Mechanism of lithium insertion in carbons pyrolyzed at low temperature

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Abstract Carbons pyrolyzed at temperature ranging from 500℃ to 1 000℃ are promising materials for high-energy density lithium batteries. These carbons not only possess a capacity higher than the theoretical value of graphite, but also display a different electrochemical behavior from that of graphite. Mechanisms now available for this phenomenon are reviewed after the presentation of mechanism of lithium intercalation in graphite. Based on the recent research, a new model for lithium insertion in carbons pyrolyzed at low temperature and some ideas for further study are proposed.

Keywords: **lithium ion batteries, anode, carbonaceous materials, mechanism.**

CARBONACEOUS materials reversibly react with lithium and can be used as the anode in lithium ion batteries[1]. To maximize the energy density of these batteries, it is very important to find kinds of carbon which reversibly react with the largest amount of lithium. Various kinds of carbon, such as graphites, cokes, active carbons, carbon blacks, carbon fibers, and carbons pyrolyzed at low temperature (500—1 000℃), etc., have been tested for this application[2—5]. Among them, carbons pyrolyzed at low temperature attract much attention. These carbonaceous materials display different electrochemical behavior from the well-known behavior of graphite. To explain this phenomenon, many reaction mechanisms have been suggested.

1 Mechanism of lithium intercalation in graphite

Graphite has layered crystal structural, and foreign atoms, ions, or small molecules can be intercalated between adjacent graphene layers to form graphite intercalation compound (GIC). The maximum extent of lithium intercalated in graphite is one lithium atom per six carbon atoms under ambient conditions. In LiC_6, the lithium atoms occupy the next nearest-neighbor sites between two adjacent graphene layers, corresponding to a theoretical capacity of 372 mA·h/g[6]. Lithium transfers most of its 2s electron density to the carbon π orbital and exists as a screened ion between graphene layers. A band-structure calculation of LiC_6 suggests a charge transfer formula Li^+C_6^-[7].

The properties of carbonaceous materials are normally tested by electrochemically reacting lithium with carbons in cells. These cells are assembled with carbon sample as one electrode and with lithium metal as counter electrode or simultaneously as reference electrode. When lithium is intercalated into graphite, the following discharge reactions occur:

anode reaction: $\text{Li} \rightarrow \text{Li}^+ + \text{e}$,

cathode reaction: $\text{Li}^+ + \text{C}_6 + \text{e} \rightarrow \text{LiC}_6$,

total reaction: $(\text{C}_6)_n + m\text{Li}(\text{C}_6)_{n-m} + m\text{LiC}_6 \quad (n \leqslant m)$.

Figure 1(a) shows the voltage-capacity relation for lithium-graphite electrochemical cell. The greater part of the charge-discharge curves lie under the line of 0.5 V.

2 Mechanisms now available for lithium insertion in carbons pyrolyzed at low temperature

Sato *et al*.[8] reported in 1994 that polyparaphenylene pyrolyzed at 700℃ can accommodate lithium up to 680 mA·h/g. Thereafter, many high capacity carbons were obtained by pyrolyzing different precursors at temperature lower than 1 000℃[8—21]. These carbons not only possess capacities higher than the theoretical capacity of graphite, but also display a different electrochemical behavior from that of graphite. The voltage profiles for most of these carbons[8—19] show large hysteresis as illustrated in fig. 1(b), that is, lithium inserted near 0.0 V is extracted near 1 V. To explain this phenomenon, many models have been proposed[5, 8, 9, 13, 14, 22, 23] so far, which can be summarized as follows.

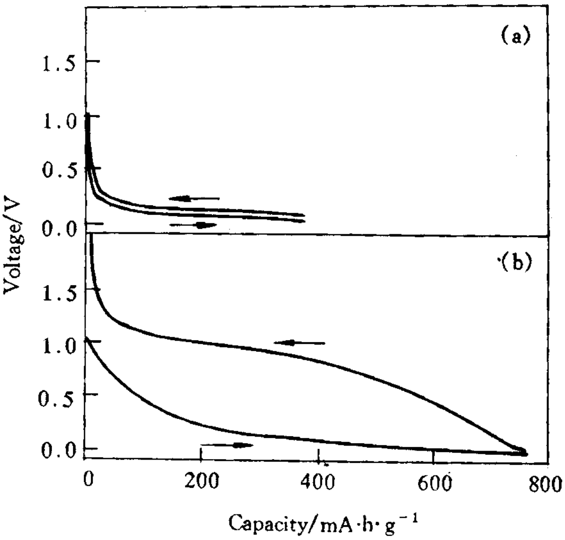

Fig. 1. Schematic illustration for discharge and charge curves of graphites (a) and carbons pyrolyzed at low temperature (b).

