



Irreversible capacity of lithium secondary battery using meso-carbon micro beads as anode material

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Abstract

One of the most important problems in lithium secondary battery using carbon anodes is the difference between the charge and discharge capacity, the so-called 'retention'. It is caused partly by the reaction of Li ion with functional groups on the surface of the carbon. Especially, carbons heat-treated at lower temperatures than 1000 °C, have many functional groups such as -COOH and -OH on the surface. As these functional groups are very reactive, Li ions might smoothly react with them in the initial charge-reaction process. In order to evaluate these contributions to the irreversible capacity, the *n*-butyllithium method was applied for meso-carbon micro beads (MCMB) heat-treated at lower temperatures than 1000 °C. As a result, there are some reactive sites such as functional groups and cavities against Li ions except interlayers. However, the irreversible capacity due to the functional groups is a minor factor, and the dominant factor is due to the decomposition of the solvent followed by the film formation on the surface of the carbon electrode or/and the doping of Li species into the reactive sites such as cavities.

Keywords: Secondary lithium batteries; Carbon; Anodes

1. Introduction

Carbon materials have received much attention as the anode material in Li secondary battery. It is pointed out that the difference between the charge and discharge capacity, the so-called 'retention', is one of the most crucial problems. Especially, the retention in the initial charge/discharge process cannot be ignored from the viewpoint of cell manufacture. Several factors are considered to cause such irreversible capacities. The first one is due to the decomposition of the solvent on the carbon electrode. For instance, propylene carbonate is reported to decompose to gaseous propylene and lithium carbonate [1]. The second is due to the reaction between Li ion and the adsorbed water on the carbon. However, this problem will be conquered to some extent by sufficient dehydration of the carbon before the cell assembly. The third is the reaction between Li ion and the functional groups on the surface of the carbon. The carbons heat-treated below 1000 °C, have many functional groups such as -COOH and -OH on the surface. Since these functional groups are very reactive, Li ions would easily react with them in the initial charge-reaction process. A detailed estimation for each factor should be given in order to improve the performance of the carbon electrode.

Armand and co-workers [2,3] firstly proposed to use *n*-butyllithium (*n*-BuLi) to mimic chemically an electrochemical reaction in connection with work on the chromium oxide/graphite electrode. Whittingham and Dines [4] estimated the discharge capacity of several cathode materials of an Li primary battery with this method being in good agreement with the electrochemical behavior of any electrodes except Al₂O₃ and graphite electrodes, to which this method cannot be applied, because Li ion does not chemically intercalate into graphite by means of the *n*-BuLi method. However, the functional groups on the carbon surface are expected to react with *n*-BuLi. Consequently, the reaction of the surface functional groups on carbon can be assessed with this method.

In the present study, *n*-BuLi method was applied to estimate the irreversible capacity caused by the effect of functional groups on the surface of meso-carbon micro beads (MCMB) heat-treated below 1000 °C.

2. Experimental

2.1. Characterization of MCMB

MCMB (Osaka Gas Co., Ltd.), which were heat-treated in the temperature range from 700 to 1000 °C,

were used as the anode material. They were characterized by the elemental analysis with CHN Corder (Yanaco Co., Ltd.) and by electron spectroscopy for chemical analysis (ESCA) with a Shimadzu ESCA 850 spectrometer.

The total cavity amount in carbons in a unit volume (cavity index, CI) was also assessed by the following equation [5]:

$$CI = 1 - \frac{D}{D^0} \times \frac{d_{002}}{d_{002}^0} \times \frac{d_{100}^2}{d_{100}^0{}^2} \times \frac{L_c}{L_c + d_{002}} \times \frac{L_a^2}{(L_a + d_{100})^2} \quad (1)$$

where D , d_{002} , d_{100} , L_c and L_a are the specific gravity, lattice constants of a , c -axes and crystallite sizes of carbons, respectively, and D^0 , d_{002}^0 and d_{100}^0 are those of ideal graphite.

The lattice constants and crystallite size of each carbon were determined by the X-ray diffractometry with silicon as internal standard. Specific gravity was measured at 30 °C with butanol as the solvent (Japanese Industrial Standard R7212).

2.2. Discharge characteristics of the MCMB anode

The working electrodes were manufactured by mixing MCMB obtained with 4 wt.% binder (Daikin, DAIFLON 7-J) dissolved in distilled water. The paste-like mixture of about 1 mg was spread in a thin film on to a nickel mesh (5 mm × 5 mm) and pressed at the pressure of 4 ton cm⁻². It was vacuum-dried for 6 h at 200 °C.

