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Lithium insertion in carbons prepared from phosphorus-containing polymers

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Abstract

Phosphorus-containing carbon has been prepared by the pyrolysis of phenolic resin containing chemically bonded phosphorus atoms, which is synthesized through the esterification of phenolic hydroxyl group by phosphoric acid. The electrochemical insertion of lithium in as-prepared carbon is also investigated. It is found that, at a pyrolysis temperature of 500°C, the addition of phosphoric acid in the precursor lowers the reversible capacity of the resultant carbon, but at 900°C, the addition of phosphoric acid in the precursor resin increases the reversible capacity of resultant carbon. Especially, the phosphorus-containing carbon prepared by the above method at 900°C gives a capacity beyond the theoretical value of graphite and reasonable discharge/charge curves. The phosphorus-containing carbon prepared by the pyrolysis at 500°C shows a similar electrochemical behavior to that of pure carbon and the effect of phosphorus atoms is little. Its reversible capacity is mainly determined by the content of hydrogen atoms rather than phosphorus atoms. However, at a relatively high pyrolysis temperature, 900°C, more phosphorus atoms are bonded with carbon atoms and are introduced to the microcrystallite structure of carbon. Hence, phosphorus element exerts a strike effect on the electrochemical behavior of carbon and, because of its different electronic effect from carbon element, more lithium species are inserted into carbon matrix. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Carbon materials have attracted much attention as anode for secondary lithium batteries because a carbon anode reduces the formation of lithium dendrites on the surface of the anode and thus higher reliability and safety are obtained [1]. To further refine the technology, improvements of the capacities of carbon materials for lithium accommodation are needed [2]. With this purpose, many efforts have been made in testing carbon materials prepared from various precursors over a wide range of pyrolysis temperature. These include petroleum coke [3], carbon fiber [4–6], and polymeric material [7] heated to temperatures from 400 to 3000°C. As a result, two typical kinds of carbon have been distinguished. One is graphite, the most extensively studied carbon material [8–10]. Graphite can accommodate lithium to a maximum extent of one lithium per six carbons, which corresponds to a specific capacity of 372 mA h/g [11]. The intercalation and de-intercalation of lithium in graphite occurs at a potential range of 0.1 to 0.0 V versus Li/Li⁺ reference. The other interesting type is carbons prepared by

the pyrolysis of organic precursors at temperatures near 700°C [12–19], which possess high contents of hydrogen and specific capacities exceeding the maximum of graphite. This type of carbon exhibits a large hysteresis during discharging and charging process, viz. lithium inserted at near 0 V is removed at about 1 V versus Li/Li⁺.

There has been some other work on the effect of adding heterogeneous elements to carbons, including boron [20–22], phosphorus [23,24], and nitrogen [20,25]. Carbons with an upmost composition of B_{0.17}C_{0.83} were made by Dahn and coworker through chemical vapor deposition at 900°C of benzene and boron chloride, which show substantial increases in specific capacity [22]. Azuma et al. reported a phosphorus-containing carbon with a capacity of 380 mA h/g, a 19% increase relative to the pure carbon with same structure, prepared by the pyrolysis at 1200°C of a mixture of furfural resin with phosphorus pentoxide [23]. Mayer et al. soaked foam-shaped polyacrylonitrile in phosphoric acid solution as the precursor and the specific capacity of resultant carbon increased from 240 to 330 mA h/g [24]. In these studies, two methods were applied to prepare carbons containing heterogeneous atoms. A physical mixing method was taken in the initial work, i.e. to pyrolyze a simple mixture of a carbon precursor with a

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compound of heterogeneous atom. Another method was the chemical vapor deposition, which seemed not to be an economical synthesis method for large-scale producing.

In this paper, we adopt a chemical method to prepare phosphorus-containing carbons, which enables a well distribution of phosphorus element even at a molecular level. Different from the simply physical addition of phosphorous compounds into precursors, here phosphorus element is introduced in phenolic resin through the chemical esterification of hydroxyl group of phenol by phosphorus acid. That is, phenolic resin with chemically bonding phosphorus is first synthesized and then pyrolyzed to prepare phosphorus-containing carbon. The effect of phosphorus on the electrochemical properties of as-prepared carbon is further investigated.

