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# Electrochemical characteristics of graphite, coke and graphite/coke hybrid carbon as negative electrode materials for lithium secondary batteries

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## Abstract

Electrochemical characteristics of various carbon materials have been investigated for application as a negative electrode material in lithium secondary batteries with long cycle life. Natural graphite electrodes show large discharge capacity in a mixed solvent of ethylene carbonate (EC) and diethyl carbonate (DEC). However, their charge/discharge performance is largely influenced by electrolytes. There is a possibility that a rapid rise in the discharge potential of the natural graphite electrode at the end of the discharge would cause a side reaction such as decomposition of the electrolyte because of an unequal reaction over an electrode. In order to improve the cycle performance of natural graphite electrodes, mixtures of graphite and coke electrodes are prepared by adding coke to natural graphite. It is found that the mixture of graphite and coke electrode shows a better cycle performance than that of a natural graphite or coke electrode. The deterioration ratio of the mixture of graphite and coke negative electrode measured by using AA-type test cells is 0.057%/cycle up to the 500th cycle. The mixture of graphite and coke is a promising material for a negative electrode in long-life lithium secondary batteries for energy storage systems because of its excellent cycle performance and large discharge capacity. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Lithium secondary batteries; Negative electrode; Carbon; Graphite; Coke; Mixture of graphite and coke

## 1. Introduction

Recently, there has been a considerable demand for the development of long-life lithium secondary batteries for dispersed type energy storage systems, such as a home-use load leveling system [1]. Lithium secondary batteries for energy storage systems need to show a much longer cycle life than those used for consumer electrical devices to achieve long-term use of as long as 10 years with a charge/discharge cycle once a day. Carbon materials have attracted great interest and are used as negative electrodes for consumer lithium ion batteries because they are more advantageous than lithium metal negative electrodes in terms of cycle performance and safety [2–6]. For use as lithium secondary batteries in energy storage systems, however, it is necessary to develop carbon negative electrodes that show much superior rechargeability to those now in consumer batteries [7,8]. We considered it to be important to

investigate the rechargeability of various carbon materials in detail in terms of the relationships between the physical and chemical properties of carbon materials and their charge/discharge characteristics. In this study, the charge/discharge characteristics of various kinds of graphite, coke and some mixtures of graphite and coke were investigated in three-electrode test cells and AA-type test cells. The mixtures of graphite and coke are called “hybrid carbon”, as explained later.

## 2. Experimental

Various kinds of natural graphite, artificial graphite, coke and mixtures of graphite and coke were examined as negative electrode materials. Table 1 shows the physical and chemical properties of carbon materials used in this study. Lattice parameters were calculated from patterns measured by a powder X-ray diffraction (XRD) method. The XRD patterns were obtained with an X-ray diffractometer using Cu K $\alpha$  radiation. Average particle diameters were obtained

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Table 1  
Physical and chemical properties of natural graphite, artificial graphite and coke used in this study

Materials	Purity (%)	Real density (g cm <sup>-3</sup> )	Particle size (μm)	Interlayer spacing <i>d</i> <sub>002</sub> (Å)	Crystallite size along <i>c</i> -axis, <i>L</i> <sub>c</sub> (Å)
Natural graphite A	99.6	2.25	9	3.35	>1000
Natural graphite B	97.0	2.25	22	3.35	>1000
Natural graphite C	98.7	2.25	23	3.35	>1000
Artificial graphite A	99.9	2.25	8	3.36	470
Artificial graphite B	98.6	2.25	10	3.37	280
Coke A	99.9	1.96	16	3.44	32
Coke B	99.8	2.13	12	3.46	20
Coke C	99.9	2.07	14	3.47	49

by grading analysis done with a laser diffraction particle size analyzer (Shimadzu, SALD-2000). The specific surface areas were measured by a BET method using a surface area analyzer (Micromeritics, Model-1200). The mixture of graphite and coke was prepared by adding coke A to natural graphite A. The charge/discharge characteristics were measured by using three-electrode test cells with lithium metal as a counter and a reference electrode over a potential range of 0.0–1.0 V. As electrolyte solutions, we used EC/DEC or dimethoxyethane (DME) (1:1 by volumetric ratio) containing 1.0 mol dm<sup>-3</sup> of lithium hexafluorophosphate (LiPF<sub>6</sub>).

