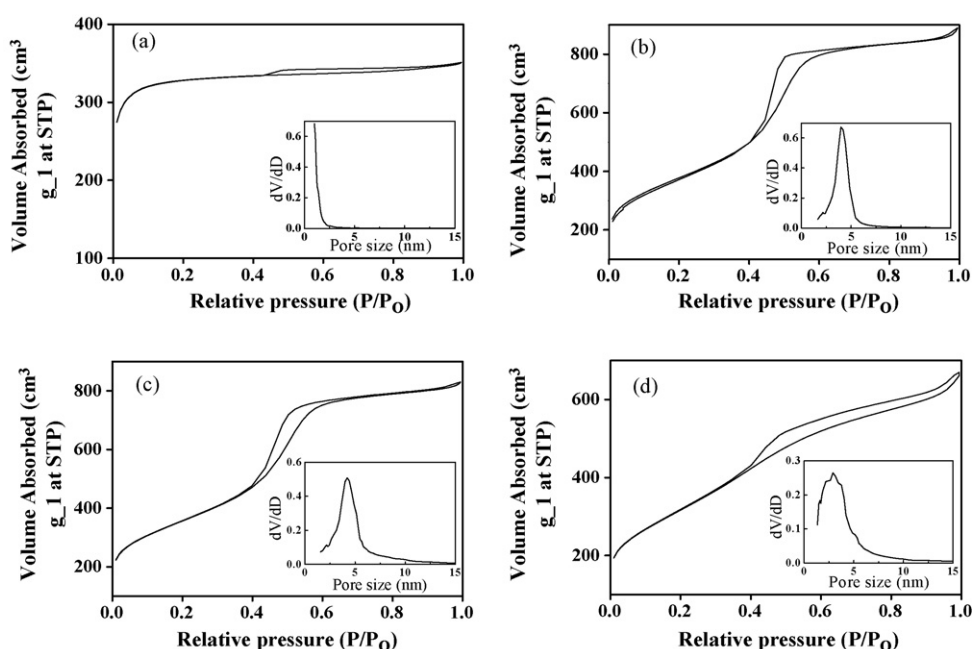


Fig. 1. Nitrogen sorption isotherms and the BJH pore-size distributions (insets) of (a) AC, (b) MC, (c) CN and (d) NC.

3. Results and discussion

3.1. Characterization of carbon materials

Nitrogen adsorption–desorption isotherms of carbon materials are shown in Fig. 1. The isotherm for CN is almost identical to that of MC, which exhibits a type IV isotherm curve with a remarkable adsorption at $P/P_0 = 0.4–0.5$ that is characteristic of a mesoporous structure [28]. The surface area and pore volume are $1271 \text{ m}^2 \text{ g}^{-1}$ and $1.3 \text{ cm}^3 \text{ g}^{-1}$ for MC and $1218 \text{ m}^2 \text{ g}^{-1}$ and $1.24 \text{ cm}^3 \text{ g}^{-1}$ for CN, respectively. By contrast, the NC shows a somewhat differently shaped isotherm compared with those of MC and CN, which indicates that its pore structure is partially destroyed during ammoxidation followed by carbonization. However, the maintenance of the mesoporosity of NC is evident, from a pore-size distribution centred at 3.5–4 nm. Compared with MC and CN, the surface area and pore volume ($1106 \text{ m}^2 \text{ g}^{-1}$ and $1.0 \text{ cm}^3 \text{ g}^{-1}$) of NC are slightly low. Although the surface area of AC ($1117 \text{ m}^2 \text{ g}^{-1}$) is found to be similar to that of NC, this results from the microporosity of AC.

As listed in Table 1, the presence of nitrogen atoms is confirmed by elemental analysis. No nitrogen can be found in AC or MC, while different nitrogen contents are observed in CN and NC depending on the sequence of ammoxidation. Compared with CN, NC has a considerably greater amount of nitrogen in its structure. The differences in the amount of nitrogen between CN and NC can be explained as follows. It appears that nitrogen will be readily introduced through ammoxidation when the sample has a functional group that is capable of accepting nitrogen. In addition, a sample with a weakly bonded structure will easily incorporate nitrogen into its structure through ammoxidation. In the case of NC, ammoxidation was carried out with the precursor state of carbon in which functional groups are more abundant and the chemical structure is weaker toward ammoxidation than the final carbon material.

