JOURNAL OF MATERIALS SCIENCE **34** (1999) 4253–4258

Carbon anode materials based on copolymers of nitrogen-containing monomers with DVB

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Through the measurement of electrochemical properties of carbon anodes based on copolymers of 4-VP and AN with crosslinker DVB, it is found that the introduction of crosslinker DVB can favor the enhancement of reversible capacity, and the highest can be up to 600 mAh g^{-1}. Measurements of Thermal gravity analysis, elemental analysis, X-ray powder diffraction, scanning electron microscopy and specific surface area indicate that the incorporation of DVB into polymer PAN can not only affect the contents of nitrogen and hydrogen, but also favor the carbonization process. In addition, it can result in improvement of the regularity of the obtained carbon structure, i.e. the formation of graphite structure, and the number of micropores is increased. By virtue of all these factors, charge capacity below and above 0.9 V enhances and charging voltages decrease with the addition amount of DVB. *© 1999 Kluwer Academic Publishers*

1. Introduction

Since the commercialization of lithium-ion secondary battery in the early 1990s, many studies [1] have been carried out to lower its cost and/or improve its properties because it has not only much market interests but also important strategic values. But materials based on graphitized carbon have limited capacity compared with lithium metal, and their preparation needs high temperature, i.e. >2000 °C, which is critical to industry, thus many methods have been tried, for example the preparation of polymeric carbons [2], the incorporation of interatoms such as B [3] and N [4, 5] and the introduction of transitional elements [6–8]. Polymeric carbons can be prepared at low temperature (<1200 °C) and their reversible capacity is larger than the theoretic one of graphite. In addition, most polymers can be got very easily in the plastic products whereas most of them can not be self decomposed and are unfriendly to environment after aged. If polymeric carbons can be commercially acceptable, they will solve some problems caused by the aged plastic products, and can reuse them as precursors for carbon anodes. Therefore, interest has been focused on these polymeric carbons. However, most of them are based on phenol-formaldehyde resins because this kind of polymers can be got from the market very easily and the cost is low [9–11].

From our obtained results [5], polymeric carbons doped with nitrogen favor the enhancement of reversible lithium capacity. In this paper, we investigated a novel kind of precursor based on copolymers of nitrogen-containing monomers and crosslinker, and studied the effects of crosslinker divinyl benzene (DVB) on electrochemical properties of the prepared polymeric carbons.

2. Experimental

Monomers 4-vinyl pyridine (4-VP) and acrylonitrile (AN) were purified by vacuum distillation and distillation under ambient pressure, respectively. The purified monomers were separately put into a 3-neck 250 ml flask with a stirring instrument. After the addition of some amount of crosslinker DVB, emulsifier PVA and initiator 0.3 wt % $(NH_4)_2S_2O_8$, the flask was bubbled with nitrogen for 30 min, and later heated at 80 °C for 6 h. When the prepared copolymers were dried, they were separately put into a tube furnace and pyrolyzed under argon atmosphere at 600 °C to prepare polymeric carbons as our reported method [5]. Samples B221, B222 and B223 were carbon products based on copolymers of AN with 1.0, 3.0 and 5.0 wt % DVB, respectively, and sample B210 was that based on homopolymer PAN.

Elemental analysis was carried out by the Heratus CHN-rapid method. X-ray powder diffraction (XRD) data were collected on a D/MAX-3B diffractometer. Thermal gravity analysis (TGA) was performed using

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a Perkin-Elmer Thermal Analysis System, 7, under a high pure nitrogen atmosphere at a heating rate of 20 °C min^{-1}. Scanning electron micrographs (SEM) were obtained using a Hitachi S530 spectrometer. In order to increase the contrast of the diagram, all carbon samples were precoated with a thin layer of gold. The measurement of specific surface area was carried out with a Sorpmatic 1800 and the results were obtained based on the well-known BET equation.

