

Microelectrode Techniques for in Situ Measurements on Electrical Conductance of a Carbon Particle and Its Composite Film during Electrochemical Lithium Insertion/Extraction

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Novel electrochemical techniques based on a filament-type and an array-type microelectrodes were developed to study in situ the conductance change of a carbon particle and its composite film during electrochemical lithium insertion/extraction reactions. Mesocarbon microbeads (MCMB, Osaka Gas Co.) heat treated at 1000 °C were investigated in an organic solution containing 1 M LiClO₄ as the electrolyte. Measurements focusing on a single MCMB particle were achieved by attaching a molybdenum-filament microelectrode to the particle; they have shown that both the voltammogram and conductance profile of MCMB itself were stable in amplitudes and shapes for successive lithium insertion. Another kind of measurement using an array-type microelectrode was performed on a composite film consisting of MCMBs and poly(vinylidene fluoride), which is an actual form of MCMB in the use for lithium secondary batteries. The composite film was prepared on an interdigitated array of nickel microelectrodes to measure in situ its conductance change. It was found that the conductance of the composite film decreased rapidly, being accompanied by a decrease of redox capacity of the film. By considering the stable behavior of MCMB itself, we concluded that the electrical contact between MCMBs was broken due probably to the volume change of MCMB induced by the lithium insertion/extraction reactions. Addition of acetylene black to the composite greatly improved the interparticle connection. In addition to these practically important results, it is also suggested that there exist at least two different insertion sites within the MCMB. As demonstrated here, microelectrode-based techniques are unique and an effective approach to study battery active materials from both fundamental and practical standpoints.

Introduction

It has been well documented that lithium ion inserted carbons possess the ability to take the place of lithium metal as an excellent anode material for rechargeable lithium batteries.^{1–9} A lot of carbonaceous materials have been manufactured and tested so far, including synthetic and natural graphites, cokes, mesophase-pitch-based carbons, etc. Since most of carbon materials are obtained as powder, they are usually used as a composite film consisting of the powdery carbon and organic polymer binders such as poly(vinylidene fluoride) (PVDF). The electrical conductivity of such a composite film is one of the most important properties for the design of high performance batteries, and therefore a conductive agent such as acetylene black is often added to ensure the conductivity of composites. The use of the conductive agent has been optimized based on the resulting battery performance (charge/discharge behavior). In contrast to such an empirical way, in situ monitoring of the film conductivity should be attractive to understand details of the conductive nature of the composites and the functions of conductive agents. The works in our laboratory have shown that the interdigitated microarray electrode (IDA electrode) is a powerful tool to study the dynamic changes in dc conductance of electroactive films in situ during their redox reactions.^{10–13} We have reported the conductive features of variety of materials such as conducting polymers,¹⁰ fullerenes,¹¹ and transition-metal oxides.¹²

In the present work, we studied the in situ conductance change of films of mesocarbon microbeads (MCMB, Osaka Gas Co.) heat treated at 1000 °C by using the IDA electrode. In addition, we also studied the in situ conductance of a single MCMB particle as a reference for discussing the results of composite films. In order to achieve the electrochemical measurements focusing on a single particle, a metal filament was maneuvered to make electrical contact with the particle.^{14,15} By piecing together the results obtained by using IDA electrodes and filament electrodes, we discuss the electrochemical behavior of the composite film and the effect of conductive additives.

The mesophase carbons heat treated at temperatures below 2000 °C are known to contain many imperfections such as turbostratic disorder and unorganized parts,^{1,7,9a} and thus the lithium insertion reaction proceeds without the formation of any staging structure characteristic of graphite-intercalation compounds (GIC). The reasons we employed the MCMB heat treated at 1000 °C are as follows: (1) Its simple spherical shape is suitable for the single particle measurements. (2) Its relatively low conductivity is profitable to evaluate conductance changes induced by lithium insertion. (3) Lithium insertion mechanism for such disordered carbon is still controversial, and thus fundamentally interesting.

