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Carbon electrode materials for lithium-ion batteries

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Abstract

Five kinds of carbonaceous materials: graphite, carbon black, coke, petroleum coke, mesophase carbon microbeads in terms of the cell carbon|EC-DEC-LiPF₆|Li, were examined by X-ray diffractometry and impedance spectrum.

Keywords: Lithium-ion batteries; Carbon; Electrodes

1. Introduction

Recently, with the development and market-testing of rechargeable lithium-ion batteries by Nagawa (Sony) [1], research work has been focused on lithiated carbon. As anode, the carbon host should fulfil three kinds of requirements: high capacity, excellent reversibility, and high current density of lithiation. Therefore, among all types of carbon tested, only a few of them have been regarded as a promising anode material for lithium-ion batteries. These carbons are graphitized to a certain degree: graphite, high temperature-treated petroleum cokes and high temperature-treated mesophase carbon microbeads (MCMB), etc. But there are still some problems related to these materials such as electrolyte decomposition that occurs during the first lithiation of carbon. In this paper, we present our results on cycling of lithium/carbon cells, electrochemical impedance spectra of these cells and X-ray patterns of the carbon hosts.

2. Experimental

Five types of carbon: graphite, coke, petroleum coke, carbon black and MCMB, named as sample G, C, P, B and M, respectively, were studied. Carbon electrodes were made directly from the carbon samples mixed with Teflon powder, compressed under pressures of about 0.6 GPa, and dried at 120 °C for 48 h. Testing cells were constructed using these carbon electrodes, Celgard 2400 microporous film and 150 μm thick lithium foil. The electrolyte was 1 M solution of LiPF₆ dissolved

in a 50:50 volume ratio mixture of ethylene carbonate (EC) and diethylene carbonate (DEC).

All cell tests were carried out by a home-made computer-controlled constant current cyclers. The charge and discharge currents were 0.5 mA/cm². All X-ray data of the carbon samples were collected from MXP 18A-HF powder diffractometer. Electrical impedance spectroscopy were measured by Solartron 1174 frequency response analyser with electrochemical interface.

3. Results and discussion

3.1. Lithium/carbon cell cycling

All cells had a plateau at 0.8 V during the first discharge state. However, in the subsequent discharge curves those phenomena have not been observed, as shown in Fig. 1. This means that some electrochemical reactions occur only during the first discharge process. Fong et al. [2] attributed this to the formation of a passivating film on the carbon surface. Our impedance spectroscopy study gave more results on this problem; a detailed discussion is given in Section 3.3.

According to the discharge curves shown in Fig. 1 and discharge capacities listed in Table 1, these samples could be divided into three groups: group A, including samples M and G; group B, including sample P; group C, including samples B and C. The properties of the three groups are different. The discharge capacity of group A is the highest, above 200 mAh/g, at a discharge current 0.5 mA/cm². Their first discharge profiles have