Electrochemical measurements were performed by using three-electrode test glass cells. Lithium metal was used as counter and reference electrodes. The electrolyte used was a 1 M solution of LiClO₄ dissolved in propylene carbonate (PC). The operations on the cell assembly were carried out in a glove box filled with argon gas where both moisture and oxygen concentration were less than 1 ppm.

The cells were charged and discharged in the potential range from 0 to 2 V versus Li/Li⁺ at a fixed current density of 0.1 mA cm⁻² (geometrical surface area of the electrode was 0.5 cm²), using a galvanostat (Hokuto Denko Co., Ltd., HJ-201B). The temperature in the glove box was kept at 25 °C.

2.3. Chemical lithiation by *n*-BuLi

MCMBs heat-treated at several temperatures were mixed with an excess amount of 1.6 M *n*-BuLi/hexane solution (Kanto Chemical Co., Ltd.) and were reacted at room temperature for 3 h. The operations were done in an argon-filled dry glove box where the moisture content was maintained at less than 1 ppm. After the

reaction, the lithium uptake into MCMB was estimated by the titration of the unreacted *n*-BuLi in the solution, method proposed by Gilman and Cartledge [6].

3. Results and discussion

3.1. Characterization of MCMB

Table 1 shows the results of the elemental analyses of MCMBs. It indicates that O/C and H/C atomic ratios decreased with increasing heat-treatment temperature (HTT), and finally reached to almost zero when MCMB was heat-treated at temperatures higher than 900 °C. The C(1s) ESCA spectra of these carbons showed two peaks, the first is a main peak at 284.2 eV attributed to C=C double bond in carbon plane, and the second, a shoulder peak at 285–293 eV, attributed to –COOH, –OH, –CHO groups, etc.

3.2. Discharge characteristics of the MCMB anode

Table 2 shows the charge/discharge capacities and the irreversible capacities of MCMB anodes in the first cycle. It is noteworthy that the discharge capacities of all MCMBs except MC1000 were higher than the theoretical value (372 Ah kg⁻¹) based on the LiC₆ composition. This fact indicates that the discharge reaction mechanism is not simply due to the de-intercalation but also composed of more complicated reactions. As shown in Fig. 1, the discharge curves of these carbons are composed of two regions. The first one is the potential range between 0 and 0.8 V versus Li/Li⁺ and the second is a plateau region of 0.8 to 1.2 V versus Li/Li⁺. A detailed discussion for the discharge mechanism is reported in Ref. [7].

The discharge reaction is considered to consist of the de-intercalation of Li ions out of the carbon (first discharge step) and the de-doping by Li species from cavities in carbon (second discharge step). As can be seen from Table 2, both the discharge and irreversible capacities decreased with increasing HTT of MCMB.

3.3. Chemical lithiation of MCMB

Although Whittingham and Dines [4] reported that the graphite is not chemically intercalated by lithium in *n*-BuLi/hexane solution, MCMBs reacted with *n*-BuLi at ambient temperature. In Fig. 2, the Li/C atomic ratio of the lithiated MCMBs and the O/C ratio of MCMBs are plotted as a function of HTT of MCMBs. One can see that Li/C ratio decreased with increasing HTT. As clarified in Section 3.1., there exist many functional groups such as –COOH and –OH on the surface of MCMB; their reactivity is considered to be very high. Hence, *n*-BuLi would react with these func-

Table 1
Results of the elemental analyses of meso-carbon micro beads

Sample	Heat-treatment temperature (°C)	Chemical composition (wt.%)				Atomic ratio		Cavity amount (cm ³ /cm ³ carbon)
		C	H	O	N	H/C	O/C	
MC700	700	90.9	1.5	0.6	2.12	0.198	0.0175	0.553
MC800	800	92.5	1.0	0.5	1.87	0.130	0.0152	0.534
MC900	900	95.4	0.3	0.6	0.40	0.038	0.0031	0.501
MC1000	1000	96.7	0.3	0.8	0.41	0.037	0.0032	0.481

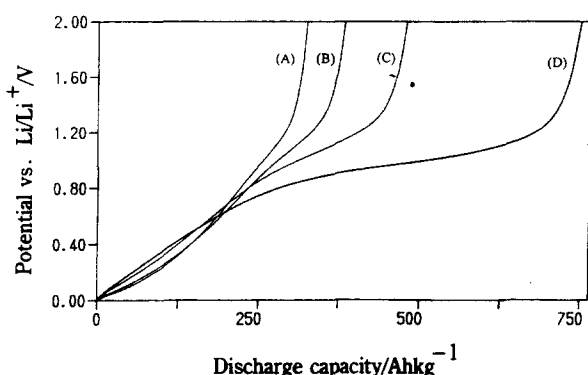


Fig. 1. Discharge capacities of meso-carbon micro beads heat-treated at: (A) 1000 °C; (B) 900 °C; (C) 800 °C, and (D) 700 °C.