Experimental Section

a. Materials. The carbon employed for the present study was spherical mesocarbon microbeads (MCMB, Osaka Gas Co.) heat treated at 1000 °C, of which specific gravity and the crystalline

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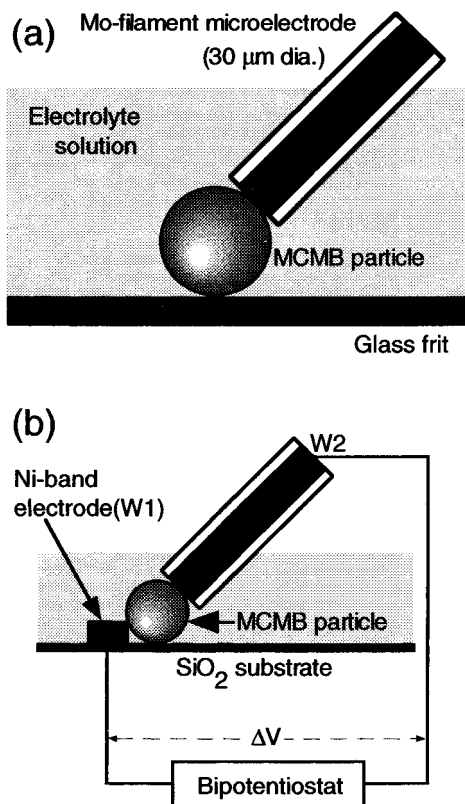


Figure 1. Schematic illustrations of (a) a MCMB particle attached with a Mo-filament microelectrode for the single particle voltammetry, and (b) the configuration for in situ measurement of the conductance change with the Mo electrode and a Ni band electrode prepared as described in the text. Electrochemical components such as reference and counter electrodes are not shown in these illustrations.

size along the *c* axis were ca. 1.8 Å and ca. 11 Å, respectively.^{7,16} An MCMB composite film was prepared as follows: MCMBs (average diameter, 6 μm) were mixed with PVDF and acetylene black (DENKA Co.) in a prescribed weight ratio using a slight amount of *n*-methylpyrrolidone (NMP) as a solvent. The resulting pastelike mixture was spread thinly on a substrate (e.g. IDA electrode) with a film thickness of ca. 20 μm by applying a doctor blade technique (Yoshimitsu Seiki YBA-1), followed by drying under vacuum at 130 °C for 12 h.

The electrolyte solution used for the electrochemical measurements was 1 M LiClO₄/propylene carbonate (PC) + ethylene carbonate (EC) (1:1 in volume) solution (Li ion battery grade, Mitsubishi Kagaku Co.). The water content in the solution was <20 ppm. A lithium foil of 1 cm² served as both the reference and the counter electrodes.

b. Measurements with a Filament-Type Microelectrode.

The cyclic voltammetry (CV) focusing on a single MCMB particle was conducted as described in our previous paper.¹⁵ Briefly, a filament microelectrode was used as a current collector for a single particle, as illustrated in Figure 1a. MCMB particles were spread on a disk of glass frit soaked in the electrolyte solution. This assembly was fixed on a *x-y-z* axis remote-controllable stage, and a Molybdenum filament (30 μm dia., Nilaco) sheathed with a thin film of Teflon (Cytop, Asahi Glass) was contacted with a targeted MCMB particle under a stereo-microscope (Nikon SMZ-U).

The in situ conductance measurements were carried out according to the configuration illustrated in Figure 1b. A single Ni band was prepared by sputtering on a SiO₂ substrate, and an MCMB particle was then pressed against the band electrode

