Composite materials of silver and natural graphite as anode with low sensibility to humidity

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Abstract

Sensitivity of anode materials to humidity is an important factor for the performance of lithium ion batteries. Here it is demonstrated for the first time that the sensitivity of composite anode materials of silver and natural graphite can be strikingly lowered. The composites are prepared by depositing silver ions onto the surface of natural graphite. After the following heat-treatment, silver ions turn into metallic silver and carbide Ag_xC by covering and/or removing active sites that absorb water very easily. Under high humidity condition (about 1000 ppm H_2O), the composite materials absorb strikingly less water resulting in still good electrochemical performance. In comparison, natural graphite without this treatment shows fast fade in capacity under high humidity even though it is good in cycling under low humidity (<100 ppm H_2O). Silver is a good matrix for lithium storage, and is assumed to contribute to reversible capacity since it enhances with the amount of deposited silver. This method can effectively lower the sensitivity of anode materials to humidity, and is promising in manufacturing lithium ion batteries under less critical conditions.

1. Introduction

The development of anode materials is of great importance in the history of lithium ion batteries, which finally entered the market after technological breakthroughs in the early 1990s. So far, a lot of anode materials have been studied, and a considerable amount of this research has been devoted to the development of anode materials with a large reversible lithium capacity [1,2]. To our knowledge, few studies have been focused on the environmental conditions for manufacturing lithium ion batteries such as the composition of atmosphere, in particular the water content, despite their importance on the performance of batteries.

The surface structure of graphite is usually different from the bulk structure and includes a lot of features such as edge planes, basal planes, surface functional groups and defects [1–3]. Recent research on anode materials indicates that the surface structure is also of great importance for the electrochemical performance [3–10]. For example, slight oxidation of graphite will lead to the formation of an efficient passivating film, and prevent the movement of graphene layers in the *a*-axis direction. Consequently, the cycling performance of the oxidized graphite is considerably improved.

Recently, we introduced copper on the surface of natural graphite and found that the surface structure is also an important factor affecting the sensitivity of anode materials to humidity [11]. After deposition of e.g. 3.8 and 10.2 wt.% copper at the surface of graphite, the deposited copper covers and/or removes some active sites on the surface of natural graphite, which absorbs water relatively easily, and the cycling behavior in the presence of high humidity (about 1000 ppm H_2O) is much improved. However, copper could undergo oxidation to form copper oxides if it is kept under ambient condition for a long time. This is a practical problem for storage. In this paper we report on the introduction of silver, which is not oxidized as easily as copper under ambient atmosphere, onto the surface of natural graphite to prepare composites. Preliminary results show that their sensitivity towards humidity is strikingly lower. Under high humidity conditions the electrochemical performance of the composite is still very good.

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2. Experimental

Composite materials were prepared by the following procedure. One gram samples of common natural graphite designated as LS17, which was standardized by mild oxidation treatment [12] of a virginal natural graphite sample from Beishu Graphite Plant, China with d_{002} 3.351 Å, L_c 120 Å and average particle size 17 μm, were immersed overnight in 10 ml of 0.3 and 0.8 mol/l $AgNO_3$ aqueous solutions at room temperature, respectively. The mixtures were dried at 60 °C under stirring. It is well known that $AgNO_3$ decomposes very easily into silver. In order to ensure silver to combine strongly with the graphite structure, the dried mixtures were heated in a tube furnace at 600 °C under flowing argon atmosphere for 4 h. The prepared products were named B1 and B2, respectively.

X-ray photoelectron spectra (XPS) were performed with an ES-300 spectrometer (KRATOS, Japan), and the relative contents of each species at the surface of the natural graphite were calculated on the integrals of their X-ray photoelectron intensities. Thermogravimetry and differential thermal analysis (TG-DTA) was performed on an instrument of PCT-1 (Beijing Analytical Instruments Co., China) under air at the heating rate of 20 °C/min. Prior to the measurement of high resolution electron microscopy (HREM) on a JEM-200CX (JEOL, Japan) under vacuum, samples were uniformly dispersed on micro-nets with cavities of micron size.