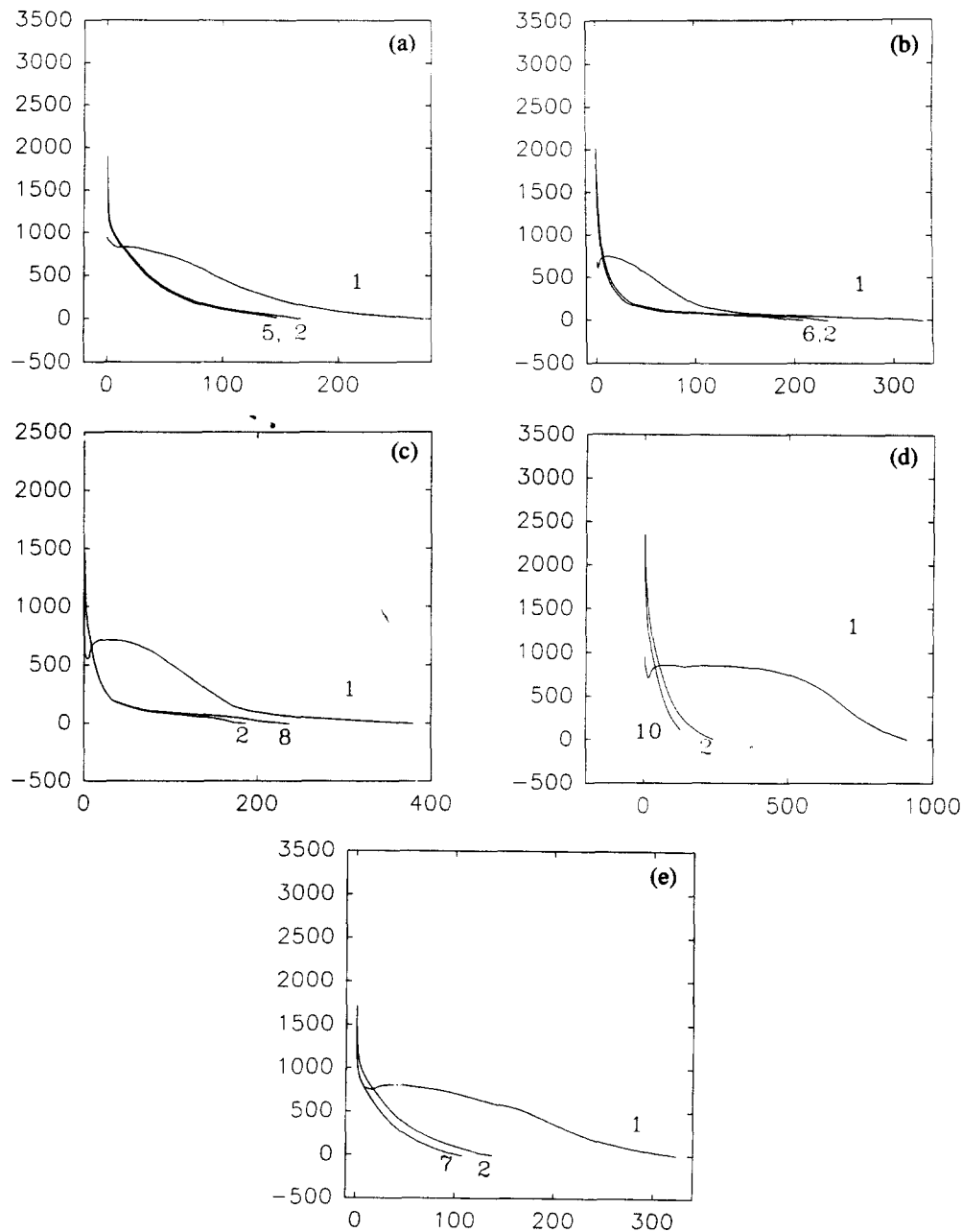


Fig. 1. Discharge profiles of samples: (a) petroleum coke; (b) mesophase carbon microbeam; (c) graphite; (d) carbon black; (e) coke. Vertical axes represent voltage (mV), horizontal axes represent capacity (mAh/g). Discharge current is 0.5 mA/cm^2 . The numbers indicate cycling numbers.

a most narrow plateau around 0.8 V and their discharge profiles have a large plateau around 0.2 V. The samples of group C have the lowest capacity, about 140 mAh/g. Their first discharge profiles have a large plateau around 0.8 V, and the consequent discharge profiles were very steep. The situation of group B was just between group A and group C with a capacity of about 160 mAh/g at a discharge current of 0.5 mA/cm^2 , a small plateau around 0.8 V compared with group A during the first discharge process, and curved subsequent discharge profiles.

What caused these differences among the three groups of materials? The main effect could be attributed to their structures. Following this idea, X-ray diffraction experiments have been carried out.

3.2. X-ray patterns

In order to find the relation between electrochemical properties and the structure of carbon anode, X-ray diffraction studies have been performed. Table 2 lists the results of X-ray diffraction of the studied samples.