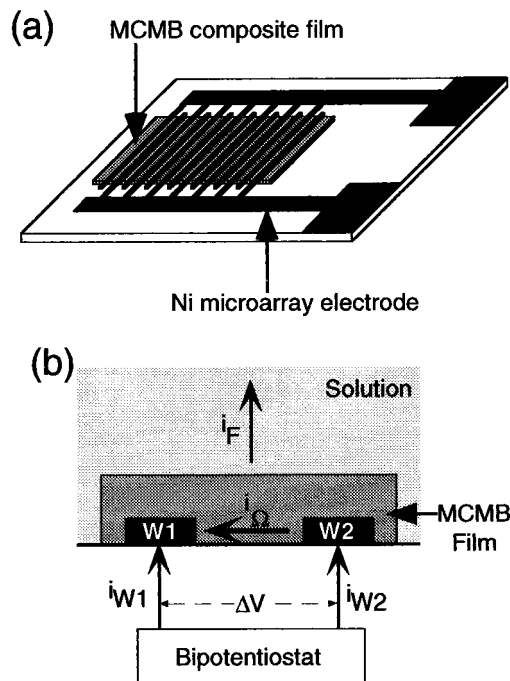


Figure 2. Schematic illustrations of (a) an interdigitated Ni microarray electrode coated with a MCMB composite film, and (b) the principle of the in situ conductance measurement for the MCMB film. The thickness of MCMB films was ca. 20 μm. The gap between arrays was 50 μm, and 7 mV potential difference was set between arrays by a bipotentiostat. Electrochemical components such as reference and counter electrodes are not shown in these illustrations.

(W1) by the Mo-filament electrode (W2). Since the sputtered Ni band (thickness, 0.1 μm) was too thin to hold the particle, it was piled up to ca. 3 μm by electroplating in a plating bath composed of 0.9 M NiSO₄, 0.2 M NiCl₂, and 0.6 M H₃BO₃ at 45 °C. By means of a bipotentiostat, the potentials of the two working electrodes (W1 and W2) were scanned with maintaining 7 mV potential difference (ΔV) between them, and the conductance of the particle was evaluated from the derived ohmic current (*i*_Ω). Importantly, as will be shown later, the faradaic current due to the lithium insertion reaction at a single MCMB was in the range of a few tenths of nA (<40 nA), which is considerably small enough to regard the observed current (μA range) as the *i*_Ω flowing through the MCMB with the 7 mV bias voltage.

Measurements were carried out in an airtight container (30 × 30 × 30 cm³) which was filled with dry air (−70 dew point). The particle dimension was determined from its optical image using a micrometer eyepiece.

c. Measurements with Microelectrode Array. The interdigitated array electrode was fabricated by photolithography with a sputter-deposited Ni film on a thermally oxidized silicon wafer, so as to have two sets of comb-type Ni arrays; each array has 10 electrode elements, 50 μm wide and 2.5 mm long, separated by 50 μm from its adjacent elements. The MCMB composite film of 20 μm thickness was prepared on the IDA electrode substrate as a 0.2 cm × 0.3 cm rectangle. Figure 2a is an illustration of the IDA electrode coated with the MCMB film. While it is not shown in the figure, a glass frit was placed on the film and pressed with a clamp to apply a constant force between the glass frit and the substrate.

The conductance of the composite film was evaluated in situ from an ohmic current (*i*_Ω) flowing through the film, as schematically illustrated in Figure 2b. The measuring principle is similar to the one described above for a single particle. In

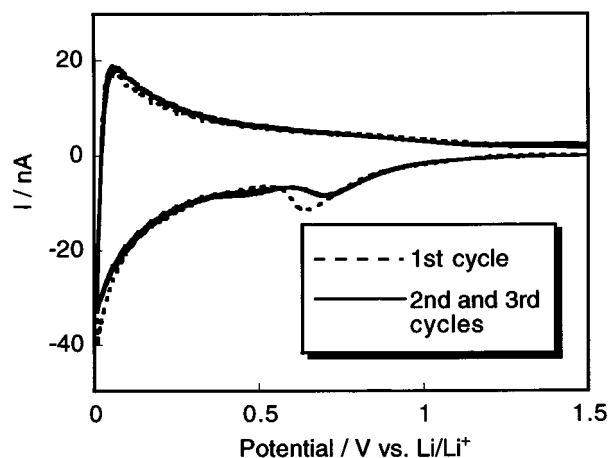


Figure 3. Cyclic voltammograms of a single MCMB particle, taken in 1 M LiClO₄/PC + EC at a scan rate of 0.2 mV s⁻¹. The diameter of MCMB was ca. 45 μm.

this case, however, significant amount of faradaic current (i_F) is superimposed on the i_Ω . Nevertheless, it would be reasonable to assume that the magnitudes of i_F at W1 and W2 are equal because of the small bias voltage, 7 mV. Consequently, the values of i_Ω and i_F can be extracted from the total currents observed at W1 (i_{W1}) and W2 (i_{W2}) by means of the following equations.

$$i_\Omega = (i_{W2} - i_{W1})/2 \quad (1)$$

$$i_F = (i_{W2} + i_{W1})/2 \quad (2)$$

In this way, we obtain both CV and conductance ($S = i_\Omega \Delta V^{-1}$) simultaneously.