Capacity was tested by a model cell that used lithium foils as the counter and the reference electrode, 1 mol/l $LiClO_4$ solution in the mixture of EC:DEC 3:7 (v/v) as the electrolyte and a homemade porous polypropylene film as separator. The anode was prepared by pressing the mixture of natural graphite and 5 wt.% polyvinylidene fluoride dissolved in N,N'-dimethyl formamide (DMF) as a binder into pellets with a diameter of ca. 1 cm. The pellets were precisely weighted, averaged about 10 mg. After drying under vacuum at 120 °C overnight, they were stored for 1 h into an argon filled box with the humidity controlled to be about 1000 ppm, then set up into model cells. Electrochemical performance was tested with a CT2001A cell test instrument (Wuhan LAND Electronic Co. Ltd., China), discharge (intercalation process) and charge (de-intercalation process) voltage ranged from 0.0 to 2.0 V versus Li^+/Li, and the electric current was constant, 0.2 mA.

3. Results and discussion

X-ray photoelectron spectrum of Ag 3d (s = 5/2) of the composite B1 (natural graphite LS17 with 3.2 wt.% silver) is shown in Fig. 1, and selected results are summarized in Table 1. Silver exists in two states: metallic silver and carbide Ag_xC, which correspond to binding energy peaks at 368.6 eV (I) and 367.5 eV (II), respectively [13] (see deconvoluted curves in Fig. 1). Their relative atomic contents are 63.46 and 36.54%. This indicates that silver nitrate decomposed completely into silver by the heat-treatment, and some part of silver reacted with the carbon atoms of natural graphite to form Ag_xC.

XPS of C 1s of the natural graphite LS17 and the prepared composite B1 are shown in Fig. 2, again selected results are summarized in Table 1. It is known that various carbon species exist at the surface of graphite and result in a complicated surface chemistry. Through deconvolution four species are identified: carbonylic carbon like e.g. in acetone/quinone, carboxylic carbon like in –COOR (R = H and/or alkyl), etheric carbon and carbon atoms in graphene planes, which correspond to peaks of binding energy at 288.9, 287.2, 286.0 and 284.4 eV, respectively [14,15]. The comparison between LS17 and B1 shows that the content of carbon atoms with a binding energy peak of around 286.0 eV increased from 9.02 to 11.85% and those of the others decreased. By the way, the peak shifted to a higher binding energy position after the deposition of silver. The increase and the shift clearly indicate a production of a new carbon species. From the above description, it is evidently Ag_xC, whose binding energy peak of C 1s is also around 286.0 eV, and this is consistent with the above result that Ag_xC was formed from the reaction of silver with carbon.

TG-DTA curves of natural graphite LS17 and the prepared composites B1 and B2 under air at heating rate 20 °C/min are shown in Fig. 3. Initially, the weight decreased slowly because of a thermal decomposition of some oxides on the surface and a slight oxidation especially of active sites. Subsequently, when the temperature arrived at above 500 °C, significant oxidation began, as indicated by substantial weight losses. The simultaneous rise of the DTA curves implies an exothermic reaction. When the rate of the combustion reaction peaked, the DTA curves passed through a maximum. Compared with natural graphite LS17, the exothermal peaks of the composites shifted very sharply

Table 1
Selected results of natural graphite LS17 and the prepared composites B1 and B2 from XPS measurement

