Rechargeable carbon anode

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Abstract

The electrochemical intercalation of lithium into carbon materials is discussed in terms of the effect of different parameters of the crystal structure and surface modifications of carbon to reduce the reaction of carbon with electrolyte solvents. The lithium intercalation capacity in the carbon materials prepared from the same raw materials and by the same preparation methods depends on the heat-treatment temperature. A higher capacity is obtained in the carbons prepared at higher temperatures, which have a graphite structure. The graphite is more reactive in reaction with organic solvents. The reaction of the graphite with solvents is reduced by a pretreatment of the carbon materials with acid and hydrazine.

Keywords: Rechargeable lithium batteries; Carbon anode

1. Introduction

In 1955, Herold prepared [1] several stages of lithium intercalation graphites, Li_xC_6, ($x = 0$–1.0), by a vapor transport method at higher temperatures. The electrochemical lithium intercalation into graphite has been reported more recently. Dey and Sullivan [2] have examined the electrochemical lithium intercalation into graphite in the electrolyte solution of propylene carbonate(PC) with $LiClO_4$. In this case, no lithium intercalation was observed, but only the decomposition of PC. In the last decade, much research efforts have been focused on the search for suitable carbon materials as an alternative anode for rechargeable lithium batteries. Lithium metal anodes have an extensive advantage because of their high energy density of 3880 mAh/g. Although some improvements in cycle life and efficiency have been achieved, the reversibility of the lithium metal electrode remains as a significant problem in aprotic solvent-based electrolytes. The major problems limiting cycle life are short circuits resulting from the growth of lithium dendrites and the macroscopic changes in their shape during the recharge processes [3,4]. Many approaches have been under taken to improve the reversibility of the lithium anode. The lithium carbon is a promising anode, because of its good rechargeability, a small change in its volume with lithium intercalation, and its safety. A potential disadvantage of this type of electrode is a low energy and a low power density compared with a lithium metal anode. The specific charge densities of LiC_6 are 372 mAh/g. However, the charge capacity exceeds that of most cathode materials for secondary lithium batteries. If the theoretical capacity of the carbon anode based on LiC_6 is obtained, the carbon materials are a quite attractive anode for the secondary lithium batteries.

Recently, Azumia et al. [5] revealed data on a lithium-ion battery claimed to be completely without metallic lithium. The battery has a energy density of three times higher than the corresponding Ni/Cd battery. This type of batteries utilizes a carbon negative electrode, prepared by thermal decomposition of polyfurfural alcohol resin, and $LiCoO_2$ as the positive electrode. Many papers on the carbon anode for lithium batteries have been published in the last five years. However, it is not clear which type of carbon materials is the best for the anode. In this paper, some results on the lithium intercalation into meso-phase carbon fiber materials prepared at different heat-treatment temperatures as well as the reaction of carbon material with the solvent has been reported. The relation of the parameters of the carbon crystal and the charge capacity has also been discussed.

2. Experimental

The carbon materials examined in this study were mainly purchased from Petca Co., Japan. These carbon materials were mesophase mealed carbon fibers prepared from petroleum pitch. The physical properties of these carbon materials are summarized in Table 1. To examine the lithium intercalation properties, coin-

Table 1
Heat-treatment temperature and crystal parameters of meso-phase pitch-based mealed carbon fibers

Carbon fiber	Heat-treatment temperature (°C)	d_{002} (Å)	L_c (Å)	Figure	
				diameter (μm)	length (μm)
A	1000	3.571	12	13	40
B	2400	3.406	220	13	60
C	3000	3.361	580	13	60

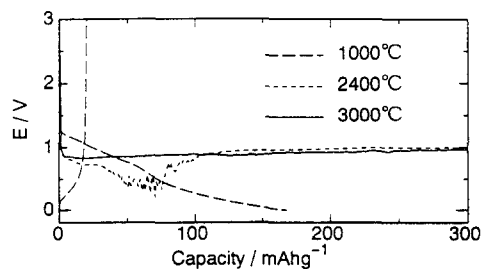

Fig. 2. Charge/discharge behavior of carbon fibers prepared at (– – –) 1000 °C, (· · · ·) 2400 °C and (——) 3000 °C in LiClO₄/EC at 0.5 mA.

