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Short communication

Effects of doped sulfur on electrochemical performance of carbon anode

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Abstract

An amorphous carbon doped with sulfur to be used as anode material for lithium ion batteries is prepared by heat-treatment of a mixture of polyacrylonitrile (PAN) and sulfuric acid. With X-ray photoelectron spectroscopy (XPS), elemental analysis, X-ray powder diffraction (XRD), scanning electron microscopy, and electrochemical capacity measurements effects of sulfur on properties of the carbon anode are investigated. The added sulfur favorably increases the charge capacity in close correlation with an increase of the size of graphite crystallites, L_c, the interlayer distance, $d_{0\,0\,2}$, and the number of micropores, and the doping of sulfur in the state of C–S–C. On the other hand, it also causes detrimental changes, for example the formation of amine-group nitrogen, sulfate/sulfonate deposits, and macropores. Nevertheless, as a result, both reversible and irreversible capacities are enhanced. This clearly shows, that added heteroatoms may have opposite influences, good and bad, on electrochemical performance of carbonaceous anode materials. Approaches towards suppressing the unfavorable ones in the application in lithium ion batteries are discussed. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Lithium ion batteries; Carbon anode; Sulfur; Doping

1. Introduction

Since the birth of lithium ion batteries in the early 1990s, many kinds of anode materials have been studied. A promising one is amorphous carbon since it can be prepared at low temperature (<1000 °C) and its reversible lithium capacity is higher than the theoretical value of graphite [1]. It was regarded as an ideal substitute for graphitic carbon [2]. Later on, effects of some kinds of dopant heteroatoms such as boron [3], silicon [4–7], nitrogen [8–11], phosphorous [12–14] and transition elements [15–17] have been studied, and much progress has been achieved. Most impressive is the effect of nitrogen. It was first reported, that doping of amorphous carbon with nitrogen by chemical vapor deposition did not result in improved electro-chemical properties of amorphous carbon because of the formation of so-called chemical nitrogen, which later on reacted with lithium and resulted in large irreversible capacity [8]. In contrast, however, another research group found that the existence of nitrogen was favorable for electrochemical performance of amorphous carbon prepared by the same chemical vapor deposition method [9]. Based on a pseudo model of carbon other researchers could not deduce definitely whether the incorporation of nitrogen was favorable for the electrochemical performance [18]. Recently, we found that both observations and considerations could be correct because of the existence of different states of nitrogen [11]. There are three states of nitrogen: graphene nitrogen, conjugated nitrogen and amine nitrogen. Their N_{1s} XPS binding energy peaks are around 398.5, 400.2 and >403 eV, respectively [11]. If the doped nitrogen atoms exist only in the state of graphene nitrogen, due to its higher electronegativity[1] (3.04) compared with C (2.55), they will enable more electrons to be introduced into the layers of graphite, i.e. more lithium to be intercalated. Conjugated nitrogen contributes perhaps not much to the reversible capacity. These states of nitrogen are both not detrimental to the electrochemical performance of the amorphous carbon. However, if nitrogen exists in the state of amine nitrogen, it will in fact react chemically with lithium resulting in a large irreversible capacity. By additional heat-treatment amine nitrogen can be removed and/or translated into conjugated nitrogen. Most likely this heat-treatment, which was employed only in one investigation [9], might

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[1] Values calculated according to Pauling.

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explain the seeming contradiction of the observed results. As a result, amorphous carbons doped with nitrogen have been widely investigated as anode materials [19]. More recently, graphite coated with C_xN has shown also a good electrochemical performance, which illustrates, that nitrogen is basically good for an increased reversible lithium capacity [20].

In the case of sulfur, it was reported that it was also favorable for lithium intercalation [21,22]. However, if it does not exist in the form of –C–S–C–, results might be different. Here, we report about another way to prepare sulfur-doped carbon by heat-treating a mixture of polyacrylonitrile (PAN) and sulfuric acid. Particular attention is paid to the effects of sulfur.