The chemical state of nitrogen present in the ammoxidized samples was further examined by XPS analysis. Fig. 2 shows the N_{1s} core level peaks of MC, CN, and NC. No peak is observed for MC. Analyzing the peaks of CN and NC reveals the existence of three contributions at binding energies of 398.3, 400.3, and 401 eV. These peaks can be assigned to pyridinic ($398.5 \pm 0.2 \text{ eV}$), pyrrolic or pyridone ($400.5 \pm 0.2 \text{ eV}$) and quaternary species ($401.2 \pm 0.2 \text{ eV}$), respectively [29]. It should be noted that NC contains a relatively higher portion of quaternary and pyridinic nitrogen than CN (Table 2). It is likely that the pyrrolic or pyridonic nitrogen introduced by ammoxidation at a relatively low temperature is transformed into nitrogen species

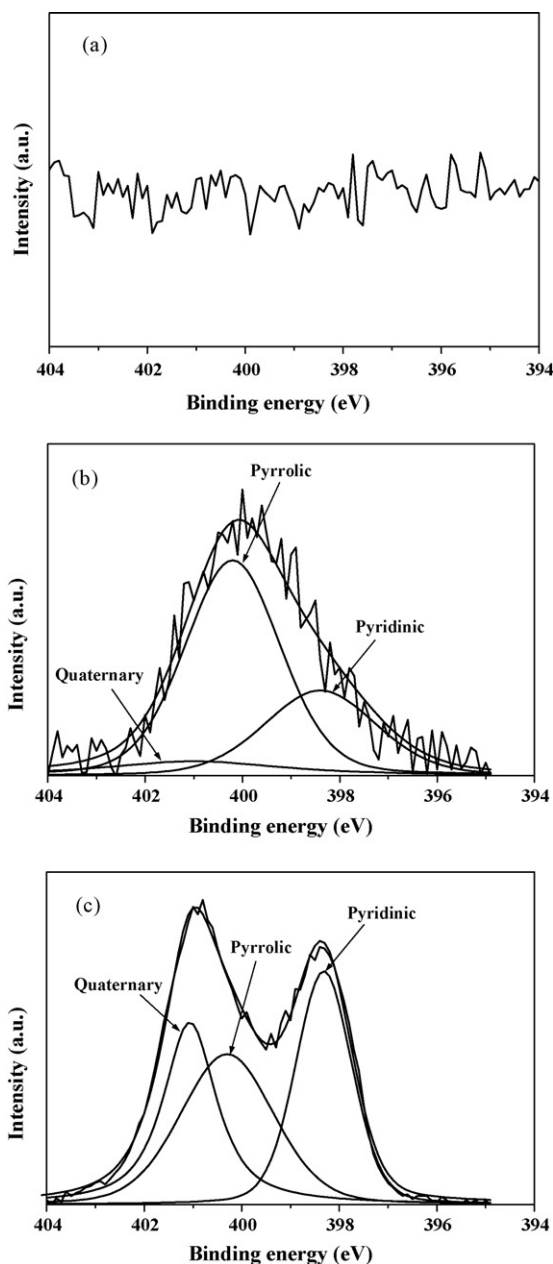


Fig. 2. XPS N_{1s} region for (a) MC, (b) CN and (c) NC.

with higher binding energy through the condensation reactions that occur during carbonization [23].

3.2. Capacitive properties of carbon materials

Typical voltammetric behaviour of AC and synthesized MC materials at the same scan rate (10 mV s^{-1}) is shown in Fig. 3. The specific capacitance is calculated to be 94.7, 119, 136 and $182 \text{ (F g}^{-1}\text{)}$ for AC, MC, CN, and NC, respectively.