The capacity of the carbonaceous materials was measured with lithium metal as the counter and reference electrode. The anode was prepared from the carbonaceous materials with 5 wt % polytetrafluoroethylene as a binder. Electrolyte used was a 1M $LiClO_4$ solution dissolved in a mixture of diethyl carbonate and ethylene carbonate (v/v 3 : 7). Discharge and charge voltages were between 2.0 and −0.03 V, and the electric current density was constantly 0.2 mA cm^{-2}. The cutoff voltage of discharge was selected at −0.03 V because overpotential resulted from internal resistance [5].

3. Results and discussion

3.1. Carbon anodes based on copolymers of 4-VP with DVB

Charging curves of carbon anodes based on copolymer of 4-VP with different content of crosslinker DVB are shown in Fig. 1. It can be seen clearly that the charge capacity enhances with the addition amount of DVB and the enhanced part situates at above 1.0 V. It is reported that micropores in carbons can act as “reservoirs” for lithium storage [12, 13] and thus the reversible lithium capacity can be very high. It is well known that the incorporation of DVB can introduce micropores into the polymer structure [14]. Of course, it will affect the prepared carbon products and part of the micropore structures can be kept, therefore, the reversible capacity increases with the addition amount of DVB. This trend is presented in Fig. 2. The highest reversible capacity can be up to 600 mAh g^{-1}.

However, the yield of the copolymer of 4-VP with DVB is quite low because its C-C bond can be destroyed very easily. Thermal gravity analysis diagrams of poly (4-vinyl pyridine) (P(4-VP)) and copolymer of 4-VP with 3.0 wt % crosslinker DVB shown in Fig. 3 present it clearly. Since its yield is very low, it couldn’t be much promising from the viewpoint of industrialization and environment protection; therefore we didn’t pursue further studies on this kind of copolymer.

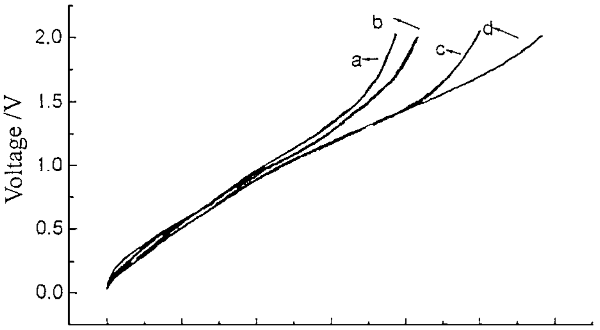


Figure 1 Charging curves of carbon anodes based on copolymers of 4-VP with different amount of DVB: (a) 0.0 wt %, (b) 1.5 wt %, (c) 3.0 wt % and (d) 5.0 wt %.

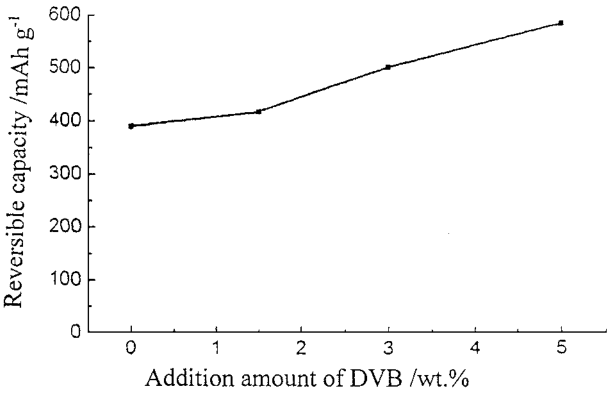


Figure 2 Relationship of reversible capacity of carbon anodes with the addition amount of DVB.

If the chain structure can not be destroyed so easily, then it will be promising for application. Whereas polyacrylonitrile (PAN) is endowed with this properties, thus we carried out further research on the copolymers from AN with DVB.

