

Short communication

On the cycle behavior of various graphitic negative electrodes in a propylene carbonate-based electrolyte for lithium ion batteries

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Abstract

We investigated the negative electrode behaviors of several mesocarbon microbeads (MCMB) heat-treated over 2000 °C in 1 M LiPF₆/propylene carbonate (PC) electrolyte under various charge–discharge current densities. A higher current density provided improved (a highly graphitized MCMB)/Li cell cycle stability as lower graphitized MCMB electrode was used. In addition, two pre-cycles at a higher current density also provided better cycle stability in subsequent cycles at a lower current density. For example, MCMB 6 μm in diameter and heat-treated at 2800 °C cycled stably at a current density of 0.2 mA cm⁻² after 2 pre-cycles at 0.5 mA cm⁻². A higher current density may provide an adequate surface film at the first charging.

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1. Introduction

The availability of graphite and graphitic carbons has enabled the development of high voltage batteries with high cycle stability and safety when used as negative electrode materials. Nowadays, commercial lithium ion batteries contain either graphite or graphitic carbons as a negative electrode. Graphite exhibits a reversible capacity as large as 372 mAh g⁻¹ and is superior to other carbons or candidate materials for negative electrodes in terms of its low irreversible capacity at first cycle and its flat and low potential profile. However, such graphitic carbons suffer from the limitation of electrolyte solutions available. For example, when an electrolyte containing propylene carbonate (PC) is selected, the decomposition of the electrolyte occurs as a main reaction, and the intercalation of a lithium ion into graphite does not occur [1–6]. This is one of the main reasons why various mixed solvents based on ethylene carbonate (EC) are utilized for the electrolyte solvent of commercial lithium batteries.

Several studies have revealed what occurs during the lithium intercalation process in PC-based electrolytes. For example, Inaba et al. reported from observations by a scanning tunneling microscope (STM) that lithium ion solvates

with PC exfoliates and ruptures a graphene sheet, since an appropriate surface film prevents fast exfoliation in EC-based electrolytes [7]. The difference in surface reactions on lithium intercalation between EC- and PC-based electrolytes has also been investigated using spectroscopic methods [8,9]. Several methods to modify the cycle stability of the graphite electrode in PC-based electrolytes have also been proposed [10–14]. These methods seem very effective in improving the cycle stability of graphitic carbons in PC-based electrolytes; however, most of them require additives to the electrolyte or the electrode surface, and these additives may decrease the charge–discharge performance of the graphite electrode.

In the present study, the authors test the hypothesis that the cycle stability of graphitic negative electrodes in PC-based electrolyte could be improved by controlling the lithium intercalation rate into the graphitic layers. This process does not require any additives to either the electrolyte or the electrode surface.

2. Experimental

The mesocarbon microbeads (MCMB) used in the present study had sphere diameters of 6 or 25 μm and were heat-treated at 2000, 2200, 2400, 2600, and 2800 °C under an Ar flow. Several crystal parameters of these MCMB were estimated from the X-ray diffraction data. Powder

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X-ray diffraction analyses were made by a Rigaku Geiger-flex diffractometer using a Cu K α beam (voltage: 30 kV, current: 40 mA). The distance at (002) layers, d_{002} , was determined using Bragg's equation, $d_{002} = \lambda/2 \sin \theta$, and the thickness of stacking along the c -axis, L_c , was estimated using Scherrer's equation, $L_c = 0.9\lambda/b \cos \theta$. Here, λ is the wavelength of the Cu K α beam, θ is the diffraction angle of a (002) peak, and b is the half width of a (002) peak. The probability of hexagonal stacking P_1 was also calculated for various MCMB according to the procedure of Houska and Warren [15].

Electrode films were fabricated as follows: MCMB were ground 15 min and then mixed with poly(vinylene difluoride) (PVdF; Kureha Chemical). The PVdF ratio was 5 wt.%. The mixture was stirred in 3 ml of N -methylpyrrolidinone (NMP) to make a slurry solution. This slurry was pasted on Cu foil (0.2 mm thick), the NMP was evaporated, and then the composite electrode film was found on the Cu foil.

