JOURNAL OF
POWER
SOURCES

Irreversible capacity loss of graphite electrode in lithium-ion batteries [1]

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Abstract

The irreversible capacity loss of the carbon electrode in lithium-ion batteries at the first cycle is caused mostly by surface film growth . We inspected an unknown irreversible capacity loss (UICL) of the natural graphite electrodes. The charge/discharge behavior of graphite and meso-phase carbon microbeads heat-treated at 2800°C (MCMB28) as the materials of the carbon anode in the lithium-ion battery were compared. It was found that the capacity loss of the natural graphite electrode in the first cycle is caused not only by surface film growth, but also by irreversible lithium-ion intercalation on the new formed surface at the potential range of lithium intercalation, while the capacity loss of the MCMB28 electrode is mainly originated from surface film growth. The reason for the difference of their irreversible capacity losses of these two kinds of carbon material was explained in relation to their structural characteristics.   © 1997 Published by Elsevier Science S.A.

Keywords: Lithium-ion batteries; Lithium/carbon cell, Carbon negative electrodes: Capacity loss, Irreversible capacity loss, Cycling behavior

1. Introduction

In the past years, considerable attention has been devoted to the investigation of rechargeable lithium-ion batteries. Many of the research efforts have been made in the search of suitable carbon materials as the alternative anodes, because lithium batteries containing lithium metal as the negative electrode has a limited cycle life performance. The carbon anode can avoid the formation of lithium dendrites on the surface of anode. So, reliability and safety of the batteries are obtained. In using a carbon anode, much work has still to be done, such as selection of carbons with a large capacity from different kinds of the materials, reducing irreversible capacity losses, as well as understanding complex mechanism of lithium-ion intercalation into carbon [1,2].

In a lithium-ion cell, the lithium supply is limited to the amount originally present in the cathode when the cell is manufactured, there is no excess lithium. In order to get the optimum cell capacity, it is critical that the reversible capacity associated with carbon should be high, but that the irreversible capacity due to lithium loss at the anode should be as low as possible. However, much work has been published on the reversible capacity of different types of carbon, but only in a few papers their irreversible capacity loss been discussed.

In this work, in order to understand on the origin of the irreversible capacity loss, we investigated the charge/dis-charge behavior of natural graphite and MCMB28 (meso-phase carbon microbeads heat-treated at 2800 °C) as well as their structural changes during the electrochemical intercalation by X-ray diffraction (XRD) analysis. We made many studies of first three cycles of an Li/C cell to evaluate irreversible capacity loss in the first cycle.

2. Experimental

The graphite samples are a commercially available native product; MCMB28 (meso-carbon microbeads heat-treated at 2800 °C) was produced from coal-tar pitch at the Osoka Japan Company. The carbon electrodes were fabricated by mixing carbon powder with 5 wt.% polytetrafluoroethylene (PTFE) binder. The mass of carbon materials of electrode was 10–12 mg/cm^2. The paste-like mixture was spread thinly onto a nickel mesh and was pressed at 500 kg/cm^2. Then carbon electrodes were dried in vacuum 120 °C for 24 h.

LiPF$_6$ was purchased from Aldrich. The salt was vacuum dried at an elevated temperature at 60 °C for 48 h to remove moisture. Ethylene carbonate (EC) and diethyl carbonate (DEC) were refluxed, then vacuum distilled twice. The simulated cells were assembled in a glove box filled with argon gas, and consisted of a carbon electrode and a metalic lithium seperated separator. The electrolyte solution used was 1 M LiPF$_6$/EC:DEC (1:1 by volume). The cells were charged and discharged in the potential range of 10 mV–1.2 V versus Li$^+$/Li at a fixed current density of 0.2 mA cm^{-2}.

Electrochemical measurements were performed in a three-electrode system, lithium metal was used as the counter and the reference electrodes. The experiments were carried out by HJ-201B charge/discharge Unit (Hokuto Denko, Japan) and EG&G Model 273 potentiostat/galvanostat. The structure of the carbon materials were characterized by X-ray powder diffraction (Richar, Japan).