2. Experimental

2.1. Synthesis of phosphorus-containing phenolic resin

35.29 g of phenol and 2.22 g of 20 wt.% sodium hydroxide solution, as a catalyst, were added, in a lump, in an aqueous solution of formaldehyde (>36 wt.%) of 62.56 g. The mixture was heated to 75°C and maintained for 1 h under nitrogen atmosphere. Then 9.13 g of phosphorus acid were added and the mixture was heated at reflux temperature for 0.5 h. The phosphorus-containing phenolic resin was obtained after distillation off the water under reduced pressure [26]. It was further heated in the air atmosphere at 110°C for 2 h to get a cured resin. The final product was named as CPPR.

For comparison, a physical method was also applied to prepare phosphorus-containing phenolic resin. In this physical mixing process, phosphoric acid was not added until the starting of the distillation operation to reduce the possibility of esterification reaction between phenolic hydroxyl group with phosphoric acid. As-prepared resin was named as PPPR.

As a control experiment, phenolic resin without phosphorus was prepared by the same process except the addition of phosphoric acid was omitted. The obtained sample was named as PR.

2.2. Preparation of carbonaceous materials

The resin sample was transferred into an electric oven and pyrolyzed in a flow of inert argon gas. The carbonaceous materials as-produced were then ground into powders with 300 mesh size. In a foregoing study, it has been found that the electrochemical behavior of carbon prepared from phenolic resin changes dramatically by the pyrolysis temperature around 700°C [27]. Hence, to gain a general evaluation of the function of phosphorus element in carbon matrix, the resin samples were pyrolyzed at 500 and 900°C, respectively.

Accordingly, resultant carbons from phosphorus-containing phenolic resin prepared by chemical method, phosphorus-containing phenolic resin by physical method, and pure phenolic resin, were separately named as CPPR500, CPPR900; PPPR500, PPPR900, and PR500, PR900.

2.3. Characterization

Powder X-ray diffraction measurements were made with a Cu K α (Rigaku RINT-2000) source. Data were collected between 10 and 60° with a scan speed of 1°/min and a receiving slit of 0.3 mm. Crystallite sizes of L_c and L_a of the carbon samples were determined, respectively, from the 002 and 10 band Bragg peaks using the Scherrer equation,

$$L_{hkl} = \frac{K\lambda}{\beta \cos \theta}$$

where K is shape factor (its values are 0.9 and 1.84 for L_c and L_a , respectively) [28], λ the X-ray wavelength, β the half-peak width, and θ the Bragg angle. The interlayer spacing was calculated using the Bragg equation

$$d_{002} = \frac{\lambda}{2 \sin \theta}$$

X-ray photoelectron spectroscopy characterization of surfaces has been carried out on a VG Scientific ESCA-LAB2200-XL spectrometer. The X-ray source is a monochromatic Al K α . The experimental data were de-convolved using in-house software to give comparable resolution.

2.4. Assembly and electrochemical measurement of cells

Typical coin-type cells were assembled in an argon-filled glove box with lithium foil as one electrode and with a particular carbon sample as the other. The electrode of the carbonaceous material was made by mixing the carbon powder with 3 wt.% binder of PTFE. The electrode was pressed between two rollers at about 1.0×10^6 Pa pressure and dried at 120°C in vacuum for 24 h. The electrolyte used was a 1 M solution of LiClO₄ dissolved in ethylene carbonate and diethyl carbonate (3:7 v/v). A microporous film wetted with the electrolyte was sandwiched between the carbonaceous electrode and the lithium negative electrode.

Electrochemical testing of the cells was performed using a computer-controlled charging–discharging cyclers at ambient temperature. The current density was set at 0.23 mA/cm² for both charging and discharging process.