We measured the properties of the resulting films as negative electrode materials with a constant-current charge–discharge cycle test using two-electrode SS coin cells and lithium foil as a counter electrode. Both electrodes were cut to 15 mm in diameter, and approximately 6 mg of active material was present on each working electrode. Both electrodes, 5 ml of electrolyte, and a porous polypropylene separator (Celgard #2500) were packed into a closed stainless cell and used for the cycle test. The electrolyte used was 1 M LiPF $_6$ /EC + DMC (1:1 in volume) or 1 M LiPF $_6$ /PC (Tomiya Pure Chemical Co., battery grade). The charge and discharge current was 0.5 or 0.2 mA cm $^{-2}$, depending on the geometric surface area of the working electrode, and thus these rates are to be interpreted as approximately $C/2$ and $C/5$, respectively. The cut-off voltage was 1.5–0.0 V. The Coulombic efficiency during the charge–discharge process of the MCMB negative electrodes was calculated through the ratio of discharge (lithium de-intercalation) capacity to charge (lithium intercalation) capacity in each cycle.

We prepared symmetrical cells to measure the impedance spectrum, using the following procedure. Two identical two(-)electrode test cells consisting of MCMB and

lithium metal electrodes were cycled under the identical constant-current condition. After the discharge of the 10th cycle, the MCMB electrodes were removed from the cells and re-constructed into one symmetric cell with the same electrolyte.

3. Results and discussion

Several structural parameters and reversible capacities (in 1 M LiPF $_6$ /EC + DMC) of various MCMB electrodes are summarized in Table 1. As reported previously, MCMB having higher crystallinity showed a larger reversible capacity in EC-based electrolyte and more closely approached the theoretical capacity of graphite (372 mAh g $^{-1}$) [16]. The cycle behaviors of these MCMB electrodes in 1 M LiPF $_6$ /PC electrolyte can be organized clearly into two categories: in one case the charge–discharge cycles are observed just as they are with an EC-based electrolyte and in the other case a large charging plateau and no discharge plateau appear even at the first cycle. The cycle stabilities of each type of MCMB electrode are also included in Table 1 as signs. It is well known that a highly graphitized negative electrode does not cycle in PC-based electrolyte, as shown in Table 1. For example, an MCMB electrode (25 μ m) heat-treated at 2800 $^{\circ}$ C did not cycle in 1 M LiPF $_6$ /PC at either 0.5 or 0.2 mA cm $^{-2}$, and an MCMB (6 μ m) heat-treated at 2800 $^{\circ}$ C showed similar behavior at a current density of 0.2 mA cm $^{-2}$.

In addition, it should be noted that the current density depended on the cycle stability of MCMB electrodes in PC-based electrolyte. The MCMB (6 μ m) heat-treated at 2800 $^{\circ}$ C, which had not cycled at a current density of 0.2 mA cm $^{-2}$, cycled at 0.5 mA cm $^{-2}$ even in LiPF $_6$ /PC electrolyte. It is clear that a high-rate charge–discharge of a MCMB electrode having graphitic structure exhibits a better cycle behavior in PC-based electrolyte.

In order to clarify the effect of a large current charge–discharge, we changed the current density after 2 charge–discharge cycles of some graphitic MCMB electrodes in 1 M LiPF $_6$ /PC. Fig. 1 shows the plots of discharge capacities

Table 1
Structural parameters and charge–discharge properties of various MCMB negative electrodes

Sphere size (μ m)	HTT ($^{\circ}$ C)	d_{002} (nm)	L_c (nm)	L_a (nm)	P_1	Reversible capacity in 1 M LiPF $_6$ /EC + DMC (mAh g $^{-1}$)	Cycle stability in 1 M LiPF $_6$ /PC
6	2000	0.344	17			110	**a
6	2200	0.343	18	32	0.14	118	**
6	2400	0.340	17	37	0.41	166	**
6	2600	0.339	16	42	0.56	181	*b
6	2800	0.338	14	46	0.64	238	*
25	2200	0.345	17		0.08	142	**
25	2400	0.340	29	42	0.44	242	–c
25	2600	0.338	27	52	0.67	248	–

^a Cycles were possible at the current density of both 0.2 and 0.5 mA cm $^{-2}$.

