



Charge/discharge characteristics of synthetic carbon anode for lithium secondary battery

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Abstract

Recent studies on carbon anodes for lithium secondary batteries have revealed that the electrochemical performances of carbon anodes largely depend on the nature of carbon precursors, heat-treatment condition, structural characteristics of carbons, and so on. In order to clarify the relationship between the carbon structures and electrochemical properties, several kinds of model carbons with different structures were synthesized from three types of pure compounds, acenaphthylene, coronene and phenolphthalein, and their electrochemical characteristics were investigated. As a result, all the model carbons carbonized at 800 °C demonstrate higher capacities than the theoretical one (372 Ah kg⁻¹). Moreover, the structures of the carbons synthesized from the admixtures of acenaphthylene and phenolphthalein were determined by the dominant component, acenaphthylene or phenolphthalein and their discharge capacities were also determined by the corresponding concentration in the carbon mixture.

Keywords: Secondary lithium batteries; Carbon; Anodes

1. Introduction

Carbon materials have recently received much attention as anode materials in lithium secondary batteries because carbon anodes reduce the formation of lithium dendrites on the surface of the anode; a higher reliability and safety are also obtained [1-4]. However, electrochemical performances of carbon electrodes vary largely with different kinds of carbons since they have a variety of structural characteristics which depend on the nature of carbon precursors and the heat-treatment conditions [5].

Carbon materials are generally classified into two categories, the graphitizable and non-graphitizable carbons, both of which can be prepared by the carbonization of hydrocarbons or similar compounds. In the present study, several kinds of model carbons with different structures were synthesized from three kinds of pure compounds and their electrochemical characteristics were investigated in order to clarify the relationship between the carbon structures and electrochemical properties.

Experimental

2.1. Preparation of model carbons

The typical graphitizable carbons were synthesized from acenaphthylene (AN) [6] or coronene (CN), the non-graphitizable from phenolphthalein (PH). The carbons were carbonized under nitrogen in a muffle furnace heated to 800 and 1000 °C at 1 °C min⁻¹ with a soak time of 1 h. Portions of these carbons were graphitized at 2780 °C, after carbonization cooled to 1000 °C. Moreover, a co-carbonization of AN and PH with different weight ratios was carried out in order to obtain a series of the carbons whose structures are between the graphitizable and non-graphitizable carbons. The carbon which was pre-carbonized at 400 °C under 60 kg cm⁻² pressure before carbonization at 800 °C was also synthesized from AN in order to investigate the pressure effect on the carbon structure.

2.2. X-ray diffraction measurement

X-ray diffraction (XRD) patterns of carbons prepared were measured with an XRD RINT-2500 with Cu K α (Rigaku Co., Ltd.). Their lattice constants and crystallite

size were determined with silicon as internal standard. For the carbons carbonized at a temperature lower than 1000 °C, Diamond's method was carried out for the estimation of the crystallite size, L_a value [7].

2.3. Specific gravity measurement

Specific gravity was measured at 30 °C with butanol as solvent (Japanese Industrial Standard R 7212).

2.4. Assessment of the total cavity amount

The total cavity amount in carbons in a unit volume (cavity index, CI) was also assessed by the following equation [8]:

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

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.

2.5. Cell assembly and electrochemical measurement

The working electrodes were fabricated by mixing carbons 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 cells made of glass. Lithium metal was used as counter and reference electrodes. The electrolyte used was a 1 M solution of LiClO₄ dissolved in a 50:50 mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) by volume. All 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 1.2 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.

3. Results and discussion

3.1. Characteristics of model carbons graphitized at 2780 °C

In Table 1 are listed the characteristics of model carbons derived from AN and PH graphitized at

2780 °C and their discharge capacity values. The structural parameters determined by XRD showed that the lamellar structure of the graphitized carbon derived from AN was fairly developed, and the amount of the cavity between the crystallites calculated from Eq. (1) was small. The discharge capacity of the carbon was 316.5 Ah kg⁻¹ which was 85% of the theoretical value (372 Ah kg⁻¹) based on the graphite intercalation compound with an LiC₆ composition. On the other hand, the non-graphitizable carbon from PH, which had the structure characterized by the strongly cross-linked system of randomly oriented small crystallites and large cavity, showed a discharge capacity of 134.4 Ah kg⁻¹. The value was much lower than the theoretical one. This result indicated that the degree of the perfectness in crystallinity correlates with the discharge capacity of the graphitizing carbon at 2780 °C.