3. Results and discussion

3.1. Phosphorus-containing carbon prepared at pyrolysis temperature of 500°C

3.1.1. X-ray powder diffraction analysis

Fig. 1 shows the X-ray diffraction patterns of the carbons prepared by the pyrolysis of precursors at 500°C. The

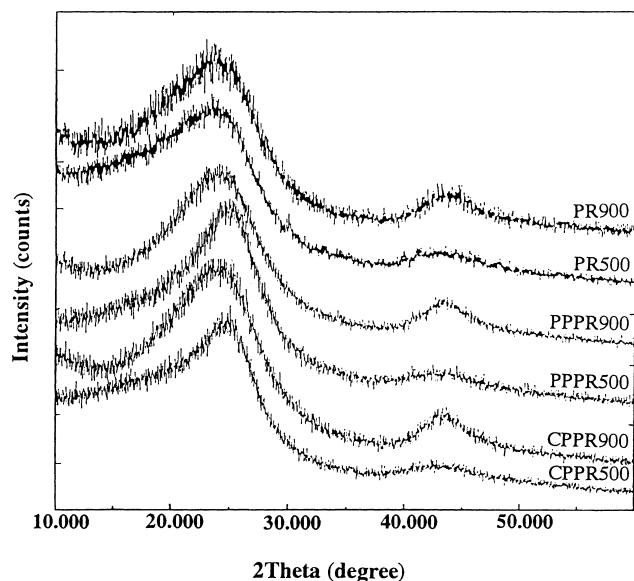


Fig. 1. X-ray diffraction patterns of carbon samples.

patterns of phosphorus-containing carbons are qualitatively similar to that of pure carbon. All samples show patterns consistent with disordered carbon with broad 002 and 100 reflections at 2θ angles of about 24° and 44° , respectively. To check for small differences between the samples with and without phosphorus, we calculate the microcrystallite parameters for all samples. In Table 1, it can be seen that phosphorus-containing carbons show larger microcrystallite size of L_a and L_c , and smaller inter-layer distance of d_{002} than pure carbon obtained from phenolic resin solely. In addition, phosphorus-containing carbon prepared by physical method presents even larger L_a and L_c and even smaller d_{002} with respect to that by chemical method. This result indicates that the addition of phosphoric acid promotes the nucleation and growth of graphene microcrystallite, especially when phosphoric acid is added into the precursor by physical method.

3.1.2. Elemental analysis

The result of elemental analysis of phosphorus-containing carbon obtained by the pyrolysis at 500°C is listed in Table 1. The residue hydrogen content of carbon is considerably affected by the addition of phosphoric acid. The H/C atomic

ratios of phosphorus-containing carbons, both CPPR500 and PPPR500, are lower than that of pure carbon sample of PR500. When phosphoric acid is added by physical method, the resultant carbon gives a lower H/C atomic ratio than does the carbon by chemical method. This result suggests that the presence of phosphoric acid accelerates the loss of hydrogen element in the form of small molecule compounds such as H_2O or CH_4 , which increases the extent of carbonization reaction of phenolic resin precursor. The above phenomenon is consistent with the result reported in the preparation of activated carbon when phosphoric acid is used as activating agent [29].

It can also be seen that the phosphorus content of the carbon obtained by the pyrolysis at 500°C is far lower than the hydrogen content. The phosphorus-containing carbon prepared by chemical method shows a little higher content of phosphorus element than that by physical method.

3.1.3. Electrochemical discharging and charging behavior

When pyrolysis temperature is 500°C , the phosphorus-containing carbon, either by chemical method or by physical method, gives a reversible capacity lower than that of pure carbon, as listed in Table 1. The phosphorus-containing carbon by physical method gives an even low capacity with respect to that by chemical method. Meanwhile, the irreversible capacity of resultant carbon is enlarged by the addition of phosphoric acid, which reduces the Faradaic efficiency during the first cycle to a value less than 50%. This result shows that the addition of phosphoric acid into resin precursor is unfavorable to the reversible capacity of resultant carbon when the pyrolysis temperature is 500°C .