Results and Discussion

a. MCMB Single Particle. Figure 3 shows the CV of a single MCMB particle heat treated at 1000 °C for the initial three cycles at a scan rate of 0.2 mV s⁻¹. The diameter of MCMB used here was ca. 45 μm. Since the background current of the Mo microelectrode alone was less than 0.3 nA, the CV response shown here is totally due to electrochemical reactions occurring at the MCMB particle. The cathodic current peak around 0.7 V vs Li/Li⁺, which was pronounced especially on the first cycle, may be ascribed to the solvent decomposition resulting in the formation of a surface-film called "solid electrolyte interface (SEI)".^{17–19} Except for this current peak at 0.7 V, no significant change in CV characteristics was observed during successive potential scans, indicating the reversibility of the lithium insertion/extraction reaction at MCMBs as well as the stability of electrical contact between the microelectrode and the MCMB particle. The lithium insertion/extraction reaction takes place continuously in the wide potential region between 1 and 0 V vs Li/Li⁺, while the reaction at the graphitized MCMB occurs only at the potential below 0.2 V associating with sharp current peaks due to the staging transformation in the Li-GIC structure.¹⁵

Figure 4 shows the current responses recorded at 0.2 mV s⁻¹ according to the configuration in Figure 2b. Since the faradaic current at a single MCMB was in the nanoampere range (Figure 3), the observed current (microampere range) should be dominantly the ohmic current derived by 7 mV bias voltage. Indeed, the current profiles at W1 and W2 are completely symmetrical to each other, confirming thus that the observed currents are almost purely the ohmic currents flowing through the MCMB, and therefore the current profile can be treated as

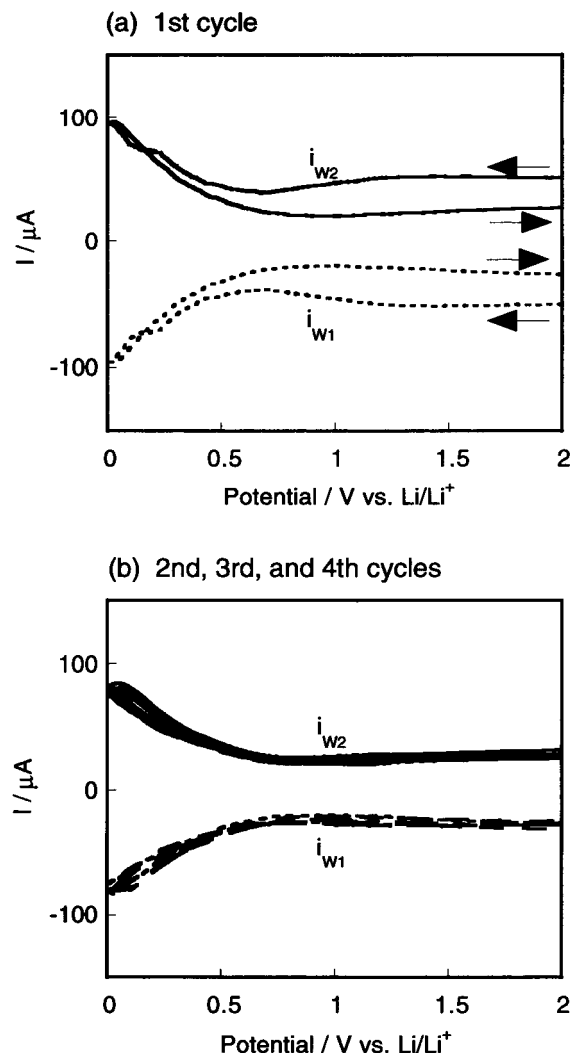


Figure 4. Current responses at W2 (Mo microelectrode) and at W1 (Ni-band electrode) attached to the MCMB particle. The potential scan rate was 0.2 mV s⁻¹, and the potential difference between W1 and W2 was 7 mV.