3.2. Carbon anodes based on copolymers from AN with DVB

3.2.1. Effect of crosslinker DVB on thermal gravity analysis

The homopolymer PAN proceeds cyclization reaction between the adjacent −CN groups at temperature below 300 °C. At the range of 350–450 °C, crosslinking reaction between the polymer chains of the cyclized PAN will take place. In this range, the dehydrogenation and denitrogenation will happen. If further heated, it will form carbon structure or skeleton [15]. Thermal gravity analysis diagram of PAN shown in Fig. 4a presents that the cyclization and crosslinking processes proceed at 263 and 435 °C, respectively.

After the introduction of DVB into PAN, the apparent molecule weight of the polymer increases, therefore its cyclization and crosslinking processes will proceed at relatively higher temperature than homopolymer PAN. Thermal gravity analysis diagrams of copolymer from AN with 5.0 wt % DVB shown in Fig. 4b clearly gives out that the cyclization and crosslinking processes proceed at higher temperature, i.e. 276 and 454 °C, respectively. It means that the introduction of crosslinker can improve the mechanical strength of PAN.

3.2.2. Effect of crosslinker DVB on the atomic ratio of N/C and H/C

Results of elemental analysis are summarized in Table I. It shows that the introduction of DVB decreases

TABLE I The change of N/C and H/C in the prepared polymeric carbons based on copolymers of AN with crosslinker DVB

Sample	Temperature (°C)	Addition amount of DVB wt %	Atomic ratio of N/C	Atomic ratio of H/C
B210	600	0.0	0.195	0.362
B221	600	1.0	0.192	0.170
B223	600	5.0	0.185	0.162

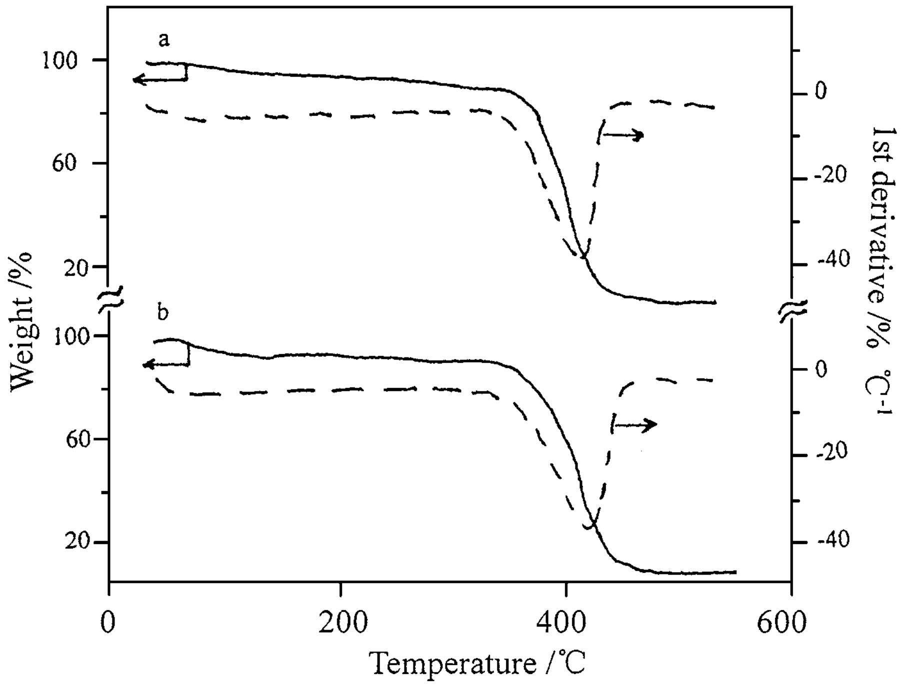


Figure 3 Thermal gravity analysis diagrams of poly(4-vinyl pyridine) (a) and copolymer of 4-VP with 3.0 wt % DVB (b).

