

Nitrogen-Containing Polymeric Carbon as Anode Material for Lithium Ion Secondary Battery

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Received 11 May 1999; accepted 10 September 1999

ABSTRACT: Nitrogen-containing polymeric carbon as anode materials for the lithium ion secondary battery is prepared from polyacrylonitrile (PAN) and melamine-formaldehyde resin (MF) at 600 and 800°C. Its physicochemical properties were investigated through elemental analysis, X-ray powder diffraction, X-ray photoelectron spectroscopy, and measurement of specific surface area. Results show that this kind of carbon is amorphous. Nitrogen atoms exist in the prepared polymeric carbon mainly as two states, that is, graphene nitrogen and conjugated nitrogen, and favor the enhancement of reversible lithium capacity. All the prepared polymeric carbon has a reversible capacity higher than that of the theoretic value of graphite, 372 mAh/g, and the highest reversible capacity can be up to 536 mAh/g. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 1735–1741, 2000

Key words: polymeric carbon; nitrogen; anode; lithium ion secondary battery

INTRODUCTION

Polymeric carbon, which is prepared from the heat treatment of polymers at a temperature generally below 1000°C, has been studied widely and can be applied in many fields such as carbon fibers, semiconductors, and capacitors. However, it was recently suggested that polymeric carbon can be used as anode materials for the next generation of the lithium ion secondary battery.¹

A lithium ion secondary battery has many advantages over traditional rechargeable batteries such as lead acid, Ni—Cd, and Ni—MH, for example, high output voltage (~ 3.6 V), lightweightness, high energy density, free of memory effect,

and long cycle life and is benign to the environment.² Since its birth in the early 1990s,³ its development has been rapid and it has been widely used as power sources for cellular telephones, cordless phones, camcorders, and portable computers. From the viewpoints of academic value and market interests, much research has been directed to lower its cost and/or to improve its electrochemical properties. One aspect of these is the study of anode materials. The generally used one is graphitic carbon or graphite. To be graphitic, carbon materials have to be heat-treated at high temperature (> 2000°C). In addition, the reversible capacity of graphitic carbon is quite limited compared with lithium metal. Consequently, other kinds of anode materials were investigated such as $\text{Li}_{3-x}\text{M}_x\text{N}$,^{4,5} tin-based oxides,^{6,7} and polymeric carbon.^{8–12} The reversible lithium capacity of these materials can be higher than the theoretical value of graphite. For future application of the lithium ion secondary battery

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Contract grant sponsors: China Natural Sciences Foundation Committee; China Postdoctor Foundation Committee.

Journal of Applied Polymer Science, Vol. 77, 1735–1741 (2000)
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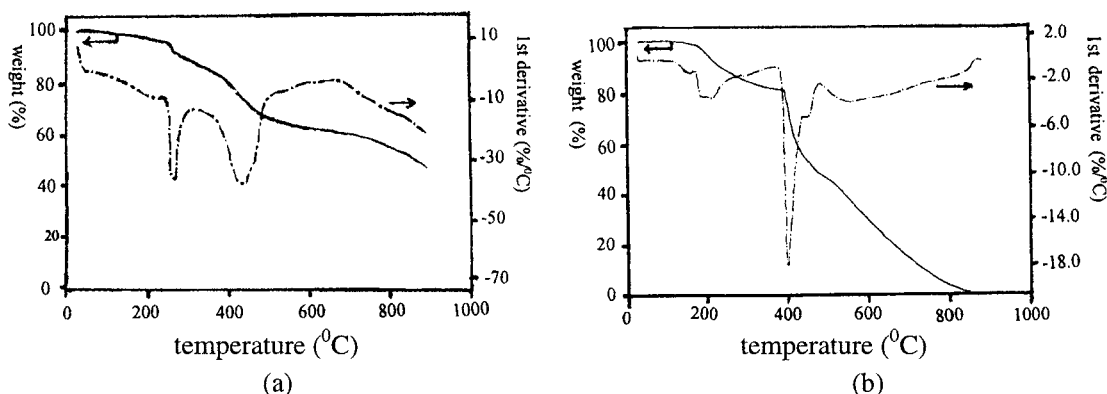