Even so, the reversible capacities of all carbon samples are over the theoretical value of graphite. Further, in Fig. 2, these carbons show discharge and charge profiles different from those of graphite. A voltage hysteresis is evident in all samples, i.e. the lithium inserted at near 0 V is removed at about 1 V versus Li/Li^+ . This result suggests that the same model is followed for lithium insertion in these three carbons. Phosphorus element exerts little effect on the electrochemical characteristics of carbon sample, which might be partly attributed to its low content in carbon matrix.

The capacity of the carbon with large hysteresis has been confirmed to depend on the residue hydrogen content.

Table 1
Characteristics of carbon samples

Sample	Crystal structure			Atomic ratio		Electrochemical property			
	L_a (nm)	L_c (nm)	d_{002} (nm)	H/C	P/C ($\times 10^{-2}$)	C_{1d} (mA h/g)	C_{1c} (mA h/g)	C_{1irrev} (mA h/g)	η_{1F} (%)
PR500	2.34	0.940	0.3743	0.333	–	941	663	278	70
CPPR500	2.72	1.136	0.3599	0.310	0.1074	1150	546	604	47
PPPR500	2.91	1.168	0.3573	0.268	0.1022	1200	482	718	40
PR900	3.67	0.948	0.3802	0.049	–	648	230	418	35
CPPR900	3.68	1.020	0.3694	0.025	0.2145	1125	449	676	40
PPPR900	3.84	1.010	0.3697	0.032	0.2054	1085	352	733	32

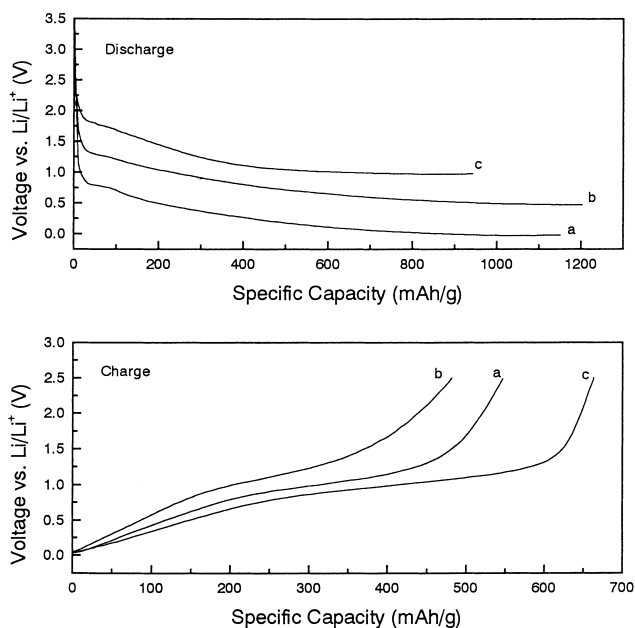


Fig. 2. Discharge and charge curves of carbons prepared by the pyrolysis at a temperature of 500°C: (a) phosphorus-containing carbon by chemical method CPPR500; (b) phosphorus-containing carbon by physical method PPPR500; and (c) pure carbon PR500. The data sets of discharge have been sequentially shifted by 0, 0.5, and 1.0 V for clarity.

Additional capacity has been attributed to the extra lithium insertion in the vicinity of hydrogen atoms located at the edge of stacking graphene layers [18,19,21]. Therefore, as the H/C atomic ratio is reduced by the addition of phosphoric acid in the precursor, especially when phosphoric acid is added by physical method, phosphorus-containing carbons show lower reversible capacities than pure carbon. And the phosphorus-containing carbon by physical method shows the lowest capacity.