Table 1
Capacities of the carbon materials

Sample	Discharge capacity (mAh/g)		
	First	Second	Final (cycle no.)
G	397.7	187.2	237.5 (8th)
M	330.9	235	209 (6th)
P	273.7	168.4	147 (5th)
B	911.7	243.9	127.6 (10th)
C	323.6	138.2	107.5 (7th)

Table 2
X-ray diffraction data

Sample	d_{002}	I/I_0	FWHM ^a
G	3.3556	100	0.23
B	3.4450	100	1.24
P	3.4267	92.4	0.60
	3.3719	100	0.44
C	3.4203	100	1.10
M	3.3606	100	0.28

^a FWHM = full width at half-maximum.

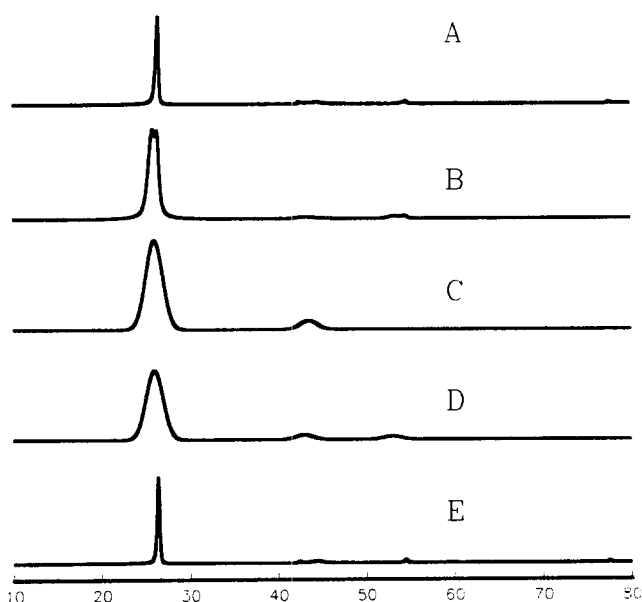


Fig. 2. X-ray diffraction patterns of the materials studied: (A) mesophase carbon microbeam; (B) petroleum coke; (C) carbon black; (D) coke; (E) graphite.

Their X-ray diffraction patterns are shown in Fig. 2. These results indicate that samples G and M are highly graphitized with a very narrow full width at half-maximum (FWHM) and very small d_{002} , which are very close to pure graphite; samples C, B are poorly graphitized with a largest FWHM and d_{002} ; sample P has two d_{002} values: one being close to pure graphite and its FWHM twice as that of sample G, the other being close to sample C and its FWHM is half of that of sample C. Thus, sample P is moderated graphitized.

The shape difference in the discharge profiles shown in Fig. 1 can be explained. Samples G and M are a graphite-type carbon. Their discharge profiles should have a plateau at 0.2 V for the formation of a staged phase during lithiation of graphite [3]. Samples B and C are a petroleum coke-type carbon. The staged phase formed during lithiation was too small. Therefore, their discharge profiles have no plateau at 0.2 V. Sample P was between samples G, M and samples B and C. So its discharge profile was an overlap of one of the two types.

These results coincided with that of the last section, where the samples have been separated into three groups according to their different electrochemical properties, and, here, according to their structure differences. It seems that the differences in electrochemical properties could be attributed to structure differences. But, the relation between these differences is still a problem. More detailed experiments are going on.

3.3. Electrical impedance spectrum

The impedance spectra of the cells studied, before and after cycling, were measured and shown in Fig. 3. It is obvious that the conductivities of the cells have been improved by cycling. One possibility of the improvement in the conductivities is the formation of Li_xC_6 in the carbon electrodes during the cycling processes of the cells. The x value in Li_xC_6 ($0 < x < 1$) reflects the amount of lithium intercalated into the carbon materials. Due to the charge transfer from lithium to the graphite layers, Li_xC_6 ($x > 0$) became a donor-type material with a high conductivity [4]. Thus, the conductivity of the whole cell has been improved. Secondly, this might be associated with the reaction in the first discharge. During the reaction, some new materials have been formed within the interface between electrode and electrolyte. Therefore, after cycling, the conductivity of these cells has been improved.