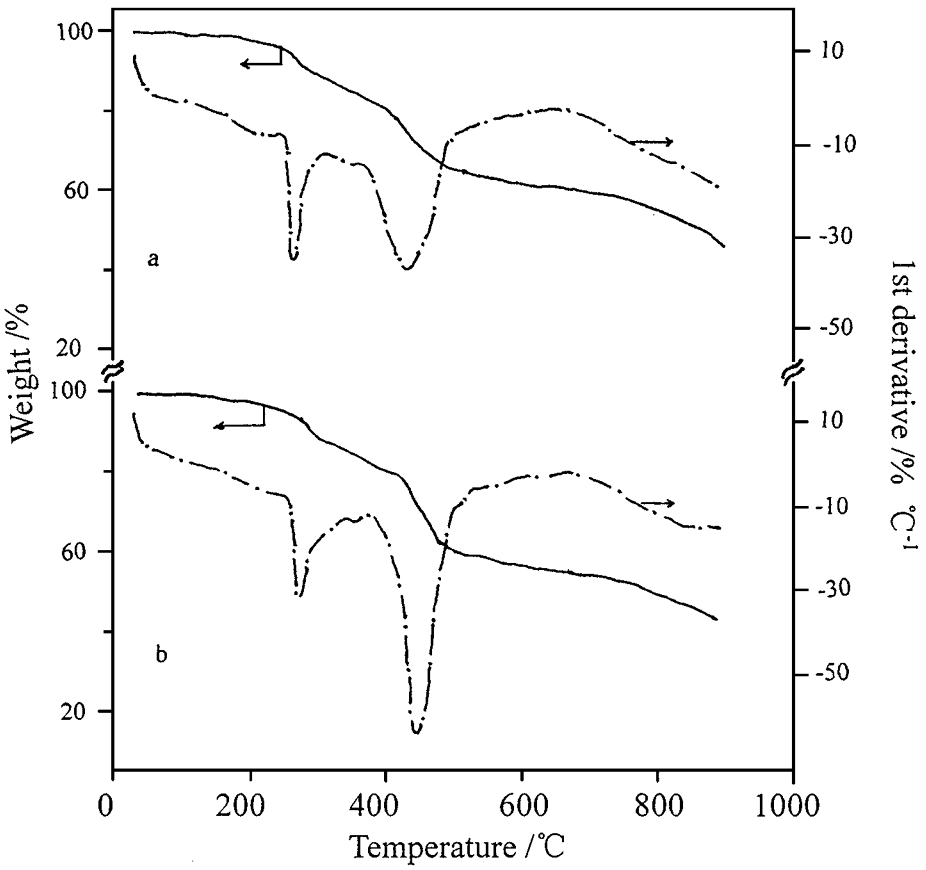


Figure 4 Thermal gravity analysis diagrams of polyacrylonitrile (a) and copolymer of AN with 5.0 wt % DVB (b).

the contents of nitrogen and hydrogen. But the decrease degree is different, the first is not much and the latter is much. The change of the content of nitrogen can be attributed to two aspects. One aspect is arisen from that the content of nitrogen in the copolymer AN-DVB is lower than that in homopolymer PAN. The other one is from that the introduced crosslinker can fix the polymer chains and favor the cyclization and crosslinking process, and thus the nitrogen atoms can be incorporated into the carbon structure more easily. However, the favored carbonization process will result in great decrease of the content of hydrogen, and thus the above results are presented. The process from copolymer to carbon structure can be schematically illustrated in Fig. 5, indicating the behavior of copolymer is different from the homopolymer PAN [15].