Fig. 1. Charge/discharge behavior of carbon fibers prepared at (– – –) 1000 °C, (· · · ·) 2400 °C and (——) 3000 °C in LiClO₄/PC–THF at 0.5 mA.

Fig. 3. Charge/discharge cyclic behavior of carbon fiber prepared at 3000 °C in LiClO₄/EC at 0.5 mA.

type cells were used. A mixture of 50 mg carbon materials and 5 mg Teflon powder was pressed into a tablet of 13 mm in diameter under a pressure of 9 MPa. The counter electrode was a disc of lithium metal foil of 15 mm in diameter. The separator was a microporous polypropylene sheet. The typical electrolyte used in these cells was 1 M solution of LiClO₄ in a propylene carbonate–tetrahydrofuran (PC–THF) mixture (50:50 vol.%) and ethylene carbonate (EC) (Mitsubishi Petrochemical Co., battery grade). The electrochemical measurements were carried out at room temperature after an overnight stand under zero current flow. The carbon electrode lithium intercalation properties were measured galvanostically. A constant current of 0.5 mA (0.375 mA/cm²) was passed through the cell. The specific charge and discharge capacities were determined from the constant-current charge and discharge coulombs of cutoff voltages of 0.00 V for charge and 2.5 V for discharge.

3. Results and discussion

Figs. 1 and 2 show typical examples of the first charge/discharge cycle for the cell Li/mealed carbon fiber with different heat-treatment temperatures using a solvent of mixture of PC–THF(1:1) and EC, respectively. The carbon fibre (A) prepared at a low temperature of 1000 °C shows only a small amount of lithium intercalation in both solvents. On the other hand, the carbon (B) heated up at 2400 °C and (C) at 3000 °C exhibit more lithium intercalation and deintercalation in the
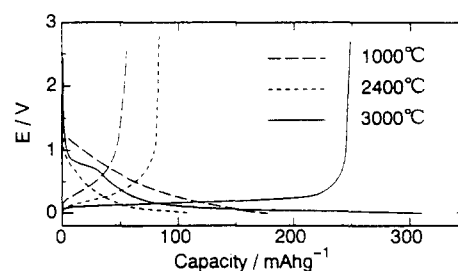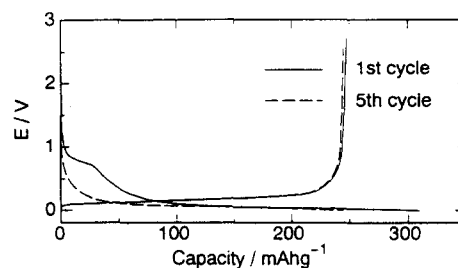
solvent of EC. The decomposition of the solvent in the mixture of PC–THF is observed for the fibers prepared at 2600 and 3000 °C. On the other hand, the carbonaceous materials prepared at 1000 °C show no typical decomposition of the solvent. The charge/discharge specific capacity was calculated to be 240 mAh/g for the carbon heated at 3000 °C and 80 mAh/g for the carbon heated at 2400 °C. In Fig. 3, the charge/discharge cyclic behaviors of the carbon fiber (C) heated at 3000 °C are shown. Within several cycling, no degradation of charge/discharge properties is observed. At the 5th cycle, there was no potential plateau at around 0.9 V, which was observed in the first cycle.

As shown in Fig. 2, the carbon electrode potential profile in the first intercalation of lithium (charging) into the high graphitized carbon (C) (heated at 3000 °C) shows a small shoulder at around 0.9 V in the solvent of EC. The shoulder may correspond to the decomposition of the solvent shown in PC–THF. As well known, the surface of carbon materials have many types of functional groups with oxygen. The functional groups may play a catalytic activity for the decomposition of the solvents. The carbon fiber (C) was treated at room temperature in different types of solution to remove the functional group: (i) 1 M hydrazine for 12 h; (ii) 60% nitric acid for 4 h, and (iii) lithium alcholate for 12 h. Fig. 4 shows the first charging profiles of lithium intercalation for the pretreated carbon (C). Apparently, the shoulder at about 0.9 V is diminished. Our previous paper has suggested that the decomposition of solvent in lithium insertion proceeded at the edges of the graphite structure [6]. The functional
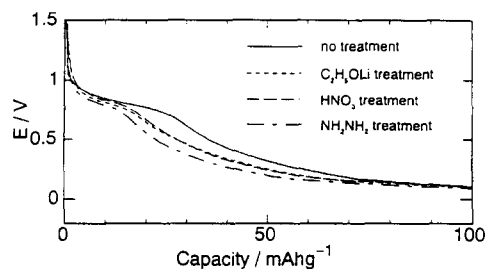
Fig. 4. Effect of pretreatment of carbon fiber prepared at 3000 °C vs. discharge behavior in $LiClO_4$/EC at 0.5 mA.

