

# RELATION BETWEEN DISCHARGE CAPACITY OF CARBON ANODE FOR LI SECONDARY BATTERY AND CARBON STRUCTURE

H. Fujimoto, A. Mabuchi, K. Tokumitsu and T. Kasuh  
 Research & Development Center, Osaka Gas Co., Ltd.  
 6-19-9, Torishima Konohana-ku Osaka 554, Japan

## INTRODUCTION

The studies on carbon negative electrodes for rechargeable lithium batteries have been extended quite rapidly in recent years. In the case of graphite anode, the theoretical discharge capacity is considered to be 372Ah/kg based on the composition of stage 1 lithium-intercalated graphite ( $\text{LiC}_6$ ). However, the observed discharge capacity is generally lower than it. The authors proposed a hexagonal crystallite model of carbon and derived the following equations for the number of carbon atoms and lithium atoms in a crystallite and the C/Li atomic ratio, respectively[1].

$$C_n = \frac{3}{2} \left( 1 + \frac{2Lc}{c_0} \right) \left( 1 + \frac{La}{a_0} \right) \quad (1)$$

$$Li_n = \frac{Lc}{6c_0} \left( 1 + \frac{3La^2}{a_0^2} \right) \quad (2)$$

$$\frac{C}{Li} = 6 \left( 1 + \frac{c_0/2}{Lc} \right) \left( 1 + \frac{2a_0(La + a_0/3)}{La^2 + a_0^2/3} \right) \quad (3)$$

where  $La$ ,  $Lc$ ,  $a_0$  and  $c_0$  are the crystallite size of a, b- and c-axes, and lattice constants. Equation (3) reveals that the C/Li atomic ratio decreases with increasing the crystallite size. This is one of the reasons that the observed discharge capacity is lower than 372Ah/kg. However, the observed discharge capacities are still lower than the value estimated from Eq.(3). It will be due to the lack of consideration of turbostratic nature of carbon. The equations above were derived by the postulation of the perfect AB stacking sequence in carbon crystallite and the formation of  $\text{LiC}_6$  with the perfect super lattice of  $p(\sqrt{3} \times \sqrt{3})R30^\circ$  by the slipping of AB-stacking to AA-stacking. Since the carbon layer planes stack randomly along c-axis in fact, the AB stacking area decreases. Hence, the formation of the super lattice would be limited to the AB-stacking area, and the discharge capacity would become lower.

In the present study, the relation between the discharge capacity and the turbostratic nature was investigated based on the theory of Houska & Warren[2].

## PROCEDURE OF ANALYSIS

As mentioned above, Equation (3) was derived based on the hypothesis of the perfect AA stacking of stage 1 lithium-intercalated graphite ( $\text{LiC}_6$ ). In order to estimate the observed discharge capacity of turbostratic carbon, a parameter,  $p_1$  which expresses the degree of graphitization, is introduced. Since the  $p_1$  value means the probability of finding the graphitic relation between the pair of adjacent carbon layer planes, it can be interpreted as the fraction of AB-stacking area. The intercalation reaction by the lithium ion causes the slipping of carbon layer plane from AB-stacking to AA-stacking. If it is postulated that the degree of the turbostratic nature does not change before and after intercalation, the number of lithium atom intercalated is considered to be calculated by the displacement of  $La$  to  $\sqrt{p_1}La$  in Eq.(2). Hence, the C/Li atomic ratio and the discharge capacity in coulomb unit,  $Q$  are expressed by

$$\frac{C}{Li} = 6 \left( 1 + \frac{c_0/2}{Lc} \right) \left( 1 + \frac{(La + a_0/3)^2}{p_1 La^2 + a_0^2/3} \right) \quad (4)$$

$$Q = \frac{F}{6M} \left( \frac{Lc}{Lc + c_0/2} \right) \left( 1 + \frac{p_1 La^2 + a_0^2/3}{(La + a_0/3)^2} \right) \quad (5)$$

where  $F$  and  $M$  are the Faraday constant and the atomic weight of carbon, respectively. If the values of  $La$  and  $Lc$  are enough large against the lattice constant, Eq.(5) are rewritten to

$$Q \approx \frac{F}{6M} p_1 \quad (6)$$

Therefore,  $Q$  is approximately proportional to  $p_1$ .

In the present study, the discharge capacities of MCMBs with different  $p_1$  were measured and were compared with the values estimated from Eqs.(5) and (6).

## EXPERIMENTAL

MCMBs heat-treated at the temperature range of 2000-3000 °C were used for the present analysis. The  $p_1$

values were obtained by the theory of Houska & Warren[2].