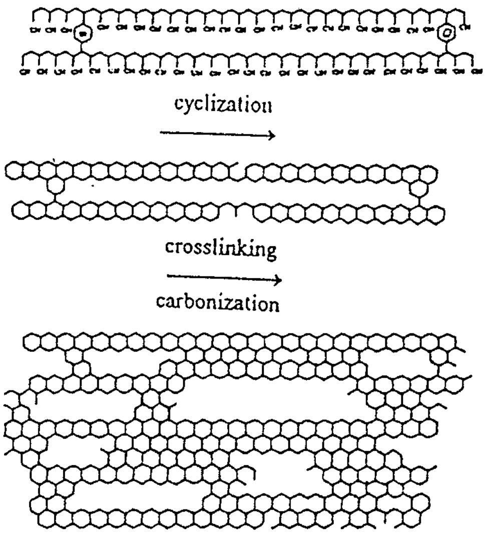


Figure 5 Cyclization, crosslinking and carbonization processes of the copolymer of AN with DVB under heat-treatment.

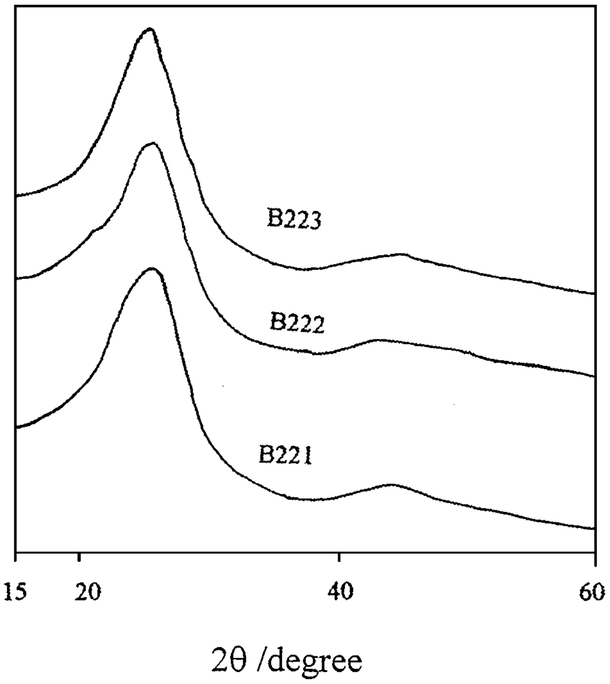


Figure 6 X-ray powder diffraction patterns of the prepared polymeric carbons based on copolymers of AN with DVB.

3.2.3. Effect of crosslinker DVB on the carbon structure

X-ray powder diffraction patterns of the prepared carbons are shown in Fig. 6. It presents that the change of distance between 002 planes, d_{002}, can be negligible. But the shape of 002 peak becomes sharper after the introduction of crosslinker DVB. This indicates that the size of graphite crystallite increases, and also presents that the introduction of DVB favors the carbonization of PAN, which partly illustrated from Fig. 5 and is consistent with results from elemental analysis.