Lithium cobalt oxide, LiCoO<sub>2</sub>, was used as a positive electrode material of AA-type test cells (diameter 14.2 mm and height 50.0 mm). The charge/discharge cycle tests of AA-type cells were carried out at a constant current of 0.2 A over a voltage range of 2.7–4.2 V.

### 3. Results and discussion

#### 3.1. Charge/discharge characteristics of carbon negative electrode

Fig. 1 (a) and (b) show discharge curves of carbon negative electrodes in EC/DME and EC/DEC, respectively. EC is known to be a superior solvent for the charge and discharge of carbon materials [9,10]. It is also well known that some carbonate compounds and ether compounds with

low viscosity are excellent solvents for non-aqueous electrolytes as they provide increased ionic conductivity for electrolytes, including EC. In this study, DME and DEC were selected as typical solvents of this type. Natural graphite and artificial graphite electrodes showed larger discharge capacities than coke electrodes in EC/DEC. The discharge capacities of carbon materials in EC/DEC depended upon their crystallinity. The carbon materials with larger crystallite size and smaller interlayer spacing, which implies higher crystallinity, showed larger discharge capacities. However, discharge capacities of graphite materials were much smaller in EC/DME. On the other hand, coke materials showed similar discharge capacities in both electrolytes. Natural graphite A showed the largest discharge capacity of 370 Ah kg<sup>-1</sup> with a very flat discharge curve in EC/DEC. The differences between the discharge capacities of natural graphite A, B and C were considered to be due to the materials' degree of purity, but a more detailed investigation is required.

Fig. 2 shows the relationship between the initial charge/discharge efficiency and the BET specific surface area of each carbon material. The initial charge/discharge efficiencies of graphite electrodes were also lower in EC/DME than those in EC/DEC. The initial charge/discharge efficiencies of the coke electrodes were quite similar in both electrolytes. The high reactivity of the graphite material with the electrolyte was considered to cause the deterioration of the initial discharge capacity in EC/DME. It was also found that the

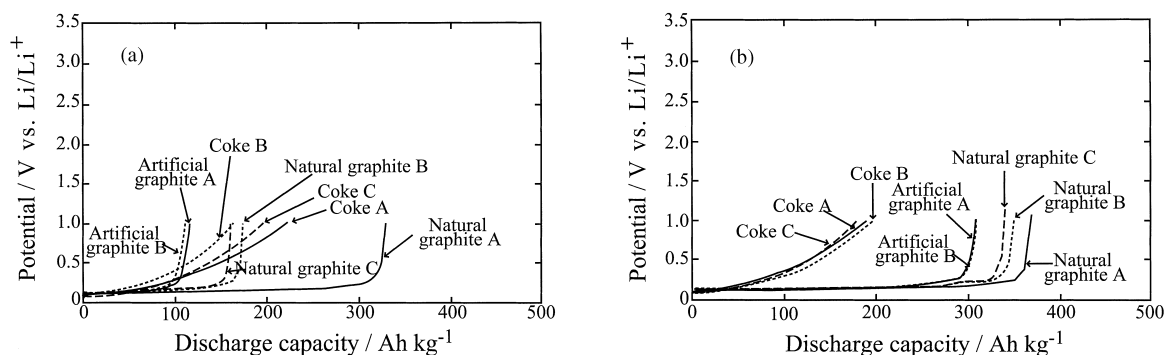


Fig. 1. Discharge curves of carbon electrodes at a rate of 0.25 mA cm<sup>-1</sup> at 25°C (a) using 1 mol dm<sup>-3</sup> LiPF<sub>6</sub>/EC + DME, (b) using 1 mol dm<sup>-3</sup> LiPF<sub>6</sub>/EC + DEC as an electrolyte.