^b Cycles were possible only at the current density of 0.5 mA cm $^{-2}$.

^c Cycles were impossible at the current density of both 0.2 and 0.5 mA cm $^{-2}$.

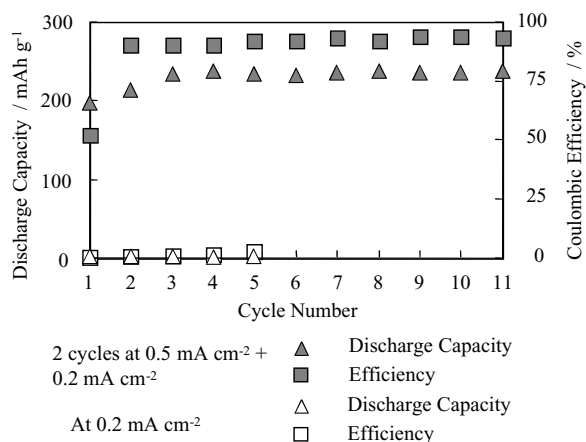


Fig. 1. The discharge capacity and Coulombic efficiency plots vs. the charge–discharge cycle number on MCMB 6 μm heat-treated at 2800 $^{\circ}\text{C}$ /1 M LiPF₆/PC/Li cells.

and Coulombic efficiencies of the MCMB (6 μm) heat-treated at 2800 $^{\circ}\text{C}$ in 1 M LiPF₆/PC at 0.2 mA cm⁻² with or without the first 2 cycles at 0.5 mA cm⁻² toward the cycle number (including cycles at 0.5 mA cm⁻²). When the cell was cycled with 2 pre-cycles at 0.5 mA cm⁻², MCMB (6 μm) heat-treated at 2800 $^{\circ}\text{C}$ could stably perform the charge–discharge cycles even under the current density of 0.2 mA cm⁻², while the cell without the pre-cycle at 0.5 mA cm⁻² would not show a stable cycle at the current density of 0.2 mA cm⁻². This result showed clearly that the cycle of graphitic negative electrodes in PC-based electrolyte becomes stable only in the pre-cycle/cycle situation, without repeating the charge–discharge at high current density.

The cycle behavior of MCMB electrodes in 1 M LiPF₆/PC electrolyte was improved by the pre-cycles with a large current in the case of another set of electrode materials and current density. Fig. 2 shows the plots of discharge capacity

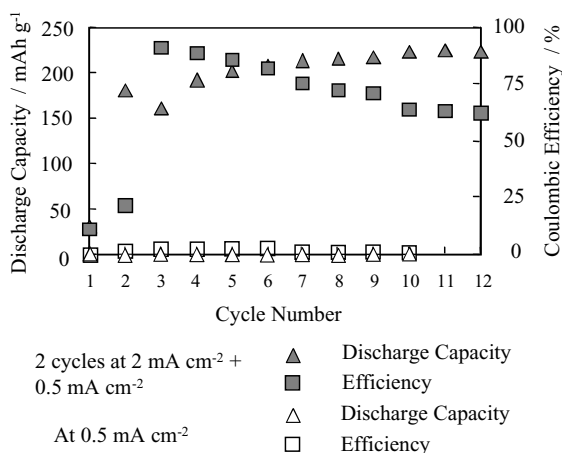


Fig. 2. The discharge capacity and Coulombic efficiency plots vs. the charge–discharge cycle number on MCMB 25 μm heat-treated at 2800 $^{\circ}\text{C}$ /1 M LiPF₆/PC/Li cells.