3.2.4. Effects of crosslinker DVB on the morphology

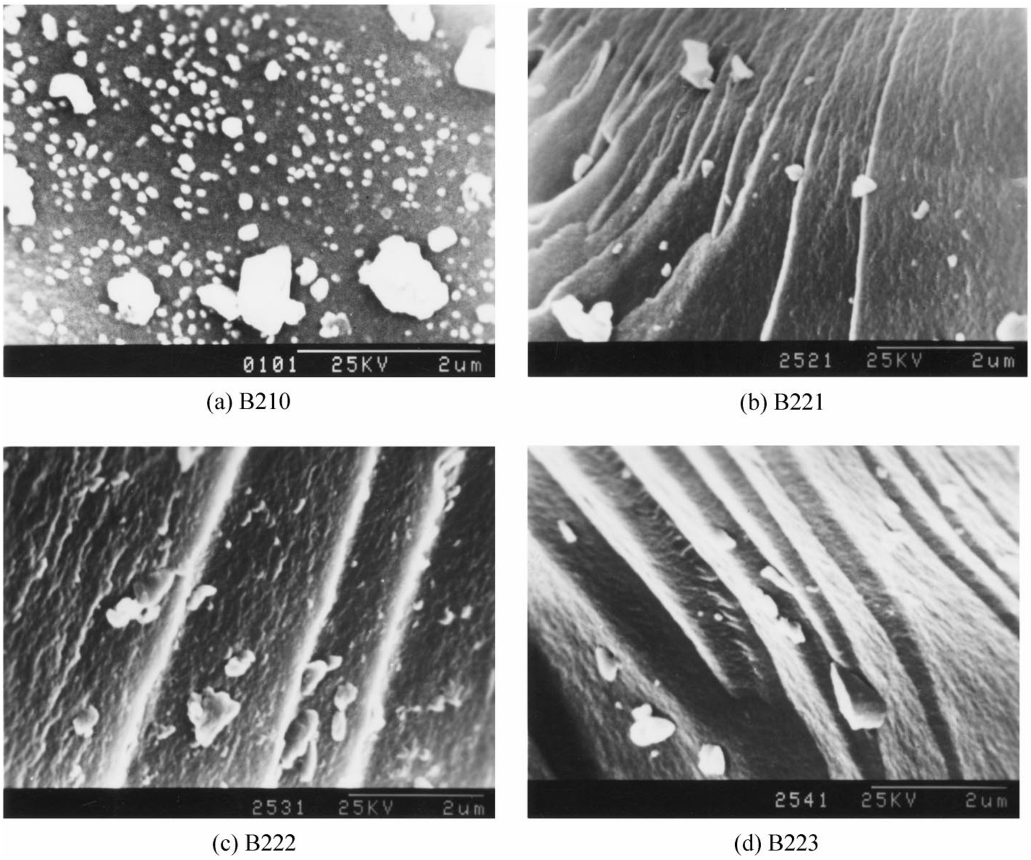
It is well known that carbon structure depends on precursors and processes [16]. The carbon structure can be divided into four kinds: plane orientation, axial orientation, point orientation and random orientation. The prepared carbons from PAN without special treatments such as elongation and orientation are generally turbostatic. It is clearly shown in scanning electron micrograph Fig. 7a. However, after introduction of crosslinker DVB, the morphology of the prepared carbon is changed. Fig. 7b–d shows that their SEM diagrams consist of layer structure, i.e. graphite structure [8]. It presents that the carbon structure is more ordered and the introduction of DVB can favor the carbonization process. The more the addition amount of DVB, the more ordered the carbon structure. As our above obtained results, the introduced DVB fixes the polymer chains and causes the molecules cyclized to joint more readily and form carbon structure. Whereas in homopolymer PAN, the cyclized polymer molecules arrange randomly according to the theory of the movement of polymer molecules, and this arrangement results in random stacking of carbon layers, i.e. turbostratic structure. The fixing action of DVB is different from the incorporation of oxides of transitional elements such as V_2O_5 [6, 7], NiO and CoO [8], which catalyze the formation of graphite. The added V_2O_5 can form complex VO (graphene)$_2$ during heat-treatment [6, 7], whose part of VO coordinates with the graphene molecules. The complex acts as nucleation agent of graphene molecules and gives rise to an increase in regularity of the formed carbon structure, and displays in SEM diagrams as layered structure.

3.2.5. Effects of crosslinker DVB on the specific surface area

No evidence of the existence of pores can be seen from Fig. 7. However, it has been reported that the introduced crosslinker DVB would affect the number of pores in polymers [17, 18]. Since there is no evidence of the existence of macropores from SEM diagrams, we carried out the measurement of specific surface area with N_2 absorption and desorption method by the use of BET equation, and the results are presented in Fig. 8. The specific surface area increases with the addition amount of DVB. This clearly indicates that the introduction of crosslinker can increase the number of micropores in the prepared carbon product. From Fig. 5 it can be seen that the introduced DVB acts as support of micropores during heat-treatment, which is different from the method by the introduction of a large amount of inorganic or organic salts into the polymer precursors [19]. After heat-treatment, the salts were removed and the spaces occupied by the salts were left. This kind of pores are larger and can only act as "reservoirs" for the storage of anions such as ClO_4^- and couldn't effectively store lithium while the introduction of crosslinker DVB can increase the lithium storage from our following results.