3. Results and discussion

The first charge/discharge curves for different carbon electrodes were shown in Fig. 1. There was a voltage plateau from 0.8 to 0.6 V at the first cycle due to the surface film growth. The plateau between 0.25 and 0 V was attributed to the lithium-ion intercalation into carbon electrode. Obviously, the first voltage plateau of natural graphite was more narrow than that of MCMB28. Table 1 shows the charge/discharge data at the first cycle and structure parameters for various carbon materials. The charge/discharge behavior at the first three cycles and irreversible capacity losses at the first cycle by the final analysis to the charge/discharge data for different carbon materials were shown in Table 2. Obviously, the irreversible capacity loss happens mostly at first charge/discharge cycle of the carbon electrode. In the following cycles, the charge/discharge process of the carbon electrodes was almost reversible. The item loss A (3–0.25 V) in Table 2 was referred to the consumed electrical quantity
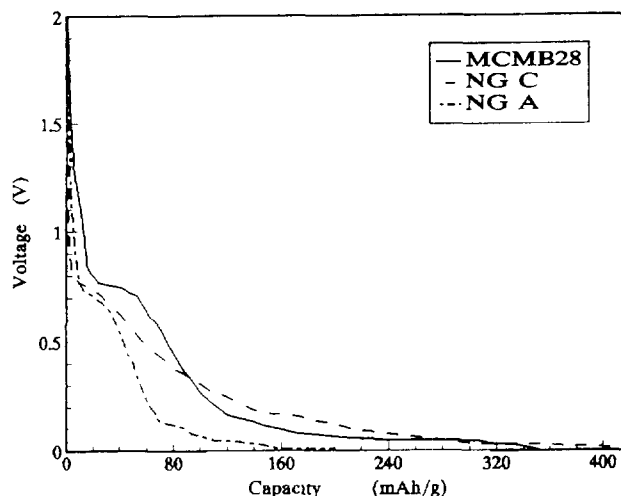

Fig. 1. Discharge curves of different carbons at first cycle, $I_0 = 0.2$ mA/cm^2

from open-cicruit voltage to 0.25 V which represents the irreversible capacity loss due to surface film growth. Loss B occurs in the 0.25–0 V voltage range. Loss C showed the whole capacity loss at the first cycle. The data of NG1* and NG2* were obtained according to data in the literature [3].

The different kinds of capacity loss were compared thoroughly in Fig. 2. Generally, it was considered that the irreversible capacity loss of carbon electrode was completely caused by the surface film growth due to solvent decomposition. On the basis of results shown in Fig. 2, this viewpoint

Table 1
Charge/discharge data and structure parameters of different carbons

Sample	Electrolyte solution	Discharge 1 (mAh/g)	Charge 1 (mAh/g)	Loss (mAh/g)	d_{002} (Å)	L_c (Å)
Petroleum coke	PC/DME	217	171	46	3.439	52
	PC/EC	202	155	47		
Pitch coke	PC/DME	250	174	76	3.466	28
	PC/EC	196	159	37		
MPA-17	EC/DEC	133	100	33		
MCMB28	EC/DEC	353	240	113	3.378	134
NG A	EC/DEC	270	62	208	3.365	415
NG B	EC/DEC	300	163	137	3.365	415
NG C	EC/DEC	417	159	258	3.368	278
NG D	EC/DEC	343	237	106	3.378	194
ELEC.C	EC/DEC	97	95	2		

Table 2
Charge/discharge behavior at the first three cycles and capacity loss at the first cycle for carbons (mAh/g)

Sample	Discharge 1	Charge 1	Loss A (3–0.25 V)	Loss B (0.25–0 V)	Loss C (A+B)	Discharge 2	Charge 2	Discharge 3	Charge 3	Loss total
MCMB28	353	240	107	6	113	253	232	232	230	136
NG B	300	163	53	84	137	153	147	133	130	145
NG C	417	159	120	138	258	185	149	179	147	326
NG D	343	237	59	47	106	210	189	197	173	151
NG 1*	600	275	265	60	325	280	250	220	190	385
NG 2*	462	298	49	115	164	231	168	175	160	244
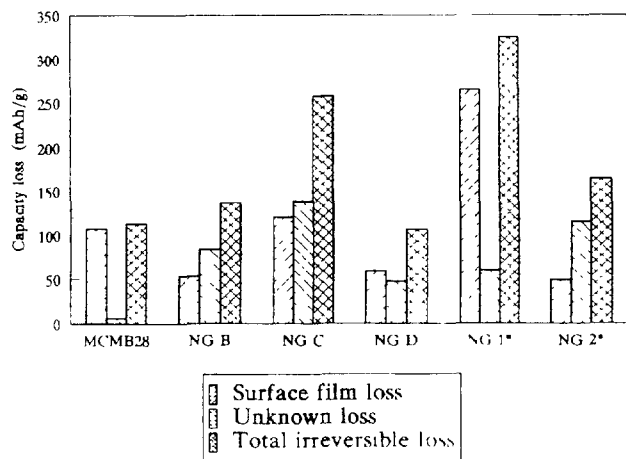
Fig. 2. Irreversible capacity loss of different carbon electrodes at the first cycle.