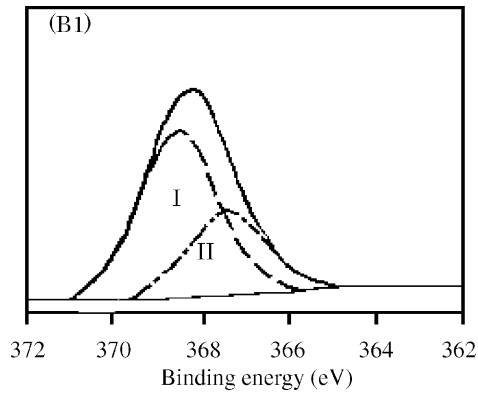| Sample	Content of Ag (wt.%)	Atomic ratio of silver species at different position of binding energy peaks (%)		Atomic ratio of carbon species at different position of binding energy peaks (%)			
		367.5 eV	368.6 eV	288.9 eV	287.2 eV	286.0 eV	284.4 eV
LS17	0.0	–	–	4.38	6.10	9.02	80.50
B1	3.2	36.54	63.46	3.25	5.15	11.85	79.75
B2	8.6	–	–	–	–	–	–

Fig. 1. XPS spectrum of Ag 3d (s = 5/2) of the prepared composite B1.

towards lower temperatures, from 752 to 695 and 686 °C, respectively. It is well known that metals or metal oxides such as Cu, Co and Ni deposited on the surface of graphite can act as catalysts to favor the thermal oxidation under air [5,16,17], as a result, exothermal peaks shift towards lower temperatures.

In order to observe the distribution of the deposited silver on the surfaces of the composites B1 and B2, scanning electron micrographs were at first obtained. No evidence of large clusters of silver at the surface of natural graphite was obtained because the resolution was not high enough (the largest magnification was only 10,000:1). Of course, this does not prove that silver was deposited homogeneously on
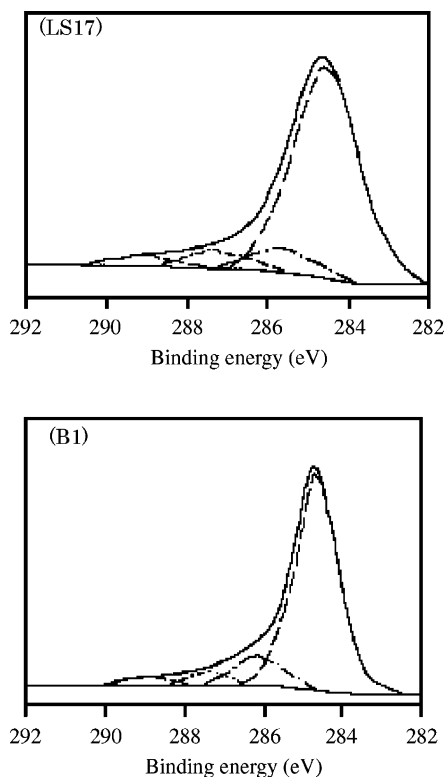

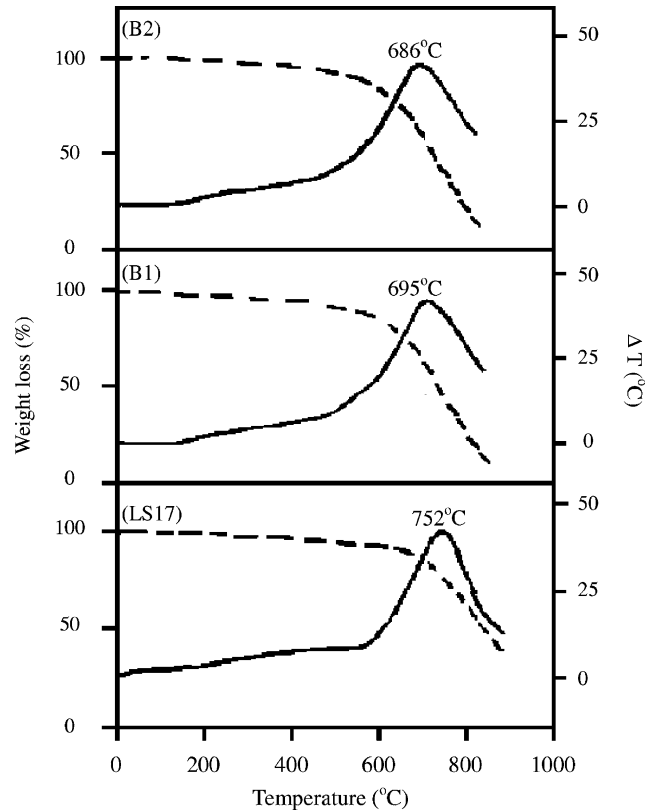Fig. 2. XPS spectra of C 1s of natural graphite LS17 and the prepared composite B1.