3.2. Phosphorus-containing carbon prepared at pyrolysis temperature of 900°C

3.2.1. X-ray powder diffraction analysis

As the pyrolysis temperature increases to 900°C, two major changes to the X-ray pattern are observed in Fig. 1. First, the 002 peak moves a little to the low angle direction, which corresponds to an increased value of d_{002} . A detailed study has been done on carbons prepared at a pyrolysis temperature ranged from 500 to 900°C, but the same trend was observed, as was also reported by Fujimoto and co-workers for heat-treated mesocarbon microbeads [30]. Further work is needed to understand this result. Second, the 100 peak near 44° becomes sharp against the background. This indicates the enlarged size of graphene layers in carbons prepared by the pyrolysis at 900°C, as is clearly shown in Table 1. Also in Table 1, it is noted that the introduce of phosphoric acid, no matter how the acid is introduced, by a chemical method or by a physical method,

accelerates the growth of microcrystallites and shortens the inter-layer distance d_{002} .

3.2.2. Elemental analysis

When pyrolysis temperature is set at 900°C, the residue hydrogen content of carbon is largely reduced. The H/C atomic ratios of these carbon samples listed in Table 1 are no more than 0.05. Moreover, the hydrogen content of phosphorus-containing carbon is close to that of pure carbon.

However, the residue phosphorus content is obviously elevated at pyrolysis temperature 900°C. Compared with that of phosphorus-containing carbon prepared by physical method, a higher percentage of phosphorus is remained in carbon matrix when phosphorus-containing phenolic resin prepared by chemical method is used as a precursor.

3.2.3. Electrochemical discharging and charging behavior

The reversible capacity of carbon samples is reduced with the pyrolysis temperature (see Table 1). In peculiar, pure carbon prepared by the pyrolysis of phenolic resin solely shows the largest loss of capacity, which is mainly attributed to the diminished potential plateau at approximately 1 V versus Li/Li⁺ during the charge process (see Fig. 3). The carbons prepared by the pyrolysis at 900°C show little hysteresis in the discharge/charge process and is appropriate to the practical application, though the capacity is reduced at the same time. Because the voltage hysteresis lowers the output voltage and power of lithium ion batteries if the

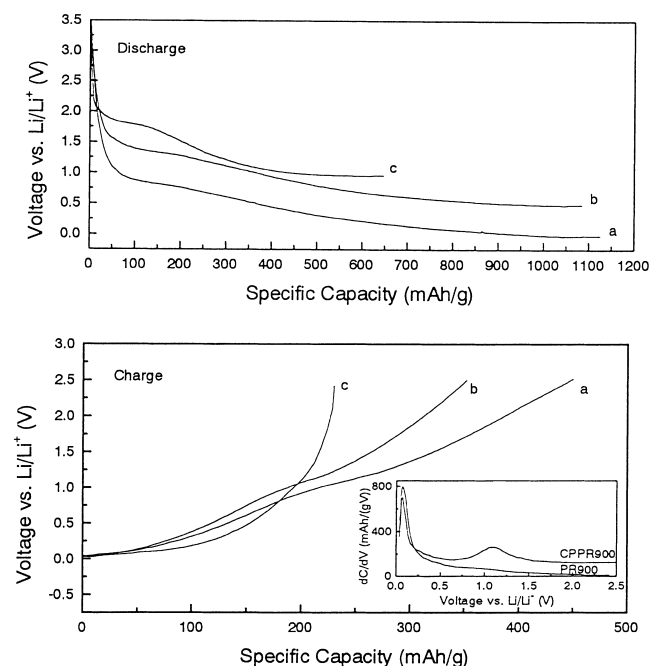


Fig. 3. Discharge and charge curves of carbons prepared by the pyrolysis at a temperature of 900°C: (a) phosphorus-containing carbon by chemical method CPPR900; (b) phosphorus-containing carbon by physical method PPPR900; and (c) pure carbon PR900. The data sets of discharge have been sequentially shifted by 0, 0.5, and 1.0 V for clarity.

carbons prepared by the pyrolysis at 500°C is used as the anode.