Table 2
Results of the charge/discharge capacities of meso-carbon micro beads and chemical lithiation by n-BuLi

Samples	Charge/discharge capacity (Ah kg ⁻¹)		Irreversible capacity (Ah kg ⁻¹)	
	Charge	Discharge	Observed in real cell	Evaluated from n-BuLi method
MC700	1190	750	440	96
MC800	837	485	352	55
MC900	656	382	274	25
MC1000	531	325	206	8

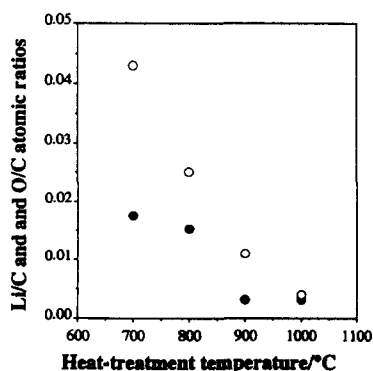
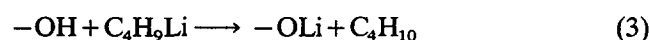
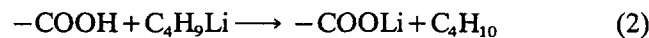


Fig. 2. Effect of the heat-treatment temperature on the (O) Li/C and (●) O/C atomic ratios.

tional groups according to:



In the case of MC1000, the Li/C ratio is in good agreement with the O/C ratio. This fact supports the result of Whittingham and Dines [4] that Li ions do not intercalate into the carbon layer in an n-BuLi/hexane solution. However, the lithium uptake into other MCMBs heat-treated below 900 °C are much larger than the O/C ratio. It indicates that there are reactive sites against n-BuLi other than functional groups and interlayers. We recently reported the evaluation method of cavity amount in carbons using the structural parameters such as lattice constants, crystallite sizes and specific gravity based on Eq. (1) [5]. Column 9 in Table 1 shows the calculated cavity amount in a unit volume. Such cavities are capable of accommodating a large amount of Li species. The higher capacity than the theoretical value is considered to come from the contribution of cavity. Most of the Li species doped into cavities contribute to the second discharge step and the rest remains undischarged in the cavities. In case of the reaction in n-BuLi/hexane solution, although the detailed reaction mechanism has not been clarified yet, some parts of the cavities are considered to contribute to the accommodation of Li species reacting with n-BuLi.

As shown in Table 2, the lithium uptake by the chemical lithiation by n-BuLi expressed in Ah kg⁻¹ unit is considerably smaller than the total irreversible capacity observed in a real cell. Two possible reasons are considered. The first one is due to the different reactivity between the chemical lithiation by n-BuLi and the electrochemical one by Li ions. Secondly, it is considered that the effect of the reaction of functional groups with Li ion on the irreversible capacity is a minor factor. The dominant factors on the irreversible capacity is probably due to the decomposition of the solvent followed by the formation of a film on the surface of carbon electrode or/and the doping of Li species into the reactive sites such as cavities, which cannot be all detected by the n-BuLi method.

4. Conclusions

The evaluation of the reactivity between n-BuLi and carbons revealed that there are some reactive sites such as functional groups and cavities against Li ions, other than interlayers. However, the irreversible capacity due to the functional groups is a minor factor, and the dominant factor is due to the decomposition of the solvent followed by the formation of a film on the surface of the carbon electrode or/and the doping of Li species into the reactive sites such as cavities.

References

- [1] A.N. Dey and B.P. Sullivan, *J. Electrochem. Soc.*, 117 (1970) 222–224.
- [2] H. Djellab, F. Dalard, D. Deroo and M.B. Armand, *J. Power Sources*, 16 (1985) 45–51.
- [3] M.B. Armand, in W. Van Gool (ed.), *Fast Ion Transport in Solids*, North-Holland, Amsterdam, 1973, pp. 665–673.
- [4] M.S. Whittingham and M.B. Dines, *J. Electrochem. Soc.*, 124 (1977) 1387–1388.
- [5] H. Fujimoto, A. Mabuchi, K. Tokumitsu and T. Kasuh, *Carbon*, submitted for publication.
- [6] H. Gilman and F.K. Cartledge, *J. Organomet. Chem.*, 2 (1964) 447–454.
- [7] A. Mabuchi, H. Fujimoto, K. Tokumitsu and T. Kasuh, *7th Int. Meet. Lithium Batteries, Boston, MA, USA, May 1994*.