(i) Lithium occupation nearest-neighbor benzene rings. The ^{7}Li NMR spectrum of Li-doped polyparaphenylene-based carbon has two bands around 0.0 ppm. The band at high chemical shift was attributed to ionic lithium and the other was thought to be caused by the existence of molecular Li_2. Sato *et al*.[8] proposed that lithium ions occupy the next nearest-neighbor sites similar to that in GIC, and lithium molecules with a covalent characteristic in the Li-Li bond occupy nearest-neighbor benzene rings. The capacity higher than the theoretical value of graphite just results from the extra occupation of lithium molecules in carbon host.

(ii) Multilayer lithium deposit on the carbon surface. Yazami *et al*.[9] observed that mesocarbon micro-beads heat-treated at 1 000℃ could reversibly store lithium up to 410 mA·h/g. They believed that lithium can either occupy the available space between the carbon layers (intercalated lithium) or can be deposited as a multilayer on the carbon surface (multilayer lithium) or even interact with the carbon surface functions (oxygen, nitrogen, etc.). Three layers of lithium can be deposited on the carbon surface with a successively decreasing charge transfer between lithium and the π orbital of graphite crystallite. If more lithium is deposited, there must be a strong tendency to form pure alkali metal as a result of the total screening of the carbon layers.

(iii) Lithium storage between graphene layers, at the edge, and on the surface of crystallite. Matsumura *et al*.[10—13] investigated the variation of reversible capacity and crystallite size L_c of pyrolyzed mesophase pitches with heat-treatment temperature in the range of 600—700℃. The result showed that the carbon sample with large L_c has low capacity and the sample with small L_c has high capacity. They assumed that for the disordered carbon with a small crystallite size, Li species are not only intercalated between graphene layers but also doped at the edge of the graphene layers, and in addition even more Li species are doped onto the surface of the crystallite.

(iv) Lithium ion clusters in cavities. Fujimoto *et al*.[14, 15] proposed a cavity index (CI) to estimate the cavity amount in mesophase pitches heat-treated at 700—2 800℃. They noted a good linear relationship between CI and the capacity of hysteresis plateau region. Consequently, it was proposed that lithium species can be doped into the cavities in the form of lithium ion clusters and contribute to the capacity of hysteresis plateau.

(v) Lithium binding in the vicinity of hydrogen atoms. Dahn *et al*.[5] noticed that there remains substantial hydrogen in high-capacity carbon prepared by Fujimoto[14, 15] and Yata *et al*.[17,18]. They synthesized a series of materials at different temperatures (550—1 000℃) from petroleum pitches, polyvinyl chloride, and polyvinylidene fluoride. It was found that the H/C atomic ratio and the specific capacity of these materials share a changing tendency when heat-treatment temperature is lowered. Therefore, they considered that Li atoms can bind in the vicinity of hydrogen atoms and transfer part of their 2s electrons to nearby hydrogen atoms, resulting in a corresponding change to the H—C bond. These bonding changes would be activated processes, which can lead to hysteresis.

3 Shortcomings of mechanisms now available for lithium insertion in carbons pyrolyzed at low temperature

Mechanisms mentioned above are suggested on different experimental bases and reveal respectively partial physical or chemical features of the carbons pyrolyzed at low temperature. Hence these mechanisms appear far from each other and have respectively one shortcoming or another.

The difficulty for lithium occupation on nearest-neighbor sites is how to overcome under ambient condition the large screened Coulomb repulsion between ions on nearest-neighbor sites. Although highly saturated lithium GIC (LiC_2, 1 116 mA·h/g) was chemically synthesized, this high capacity was obtained under the extreme condition of $(5.0—6.0) \times 10^9$ Pa.

According to Yazami's mechanism, lithium species deposited on the carbon surface have a stronger and stronger metallic character with the increase of C-Li distance between lithium layer and carbon surface. Nevertheless, the result of ^{7}Li NMR analysis reveals that lithium extra inserted in high-capacity carbon with large hysteresis shows strong ionic character, even compared with lithium intercalated in graphite[8, 23, 25]. In addition, the reason for hysteresis was not given in this mechanism.

