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# Surface active sites: an important factor affecting the sensitivity of carbon anode material towards humidity

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## Abstract

In this paper, we report that various kinds of active sites on graphite surface including active hydrophilic sites markedly affect the electrochemical performance of graphite anodes for lithium ion batteries under different humidity conditions. After depositing metals such as Ag and Cu by immersing and heat-treating, these active sites on the graphite surface were removed or covered and its electrochemical performance under the high humidity conditions was markedly improved. This suggests that lithium ion batteries can be assembled under less strict conditions and that it provides a valuable direction to lower the manufacturing cost for lithium ion batteries.

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So far, many kinds of anode materials for lithium ion batteries have been studied.<sup>1,2</sup> However, graphitic carbons are still primarily available on the market, and this shows the importance of carbonaceous materials. A current research focus on the carbonaceous anode materials for lithium ion batteries is the modification of graphite by e.g. mild oxidation, deposition of metals or their oxides, coating with polymers and other kinds of carbons on the graphite surface.<sup>1-12</sup> Nevertheless, few studies are devoted to investigate the sensitivity of anode materials towards humidity.<sup>13,14</sup> It has long been realized that the electrochemical performance of carbon anode materials is more sensitive to humidity than that of cathodic ones. When the humidity is high, anode materials easily absorb water resulting in rapid fading of the reversible capacity. Unfortunately, the water content in a manufacturing facility is very difficult to maintain at a desirably low level of essentially 0 ppm. If sensitivity of anode materials to humidity can be decreased, the requirements for controlling the atmosphere in the manufacturing unit will be lowered and lithium ion batteries can be produced under less demanding conditions. In this paper, at first the sensitivity of graphitic carbon with hydrophilic active sites to humidity was studied, then the graphite surface was modified by covering or removing the surface active sites with deposited metals and the electrochemical performance of the composites prepared under high humidity condition was investigated.

### Experimental

A natural graphite from mild oxidation (designated as LS17,  $d_{002}$  3.351 Å,  $L_c$  120 Å and average particle size 17 μm) as described in ref. 8 was used for this study. Capacity measurements were performed as follows. A mixture of graphitic material and 5 wt.% (based on the graphite) polyvinylidene fluoride (binder) was pressed into pellets with a diameter of *ca.* 1 cm. After drying under vacuum at 120 °C overnight, the pellets were kept in an argon glove box at different humidities (<100 ppm and about 1000 ppm) for 1 hr; later they were assembled into model cells under the same

humidity conditions as the working electrode. Lithium foil was used as the counter and reference electrode, a solution of 1 M LiClO<sub>4</sub> in EC/DEC (v/v = 3:7) as the electrolyte and a homemade porous polypropylene film as the separator. Electrochemical performance was measured galvanostatically with a CT2001A cell test instrument (Wuhan LAND Electronic Co., Ltd., China) in a voltage range of 0.0 - 2.0V *versus* Li<sup>+</sup>/Li at 0.2 mA.

Modification on the natural graphite was performed as follows. Two pieces of 1 g LS17 were immersed in 10 ml aqueous solutions of 1.6 mol/l Cu(NO<sub>3</sub>)<sub>2</sub> and 0.8 mol/l AgNO<sub>3</sub>, separately, at room temperature overnight. The water in the solutions was evaporated at 80 °C during continuous stirring, and then the obtained remains were heat-treated in a tube furnace at 200 °C and following 600 °C for 2.5 hrs and 10 hrs, respectively, under an argon atmosphere. The prepared composites were named A and B, respectively.