In order to get a clear answer to this problem, some more experiments were carried out for sample G. The impedance spectra of the cell containing material G were measured before discharge, discharged to 0.8 V, discharged to 0.2 V, and charged to 0.2 V, charged to

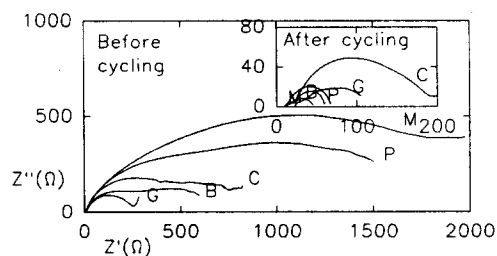


Fig. 3. Impedance spectra of Li/carbon cells studied. P, petroleum coke; M, mesophase carbon microbeam; G, graphite; B, carbon black; C, coke.

2.0 V, respectively. The impedance spectra are shown in Fig. 4. R_0 is the resistance of the electrolyte, lithium anode bulk, and carbon cathode bulk. R_1 and R_2 are the resistances of the interface between the electrolyte and carbon, and of the interface between electrolyte and lithium, respectively. Their values are given in Table 3. As the discharge and charge proceed, resistance R_0 increased. This might be attributed to two factors:

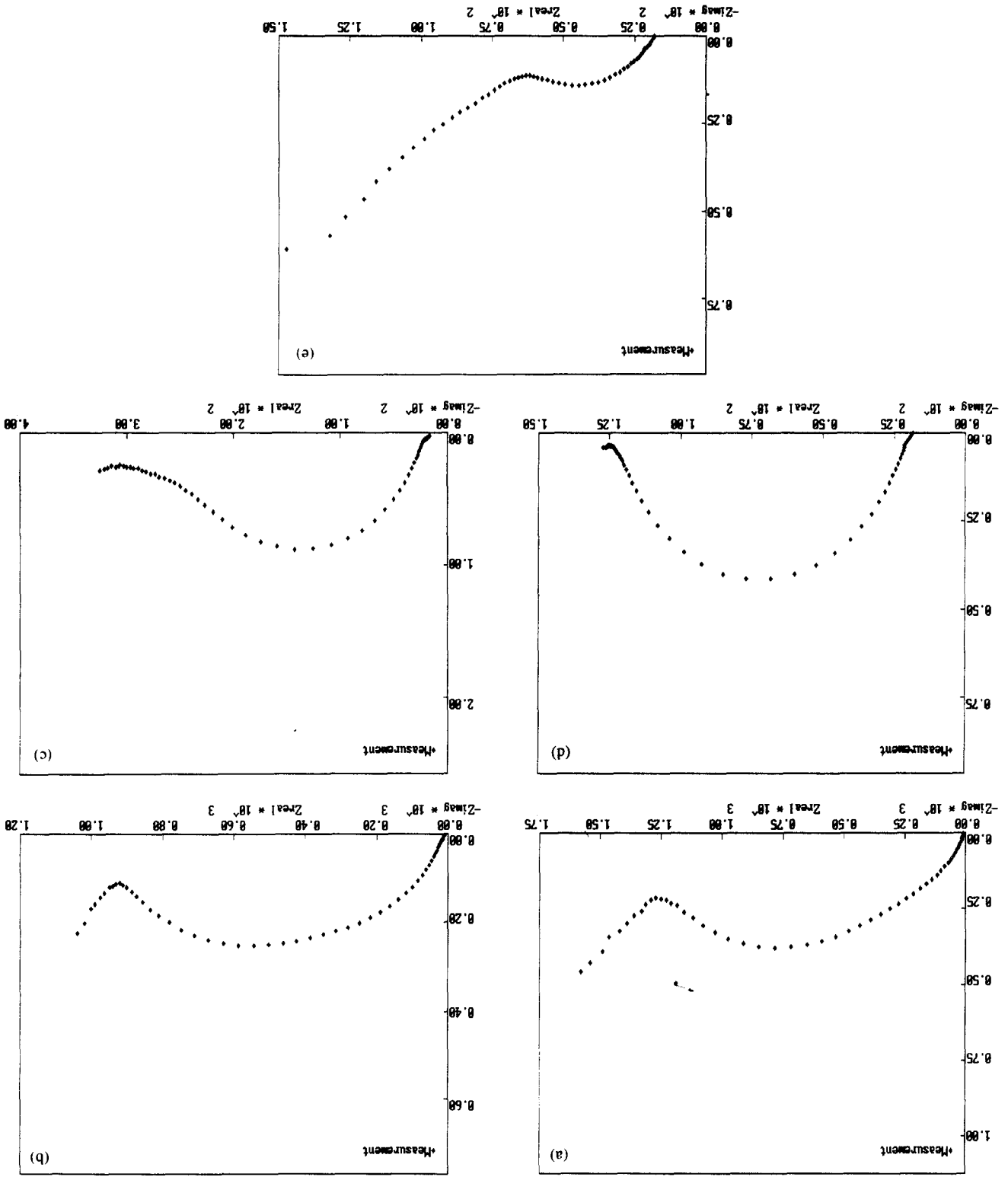


Fig. 4. Impedance spectra of Li/graphite cell: (a) new cell; (b) discharged to 0.8 V; (c) discharged to 0.2 V; (d) charged to 0.2 V; (e) charged to 2.0 V.

Table 3
Analysed resistances of the cell

Condition	R_0 (Ω)	R_1 (Ω)	R_2 (Ω)
New cell	6.87	353.3	820
Discharged to 0.8 V	8.00	353.3	530
Discharged to 0.2 V	14.00	220	460
Charged to 0.2 V	14.80	$R_1 + R_2$ (Ω)	
		106	
Charged to 2.0 V	18.00		41.3

the resistance increase of the electrolyte and the resistance change of carbon bulk. The resistance of lithium bulk did not change during the discharge and charge processes. Thus, the resistance of lithium bulk could be regarded as a constant. Because of the large differences