Figure 1 Thermal gravity analysis diagrams of (a) PAN and (b) MF.

as a power source for electric vehicles, polymeric carbon is a promising candidate.²

Most kinds of polymeric carbon are prepared from the very common phenol–aldehyde resin.^{8–10} While polyacrylonitrile (PAN) and melamine–aldehyde resin (MF) are also common polymers, as far as we know, which are rarely reported except in a recent publication related to PAN.¹³ One reason may be that the existence of nitrogen is suggested to be unfavorable to the electrochemical properties of the carbon anode because of the existence of the so-called chemical nitrogen which reacts irreversibly with lithium.¹⁴ However, our results and others illustrate that if nitrogen is bonded satisfactorily, that is, nitrogen does not exist as the above-mentioned chemical nitrogen or amine-group nitrogen, the electrochemical properties of the prepared polymeric carbon will be improved.^{15,16} Consequently, here, polymeric carbon based on PAN and MF was studied for anode materials of a lithium ion secondary battery and results show that the electrochemical properties of this kind of polymeric carbon are also satisfactory.

EXPERIMENTAL

Purified monomer acrylonitrile (AN) was put into a three-neck flask which contained the solvent dimethylformide (DMF) and the purified initiator AIBN. After the flask was degassed with nitrogen for 30 min, the polymerization was carried out at 80°C for 8 h. When cooled, the solution was poured slowly into ethanol and PAN was precipitated. After filtration, it was dried under ambient pressure and later under a vacuum.

MF was prepared from the condensation polymerization of melamine and formaldehyde (molar ratio 1 : 2) at 80°C with pH 10.0. When the polymerization reaction was completed, the product solution was cast onto a plate. After drying, a thin film was formed.

Thermogravimetric analysis diagrams of PAN and MF, under a high purity nitrogen atmosphere at 20°C/min, are shown in Figure 1(a,b) and illustrate that the carbon structure begins to form at a temperature above 500°C. Thus, the heat-treatment temperature was selected as 600 and 800°C, respectively, to prepare polymeric carbon.

The dried polymers were put into a tube furnace and pyrolyzed under an argon atmosphere at the above-mentioned temperature, that is, 600 and 800°C, respectively, to prepare polymeric carbon. Carbon samples A1, A2 and B1, B2 were prepared from PAN and MF, separately. The prepared polymeric carbon was powdered through a 320-mesh sieve and used for the following analysis of physicochemical properties:

Specific surface area was acquired on a Sorp-matic 1800 series instrument based on the well-known Brunauer, Emmett, and Teller (BET) equation. Elemental analysis was performed by the Heratus CHN-rapid method. X-ray powder diffraction measurement was made using a D/MAX-3B diffractometer equipped with a copper target and a diffracted beam monochromator. The size of the graphite crystallite, L_c , was calculated based on the following well-known Sherrer equation:

$$L_c = k\lambda/B \cos \theta$$

Table I Results from Elemental Analysis, X-ray Powder Diffraction, and X-ray Photoelectron Microscopy of the Prepared Polymeric Carbon

Sample	Polymer	Heat-Treatment Temperature (°C)	Ratio of N/C	Ratio of H/C	Interlayer Distance d_{002} (Å)	Size of Graphite Crystallite (Å)	Relative Content of Graphene Nitrogen (%)	Relative Content of Conjugated Nitrogen (%)	Relative Content of Amine-Group Nitrogen (%)
A1	PAN	600	0.178	0.351	3.520	11.4	46.52	53.48	0.0
A2	PAN	800	0.057	0.155	3.602	12.9	39.74	60.26	0.0
B1	MF	600	0.217	0.241	3.434	12.2	49.37	50.63	0.0
B2	MF	800	0.067	< 0.03	3.411	14.2	34.22	65.78	0.0
B0	MF	20	1.190	0.960	—	—	0.0	49.99	50.01

where k is the shape factor; λ , the X-ray wavelength; B , the full-width at half-maximum (fwhm) of the 002 peak in radians; and θ , the Bragg angle. Since this kind of carbon is amorphous, the shape factor k is 0.9. X-ray photoelectron spectroscopy was performed with a spectrometer of ES300 from Karatos Ltd. under a high vacuum. Its X-ray source was $MgK\alpha$ and graphite was used as a reference.