2. Experimental

A 30 ml sample of acrylonitrile monomer, purified by distillation, was put into a 3-neck flask with 120 ml dimethyl formamide under flowing nitrogen gas. After adding 0.3 wt.% initiator azo-*bis*-isobutyronitrile, the polymerization was conducted at 60 °C for 8 h. under stirring. The solution was then cast into a plate and dried under vacuum. The resulting thin film of PAN was put into a tube furnace and heat-treated at 600 °C under an argon atmosphere to prepare an amorphous carbon. The obtained carbon product was powdered through a 320-mesh sieve (marked A).

Sulfuric acid 20 wt.% was mixed thoroughly with the powdered PAN in a ball mill. The mixture was pyrolyzed in the way described above to prepare an amorphous carbon doped with sulfur atoms (marked AS).

Elemental analysis was performed with the Heraeus CHN-rapid method. X-ray powder diffraction (XRD) patterns were collected on a D/MAX-3B instrument. Scanning electron micrographs (SEM) were obtained with a Hitachi S530 microscope. Prior to SEM measurements, carbon samples were coated with a thin film of gold to suppress charging effects. XPS was performed on an ES300 instrument (Kratos) with Mg Kα radiation.

By pressing the mixture of the carbonaceous materials A or AS with 5 wt.% PVDF as a binder into a thin film, pellets with a diameter of ca. 1 cm used as the working electrodes were manufactured; their weight was precisely determined (about 10 mg). Before transfer into a glove box filled with argon gas free of water and oxygen, the pellets were dried overnight at 120 °C under vacuum. Button-type model cells were constructed with these electrode pellets, using an in-house made porous polypropylene film as the separator and lithium foil as both the counter and reference electrode. The electrolyte used was a 1 M solution of $LiClO_4$ dissolved in a mixture of EC and DEC (3/7, v/v). The cells were galvanostatically discharged and charged in the voltage range −0.03 to 2.0 V versus Li^+/Li using a computer-controlled constant current cycler, and the current was 0.2 mA.

3. Results and discussion

An X-ray photoelectron spectrum of S_{2p} in the prepared carbon AS is shown in Fig. 1. The peak assigned to sulfur actually consists of two peaks located at 164.2 and 168.4 eV. The two peaks suggest that sulfur exists in two forms. One is in the state of –C–S–C–, the other one is in the state of sulfate (–C–SO_4–C–) or sulfonate (–C–SO_3–C–) [23]. After the described treatment including a heat-treatment at 100 °C for some time the sulfuric acid was dispersed homogeneously in the bulk structure of the carbonaceous material. Therefore, sulfur does not only exist at the surface of the prepared carbon, but also in the bulk as a dopant.

Elemental analysis results of carbons doped with sulfur (AS) and without (A) sulfur are given in Table 1. The data show that the content of nitrogen increases from 0.195 to 0.209, and that of hydrogen decreases sharply from 0.362 to 0.166, and that of sulfur kept in the carbon is 0.0021, less than one-tenth of the amount added before the heat-treatment. It shows, that this method can incorporate sulfur into the amorphous carbon though it is not very effective to incorporate a large amount of sulfur.

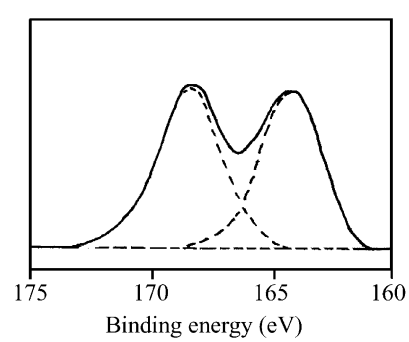

Fig. 1. X-ray photoelectron spectra of S_{2p} in the prepared disordered carbon doped with sulfur.