As for the formation of lithium ion clusters in cavities, it was thought to be not probable because no bands in ^{7}Li NMR spectrum were observed in the chemical shift range above that of lithium intercalated in graphite[26].

Matsumura *et al*. realized that the capacity of carbons is largely affected by crystallite size, especially by L_c. However, it can be found from their experimental data that a small increase of L_c results in a dramatic decrease of the capacity when heat-treatment temperature is below 1 000℃; a dramatic increase of L_c only leads to a small decrease of the capacity when heat-treatment temperature is above 1 000℃. This indicates that the capacity of carbons might be affected by other factors besides L_c.

Dahn's mechanism gave a better explanation for the voltage hysteresis, but it is still needed to further elucidate the position where lithium is stored in carbon and the concrete interaction between lithium and hydrogen.

Briefly, there are separately different kinds of shortcoming in all the mechanisms now available. It is especially needed to draw a new, general and integrated model for lithium insertion in carbons pyrolyzed at low temperature.

4 New model for lithium insertion in carbons pyrolyzed at low temperature

Although there is a long distance between different mechanisms now available, all of them have something in common to some extent. All mechanisms, except those proposed by Fujimoto and Dahn, investigated the contribution of crystal structure to the capacity of carbons. Fujimoto's mechanism even used crystal parameters to calculate the cavity index.

(ⅰ) Lithium doping at the edges of graphene layers. Recently, high-capacity carbons were prepared in our group by altering the cross-linking density of polymeric precursors[27, 28]. It was founded that the cross-link structure of precursors hinders the growth of graphene layers and hence graphene layers are more liable to form stacking layers. With the increase of cross-linking density, L_a of the crystallite decreases, L_c increases, and the capacity of the carbon increases at the same time. There is a linear relation between the capacity of the plateau and the edge length of stacking graphene layers. As we know, the frontier electron density exists only in the carbon atoms at the edge of graphene layers[29, 30]; carbon atoms in hybridization state other than sp^2 and even other kinds of atoms are linked with the stacking graphene layers at their edge area[31]. We consider that, except for the lithium intercalated between graphene layers, lithium is mainly doped at the edges of the graphene layers rather than on the surfaces.

(ⅱ) Type of atoms at the edge of graphene layers. High-capacity carbons pyrolyzed at low temperature possess not only a crystal structural feature of large edge area of graphene layers but also a chemical composition feature of high H/C atomic ratio. However, polymer precursors, which possess a larger H/C atomic ratio than the corresponding carbonaceous materials obtained after pyrolyzing, have no ability to accommodate lithium species. The linear relation between the capacity and the H/C atomic ratio is effective only when heat-treatment temperature is higher than the carbonization temperature of the precursor, at which the formation and growth of graphene crystal nuclei begin. These results indicate that extra insertion of lithium species results from the co-contribution of the edges of graphene layers and the hydrogen in carbon and, furthermore, the hydrogen having contribution should be bound at the edges of graphene layers.

We think that the so-called lithium insertion in the vicinity of hydrogen is essentially the lithium doping at the edges of graphene layers binding hydrogen atoms.

(iii) Interaction of lithium with atoms at the edges of graphene layers. It is the hydrogen at the edges of graphene layers but not the hydrogen of precursors that has the ability to cause extra insertion of lithium species. This fact suggests that this ability of the hydrogen at the edges cannot remain in the absence of the edges of graphene layers, and accurately in the absence of the carbon atoms at the edges of graphene layers. Therefore, the doping of lithium at the edges of graphene layers binding hydrogen atoms would be a three-membered interaction among lithium, hydrogen and carbon atoms in the edge area, which leads to the hysteresis during the lithium extraction process. An ionic complex such as lithium naphthalene should be formed and gives the lithium a strong ionic characteristic.

(iv) Texture of carbon pyrolyzed at low temperature. Fujimoto *et al*.[14] noticed that the carbon with low density shows a high capacity and suggested that lithium species can be doped into the cavities in the carbon. It is also observed in our study that, when the cross-linking density of precursors is raised, the density of carbons obtained decreases and the capacity increases. As the cross-link structure of precursors hinders the growth of the graphene layer, the disorganized region with low density and the disordered stacking of crystallites are formed around the cross-linking sites, which could lead to the cavities in carbon. We consider that the so-called cavities by Fujimoto *et al*. are actually the cavities formed in the disordered texture of crystallites and that the essence of lithium doping into cavities is lithium doping on the inner surface of the cavities constructed by the edges of disorderly stacking crystallites.