Fig. 3. XRD spectrum of graphite B: (a) before discharge, and (b) after discharge.

is only suitable for MCMB28. For natural graphite, the surface film capacity loss is less than the whole capacity loss. Therefore, there must exist another kind of the capacity loss for natural graphite. The origin of the second kind of the capacity loss was unknown, thus, it is called here 'unknown irreversible capacity loss' (UICL). UICL occurs in the 0.25–0 V range of intercalating voltage of lithium ions (Fig. 1 and Table 2). We compared the structural characteristics of two kinds of carbon materials and supposed that two elements of structural difference brought about UICL of the natural graphite electrode. The shape of carbon particle is the first element. Natural graphite with a flake structure has a large area of exposed hexagonal plane. The structure of the graphite microcrystal may be split forming new surfaces, on which the delocalized electrons would absorb irreversibly lithium ions. This kind of surface reaction is not same as that of solvent decomposition and is attributed to UICL. XRD measurement indicated that L_c decreased from 415 Å (before) to 215 Å (after the charge/discharge cycle) demonstrating the phenomenon of splitting of the graphite microcrystal along the equatorial surface. The L_c value (215 Å) after the charge/discharge cycle corresponds to the result in Fig. 3(b). The splitting phenomenon of the graphitizing microcrystal along the equatorial surface was reported in Ref. [4]. Fig. 3 shows the XRD spectrum of graphite B before and after discharge. MCMB28 has the unique sphere structure; spherical particles give a close packed arrangement resulting in the electrodes with high density, and low exposed surface area.

The structure parameters of the two kinds of carbon were obtained using the XRD technique. Before the charge/discharge cycle, $d_{002} = 3.378$ Å, $L_c = 55$ Å for MCMB28, $d_{002} = 3.365$ Å, $L_c = 415$ Å for natural graphite B. Natural graphite has a greater L_c and a smaller d_{002} than that for MCMB28; natural graphite will be exfoliated more easily and can provide more exposed layers. The crystallinity of natural graphite is higher than that of MCMB28.
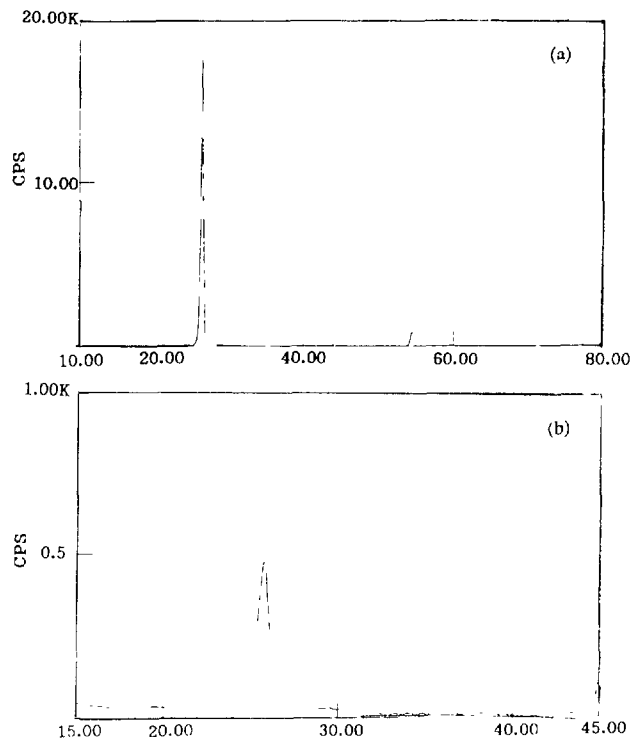
Usually, there are about hundreds of graphite layers in the natural graphite microcrystal. When small lithium ions are intercalated reversibly into or de-intercalated from a graphite crystal, the interlayer distance of the graphite crystal can be extended or compressed reversibly. It is obvious that the expansion for microcrystal with hundreds of layers is more difficult than that with tens of layers. It was reported [5] that when the lithium ions were intercalated into graphite to the extent of LiC$_6$, the interlayer distance (d_{002}) would increase from 3.355 to 3.70 Å and the size (L_c) of a microcrystal with 1000 Å would be also changed to 1100 Å. Therefore, the microcrystal with a great L_c is easy to be split.

4. Conclusions

Irreversible capacity loss of natural graphite consists of a loss due to formation of a surface film and UICL that occurs in the range of lithium-ion intercalating voltage. It is clear that if we wish to reduce the irreversible capacity loss associated with carbon electrodes we need to understand the origin of the irreversible capacity loss: how and where the lithium is lost. It is suggested that irreversible capacity loss would be decreased by selecting natural graphite with small crystallinity and a sphere structure carbon material with a low surface area.

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