3.2. Characteristics of model carbons heat-treated at 800 and 1000 °C

In Table 2 are listed the structural parameters of model carbons carbonized at 800 and 1000 °C and their discharge capacities. The discharge capacities of all model carbons treated at 800 °C were higher than the theoretical one. Although the crystallite size of the carbons from graphitizable precursors of AN and CN were almost same, the discharge capacities were rather dispersed. However, the trends in the cavity amount coincided with those of discharge capacities. On the other hand, the carbons from non-graphitizable precursor of PH, whose cavities were more than other carbons, showed poorer discharge capacities. These results may be interpreted that dischargeable lithium species are not only the intercalate between carbon planes but also the lithium trapped in the cavity, and that the structure with a certain amount of the cavity and a certain degree of the crystallinity are necessary for the carbon with a high capacity.

In order to clarify the contribution of the cavity amount on the discharge capacity, the carbon derived from AN was synthesized by pre-carbonizing under high pressure before carbonization at 800 °C. As shown in Table 3, the cavity amount of the carbon treated under high pressure was less than that of the pristine treated under a normal pressure, although the crystallite size of both carbons are same. The variations in the discharge capacity showed the same trend. This result also supported the hypothesis that the discharge capacity partially depended on the cavity amount.

3.3. Characteristics of carbons synthesized from the mixture of AN and PH

Since it is expected that the carbons containing both a moderate cavity amount and a certain degree of

Table 1
Characteristics of model carbons graphitized at 2780 °C and their discharge capacities

Feedstock compound	XRD			SG ^a (-)	CI ^b (vol.%)	Discharge capacity (Ah kg ⁻¹)
	d_{002} (Å)	L_c (Å)	L_a (Å)			
Acenaphthylene	3.37	823.3	1081.0	2.22	2.6	316.5
Coronene	3.36	559.0	696.0	2.23	2.9	291.9
Phenolphthalein	3.44	25.8	40.0	1.42	49.8	134.4

^a Specific gravity.

^b Cavity index.

Table 2
Characteristics of model carbons carbonized at 800 and 1000 °C and their discharge capacities

Feedstock compound	HTT ^a (°C)	XRD			SG ^b (-)	CI ^c (vol.%)	Discharge capacity (Ah kg ⁻¹)
		d_{002} (Å)	L_c (Å)	L_a (Å)			
Acenaphthylene	800	3.39	21.7	19.7	1.65	49.7	497.4
	1000	3.43	21.8	20.1	1.91	41.0	264.3
Coronene	800	3.43	18.6	18.2	1.69	51.6	675.0
	1000	3.43	20.8	20.2	1.84	43.5	289.3
Phenolphthalein	800	3.55	11.1	19.7	1.54	57.0	385.7
	1000	3.52	20.0	20.0	1.43	55.5	282.1

^a Heat-treatment temperature.

^b Specific gravity.

^c Cavity index.

Table 3
Characteristics of model carbons from acenaphthylene carbonized at 800 °C, (1) pristine; under normal pressure and (2) pressure; pre-carbonization under 60 kg cm⁻² and their discharge capacities

	XRD			SG ^a (-)	CI ^b (vol.%)	Discharge capacity (Ah kg ⁻¹)
	d_{002} (Å)	L_c (Å)	L_a (Å)			
Pristine	3.39	21.7	19.7	1.65	49.7	497.4
Pristine under pressure	3.41	20.5	20.9	1.76	45.9	300.0

^a Specific gravity.

^b Cavity index.

crystallinity show high capacity, a series of carbons carbonized at 800 and 2780 °C were synthesized from a mixture of AN and PH.