Fig. 3. TG-DTA curves of natural graphite LS17 and the prepared composites B1 and B2 under air with heating rate 20 °C/min (dashed lines: TG curves; solid lines: DTA curves).

the surface of graphite. HREM was additionally employed. The obtained micrographs are shown in Fig. 4. They indicate that silver exists in nano-meter clusters or particles and the size distribution of these clusters is not very uniform. At the surface of natural graphite there are some active sites adsorbing water easily. They adsorbed preferentially silver ions in the solutions, consequently, silver ions were concentrated at these sites. During the heat-treatment, the concentrated silver ions turned into metallic silver and part of the formed silver reacted with carbon atoms at these active sites to produce Ag_xC. As a result, silver clusters on the nano-meter scale could be observed in micrographs. The identification of their exact location requires further studies, but we suggest that they can exist on basal planes and edge ones. Of course, most of them will deposit on edge planes since they are more active than the basal planes [3], and there are also active sites at the basal planes though it is much less than those at the edge planes [18].

Discharge (lithium intercalation) and charge (lithium de-intercalation) profiles in the first cycle and discharge profiles in the second cycle of natural graphite LS17 and the composite materials B1 and B2 manufactured into cells in the presence of high humidity (about 1000 ppm H_2O) are given in Fig. 5. The discharge capacity above 0.3 V in the first cycle for LS17 was a little higher than that for B1 and B2. Charge capacity (reversible capacity in these cases)
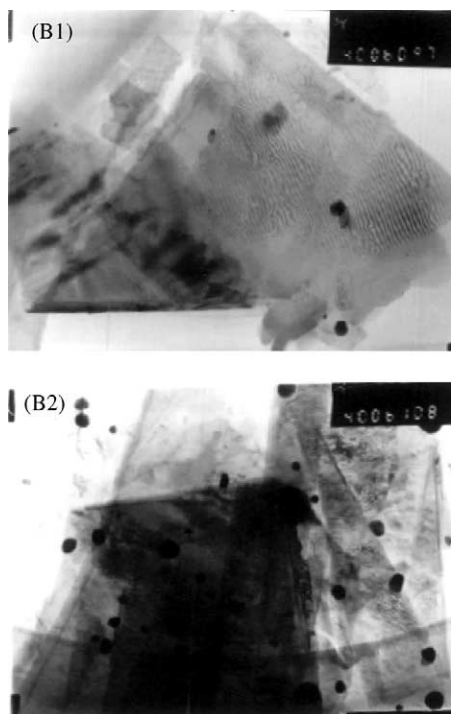
Fig. 4. HREM micrographs of the composites B1 and B2 with a width of 310 nm.

changed from 320 to 321 and 333 mAh/g, respectively. The coulombic efficiency in the first cycle was different, increased from 77.8 to 80.7 and 83.1%. When the natural graphite LS17 was built into cells under low humidity conditions (<100 ppm H_2O), its reversible capacity was 335 mAh/g and the coulombic efficiency in the first cycle was 88.5% (see Fig. 5 curve d).

