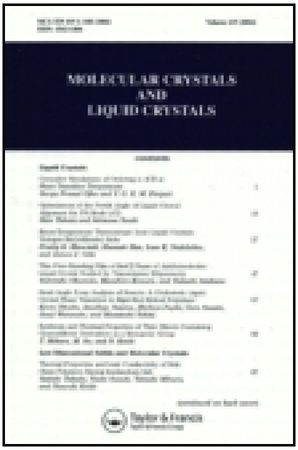

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Carbonaceous Materials for Lithium Ion Secondary Battery Anodes

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Carbonaceous Materials for Lithium Ion Secondary Battery Anodes

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Graphite, graphitizable carbon (soft carbon) and non-graphitizable carbon (hard carbon) have been investigated as anode materials for lithium ion secondary batteries. Graphite and hard carbon are now mainly put to practical use and both have their merits and demerits. In this article, characteristics and properties of graphite and hard carbon as lithium intercalation hosts are described and the possibility is discussed of novel hard carbon anode materials prepared from agricultural wastes such as bamboo saw dusts or coffee grounds.

Keywords: lithium ion secondary battery; anode material; lithium intercalation host; graphite; hard carbon

INTRODUCTION

The lithium ion secondary battery (LIB) technology was pioneered by Sony Corporation. It introduced the lithium ion cells into the market first in the world in 1991. Principal features of LIB are as follows.

1) high energy density (both gravimetric and volumetric),
2) high operating voltage,
3) low self-discharge rate,
4) no memory effect,
5) high drain capability,
6) wide temperature range of operation,
7) quick charge acceptance

These characteristics have enabled LIB to be applied to diverse portable electronic products such as notebook PC's, cellular phones,camcorders etc.

The carbon anode is a key component of the lithium ion secondary battery, and various carbon materials ranging from graphite to amorphous carbon have been proposed.

ANODE CARBON

Graphite has a layered structure and it is well known that graphite can be intercalated (or doped) with lithium to form lithium graphite intercalation compounds (Li-GIC), LiC_6. In an aprotic organic solvent containing lithium salts, graphite is reduced by electrochemical doping with lithium to form Li-GIC, and a Li-GIC can be electrochemically oxidized by lithium undoping. This indicates that a Li-GIC can be charged and discharged as anodes for nonaqueous rechargeable cells according to the following equation.

$$\mathrm{Li_aC} = \mathrm{Li_{a\text{-}dx}C} + \mathrm{dxLi^+} + \mathrm{dxe^-}$$

When the anode is discharged, lithium deintercalates from graphite and lithium ions dissolve into the electrolyte, and when the anode is charged, lithium intercalates between the layers of graphite.

Several types of carbonaceous materials as well as graphite can be intercalated with lithium to form similar intercalation compounds. We have given by analogy the name 'carbon intercalation compounds' (CIS) to these compounds.

It has been confirmed that certain carbonaceous materials are reduced / oxidized by electrochemical lithium doping / undoping in aprotic nonaqueous electrolytes to form Li-CIC's and that some carbonaceous materials can be utilized as anodes of LIB in place of graphite.

The ionic states of lithium species intercalated into carbon layers were determined by the ^{7}Li-NMR analysis. Knight shifts of lithium species doped into carbon with doping rates ranging between 0 to 100% were almost the same as that of LiCl, the typical ionic lithium compound. It was concluded from this experiment that lithium doped into the carbon layers is in the ionic state and that no metallic lithium is present in the system. The name of "lithium ion secondary battery" has been given to this battery system for this reason.

GRAPHITE AND HARD CARBON ANODES

At present, graphite and hard carbon are mainly put to practical use and both have their merits and demerits. TABLE I shows the comparison between graphite and hard carbon as the anode materials for LIB.

TABLE I Comparison of Graphite and Hard Carbon

Description	Graphite	Hard Carbon
Cyclability	Acceptable	Excellent
Anode Bulging	Large	Very Small
Discharge Curve Profile	Flat	Sloping
Lithum Doping Capacity	< 370 mAh/g <825 mAh/cm^3	< ca. 700 mAh/g < ca.1000 mAh/cm
Efficiency at 1st cycle	>95%	>85%

It is well known that the d$_{002}$ spacing of graphite is 0.335 nm and when lithium intercalates between the layers of graphite, d$_{002}$ spacings expand up to 0.372 nm, then shrink back to 0.335 nm again by lithium deitercalation. In the case of the graphite anode, significant deformation of the electrode is brought about by this expansion / shrinkage of d002 spacings during charge / discharge cycles, which results in poor cyclability of the graphite anode cell.

On the other hand, d$_{002}$ spacings of hard carbon are over 0.372nm, and the expansion of d$_{002}$ spacings and the electrode deformation due to Li doping cannot be observed. Cyclability of the hard carbon cell is excellent and this is attributed to this structural stability and no deformation of the anodes during cycles.

Graphite has an orderly layered structure and lithium can intercalate only into the spacings between the layers to form LiC6, and the lithium doping capacity of graphite is subject to the stoichiometry of LiC_6 (370 mAh/g). Hard carbon, however, consists of randomly oriented small crystallites, and lithium can be electrochemically inserted into the ultramicropores (with diameters of about 0.7 to 0.8 nm). These ultramicropores are assumed to be able to trap lithium in clusters, and this cluster lithium can also be discharged. Thus the capacity limitation due to LiC6 stoichiometry can be eliminated in the case of the hard carbon anode as a whole.

The discharge curve profile of the graphite anode cell is flat while that of the hard carbon cell is sloping. This sloping profile of the latter is favorable for a state-of-charge indicator, because open circuit voltages (OCV) correspond to the remaining capacity and the state of charge or the depth of discharge can be easily determined by measuring OCV of the cell.

The hard carbon cell, however, is not suitable for the application to electronic devices with cut-off voltages higher than around 3.0 V. When discharge is cut off at these voltages, the energy corresponding to the voltage range below 3.0 V cannot be utilized.

NOVEL HARD CARBON AS ANODE MATERIALS

It should be stressed that hard carbon can be economically prepared from agricultural wastes. We have been developing anode carbonaceous materials by carbonization of bamboo saw dusts and coffee grounds followed by heat treatment at various temperatures.

TABLE II shows charge / discharge capacities of bamboo saw dusts and coffee grounds derived carbonaceous materials.

TABLE II CHARGE AND DISCHARGE CAPACITY OF BAMBOO AND COFFEE GROUNDS DERIVED CARBONACEOUS MATERIALS

Raw Materials	HTT/°C	CC/mAh/g	DC/mAh/g	Eff/%
Bamboo	1100	775	630	81.3
	1200	710	580	81.7
	1300	560	500	89.3
Coffee Grounds	1200	615	525	85.4

HTT: Heat Treatment Temperature, CC: Charge Capacity
DC: Discharge Capacity, Eff: Efficiency at first cycle

These data are encouraging to further studies on these materials. Focus should be on improvement of efficiency or verification in practical cells.