groups may be concentrated near the edges. For the practical applications of carbon materials as the anode, the powdered materials are more convenient to obtain high packing density than the long size fibers. The powdered carbon materials have a lot of edge parts and the decomposition of the solvent is more significant. Although the pretreatments of carbon materials are not perfect it suggests the possibility to have more stable carbon materials as the anode of secondary lithium batteries by pretreatment.

Carbon materials have large variations in their structure and texture, depending on the starting materials and their preparation processes. Petroleum coke, carbon fiber, pyrolytic carbon, and carbonaceous materials have been extensively examined. In Table 2, Coulomb densities for various types of carbon materials are summarized along with X-ray diffraction data. Table 2 shows that the specific charge capacity does not depend on the crystallinity, which corresponds to the d_{002} spac-

ing. The pyrolytic graphite prepared by thermal decomposition of benzene vapor at about 1000 °C and the thermal decomposition of carbon of a furan-based polymer at 1100–1200 °C, which are carbonaceous materials, show high capacity, and natural graphite has a similar Coulomb capacity compared with the non-graphitic carbon. The crystallinity of carbon materials is only one of the factors affecting the specific charge density, the other properties, such as macroscopic structure, being also important. Recently, quite interesting results have been reported that a long size carbon fiber showed a high specific charge capacity for lithium intercalation that was deteriorated by grinding to a fine powder [12]. In the case of the high crystalline graphite, the lithium insertion properties depended greatly on the character of the electrolyte solvents. Generally, the high crystalline graphite may tend to decompose the solvents such as PC and THF; EC is stable in the lithium intercalation. The decomposition mechanism of the solvents is not yet elucidated. As shown by Imanishi et al. [6] and Morikawa et al. [12], the edges or surface of the graphite structure, where a functional group is concentrated, could play a catalytic activity in the decomposition of solvent. It is quite interesting that carbonaceous materials such as the thermal decomposition of carbon of furfuryl alcohol resin showed a high capacity for lithium intercalation. This result suggests a possibility of some capable positions for lithium intercalation beside of crystalline lithium sites in the LiC_6 structure.

Table 2
Charge capacity and crystal parameters for various carbon materials

Carbon material	Crystal parameter		Capacity (mAh)	Solvent	Ref.
	d_{002} (Å)	L_c (Å)			
PPCA [a] thermally decomposed carbon	Amorphous		146	PC [c]–DME [d]	[6]
FFAR [b] thermally decomposed carbon	3.80		320	PC–DEC [e]	[7]
Meso-phase pitch-based carbon fiber	357	12	50	EC [f]	this work
Benzene thermally decomposed carbon	3.49	100	300	PC	[8]
PAN-based carbon fiber	3.42		80	PC–DME	[6]
Meso-phase pitch-based carbon fiber	3.41	220	80	EC	this work
Pitch-based carbon fiber	3.39	236	180	PC	[9]
Pitch-based carbon bead	3.36	635	250	AN [g]–EC	[10]
Meso-phase pitch-based carbon fiber	3.36	580	240	EC	this work
Artificial graphite	3.357	600	100	AN–EC	[10]
Kish graphite	3.354	1000	0	PC	[9]
Natural graphite	3.35		370	EC	[11]

[a] PPCA = poly-2-chloro-1-phenylacetylene.
[b] FFAR = furfuryl alcohol resin.
[c] PC = propylene carbonate.
[d] DME = 1,2-dimethoxyethane.
[e] DEC = diethyl carbonate.
[f] EC = ethylene carbonate.
[g] AN = acetonitrile.

4. Conclusions

The lithium intercalation into the meso-phase petroleum pitch-based mealed carbon fiber has been examined. The Coulomb capacity of lithium intercalation in the EC solvent increases with increasing preparation temperature of the carbon fiber. In the first insertion of lithium into the carbon (C), a decomposition of the solvents was found. The decomposition reaction in the solvents is diminished by the pretreatment of carbon with acid and hydrazine.

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