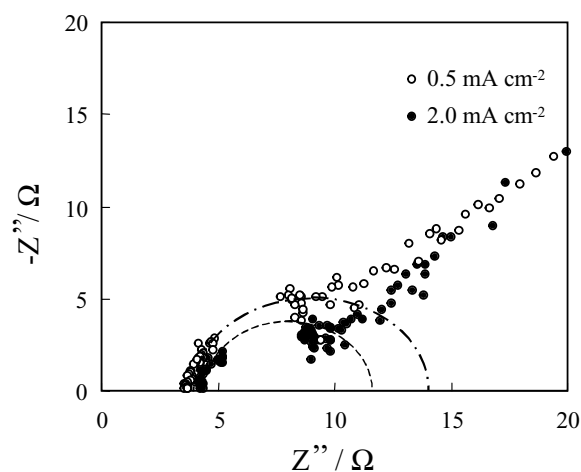


Fig. 3. Cole–Cole plots of the symmetrical cells consisting of the MCMB electrodes after 10 cycles in MCMB/1 M LiPF₆/PC/Li cells. Voltage amplitude: 10 mV, frequency range: 10⁵ to 1 Hz.

ities and Coulombic efficiencies of the MCMB (25 μm) heat-treated at 2800 $^{\circ}\text{C}$ in 1 M LiPF₆/PC at 0.5 mA cm⁻² with or without the first 2 cycles at 2.0 mA cm⁻² toward the cycle number (including cycles at 2.0 mA cm⁻²). Again we found that the cycle property of the MCMB electrode having the more graphitic structure improved, with a discharge (Li de-intercalation) capacity as large as 200 mAh g⁻¹ exhibited over 10 cycles, since its Coulombic efficiency was decreasing with each cycle.

These results clearly show that the modification of MCMB electrodes during high-rate pre-cycles is an irreversible process. The high-rate pre-cycles change the structure of the surface film on MCMB electrodes, which can improve their cycle stabilities in PC-based electrolytes. In order to estimate the difference of the surface film on MCMB (we performed) AC impedance measurements for MCMB/1 M LiPF₆/PC/MCMB symmetrical cells consisting of MCMB (6 μm) heat-treated at 2800 $^{\circ}\text{C}$ cycled 10 times beforehand in MCMB/1 M LiPF₆/PC/Li cells under the same condition. Fig. 3 shows the Cole–Cole plots for these measurements in the case of current densities of 0.5 and 2.0 mA cm⁻². In both cases the lithium–MCMB half-cell could be cycled stably. The semi-circle shown in both series around 4–15 Ω is expected to indicate the sum of the resistances of a surface film on electrodes [17]. The resistance in this region was smaller when the MCMB/Li cells were cycled at 2.0 mA cm⁻² (about 8 Ω) than when they were cycled at 0.5 mA cm⁻² (about 10 Ω); nevertheless, the average value of the first cycle irreversible capacity was larger in the former case (157 mAh g⁻¹) than in the latter (141 mAh g⁻¹). This result implies that the surface film produced on MCMB at the current density of 2.0 mA cm⁻² is structurally different from that at the current density of 0.5 mA cm⁻²; the former seems more compact than the latter.

Kanno et al. examined the lithium intercalation–de-intercalation test with regard to a kind of carbon fiber electrode

in a PC-based electrolyte and claimed that the irreversible capacity on the first cycle contained two alternative processes [18]. Aurbach et al. proposed that various reactions were likely to occur on the surface of negative electrodes in lithium and lithium ion batteries [19]. Some of these reaction products may stabilize the surface during the lithium intercalation into a graphitic negative electrode in PC-based electrolyte, though it is impossible to point out which reaction product did so, based only on the result of the present study. The pre-cycling at a large current is thought to provide a modified surface film on the MCMB electrode that in turn stabilizes further cycles in the PC-based electrolyte.

The poor cycle stability of a graphitic negative electrode in PC-based electrolyte is often treated as a homologue of the irreversible capacity at the first cycle in EC-based electrolyte. The charge current dependence of the first cycle irreversible capacity in EC-based electrolyte has been revealed in several reports [20]. However, it is not certain that the surface film formation process, especially in EC-based electrolyte, has an identical basis to that of the degradation process of a graphitic electrode in PC-based electrolyte. For example, Fong et al. assumed that these two processes must be different [21]. Therefore, the authors believe that it is worth revealing the rate dependence of the performances of graphitic carbons in PC-based electrolyte, even if these can be predicted from what is already known about surface film formation.