Electrochemical measurements were performed by using three-electrode test cells made of glass. Li metal was used as a counter and a reference electrode. Working electrode was fabricated by mixing heat-treated MCMBs with 4 wt% of PTFE binder. The electrolyte used was a 1M LiClO<sub>4</sub> / ethylene carbonate + diethyl carbonate (1:1). The cell assembly was carried out in an Ar glove box where both water and oxygen concentrations were less than 1 ppm. The cells were charged and discharged in the potential range of 0 to 2 V vs. Li/Li<sup>+</sup> at a constant current density of 0.1 mA•cm<sup>-2</sup>.

## RESULTS AND DISCUSSION

Figure 1 shows the discharge curves of MCMBs heat-treated at 2000 - 3000°C. One can see that the discharge capacity of MCMBs increases with increasing the heat treatment temperature. The plateau regions in the range of 0 - 0.25V of the discharge curves are generally considered to be due to the deintercalation reaction. Hence, in order to verify the relation of Eqs.(5) and (6), the capacity ranging from 0 to 0.25V was plotted as a function of  $p_1$  value in Fig.2. As expected from Eq.(6), the capacity was proportional to the  $p_1$  value. It indicates that the lithium storage mechanism in this potential range corresponds to the lithium-intercalation reaction into the graphitic layers with the AB-stacking.

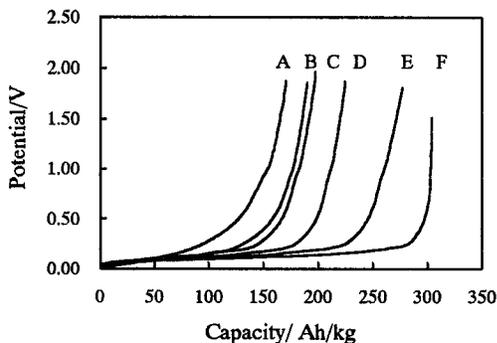


Fig.1 Discharge curves of MCMBs heat-treated at; A:2000°C, B:2200°C, C:2400°C, D:2600°C, E:2800°C, F:3000°C

According to the theory of Houska & Warren, the projected probability function (PPF) can be synthesized from the  $p_1$  value, from which the angle of misorientation can be estimated. Figure 3 is the simulation of the turbostratic nature of carbon layer stacking for MCMBs based on the angle of misorientation estimated from the PPF. In any case, there observed a moiré pattern formed by a pair of the adjacent layer planes exhibiting the coexistence of AB and AA stackings. The compound of

LiC<sub>6</sub> with the in-plane ordering of  $p(\sqrt{3} \times \sqrt{3})R30^\circ$  can be formed only in the area of AB-stacking. As a result, the discharge capacity decreases with decreasing the heat treatment temperature.

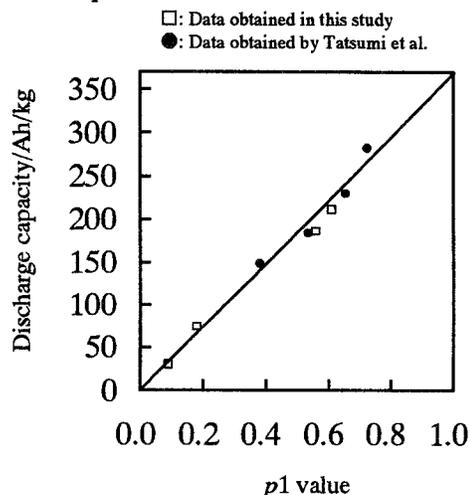


Fig.2 Relation between the  $p_1$  value and the discharge capacity

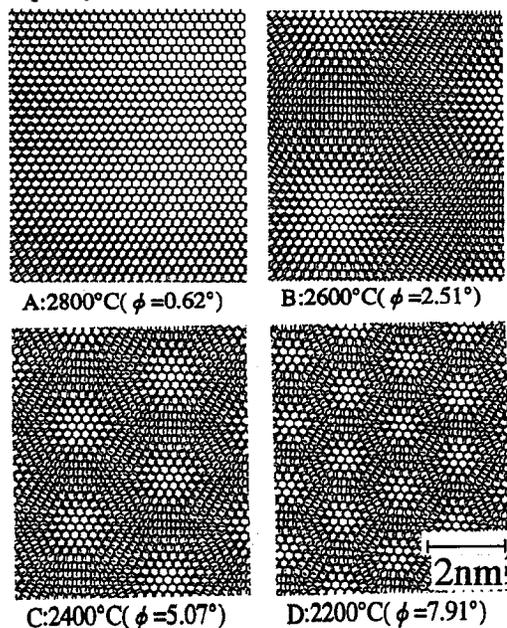


Fig.5 Simulation of the rotational misorientation between the adjacent layer planes for MCMBs heat-treated at different temperatures

## References

1. Fujimoto, H., Mabuchi, A., Tokumitsu, K., Kasuh, T. and Akuzawa, N., *Carbon*, **32**, 193 (1994).
2. Houska, C. R. and Warren, B. E., *J. Appl. Phys.*, **25**, 1503(1954)