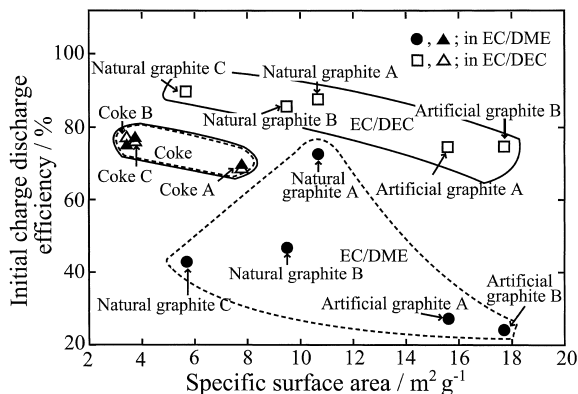


Fig. 2. Relationship between initial charge/discharge efficiency and specific surface area of carbon materials.

initial charge/discharge efficiency became lower in EC/DEC when using carbon materials with larger specific surface areas. From these results, it was concluded that the charge/discharge characteristics of graphite materials were largely influenced by the electrolyte because of a side reaction such as decomposition of electrolytes [9,10]. Consequently, EC/DEC was evaluated as a suitable electrolyte for the graphite electrode.

In order to examine charge/discharge cycle performance of the graphite and coke electrodes, AA-type test cells were used. Natural graphite A was selected from graphite materials as a negative material for AA-type test cells because it showed the largest discharge capacity in both electrolytes. Coke A, B and C showed almost the same discharge capacity in EC/DEC. From the results in EC/DME, coke A was selected from coke materials. Fig. 3 shows the cycle performance of AA-type test cells using natural graphite A and coke A as negative electrode materials. Test cells using natural graphite A showed a larger discharge capacity than that using coke A during all cycles up to the 1000th cycle. The deterioration ratios of the discharge capacity at certain cycle periods are shown in Table 2. The deterioration ratio of the discharge capacity was changed according to the charge/discharge cycle periods. Natural graphite A and coke A

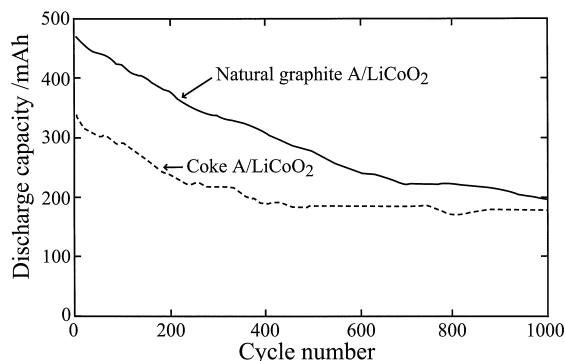


Fig. 3. Charge/discharge cycle performance of AA-type test cells using LiCoO<sub>2</sub> and natural graphite A and coke A at a charge/discharge current of 0.2 A.

Table 2

Deterioration ratios (%/cycle) of the discharge capacity of AA-type test cells using LiCoO<sub>2</sub> with natural graphite A and with coke A at various cycle periods

Cycle periods	1–100	100–500	1–500	500–1000	1–1000
Natural graphite A	0.089	0.088	0.083	0.054	0.057
Coke A	0.170	0.086	0.091	0.016	0.050

showed different tendencies in the change of deterioration ratio, which indicated that these materials had different deterioration mechanisms. In the case of coke A, the deterioration ratio was very large during the initial 100 cycles. However, the deterioration ratio of the coke A electrode was very low after the 500th cycle. On the other hand, the deterioration ratio in discharge capacity of graphite A from the 500th to 1000th cycle was larger than that of coke A. It is considered that the large potential change of natural graphite A at the end of discharge caused side reactions and heterogeneous reactions. Therefore, it is expected that the deterioration ratio in the discharge capacity of natural graphite A during a long cycle life test would be depressed by adding coke.