Table 1
Results of elemental analysis, XRD and XPS of disordered carbons doped with (AS) and without (A) sulfur

Sample	Temperature (°C)	Amount of added H_2SO_4 (wt.%)	Atomic ratio of N/C	Atomic ratio of H/C	Atomic ratio of S/C	d_{002} (Å)	L_c (Å)	Relative content of graphene nitrogen (%)	Relative content of conjugated nitrogen (%)
A	600	0.0	0.195	0.362	0.0	3.520	11.41	53.6	46.4
AS	600	20.0	0.209	0.166	0.0021	3.553	12.90	49.8	46.2

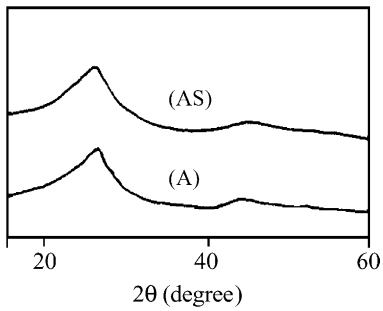

Fig. 2. X-ray powder diffraction pattern of the prepared disordered carbons with (AS) and without sulfur (A).

During the heat-treatment, PAN initially forms cyclical structures, then the cross-linking starts. After the following dehydrogenation, the cross-linked structure turned into a carbon structure [24]. Since the acid accelerated the cyclization process [25], more –CN groups were incorporated into the "cyclic" form, thus, slightly more nitrogen atoms were kept in the carbon structure. The sharp decrease in the content of hydrogen is presumably due to the fact, that "cyclic" PAN is dehydrogenated more easily and is carbonized faster.

X-ray diffractograms of the prepared carbons with (AS) and without (A) sulfur are shown in Fig. 2. Only the diffraction peak around 25° corresponding to 0 0 2 planes can be identified easily. The crystal size L_c was estimated using the Scherrer equation $L_c = A\lambda/(B\cos\theta)$ where A is the shape factor (for amorphous carbon 0.90); λ the X-ray wavelength; θ the Bragg angle; and B is the full width at half maximum of the peak in radians. The estimated data are summarized in Table 1. Around 42.5° there are very weak diffraction peaks corresponding to 0 0 4 planes and/or 1 0 0 planes. Since the heat-treatment temperature of 600 °C was low, the prepared carbons are amorphous, and consist of graphite crystallites and disordered areas, which is consistent with all previously reported results [1–11]. The interlayer distance $d_{0\,0\,2}$ increases a little after the addition of H_2SO_4 from 3.520 to 3.553 Å. The 0 0 2 peak becomes slightly narrower and the size of graphite crystallite L_c increases somewhat from 11.41 to 12.90 Å after the introduction of sulfur. Since the added H_2SO_4 may accelerate the cyclization of PAN, the carbonization process was also accelerated, which is consistent with the results of the elemental analysis, viz. the decrease in the content of hydrogen. Usually an increase in the carbonization degree will accompany a decrease in $d_{0\,0\,2}$. In the present case, sulfur is incorporated in the form of sulfur and sulfate/sulfonate. The diameter of a sulfur atom (2.04 Å) is larger than that of a carbon atom (1.54 Å), let alone that of sulfate/sulfonate groups, which is even much larger. Consequently, the interlayer distance $d_{0\,0\,2}$ increases a little after the introduction of sulfur.

X-ray photoelectron binding energy spectra of nitrogen N_{1s} in carbons added with (AS) and without (A) sulfur are given in Fig. 3. Nitrogen in carbon A without added sulfuric acid exists in two states [11], viz. graphene nitrogen and conjugated nitrogen, with peaks at 398.2 and 400.1 eV, respectively. In the sulfur-containing carbon AS nitrogen exists in three states, viz. graphene nitrogen, conjugated nitrogen and amine-group nitrogen [23]. The latter one which is also called chemical nitrogen [8,11], corresponds to a binding energy peak at 406.2 eV. In contrast to phosphoric acid [14] the acidity of H_2SO_4 is stronger. This results in a higher degree of protonation of the nitrogen atom, thus amine-group nitrogen was left in the amorphous carbon and its relative content is 4.0%. As listed in Table 1 the relative content of conjugated nitrogen in carbon doped with sulfur decreases from 53.6 to 49.8%, and that of graphene nitrogen was changed not much staying at about 46%. The absolute content of graphene nitrogen is almost the same, 0.105 and 0.104 (atomic ratio of N/C).