The voltammogram of AC shows a tilted shape rather than a rectangular shape. This is due to the influence of the ohmic resistance from electrolyte motion in carbon pores on the mechanism of double-layer formation [30,31]. This distortion becomes significant at a high voltage sweep rate, and indicates that

Table 1
Elemental analyses of AC, MC, CN, and NC

Sample	C (wt.%)	H (wt.%)	N (wt.%)
AC	92	1	0
MC	95	0.8	0
CN	91	1	1.6
NC	74	1.6	8

Table 2
Ratios of quaternary, pyrrolic and pyridinic nitrogen of all samples evaluated by the peak separation analyses of N_{1s} core level peaks

Sample	N _{Quaternary} (%) 401.2 ± 0.2 eV	N _{Pyrrolic} (%) 400.5 ± 0.2 eV	N _{Pyridine} (%) 398.5 ± 0.2 eV
AC	–	–	–
MC	–	–	–
CN	9.5	61.9	28.6
NC	31.1	35.6	33.3

AC is not suitable for rapid charge–discharge operations. Conversely, mesoporous carbons such as MC, CN, and NC show fast charge–discharge responses at the beginning of both positive and negative sweeps. It has been accepted that when the ions are more easily accessible to the electrochemically active surface, the charge–discharge characteristics are faster even at a high voltage sweep rate [16], which is important for the reversibility of electrochemical capacitors. It is believed that the pore structures of mesoporous carbons, which have large pore-sizes with a narrow pore-size distribution, favour ionic penetration into pores and thereby lead to the fast charge–discharge characteristics found for MC, CN, and NC [16].

It is known that nitrogen incorporated on a carbon framework has a beneficial effect on capacitive behaviour in acidic medium [32]. CN and NC exhibit redox currents on both positive and negative sweeps that can be attributed to the pseudo-capacitive effect of incorporated nitrogen heteroatoms and thus cause an increase in capacitance. It is interesting to note that the effect of pseudo-capacitance is dominant in NC. This is, in part, due to the fact that the total amount of nitrogen incorporated is higher in NC than in CN. This enhancement of pseudo-capacitance may also be attributed to the chemical state of the nitrogen. It has been suggested that pyridinic nitrogen at the periphery of the graphene layers provides a pair of electrons that could introduce electron donor properties to the layer [33]. Such a feature could result in the attraction of ions, such as protons, and consequent pseudo-capacitive interaction [23,33]. In this study, NC is confirmed to contain a relatively large amount of pyridinic nitrogen in its structure, the nitrogen species of which will contribute to further enhancement of the pseudo-capacitance.

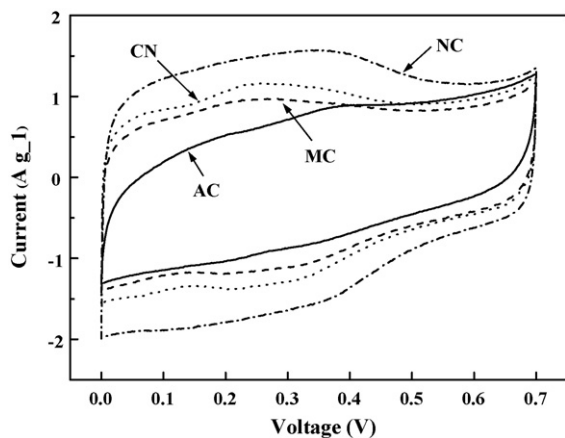


Fig. 3. Cyclic voltammograms of AC, MC, CN and NC in 1 M sulfuric acid. Cyclic voltammetry measurement performed in potential range of 0–0.7 V vs. SCE at a scan rate of 10 mV s⁻¹.

4. Conclusion

For use as electrode materials in electrochemical capacitors, mesoporous carbons with a moderate amount of nitrogen have been prepared by ammoxidation performed at different stages of the MC preparation process, namely, ammoxidation before (NC) and after carbonization (CN). The physical characteristics of N-doped MCs are similar to those of MC regardless of the ammoxidation sequence. On the other hand, the contents and chemical state of incorporated nitrogen are found to be affected by the sequence of ammoxidation. The amount of incorporated nitrogen in NC (8 wt.%) is greater than that in CN (1.6 wt.%). In addition, pyridinic species are more abundant in NC than in CN. Both mesoporosity and nitrogen functionality have positive influences on the capacitive performances of the materials examined in this study. The specific capacitances are in the order of: NC (182 F g⁻¹) > CN (136 F g⁻¹) > MC (119 F g⁻¹) > AC (activated carbon, 94.7 F g⁻¹). The large amount of incorporated nitrogen in NC is mainly responsible for the high specific capacitance. In addition, the large amount of pyridinic species in NC enhances the electron donor/acceptor properties and this would further improve its pseudo-capacitance. Since ammoxidation is conducted simply in a mild condition, the method proposed in this study is an easy process that can be used for the preparation of carbon electrodes that give high performance in electrochemical capacitors.

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