### 3.2. Charge/discharge characteristics of mixture of graphite and coke negative electrode

Fig. 4 shows the discharge curves of the natural graphite, coke and mixture of graphite and coke electrodes. The discharge capacities of the mixture of graphite and coke electrodes, prepared by mixing natural graphite with coke at certain weight ratios, did not simply equal the discharge capacities of graphite and coke multiplied by their proportions in the mixtures. Accordingly, we refer to the mixtures of graphite and coke as “graphite/coke hybrid carbon”, in this study because we considered that there is a mutual interaction between the graphite and coke caused by the change in electrical conductivity and other factors. The most significant feature of the mixture of graphite and coke negative electrode was that the change in discharge potential

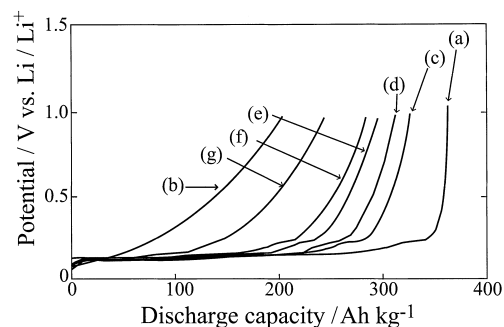


Fig. 4. Discharge curves of (a) natural graphite, (b) coke and mixtures of graphite and coke, (c) natural graphite/coke = 8/2, (d) natural graphite/coke = 7/3, (e) natural graphite/coke = 6/4, (f) natural graphite/coke = 5/5, and (g) natural graphite/coke = 2/8 at a rate of 0.25 mA cm<sup>-2</sup> at 25°C.

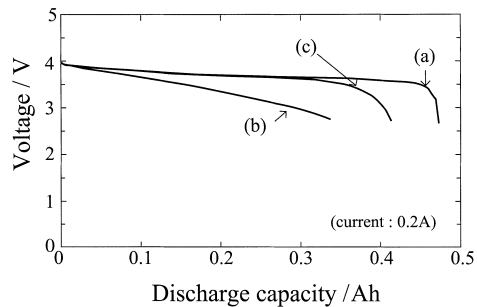


Fig. 5. Discharge curves of AA-type test cells using  $\text{LiCoO}_2$  and (a) natural graphite, (b) coke and (c) mixture of graphite and coke (natural graphite/coke = 8/2) at a discharge rate of 0.2 A.

at the end of the discharge was smaller than that of natural graphite. The slope of the discharge curve of the mixture of graphite and coke (natural graphite/coke = 8/2) at 0.8 V near the end of discharge ( $0.05 \text{ V kg Ah}^{-1}$ ) was only the third of that of the natural graphite ( $0.16 \text{ V kg Ah}^{-1}$ ).

Fig. 5 shows the discharge curves of AA-type test cells using natural graphite, coke and a mixture of graphite and coke (natural graphite/coke = 8/2). Test cells using the mixture of graphite and coke negative electrodes also showed intermediate discharge characteristics between those using natural graphite and coke. Fig. 6 shows the results of charge/discharge cycle tests. The mixture of graphite and coke negative electrodes showed the smallest deterioration ratio (0.057%/cycle) in the discharge capacity up to the 500th cycle. It was found that by adding coke to natural graphite the initial discharge capacity became lower, but cycle performance became much better. The natural graphite with highest crystallinity among carbon materials showed the largest discharge capacity. However, there is a possibility that a rapid rise in the discharge potential of the natural graphite electrode at the end of the discharge would cause a side reaction such as decomposition of the electrolyte because of an unequal reaction over an electrode. Thus, it was thought that the reactivity of the natural graphite