Different with the results observed for pyrolyzate at 500°C, phosphorus-containing carbons heated at 900°C, both by chemical method and by physical method, show higher capacities than those of pure carbon. Especially, as listed in Table 1, the carbon by chemical method shows an even higher capacity than that by physical method. This carbon sample by chemical method still holds a capacity higher than the maximum of graphite, yet the capacity values of the other two samples PPPR900 and PR900 are only 352 and 230 mA h/g, respectively. Cyclic discharge/charge analysis in the following 20 cycles shows that the reversible capacity of carbons prepared at 900°C deteriorates little and the Faradaic efficiency is near 100% from the second cycle.

In respect that the direct proportion relationship of the reversible capacity with the H/C atomic ratio of carbon is no longer observed, the high capacity of CPPR900 cannot be assigned to the interaction of lithium with hydrogen atoms located at the edge of stacking graphene layers. The characteristic of discharge and charge curves shown in Fig. 3 is consistent with this judgment. Because, as a control sample, pure carbon pyrolyzed at 900°C shows an electrochemical behavior similar to that of lithium graphite intercalation compound, rather than that of high-capacity carbon with large hysteresis.

It can be found from Table 1 that the phosphorus content changes in the same trend with the reversible capacity of phosphorus-containing carbon. Moreover, as shown in Fig. 3, most of the reversible capacity of phosphorus-containing

carbon by chemical method is found at relatively higher voltage range than 0.5 V. The inset in Fig. 3 shows the differential capacities, dC/dV , versus voltage for the carbon samples of CPPR900 and PR900. The derivative profile of pure carbon, PR900, shows only one peak in the voltage region lower than 0.1 V, the area of which corresponds to the amount of lithium intercalated between adjacent graphene layers. Nevertheless, in the derivative profile of CPPR900, there appears another peak near 1.1 V. This indicates that another model for lithium insertion in phosphorus-containing carbon prepared by the pyrolysis at 900°C is needed to understand its high capacity over the maximum of graphite. On the basis of the above arguments, it appears clear that this high capacity might and could only be related with the presence of phosphorus atoms in the carbon matrix.

3.3. XPS analysis of phosphorus-containing carbons

Dahn and coworkers found that nitrogen or boron can be substitutionally incorporated in the carbon crystal lattice in the heteroatom-containing carbons prepared by chemical vapor deposition method [22,25]. A shift of the reversible capacity to low or high voltage was reported for nitrogen- or boron-containing carbon, respectively. This was attributed to the different electronic effects of nitrogen and boron, the former acts as an electron donor and the latter as an electron acceptor. However, in the case of our samples, a rough analysis of the open circuit voltage for the carbon samples with or without phosphorus shows no obvious difference. The cause may lie in the difficulties for phosphorus atoms to break all the P–O bonds and be incorporated substitutionally