In Fig. 1 is shown the relationship between the AN content in a mixture of AN and PH and the discharge capacity. The discharge capacities of the carbons in each series are classified into two groups, their discharge capacities are almost equal to either 100% or 0% AN. None of discharge capacities exceeds the discharge values of the 100% AN carbons. The threshold value of AN ratio is 40 to 50%. The reason why the optimum mixing ratio was not obtained can be found in the structure of the resultant carbons.

Figs. 2 and 3 illustrate the relationship between the mixing ratio of AN and the structural parameters such

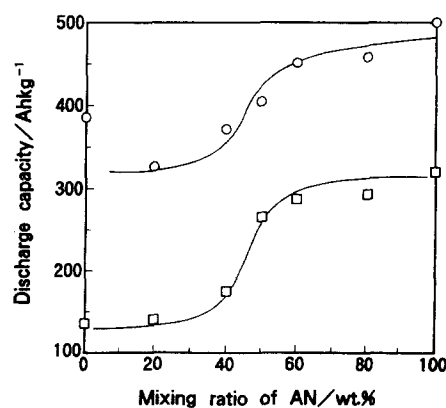


Fig. 1. Relationship between the mixing ratio of AN and discharge capacity of the carbon from the mixture of AN and PH treated at (◇) 800 and (□) 2780 °C.

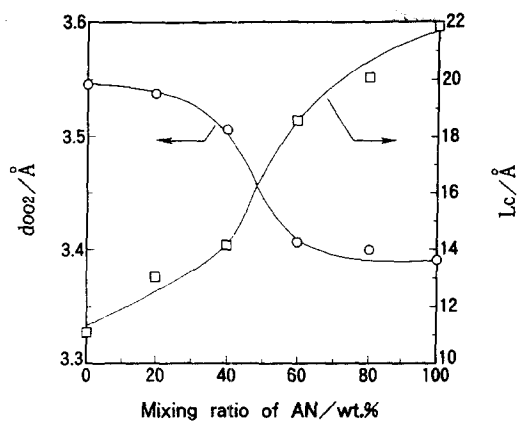


Fig. 2. Relationship between the mixing ratio of AN and structural parameters (○) d_{002} and (□) L_c in the carbon from the mixture of AN and PH carbonized at 800 °C.

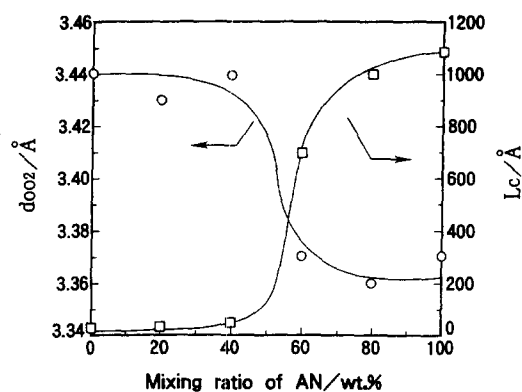


Fig. 3. Relationship between the mixing ratio of AN and structural parameters (○) d_{002} and (□) L_c in the carbon from the mixture of AN and PH graphitized at 2780 °C.

as d_{002} or L_c of carbons carbonized at 800 °C and graphitized at 2780 °C, respectively. The trends in the variations in d_{002} and L_c of the carbons at 800 °C is similar to those in discharge capacities. The pronounced tendency is seen in those of carbons heated at 2780

°C. These facts indicate that the structure of the carbon materials is determined by the dominant component, AN or PH.

Conclusions

1. The discharge capacities of all model carbons carbonized at 800 °C were greater than that of the theoretical one (372 Ah kg⁻¹).

2. The carbons from graphitizable precursors such as AN or CN had well-developed lamellar structure with a small cavity, resulting in the discharge capacity of 85% of the theoretical value based on an LiC₆ graphite intercalation compound.

3. The structures of the carbons synthesized from AN/PH mixtures was determined by the dominant component, AN or PH.

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