the variation of conductance of the particle. On the first cathodic potential scan, the conductance decreased slightly at the potential region from 1 to 0.5 V, and increased again at potentials below 0.5 V. The decrease in conductance might be ascribed to the formation of SEI,^{17–19} whereas the following increase is due to the insertion of lithium. Owing to the presence of SEI, the conductance did not return to the original value even if the electrode potential was scanned back to the initial potential, 2 V. For the following potential cycling, the conductance profile showed only the reversible increase upon the lithium insertion and was stable up to at least 10 cycles. The data shown here can be defined as the pure conductance behavior MCMB itself.

By comparing Figure 3 and Figure 4, an interesting discrepancy was noticed; the increase of conductance (i_Ω) began around 0.6 V, while the CV current was observed at wider potential region. This result indicates that the reaction taking place at the potential more positive than 0.6 V would be of a type which brings no change in conductance. The mechanism of lithium insertion/extraction at disordered carbons is still controversial. Dahn et al.^{1,20} have successfully proved that lithium can bind on the hydrogen-terminated edges of graphene sheets, but the MCMB heat-treated at 1000 °C would not contain such residual hydrogen atoms.^{20a} Mabuchi et al.⁷ proposed a model which describes that lithium ions insert not only into the stacked

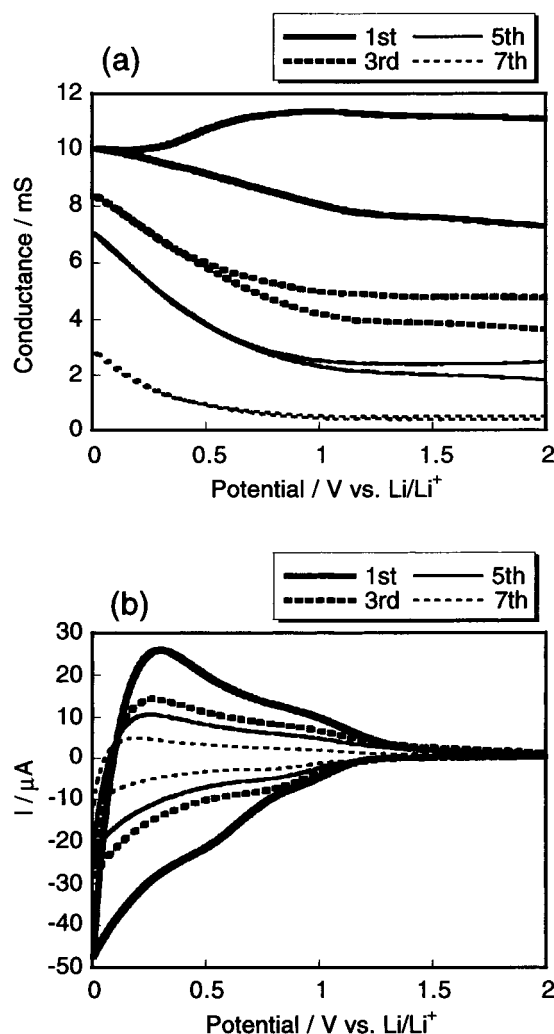


Figure 5. (a) Potential-conductance profiles and (b) cyclic voltammograms of a composite film (MCMB:PVDF = 100:5.5 in weight) measured simultaneously using the IDA electrode. The film thickness was ca. 20 μ m. The scan rate of electrode potential was 0.2 mV s⁻¹. The potential difference between arrays (W1 and W2) was 7 mV. The results on first, third, fifth, and seventh cycles are presented.