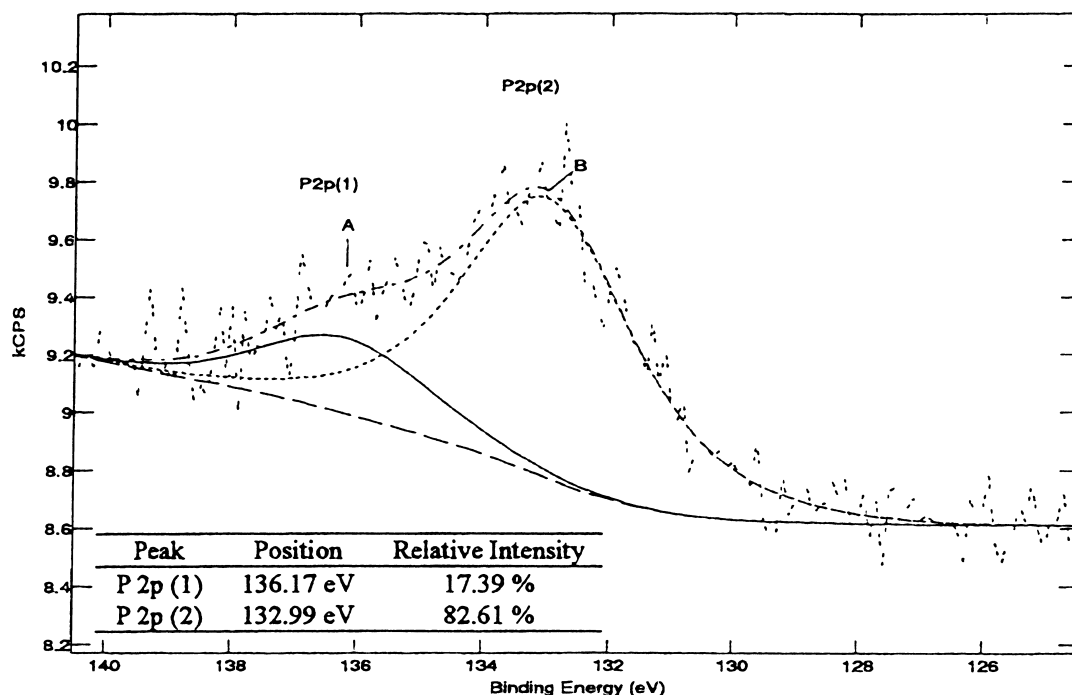


Fig. 4. X-ray photoelectron spectrum of CPPR500, phosphorus-containing carbon by chemical method prepared by the pyrolysis at 500°C.

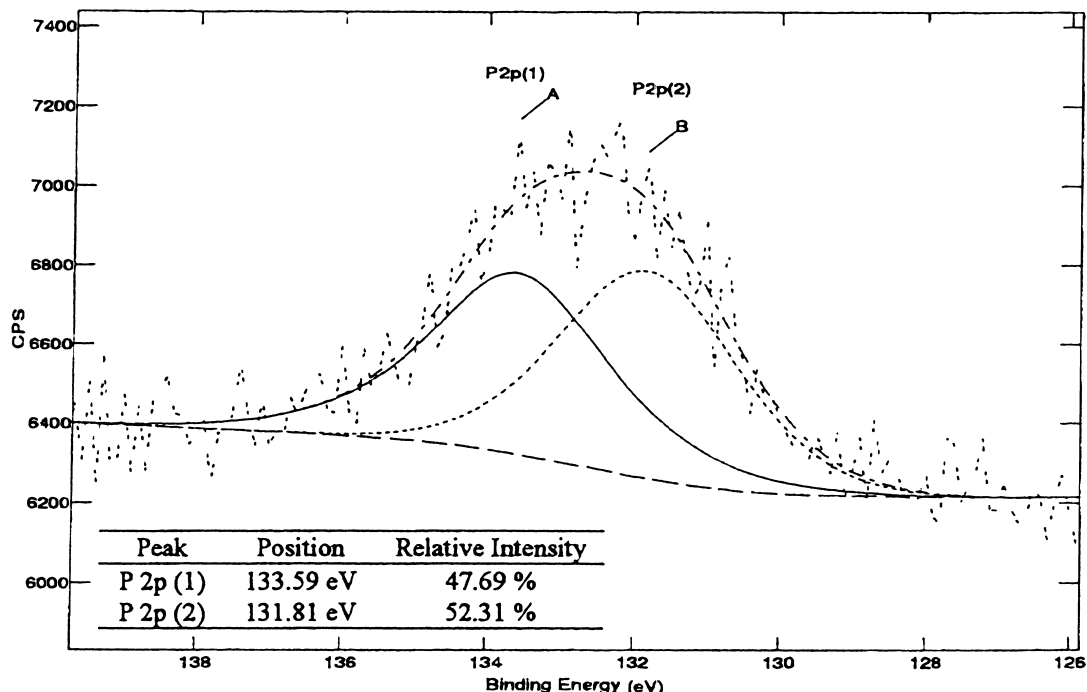


Fig. 5. X-ray photoelectron spectrum of CPPR900, phosphorus-containing carbon by chemical method prepared by the pyrolysis at 900°C.

into the carbon lattice in our samples. The structure of phosphorus-containing carbons prepared by the pyrolysis of polymeric precursors is rather complicated than that prepared by chemical vapor deposition. Its structure is far from that of ideal graphite and there are disorganized regions besides the crystallized fields. Nevertheless, it is still possible for phosphorus atoms to be introduced into the vicinity of crystal surface and to affect the electrochemical properties to some extent. To further understand the role of phosphorus atoms, X-ray photoelectron spectroscopy is used to investigate the chemical state of phosphorus in carbon matrix.