3.2.6. Effects of crosslinker DVB on reversible lithium capacity

Charging curves of the prepared carbon anodes are shown in Fig. 8. Not only the reversible lithium capacity enhances but also the charging curves decrease



(a) B210 (b) B221

(c) B222 (d) B223

Figure 7 Scanning electron micrographs of the prepared polymeric carbons based on copolymers of AN with DVB.

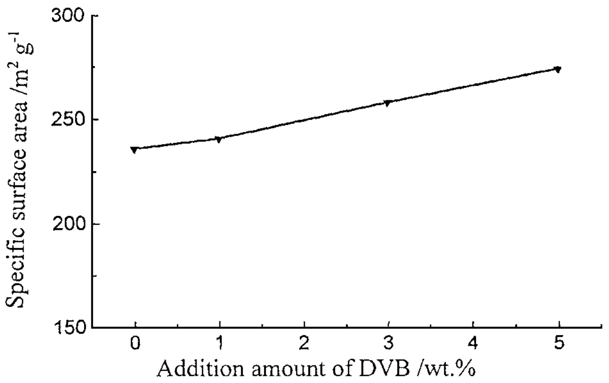


Figure 8 Change of specific surface area with the addition amount of DVB.

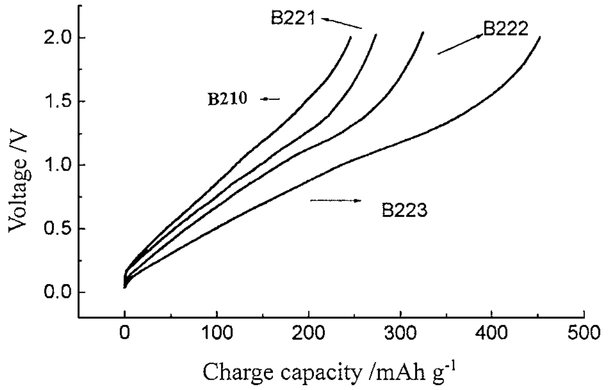


Figure 9 Charging curves of carbon anodes based on copolymers of AN with DVB.

with the addition amount of DVB. The enhanced part of reversible capacity is divided into two parts. One part is below 0.9 V, corresponding to the change of graphite structure [12, 20]. The more the content of graphite structures, the lower the charging voltage and the higher the reversible lithium capacity. The other one is above 0.9 V, which is arisen from the change of micropores. Though the effect of the change of nitrogen content is beyond this range [5], it is very little, and the main is from the micropores from mechanism of lithium storage in micropores [12, 13]. As to why the voltage is higher than 0.9 V, it is resulted from that the carbon structure is disordered. Lithium bonds partly with the imperfect structure in the micropores of carbons and deintercalates through the graphite crystallites. This process is different from graphite, in which the introduction of micropores or nanometer channels [13], can also enhance reversible lithium capacity but not result in voltage hysteresis.

4. Conclusion

The incorporation of crosslinker DVB into nitrogen-containing polymers P(4-VP) and PAN can result in the enhancement of reversible lithium capacity thereof based carbon anode, and the highest can be up to 600 mAh g^{-1}. As to PAN, the crosslinker can not only result in an increase of temperature at which cyclization and crosslinking processes proceed and affect the contents of nitrogen and hydrogen, but also increase the carbonization degree, and favor the formation of graphite structure. In addition, the number of micropores in the prepared carbons is increased. All these factors lead to the enhancement of reversible lithium capacity below and above 0.9 V, corresponding to graphite structure and micropores or disordered carbon structure, respectively, and decrease of charge voltage. It is also true to other addition polymers such as polymethyl acrylonitrile [21]. It indicates that this method is much promising from the viewpoint of application.

Acknowledgement

China Natural Sciences Foundation Committee supplied part funds of this work.

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Received 28 January 1998
and accepted 2 March 1999