## Results and discussion

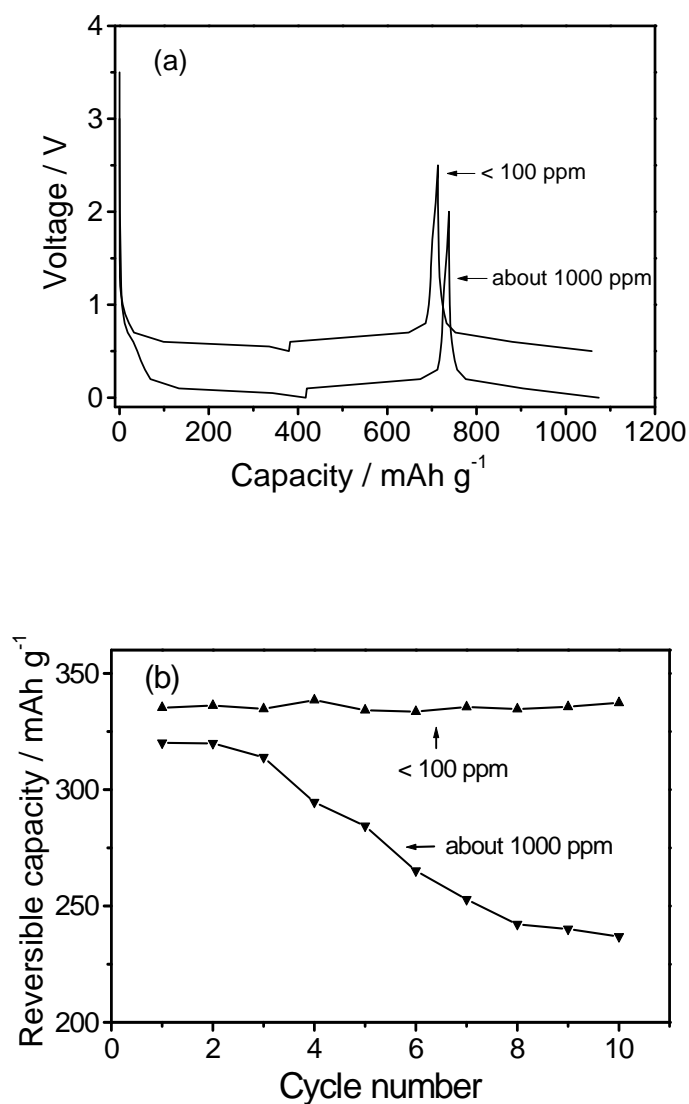


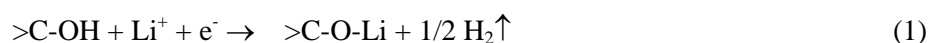
Fig. 1 Discharge and charge curves in the first cycle and discharge curves in the second cycle (a) and cycling behavior in the first 10 cycles (b) of natural graphite LS17 at low (<100 ppm H<sub>2</sub>O) and high humidity (about 1000 ppm H<sub>2</sub>O).

Fig. 1 shows (a) the discharge and charge curves in the first cycle and discharge curves in the second cycle and (b) cycling behavior in the first 10 cycles of natural graphite LS17 at different humidity. At the lower humidity (< 100 ppm), the reversible capacity of LS17 is 335 mAh/g, and the coulombic

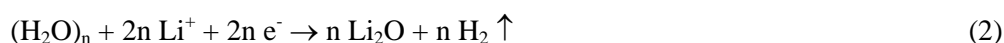
efficiency in the first cycle is 88.5 %. Its cycling was also satisfactory and there was no evident capacity fading in the first 10 cycles. This clearly indicates that this kind of graphite can be a good candidate for commercial lithium ion battery. However, under the high humidity (about 1000 ppm), its reversible capacity decreased to 320 mAh/g, and the coulomb efficiency in the first cycle became low, 77.8%. In addition, the reversible capacity faded quickly to 230 mAh/g in the first 10 cycles.

It is evident that the marked different electrochemical behavior of the same graphite LS17 is from the different humidity environment. As mentioned above, the graphite LS17 was subjected to the mild oxidation treatment and there are some micropores,<sup>8</sup> whose internal volume can be reflected in the inner specific surface area of the graphite, about 4 m<sup>2</sup>/g, comprising of most of the total specific surface area from BET measurement (about 5 m<sup>2</sup>/g). It is known that micropores can be sites for reversible lithium intercalation and deintercalation<sup>1,2,16,17</sup> and there are active sites including hydrophilic ones around the micropores.<sup>15</sup> Consequently, under the low humidity the formed solid-electrolyte interface (SEI) between graphite and electrolyte is compact, and only lithium ions can pass through this film.<sup>18</sup>

However, under the high humidity condition the active sites on graphite surface adsorbed much water. As shown in Fig. 1 for high humidity case, the adsorbed water influenced lithium intercalation into graphite and led to poor electrochemical performance. These effects can be mainly ascribed to the following reaction scheme. (1) Part of the absorbed water formed a thin layer of >C-OH on graphite surface, and the following side reaction happened:



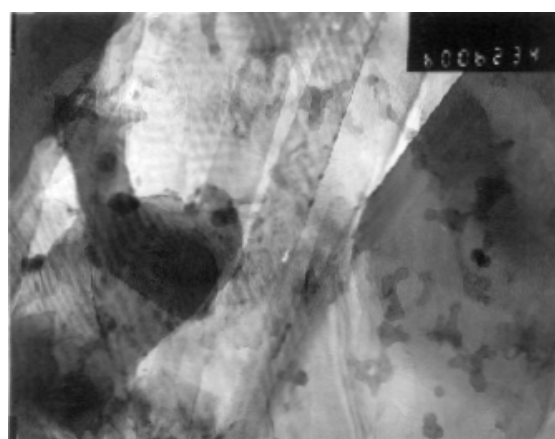
leading to a dense layer of SEI film, and the formed >C-O-Li cannot be reduced during the successive reduction process causing initial irreversible capacity. (2) Some absorbed H<sub>2</sub>O might form tiny water aggregates (H<sub>2</sub>O)<sub>n</sub>. During reduction process, the following reaction is expected to take place:



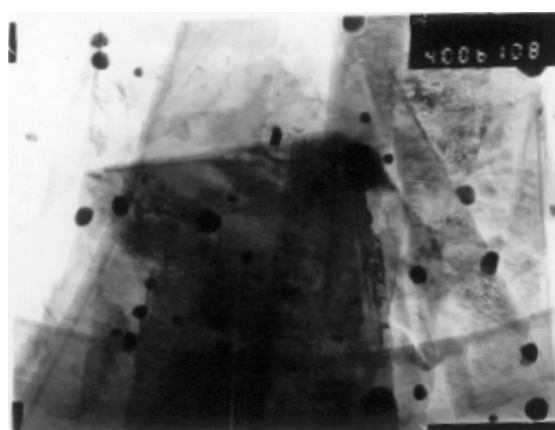
where Li<sub>2</sub>O cannot be reduced and is supposed to form nonconductive lumps spreading over the

graphite surface causing to block the successive electrochemical reactions. (3) Some part of the absorbed water would diffuse into the electrolyte prior to lithium intercalation since the anode pellets were in contact with the electrolyte for some time prior to the capacity measurement. This part of water likely to behave as the added water in the organic electrolyte causing thicker SEI film, which did not favor the intercalation of lithium, and resulting in irreversible capacity.<sup>18-20</sup> (4) The absorbed water around micropores reacted with lithium ions to produce LiOH or Li<sub>2</sub>O during the electrochemical reduction. In this case, the occupation of micropores by LiOH or Li<sub>2</sub>O naturally resulted in fewer sites for lithium storage and a consequent decrease in reversible capacity. By the way, they also blocked the successive electrochemical reactions. As a result, high initial irreversible capacity, reduced reversible one, and rapid fading in capacity are expected.<sup>21</sup>

As the above discussion mentioned, if the graphite surface is changed, then a different electrochemical performance will be obtained. This has been clearly shown by changing the surface structure,<sup>1-12,22,23</sup> and here we tried to modify the graphite surface by depositing metals.



500 nm  
(A)



310 nm  
(B)

Fig.2 HREM micrographs of the composites A and B.

Fig.2 shows the high resolution electron micrographs of our prepared composites A and B from the modification of graphite LS17 by depositing with copper and silver. The deposited copper and silver exist in nanometer clusters or particles and their distribution is not very uniform. As mentioned above, there are some very active sites (also called hydrophilic sites) at the surface of graphite, which adsorb water easily.<sup>15</sup> They preferentially adsorbed metal ions such as  $\text{Cu}^{2+}$  and  $\text{Ag}^+$  from the solutions. As a



result, metal ions were concentrated at these active sites. During the following heat-treatment, the nitrates were turned into oxides at first, then metal oxides reacted with carbon atoms at these active sites to form metals and carbides  $M_xC$  ( $M = Cu$  and  $Ag$ ),<sup>24,25</sup> or decomposed into metal and thus nanometer clusters or aggregates of the deposited metals could be observed in micrographs. If there are no active sites, the deposition of Cu and Ag would be preferably uniform and clusters could not be observed.

Discharge and charge profiles in the first cycle and discharge profiles in the second cycle and cycling behaviors in the first 10 cycles of the composites A and B manufactured into cells in the presence of high humidity (about 1000 ppm) are shown in Fig. 3.