Capacity of the prepared polymeric carbon was tested with a model cell with lithium metal as the counter and reference electrode. A mixture of polymeric carbon with 5 wt % polytetrafluoroethylene as a binder was pressed into pellets as anode of the model cell. The electrolyte used as a 1M solution of $LiClO_4$ dissolved in a mixture of diethyl carbonate (DEC) and ethylene carbonate (EC) (v/v = 7 : 3). The separator was home-made of porous polypropylene. Because there is overpotential and internal resistance, discharge and charge voltages were selected in the range of -0.03 – 2.0 V. From comparison of discharge and charge profiles, there is no lithium plating at the cutoff voltage of -0.03 V. Electric current density was constant, that is, 0.25 mA/cm².

RESULTS AND DISCUSSION

The results of elemental analysis are shown in Table I. From their comparison, it can be seen that the contents of interatoms such as H and N decrease when the heat-treatment temperature increases, which is consistent with what others reported.^{8–10} When the nitrogen content in the precursor is high, that in the prepared polymeric

carbon will be high. However, the nitrogen content is considerable. Thus, it may affect the physicochemical properties of the prepared carbon.

X-ray powder diffraction patterns of the prepared polymeric carbon are presented in Figure 2 and results are summarized in Table I. A weak and broad (002) Bragg peak near 26° is observed. The Bragg peak of the other planes such as the 100, 101, and 004 planes are not discernible. This indicates that the prepared polymeric carbon is amorphous and consists of graphite crystallites and disordered areas.¹⁷ However, compared with other kinds of amorphous carbon prepared also at low temperature,^{8–10} the interlayer distance,

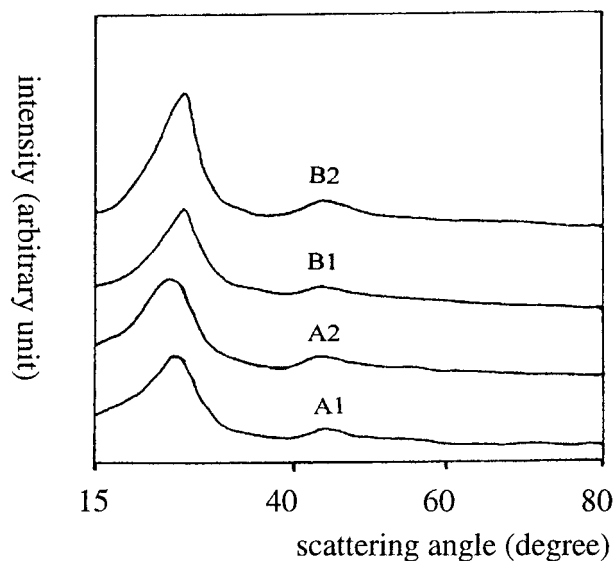


Figure 2 X-ray powder diffraction patterns of the prepared polymeric carbon.