graphene layers but also into the unorganized parts "cavity" with forming lithium clusters. Further work is needed for the exact explanation of the conductance profile; however, it is clear at present that there are at least two different insertion sites within the MCMB from the conductometric point of view. Interestingly, we have recently found that the diffusion coefficient of lithium within the MCMB changes around 0.6 V also.¹⁶

b. MCMB Composite Film. Taking into consideration the stable electrochemical behavior of MCMB particle itself, we have studied next the MCMB composite film which is an actual form of MCMB in battery applications. The average diameter of the MCMBs used for making composite films was 6 μ m. Figure 5 shows the (a) in situ conductance profiles and (b) CVs of a MCMB/PVDF (100:5.5 in weight) composite film, recorded at a scan rate of 0.2 mV s⁻¹. Note that a conductive additive such as acetylene black is absent in this composite. The conductance profile is "basically" the same as that of the MCMB particle (Figure 4); the conductance increased with lithium insertion, while a remarkable decrease was observed on only the initial cathodic scan probably due to the SEI formation. However, in contrast to the stable behavior of MCMB particle, the magnitude of film conductance was decreased drastically

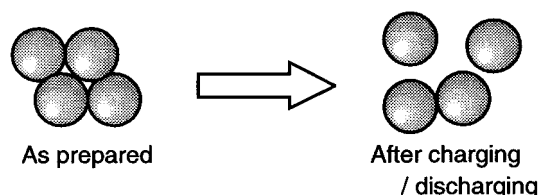


Figure 6. Schematic illustration of the proposed microstructure change in MCMB/PVDF composites during the successive discharge/charge (PVDF is not shown).

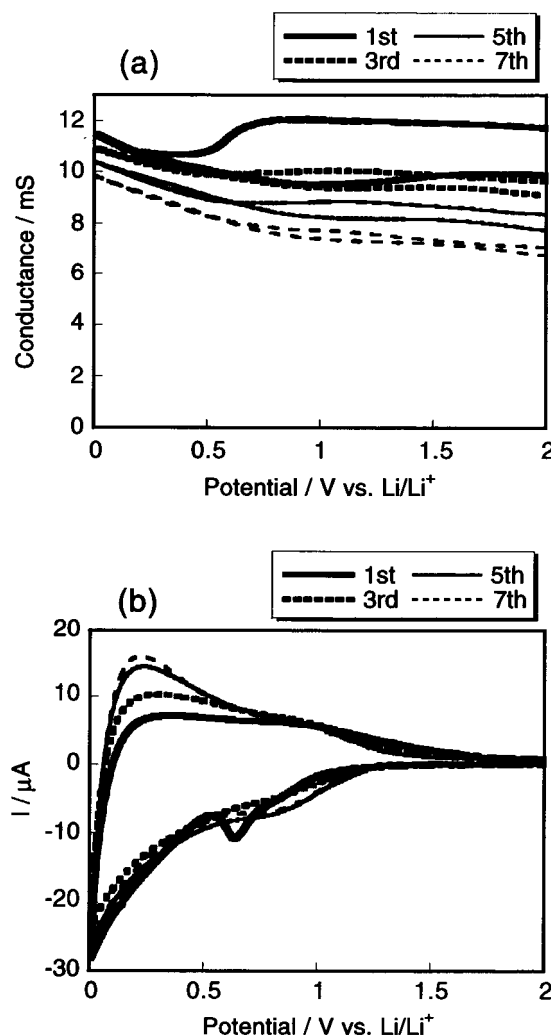


Figure 7. (a) Potential-conductance profiles and (b) cyclic voltammograms of a composite film (MCMB:PVDF:AcB = 100:5.5:27.5 in weight) measured simultaneously using the IDA electrode. Experimental conditions were the same as that in Figure 5.

by discharge/charge cycles and reached only 4% of the initial conductance in the seventh cycle. As seen in Figure 5b, the CV response of the film weakened in such a way as to synchronize with the decrease in conductance. These results were reproducible for other three samples. The observed decrease in conductance and CV activity of the composite film may be explained by supposing an electrical isolation of MCMB particles, as schematically modeling in Figure 6. During the lithium insertion/extraction reaction, the MCMB particles would incur expansion and contraction in their volume to some extent, causing a change of microstructure in the composite. If a particle is once isolated from the MCMB network within the composite, this particle can never take part in redox events. Similarly, the total conductance of the composite film would be decreased due to such in situ defect formation in the conduction path.