As mentioned in Section 2, the time interval that anode materials were exposed to the high humidity environment was not very long (1 h), and the amount of water absorbed prior to the assembling was accordingly limited. However, our above results show that this amount of water had a great
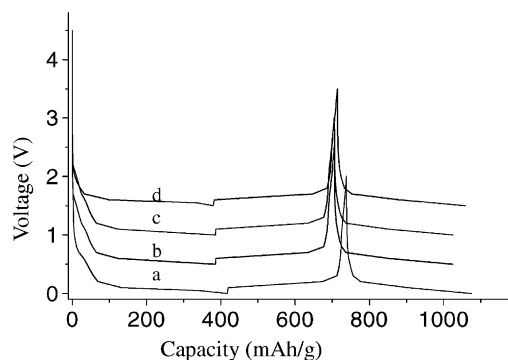

Fig. 5. Discharge and charge curves in the first cycle and discharge curves in the second cycle of natural graphite LS17 (a and d) and its composites B1 (b) and B2 (c). Curves a–c were obtained when the materials were assembled into model cells under high humidity (about 1000 ppm H_2O), curve d under low humidity (<100 ppm H_2O). For clarity, voltages of b–d were shifted upwards by 0.5, 1.0 and 1.5 V, respectively.

influence on lithium intercalation/de-intercalation. Lithium usually intercalates via the edge planes. Under low humidity lithium intercalation via defects at edges was favored because more passages remain available. However, when these active defects were occupied by water, part of the absorbed water at the surface of graphite would at first diffuse into the organic solution. It is known that the electrolyte is generally reduced to form a surface film only to a thickness that electrons can reach through electron tunneling, and there occur no more electrochemical reactions between the electrolyte and the surface after the completion of surface formation reactions [18]. However, in the presence of water it is reported that the electronic conduction through the surface film towards electrolyte was improved, and thus an enhanced electrochemical reduction of electrolyte at the interface happened as a side reaction producing thicker surface film [19]. In our case, part of the absorbed water, which diffused into the electrolyte solution, would also result in an enhanced electrochemical reduction of the electrolyte in comparison with the process under low humidity. Moreover, some of the absorbed water would react with the passivating film components such as lithium alkyl-carbonate producing LiOH and ROH. The produced ROH reacted with lithium as the following equation [20]:

$$2Li^+ + 2e^- + 2ROH \rightarrow 2LiOR + H_2 \uparrow \qquad (1)$$

As a result, the coulombic efficiency in the first cycle is lowered under high humidity condition when the graphite is not modified. In addition, natural graphite LS17 was treated by removal of minerals through dipping in KOH aqueous solution and the following mild oxidation, and thus there were micropores left [12]. Some part of water situated at the active sites around micropores did not diffuse into the electrolyte, reacted with lithium to form LiOH, and did not favor lithium intercalation at/via these sites. Consequently, the reversible capacity under the high humidity conditions was lowered, from 335 to 320 mAh/g, and the coulombic efficiency in the first cycle decreased.

When 8.6 wt.% silver (B2) was deposited onto the surface of natural graphite, the reversible lithium storage capacity is evidently enhanced. Nevertheless, it is still not markedly above that of the pure natural graphite (LS17) handled under low humidity. One reason is that the deposited silver removed/covered some amount of active sites in micropores, and thus these kinds of sites did not absorb water and once again served as 'reservoir' for lithium storage under high humidity [21,22]. Another reason is perhaps that the deposited silver formed reversibly alloys with lithium and contributed to reversible capacity. It is reported that silver reversibly forms alloys with lithium below 0.2 V, the same voltage range as that for lithium to intercalate into graphite [23,24], and thus the contribution of the deposited silver to the reversible capacity cannot be clearly identified. But in the case of the deposited copper, there was slight evidence from the discharge and charge curves illustrating that the deposited copper contributed to reversible capacity [11].
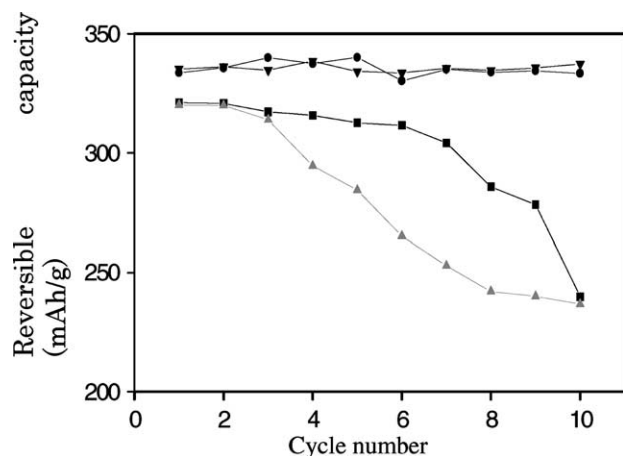
Fig. 6. Cycling behavior of natural graphite LS17 and the prepared composites B1 and B2. (▼) LS17 under low humidity (<100 ppm H_2O); (▲) LS17 under high humidity (about 1000 ppm H_2O); (■) B1 under the high humidity (about 1000 ppm H_2O); and (●) B2 under the high humidity (about 1000 ppm H_2O).