SEM of carbons A and AS are presented in Fig. 4. These micrographs show that the number of pores increases greatly after the addition of H_2SO_4, and some of them are not micropores/nanopores, they may be called more approximately macropores, larger than 100 nm. These structural changes must have been caused by the added H_2SO_4. From the results of the elemental analysis, less than one tenth of the added sulfur was left in the carbon. This means that most of the added H_2SO_4 was used up in pore formation during the heat-treatment, and could not act as a setting agent to cause the graphene molecules to arrange more ordered like phosphoric acid [14]. Of course, the number of pores is larger than that in carbon from the addition of H_3PO_4 from the comparison of the SEM micrographs [14].

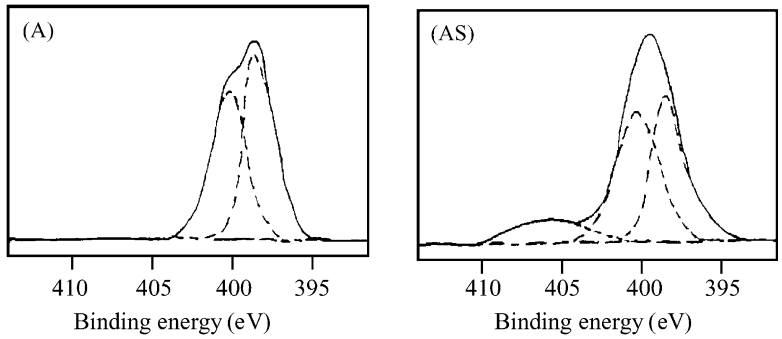

Fig. 3. X-ray photoelectron spectra of N_{1s} in the prepared disordered carbons with (AS) and without sulfur (A).

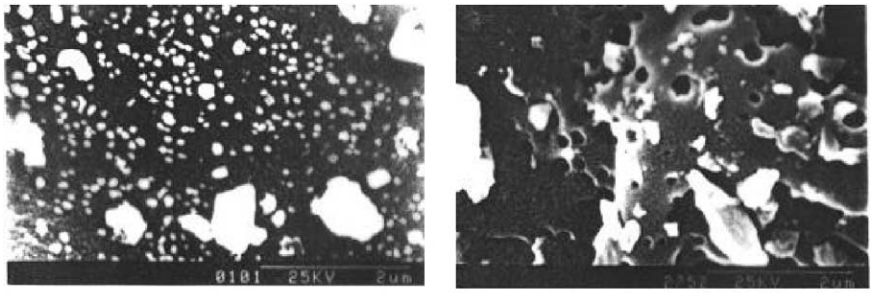

Fig. 4. Scanning electron micrographs of the prepared disordered carbons with (AS) and without (A) sulfur.

The discharge and charge profiles in the first cycle are shown in Fig. 5a and b. The discharge and charge capacity is larger after the addition of sulfur. It increases from 440 to 647 mAh/g and from 251 to 380 mAh/g, respectively. The coulombic efficiency in the first cycle is almost the same, 57.3 and 58.7% for A and AS, which is typical for a lot of amorphous carbons. From the discharge curve of AS, it can be seen that the discharge voltages decreases slowly below 0.8 V. There is no evident discharge plateau as observed with graphite. In the case of A, its discharge curve above 0.5 V, corresponding completely to irreversible capacity such as formation of a passivating film, is shorter than that of AS, and it indicates that the irreversible capacity is higher after the introduction of sulfur.

As mentioned above, the content of nitrogen increases slightly, but the absolute content of graphene nitrogen does not increase. This will not result in an increase of charge capacity. Only one form of the incorporated sulfur, –C–S–C–, will contribute to an increased charge capacity [21,22]. In addition, the slight increase in d_{002} and L_c will favor lithium intercalation into graphite crystallites [12,13]. Furthermore, perhaps the most important, the number of micropores increases, which are well known to act as matrixes for lithium storage [26–28]. Finally, these factors cause a considerable increase in charge capacity beyond the theoretic level of graphite.