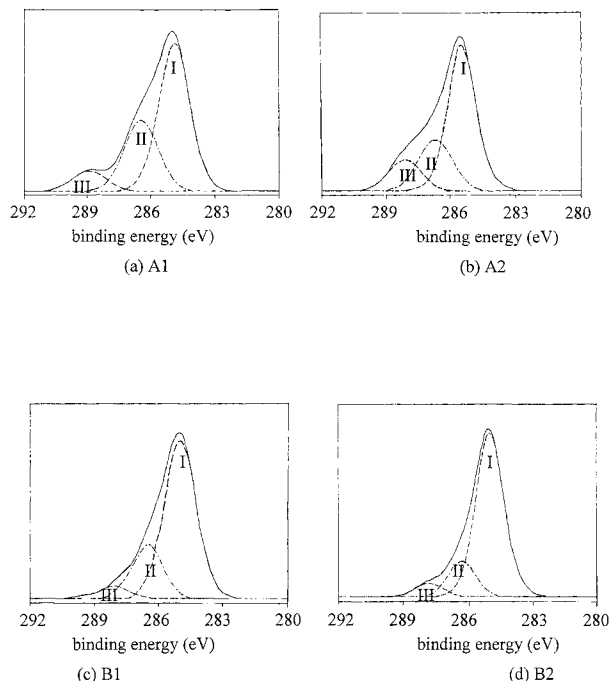


Figure 3 X-ray photoelectron spectra of C_{1s} in the prepared polymeric carbon.

d_{002} , is a little smaller. Since the diameter of nitrogen is smaller than that of carbon, 1.50 versus 1.54 Å, the substitution of carbon by nitrogen will cause a decrease in the spacing between adjacent sheets.^{15,16} Meanwhile, the nitrogen atoms can favor carbonization, which will result in a more compact carbon structure.^{14,16}

X-ray photoelectron spectra of C_{1s} in the prepared polymeric carbon are shown in Figure 3. The spectra divide into three peaks, that is, I, II, and III. Peak I is around 285 eV, corresponding to carbon atoms in graphene molecules. Parts of graphene molecules consist of graphite crystallite and others form the skeleton of the disordered areas. Peaks II and III correspond to carbon atoms in the state of C—N bonding, —C—H, and edge atoms.¹⁶ When the temperature is high, the relative content of peak I increases and that of the peak II decreases, which results from the high carbonization degree and low content of nitrogen. This indicates that the carbon structure has been cast into shape; however, it is not still completely graphitic, which is consistent with the above results from X-ray powder diffraction.

X-ray photoelectron spectra of N_{1s} in the prepared polymeric carbon and MF are given in Figure 4 and the relative content of each kind of

nitrogen is presented in Table I. Nitrogen in the prepared polymeric carbon exists mainly in two states, namely, graphene nitrogen and conjugated nitrogen, corresponding to binding energy peaks at 398.5 and 400.2 eV, respectively.¹⁶ The first kind of nitrogen is so-called since it situates at the graphene molecules of the graphite crystallite while the latter exists only as —C=N bonding and does not join in the graphene molecules. There is no indication of the existence of amine-group nitrogen, corresponding to a binding energy peak at around 403 eV. Consequently, nitrogen atoms are bonded satisfactorily and will not contribute to the enhancement of irreversible capacity. Because the electronegativity of nitrogen (3.5) is higher than that of carbon (3.0), and its diameter is smaller than that of carbon, the interaction between the formed carbon structure and lithium will be stronger, and thus more lithium can be intercalated.^{15,16} Therefore, to the contrary, the reversible capacity of the prepared carbon will be