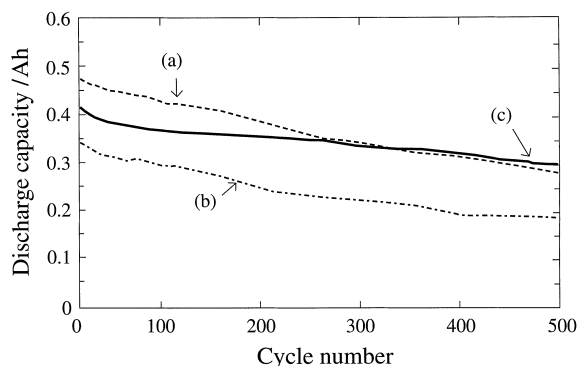


Fig. 6. Charge/discharge cycle performance of AA-type test cells using  $\text{LiCoO}_2$  and (a) natural graphite, (b) coke and (c) mixture of graphite and coke (natural graphite/coke = 8/2) at a discharge rate of 0.2 A.

electrode with the electrolyte at the end of the discharge could be reduced by the addition of coke, and the mixture of graphite and coke electrode showed a superior cycle performance to the natural graphite electrode.

#### 4. Conclusions

The charge/discharge characteristics of various carbon materials with different crystallinities and physical and chemical properties were examined in EC/DEC and EC/DME. The discharge capacities of carbon materials in EC/DEC depended on their crystallinity. Natural graphite showed the largest discharge capacity among the carbon materials used in this study. In order to improve the cycle performance of natural graphite, the mixture of graphite and coke electrode was investigated. As a result, it was found that the mixture of graphite and coke electrode showed a superior cycle performance to the natural graphite electrode. It was thought that the excellent cycle performance of the mixture of graphite and coke electrode could be attributed to a repression of a side reaction between the graphite and the electrolyte owing to the small change of the discharge potential at the end of discharge. Mixture of graphite and coke was found to be a promising material for long-life lithium secondary batteries because it showed both a high capacity and an excellent rechargeability.

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#### References

- [1] T. Hazama, M. Miyabayashi, H. Ando, R. Ishikawa, S. Furuta, H. Ishihara, J. Shonaka, *J. Power Sources* 54 (1995) 306.
- [2] R. Kanno, Y. Takeda, T. Ichikawa, K. Nakanishi, O. Yamamoto, *J. Power Sources* 26 (1989) 535.
- [3] M. Mohri, N. Yanagisawa, Y. Tajima, H. Tanaka, T. Mizuki, H. Wada, *J. Power Sources* 26 (1989) 545.
- [4] N. Imanishi, S. Ohashi, T. Ichikawa, Y. Takeda, O. Yamamoto, *J. Power Sources* 39 (1992) 185.
- [5] B. Scrosati, *J. Electrochem. Soc.* 139 (1992) 2776.
- [6] M. Fujimoto, K. Ueno, T. Nohma, M. Takahashi, K. Nishio, T. Saito, in: *Proceedings of the Symposium on New Sealed Rechargeable Batteries and Supercapacitors*, 1993, p. 280.
- [7] H. Kurokawa, T. Nohma, M. Fujimoto, T. Maeda, K. Nishio, T. Saito, in: *Ext. Abstr. of the International Workshop on Advanced Batteries*, Japan, 1995, p. 332.
- [8] T. Maeda, H. Kurokawa, M. Fujimoto, T. Nohma, K. Nishio, in: *Ext. Abstr. of 36th Meeting on Battery Symposium*, Japan, 1995, p. 121.
- [9] M. Fujimoto, Y. Kida, T. Nohma, M. Takahashi, K. Nishio, T. Saito, *J. Power Sources* 63 (1996) 127.
- [10] M. Fujimoto, Y. Shoji, Y. Kida, R. Ohshita, T. Nohma, K. Nishio, *J. Power Sources* 72 (1998) 226.