To sum up, a new model for lithium insertion in carbons pyrolyzed at low temperature (shown in fig. 2) is proposed: i) except for the lithium intercalated between graphene layers, lithium is mainly doped at the edges of graphene layers rather than on the surface of crystallites; ii) the atoms, including hydrogen atoms, in the edge area of graphene layers contribute to lithium doping at the edges; iii) there is a three-membered interaction among lithium, hydrogen and carbon atoms in the edge area, which leads to the hysteresis during the lithium extraction process; iv) the disorderly stacking of crystallites forms cavities in carbon; the so-called lithium doping in cavities is actually the lithium doping on the inner surface of the cavities constructed by the edges of crystallites.

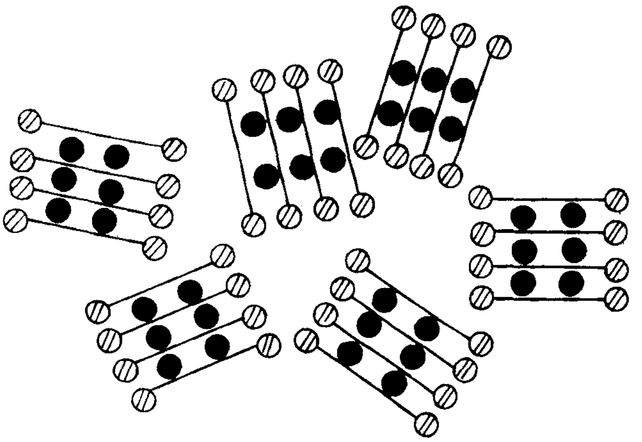

Fig. 2. A new model for lithium insertion in carbons pyrolyzed at low temperature. ●, Lithium intercalated between graphene layers; ○, lithium doped at the edges of graphene layers.

This model reveals the interal relations among Matsumura's, Fujimoto's, and Dahn's explanation and gives a general understanding of lithium insertion in carbons pyrolyzed at low temperature. The results from X-ray photoelectron spectrometry also sustain the above new model1).

5 Prospects

Further studies on lithium insertion in carbon pyrolyzed at low temperature may focus on the following aspects:

(i) Effect of the composition and structure of precursors. The previous work was mainly about the effect of heat-treatment temperature on the structure and electrochemical properties of the carbon, for the structural variation of the carbon is usually accomplished by altering heat-treatment temperature. Hence a basic limitation is brought to the better understanding of lithium insertion. It is found that the cross-linking structure of precursors exerts a large influence on the electrochemical behavior of resultant carbons[27, 28]. This opens a new way to the study of lithium insertion, that is, with the same kind of precursor and the same heat-treatment temperature, to vary the structure and electrochemical properties

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1) Xiang, H. Q., *Ph. D. Thesis*, Institute of Chemistry, the Chinese Academy of Sciences, 1997.

of carbons simply by altering the composition or structure of precursors.

(ⅱ) Generally analyzing the structural features of carbons pyrolyzed at low temperature. The structure of carbons pyrolyzed at low temperature is far from that of ideal graphite. The crystallites of high-capacity carbons have a small size and random orientation. Moreover, there are disorganized regions besides crystallized fields. Therefore, in order to gain an overall understanding of the relation between lithium insertion and the structure of high-capacity carbons, it is needed to dissect the structure of carbons by various characterization means.

(ⅲ) Effect of the atoms in transition boundary region between disorganized region and crystallized field. The reversible insertion of lithium in carbonaceous materials is essentially associated with the crystal structure. Therefore, although carbons pyrolyzed at low temperature display a different electrochemical behavior from that of well-crystallized graphites, a better knowledge of lithium insertion cannot be gained without the consideration of crystal structure.

The physical and chemical state of atoms in crystal boundary region is largely different from that of atoms in the inner part of crystallite. Both disorganized region and crystallized field are not isolated and they are chemically linked. There is a transition boundary region between disorganized region and crystallized field. Recently, it was reported that graphite ground mechanically shows a capacity higher than 372 mA·h/g[32]. The reason is just assigned to the increased total edge area of ground crystallites and atoms including hydrogen thereon. In addition, Dahn *et al*. also believe in their further studies that the lithium atoms may bind on hydrogen terminated edges of hexagonal carbon fragments[33, 34]. Therefore, a better knowledge about characteristics of the atoms in transition boundary region is crucial to elucidate the mechanism for lithium insertion in carbons and to improve the electrochemical properties of lithium ion batteries.

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