With respect to the effect of hydrogen on charge capacity we have shown, that it did not cause any significant effect with this kind of amorphous carbon [11]. From the elemental analysis results we know, that the content of hydrogen is much larger in the carbon prior to incorporation of sulfur, but its discharge and charge capacity is much smaller.

After incorporation of sulfur the enhancement in irreversible capacity can be ascribed to the following factors. The added H_2SO_4 causes the formation of amine-group nitrogen, which subsequently reacts irreversibly with lithium [8,11]. In addition, one form of sulfur (sulfate/sulfonate) can also irreversibly react with lithium. Finally, additional macropores are formed by the treatment with H_2SO_4. As a result, the surface area increases. In order to form the required additional passivating film, more electrolyte molecules will be consumed. Further imperfections on the surface will also irreversibly absorb lithium [29].

In fact, the reversible capacity of the amorphous carbon prepared from pure PAN can be above the theoretical value of graphite when the heat-treatment conditions are adjusted properly [17]. If more sulfur is incorporated and the experimental conditions are optimized, the properties of the disordered carbon will improve even more. As to the specific actions of different states of sulfur such as –C–S–C– and sulfate/sulfonate, further investigations are required. Results obtained so far definitely indicate, that incorporation of sulfur leads to an improvement of the electrochemical properties of the carbon.

With respect to the cycling behavior, the fading in the reversible capacity is not yet satisfactory, although it is observed with most other amorphous carbons. The main reason is the existence of a lot of imperfections [28,30]. In

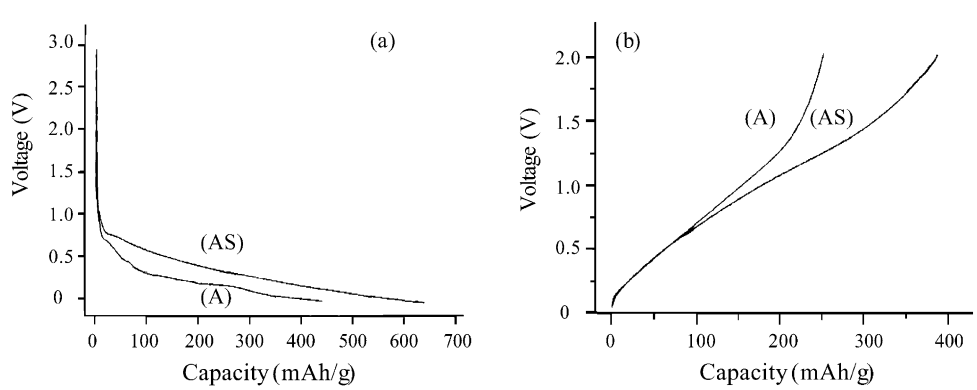

Fig. 5. Discharge profiles (a) and charge profiles (b) of carbon anodes with (AS) and without sulfur (A).

the case of graphite, there are still some active imperfect structures. Recently it was found, that the cycling behavior and the coulombic efficiency in the first cycle of graphite was improved considerably after an oxidative treatment removing these imperfections [31]. This suggests a promising method to improve its electrochemical performance, which is currently under further investigation.

4. Conclusion

Addition of H_2SO_4 can favor the cyclization process of PAN during the heat-treatment to prepare amorphous carbon. The incorporated sulfur exists in two forms: –C–S–C– and sulfate/sulfonate. This addition results in an increase in the content of nitrogen, the size of graphite crystallite, L_c, the interlayer distance, $d_{0\,0\,2}$, and the number of micropores. This addition also results in the formation of amine-group nitrogen and macropores above the nanometer level. Consequently, the incorporation of sulfur leads to an enhancement of discharge and charge capacity at the same time.

Our results as well as those of other groups suggest, that the existence of heteroatoms in amorphous carbon can serve to improve its electrochemical properties as anode [3–15,21,22]. Unfortunately, the incorporated heteroatoms will produce some unfavorable side effects when they exist in unfavorable states. When the advantageous factors are exploited and the unfavorable factors are averted as good possible the incorporation of heteroatoms may result in a great advance to the improvement of the electrochemical performance of carbon anodes.

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