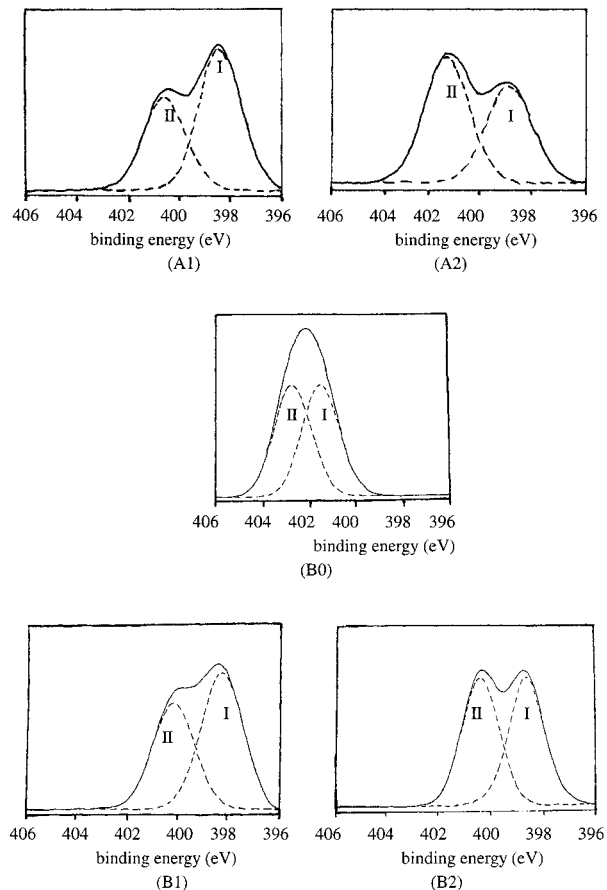


Figure 4 X-ray photoelectron spectra of N_{1s} in the prepared polymeric carbon and MF(B0).

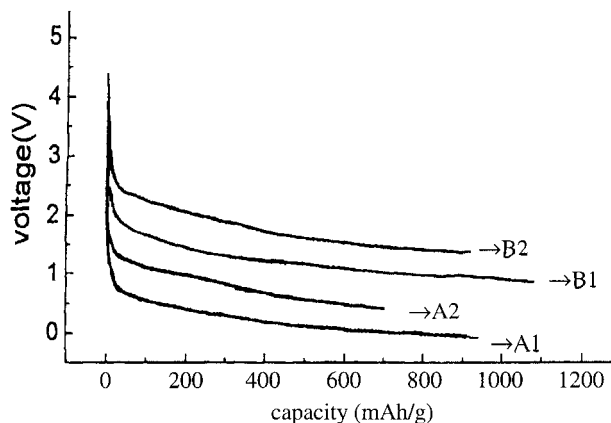


Figure 5 Discharging profiles in the first cycle of the prepared polymeric carbon. For clarity, voltage profiles of A2, B1, and B2 are shifted upward by 0.5, 1.0, and 1.5 V, respectively.

high since these kinds of doped nitrogen atoms favor the enhancement of reversible capacity.^{15,16} When the temperature increases, the relative content of graphene decreases because nitrogen atoms in graphene molecules are unstable thermodynamically.

Discharging profiles in the first cycle of the prepared polymeric carbon are shown in Figure 5. During the discharging process, there is no evident voltage plateau and, for the most part, is below 0.5 V, which is different from graphite.¹⁸

Charging profiles in the first cycle of the prepared polymeric carbon are shown in Figure 6. As reported,^{8–10} this kind of amorphous carbon does not have any evident voltage plateau during the charging process either. The reversible capacity of all samples is higher than the theoretical value of

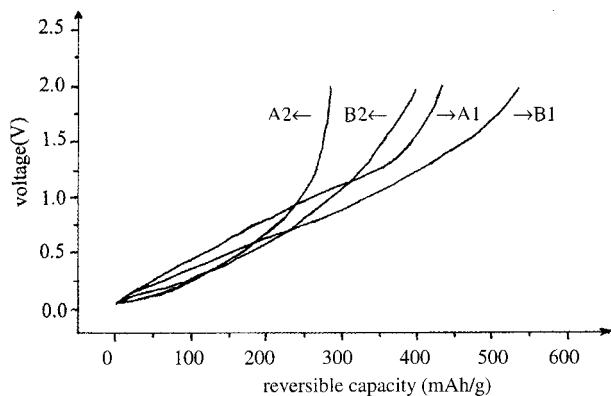


Figure 6 Charging profiles in the first cycle of the prepared polymeric carbon.

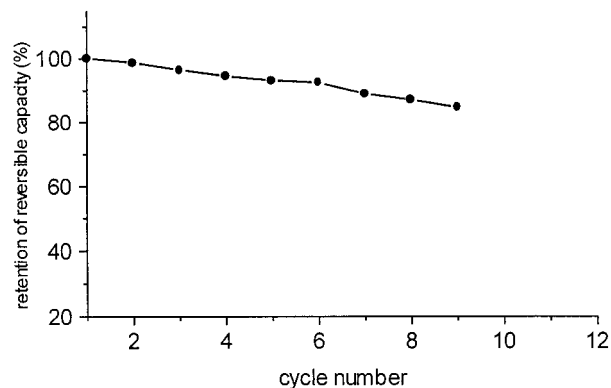


Figure 7 Relation between the reversible capacity of polymeric carbon A1 and cycle number.