As shown in Fig. 2, the current of 2.0 mA cm^{-2} seems insufficient to produce an adequate surface film for stable cycling in PC-based electrolyte. The Coulombic efficiency in this case continued to decrease during the cycles, as the current amount compensated for the imperfect region of the surface film. We also applied a high-rate charge–discharge on a natural graphite electrode, however, this experiment resulted no reversible capacities after pre-cycles at the current density range up to 5.0 mA cm^{-2} in $1 \text{ M LiPF}_6/\text{PC}$ electrolyte. These results obviously show the limitation of the high-rate pre-cycle process with graphitic negative electrode materials. It is impossible to prevent the deformation of a perfectly ordered structure of graphite by the high-rate charge–discharge process. However, it is possible that we will be able to modify the surface feature of a graphitic carbon negative electrode without any additives, by simply controlling the applied current/voltage.

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References

- [1] A.N. Dey, B.D. Sullivan, *J. Electrochem. Soc.* 117 (1970) 222.
- [2] G. Eichinger, *J. Electroanal. Chem.* 74 (1976) 183.
- [3] M. Arakawa, J. Yamaki, *J. Electroanal. Chem.* 217 (1987) 273.
- [4] R. Fong, U. von Sacken, J.R. Dahn, *J. Electrochem. Soc.* 137 (1990) 2009.
- [5] O. Ohusid, Y. Ein-Eli, D. Aurbach, M. Babai, Y. Carmeri, *J. Power Sources* 43–44 (1993) 47.
- [6] M. Fujimoto, Y. Kida, T. Nohma, M. Takahashi, K. Nishio, T. Saito, *J. Power Sources* 63 (1996) 127.
- [7] M. Inaba, Z. Siroma, Y. Kawatate, A. Funabiki, Z. Ogumi, *J. Power Sources* 68 (1997) 221.
- [8] R. Imhof, P. Novák, in: C.F. Holmes, A.R. Landgrebe (Eds.), *Proceedings of the Symposium on Batteries for Portable Applications and Electric Vehicles*, PV 97-18, The Electrochemical Society Proceedings Series, Pennington, NJ, 1997, p. 313.
- [9] M. Fujimoto, Y. Shoji, Y. Kida, R. Ohshita, T. Nohma, K. Nishio, *J. Power Sources* 72 (1998) 226.
- [10] G.H. Wrodnigg, J.O. Besenhard, M. Winter, *J. Electrochem. Soc.* 146 (1999) 470.
- [11] C. Wang, H. Nakamura, H. Komatsu, M. Yoshio, H. Yoshitake, *J. Power Sources* 74 (1998) 142.
- [12] M. Inaba, Y. Kawatate, A. Funabiki, S.K. Jeong, T. Abe, Z. Ogumi, *Electrochemistry* 67 (1999) 1153.
- [13] A. Naji, J. Ghanbaja, P. Willmann, D. Billaud, *Electrochim. Acta* 45 (2000) 1893.
- [14] H. Wang, M. Yoshio, *J. Power Sources* 93 (2001) 123.
- [15] C.R. Houska, B.E. Warren, *J. Appl. Phys.* 25 (1954) 1503.
- [16] K. Tatsumi, N. Iwashita, H. Sakaebe, H. Shioyama, S. Higuchi, A. Mabuchi, H. Fujimoto, *J. Electrochem. Soc.* 142 (1995) 716.
- [17] M. Morita, N. Nishimura, Y. Matsuda, *Electrochim. Acta* 38 (1993) 1721.
- [18] R. Kanno, Y. Kawamoto, Y. Takeda, S. Ohashi, N. Imanishi, O. Yamamoto, *J. Electrochem. Soc.* 139 (1992) 3397.
- [19] D. Aurbach, A. Zaban, Y. Ein-Eli, I. Weissman, O. Chusid, B. Markovsky, M. Levi, E. Levi, A. Schechter, E. Granot, *J. Power Sources* 68 (1997) 91.
- [20] E. Peled, in: S. Megahed, B. Barnett, L. Xie (Eds.), *Rechargeable Lithium and Lithium-Ion Batteries*, PV 94-28, The Electrochemical Society, Pennington, NJ 1995.
- [21] R. Fong, U. von Sacken, J.R. Dahn, *J. Electrochem. Soc.* 137 (1990) 2009.