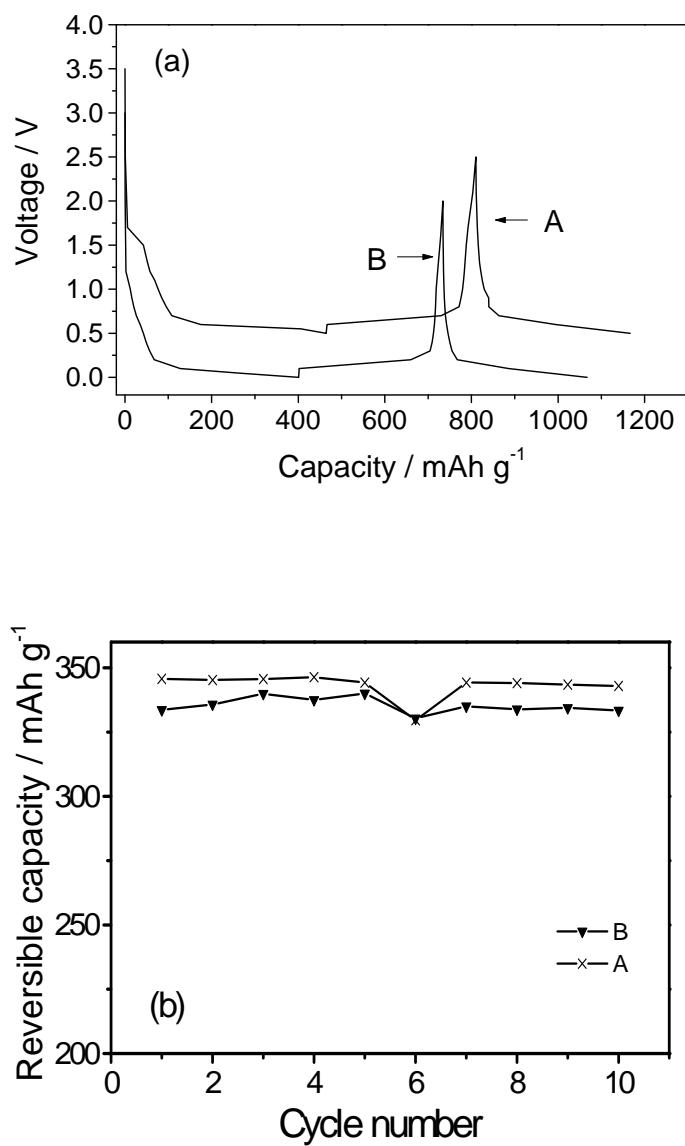


Fig.3 Discharge and charge curves in the first cycle and discharge curves in the second cycle (a) and cycling behavior in the first 10 cycles (b) of composites A and B under high humidity (about 1000 ppm H<sub>2</sub>O). For clarity, voltages of A in Fig.2(a) were shifted upwards by 0.5V.

The reversible capacity changed from 320 (for the untreated graphite under the high humidity) to 348 and 333 mAh/g for A and B, respectively. The coulombic efficiency in the first cycle increased from 77.8 % to > 83 % after the deposition of metals. In the case of the composites, their cycling behavior has been markedly improved and there was no evident capacity fading in the first 10 cycles. Compared with the behavior of LS17 under the high humidity as shown in Fig.1, it is apparent that the electrochemical performance of graphite anode is markedly improved.

The above results show that the deposited metallic elements such as copper and silver removed and/or covered the active hydrophilic sites at the graphite surface. The adsorbed amount of water decreased sharply under the high humidity and a good SEI film was formed to ensure good cycling.<sup>18</sup> In the meanwhile, the deposited metals may contribute to the enhancement of reversible capacity. For example, Ag can reversibly alloy and dealloy with Li.<sup>26,27</sup> In addition, size and surface effects of these nanometer clusters of deposited Ag and Cu might also contribute to the reversible capacity. For example, the reversible capacity of nanoparticles of tin, tin-based alloys and silicon is much higher than that of the bulky tin and silicon.<sup>2,28,29</sup> The difference in the reversible capacity of the composites A and B is presumably mainly due to the difference in the molar and weight amounts of the deposited metals and the difference in the formed alloys with Li. With respect to other conceivable roles of metals and carbides, further studies are necessary. Conceivably they will favor lithium intercalation or diffusion as the coated Ni, and thus high rate capability will be improved.<sup>30</sup>

### Conclusions

It is shown that there are active hydrophilic sites at the surface of natural graphite. When processed under low humidity (< 100 ppm H<sub>2</sub>O) they did not cause unfavorable effects. However, when processed under high humidity (about 1000 ppm H<sub>2</sub>O) they absorbed water and led to the decrease and fading of the reversible capacity. When these sites were effectively removed/covered by depositing

metal elements such as Cu and Ag, composite electrodes absorbed less water when assembled into model cells in the presence of the high humidity and provided still good electrochemical performance. These results provide a valuable direction to low the manufacture cost for lithium ion batteries since lithium ion battery can be assembled under less strict condition due to the change in surface structure.

#### Acknowledgments

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