graphite, 372 mAh/g, and the highest can be up to 536 mAh/g. The high capacity is partly due to the effects of nitrogen atoms.^{15,16} Comparison between A1 and B1, and A2 and B2, indicates that the higher the nitrogen content the higher the reversible capacity is. Of course, the effect of the micropores in the prepared carbon is also important.^{19–21} For example, the specific surface area obtained through the BET method in samples A1 and B1 is 236 and 211 m²/g, respectively. It is well known that during the heat-treatment of polymers small molecules will be given off and their vacancies will be left as micropores. During the charging process, lithium will enter these micropores as lithium clusters or lithium molecules Li_x ($x \geq 2$), while during the discharging process, the formed lithium clusters or lithium molecules will decompose and give off lithium ions and electrons via the surrounding graphite crystallites.^{19–21} Consequently, these micropores act for “reservoirs” of lithium storage and contribute to enhancement of the gravimetric reversible capacity of the prepared carbon. Because this kind of micropore is different from that derived from the addition of pore-genic agents such as inorganic salts,^{22,23} their electrochemical behavior is different. The latter can store anions such as ClO₄⁻ and act as the cathode for a lithium secondary battery with a potential of 2.0–4.0 V versus Li⁺/Li.

Changes of the reversible capacity with one kind of the prepared carbonaceous materials, A1, with the cycle number is shown in Figure 7. Reversible capacity fades gradually with the cycle number, which is similar to other kinds of low-temperature carbons. Capacity fading has been suggested to be from hydrogen atoms in the car-

bonaceous materials.²⁴ If hydrogen atoms in the carbonaceous materials react with lithium and contribute to the fade of reversible capacity, the content of hydrogen must be lowered after several cycles. After 10 cycles, the carbon anode was immersed in dilute hydrochloric acid for 24 h and washed with water until neutral, then dried under a vacuum, and the content of hydrogen in the carbon anode material was analyzed. The result shows that the hydrogen content is unchanged; thus, the function of hydrogen is not complete as suggested above. The existence of hydrogen atoms is due to the heat-treatment temperature being low and the graphitization process not being complete.

The cause of capacity fading may be due to the imperfect carbon structures such as edge carbons, tetrahedral carbons, free carbon radicals, and chain carbons.²⁵ These structures are very active and react with lithium. During repeated discharge and charge cycles, they lead to destruction of the carbon structure.²¹ Of course, since the activity of these imperfect structures is very high and can bond with lithium, they have been suggested to be the cause of the increase in reversible capacity.^{26,27} In fact, these imperfect structures are situated at the surface of graphite crystallites or exist in the disordered areas. Even though they contribute to an increase in reversible capacity, the interaction between them and lithium could not last long since the lithium thereof is very active and can react with electrolyte molecules such as DEC and EC in an electrolyte solution. Recently, it was observed, through electrochemical scanning tunneling microscopy (ECSTM), that the edges of graphite are the cause of destruction of the graphite structure since they favor the intercalation of electrolyte molecules and solvated lithium ions.²⁸ If these imperfect structures can be eliminated through oxidation, capacity fading will be negligible.^{29–31} This suggests that this kind of polymeric carbon will be promising as anode materials for a lithium ion secondary battery.

CONCLUSIONS

Nitrogen-containing polymeric carbon was prepared from the heat-treatment of common polymers such as PAN and MF. In this kind of carbon, nitrogen atoms do not exist as amine-group nitrogen and can favor the enhancement of a revers-

ible lithium capacity. It is observed that the higher the nitrogen content in the prepared polymeric carbon the higher the reversible capacity. All the prepared nitrogen-containing samples have a reversible capacity higher than the theoretic value of graphite, 372 mAh/g, and the highest one can be up to 536 mAh/g. However, its cycling property still needs to be improved.

This research was supported by the China Natural Sciences Foundation Committee and the China Postdoctor Foundation Committee.

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