in conductivity between carbon and LiC_6 , the resistance of the carbon electrode would be changed as lithium intercalated into or lithium de-intercalated from the carbon cathode. During discharge, the resistance of carbon electrode bulk should be decreased, and during the charging process, the resistance increased. Thus, the increase in resistance R_0 during the discharge process was mainly caused by the increase

in the electrolyte resistance. During the charge process, the increase in resistance R_0 was probably caused by the increase in the electrolyte resistance and the increase in the carbon electrode bulk resistance. The resistance R_1 did not change during the discharge process to 0.8 V, but the resistance R_2 had a big change. With further discharge, these two resistances R_1 and R_2 decreased very quickly. During charge, the resistances R_1 and R_2 could not be identified individually, but their total value decreased.

Following the above results, some reactions concerning the carbon electrode during the discharge process could be supposed. These reactions caused the decrease in the resistance R_1 and an increase in the resistance R_0 . These reactions caused also a plateau at 0.8 V in the first discharge profiles of the samples.

References

- [1] T. Nagaura, A lithium-ion battery, *4th Int. Rechargeable Battery Seminar, Deerfield Beach, FL, USA, 1990*.
- [2] R. Fong, U. von Sacken and J.R. Dahn, *J. Electrochem. Soc.*, **137** (1990) 2009.
- [3] D. Billaud, F.X. Henry and P. Willmann, *Mater. Res. Bull.*, **28** (1993) 477.
- [4] Y. Sasaki, *J. Mater. Sci.*, **24** (1987) 4431.