Figs. 4 and 5 show separately the P_{2p} XPS spectra of CPPR resin pyrolyzed at 500 and 900°C, together with the simulation result by computer. The CPPR500 sample shows two P_{2p} binding energy peaks at 136.17 and 132.99 eV, whilst the CPPR900 sample shows two P_{2p} binding energy peaks at 133.59 and 131.81 eV. It is noticed that, as a whole, the binding energy of P_{2p} of CPPR500 prepared by the pyrolysis at 500°C is higher than that of CPPR900 prepared at 900°C.

The binding peak at 136.17 eV is assigned to the tetra-coordinated phosphorus atoms with oxygen atoms. P_{2p} peaks with lower binding energies are attributed to the partial substitution of oxygen atoms by carbon atoms to different extent [31]. The above result shows that, during the heat treatment process, part of P–O bonds are disassociated and some P–C bonds are formed, which shifts the P_{2p} binding energy to low value direction. A higher pyrolysis temperature benefits the breaking of P–O bonds and the

forming of P–C bonds and so results in the even low P_{2p} binding energy.

According to the result of XPS analysis, we suggest that phosphorus atoms exist mainly at the state of P–O bond in the disorganized region of carbon matrix heat-treated at 500°C and exert little effect on the electrochemical behavior of carbon. The capacity of carbon is still determined by the content of residual hydrogen, i.e. by the interaction of lithium with hydrogen atoms located at the edge area of graphene layers. However, at the pyrolysis temperature of 900°C, more phosphorus atoms are bonded with carbon atoms and are introduced to the microcrystallite structure. Therefore, phosphorus element exerts a considerable effect on the electrochemical behavior of carbon and, because of its different electronic effect from carbon element, more lithium species are inserted into carbon matrix.

4. Conclusions

We have prepared a phosphorus-containing carbon by a chemical method. In this method, phenolic resin containing chemically bonded phosphorus atoms is synthesized through the esterification of phenolic hydroxyl group by phosphoric acid. Then it is pyrolyzed at 500 and 900°C, respectively, to prepare the phosphorus-containing carbon.

At pyrolysis temperature of 500°C, the addition of phosphoric acid in the precursor lowers the hydrogen content and the reversible capacity of as-prepared carbon. The phosphorus-containing carbon shows the similar electrochemical

behavior to that of pure carbon and the effect of phosphorus atoms is little. The reversible capacity is mainly determined by the interaction of lithium with hydrogen atoms located at the edge area of graphene layers.

However, when pyrolysis temperature is elevated to 900°C, the addition of phosphoric acid in the precursor resin is favorable to a high reversible capacity of resultant carbon. With respect to a physical method of simply mixing precursor with phosphoric acid, chemical method is able to more effectively increase the capacity of resultant carbon. The phosphorus-containing carbon prepared by chemical method shows a capacity beyond the maximum of graphite and reasonable discharge/charge curves, which appears to be a promising candidate for the anode material for lithium-ion batteries.

The result of XPS analysis shows that, at relative high pyrolysis temperature, more phosphorus atoms are bonded with carbon atoms and be introduced to the microcrystallite structure and hence exert a strike effect on the electrochemical behavior of resultant carbon. Because of the different electronic effect of phosphorus element from carbon element, more lithium species are inserted into carbon matrix containing phosphorus element.

We do not clearly understand the interaction between lithium and phosphorus atoms during the cycling discharge and charge process. Fundamental studies are needed to elucidate the role of phosphorus atoms in the carbon matrix.

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