Accordingly, we can assume that the deposited silver also was perhaps in action as a storage site for lithium. Certainly, further studies aimed in particular at identification of Li_xAg after lithium intercalation are necessary.

In the case of B1, there is not much increase in reversible capacity in comparison with LS17. The main reason is that the amount of silver (3.2 wt.%) is not enough to cover most active sites especially those situated at the inner surrounding of micropores. Consequently, as discussed above, its reversible capacity is just a little higher than that of LS17 under high humidity.

Cycling behavior in the first 10 cycles of natural graphite LS17 and the composite anode materials B1 and B2 is shown in Fig. 6. In the case of LS17, when the cells were built under low humidity, its reversible capacity did not fade in the first 10 cycles [12,25]. In the presence of high humidity, the reversible capacity faded very quickly in the first 10 cycles, from 320 to 230 mAh/g. With composite materials B1 and B2 the cycling behavior was different. With B1 capacity did not fade very quickly at the first two cycles, but later faded to almost the same level as that of LS17. With B2 there was no evident capacity fading in the first 10 cycles in the presence of the high humidity, which is similar to the behavior of LS17 under low humidity.

As Eq. (1) shows, the evolved hydrogen gas would lead the structure of film to become loose, and thus solvated Li^+ could pass through the passivating film to co-intercalate into graphite and result in exfoliation of the graphene planes since this kind of phenomenon has been observed to happen in EC-based electrolytes [18]. Consequently, under the high humidity condition, capacity of LS17 faded very fast.

In the case of B1, there is not much capacity fading in the first two cycles, unlike that of LS17. But later it faded almost to the same level of LS17 under high humidity. Just as said above, the deposited silver was not enough to cover all of the active sites at the surface of graphite especially those at the surrounding of micropores. These active sites unoccupied by silver absorbed water, which reacted with lithium producing LiOH and H_2 gas. As a result, the formed passivating film was either not dense enough to block the passage of solvated Li^+ [18,26], and the structure of graphite deteriorated later though part of the passivating film was good enough to prevent its passage.

As to B2, since the amount of the deposited silver was enough to remove/cover most active sites at the surface of natural graphite, the amount of adsorbed water decreased sharply, the cycling behavior improved strikingly and there is not evident capacity fading in the first 10 cycles.

With respect to other effects of the deposited silver such as an increase in electronic conductivity and other conceivable roles of metallic silver and silver carbide, further studies are necessary.

4. Conclusion

In summary, there are active sites at the surface of natural graphite adsorbing easily water, which can be removed/covered by the introduction of silver onto the surface and the following heat-treatment. The deposited silver exists in nano-meter sized clusters and in two forms, i.e. metallic silver and carbide Ag_xC. Under conditions of high humidity (1000 ppm), the composite materials of natural graphite with the deposited silver adsorb markedly less water and still provide good electrochemical performance. In contrast, the capacity of the untreated natural graphite fades very quickly due to the absorbed water when built into cells under high humidity though it is good in cycling under low humidity (<100 ppm H_2O). As to the contribution of silver to the reversible capacity, though it could not be definitely identified, it is assumed to be in action since silver can act as a good matrix for lithium storage. This method can evidently lower the sensitivity of the anode material to humidity, and is promising for the industry to manufacture lithium ion batteries under less critical conditions.

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