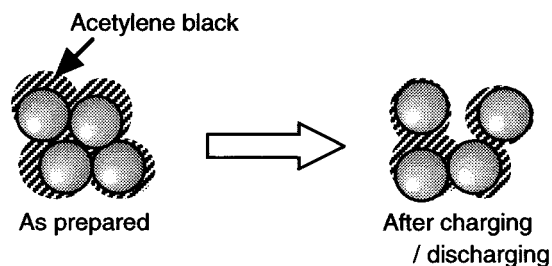


Figure 8. Schematic illustration of the proposed microstructure change in MCMB/PVDF/AcB composites taking place during the successive discharge/charge (PVDF is not shown).

For a practical use of disordered carbons, a conductive agent such as acetylene black (AcB) is often added to the composite, in order to support the relatively low conductivity of the carbon material itself and prevent the conductivity decrease shown above. Figure 7 shows the results obtained for the composite film of MCMB/PVDF/AcB (100:5.5:27.5 in weight). The conductance profile was improved greatly as shown in Figure 7a, indicating that the presence of AcB is effective to retain the film conductance. More than 60% of the initial conductance was maintained even during the seven cycles. These results were reproducible for other three films. The volume change of MCMB particle would also occur in this case. However, since the AcB would serve as a flexible conducting wire as imaged in Figure 8, few particles would be isolated electrically. The observed slight decrease in conductance is still reasonable on account of the lengthened conduction path. We have studied other AcB compositions such as MCMB/PVDF/AcB (100:5.5:5.5) which showed an intermediate behavior between Figure 5 and Figure 7; the conductance was decreased to ca. 30% of the original value during seven cycles. The amplitude of CV current of the film was no longer weakened by potential cycling, rather the anodic peak due to lithium extraction was grown to be sharp, as seen in Figure 7b. Results were reproducible for every AcB compositions investigated. While it is not elucidated at present why the early lithium extraction showed broad CV shape and improved gradually, the presence of AcB might be responsible for this strange behavior. Although the results obtained by the present CV technique cannot be compared quantitatively with those obtained from the constant-current potentiometry which has been employed more frequently, the qualitative tendencies of the in situ conductance behavior of the MCMB composite film were evaluated here for the first time.

Conclusion

We have developed microelectrode-based techniques profitable for evaluation of battery active materials. One is the filament-type microelectrode for the studies for a material's single particle, and the other is the array-type microelectrode for the material's film. We studied MCMB here and found that the conductance and redox activity of its film decreased continuously during successive charge/discharge, while an MCMB particle itself is stable. This behavior is presumably caused by the break of electrical contact between MCMBs in composite due to their volume change induced by lithium insertion/extraction reactions. Addition of acetylene black was found to be effective to retain the interparticle connection. It is worth noting that these empirically accepted tendencies were represented here by our novel microelectrode techniques from

more scientific standpoint. The present work is naturally applicable to other components of lithium ion battery. Since most of cathode oxide material such as LiMn_2O_4 is semiconductor,^{12b} the effective use of conductive additives should be critically important in making its composite film.

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References and Notes

- (1) Dahn, J. R. *Science* **1995**, 270, 590.
- (2) Dahn, J. R. *Phys. Rev. B* **1991**, 44, 9170.
- (3) Dahn, J. R.; Sligh, A. K.; Shi, H.; Way, B. W.; Weydanz, W. J.; Reimers, J. N.; Zhong, Q.; von Sacken, U. In *Lithium Batteries-New Materials, Developments and Perspectives*; Pistoia, G., Ed.; Elsevier: Amsterdam, 1994.
- (4) Levi, M. D.; Levi, E. A.; Aurbach, D. *J. Electroanal. Chem.* **1997**, 421, 89.
- (5) Levi, M. D.; Aurbach, D. *J. Phys. Chem.* **1997**, 101, 4641.
- (6) Che, G.; Lakshmi, B. B.; Fisher, E. R.; Martin, C. R. *Nature* **1998**, 393, 346.
- (7) Mabuchi, A.; Tokumitsu, K.; Fujimoto, H.; Kasuh, T. *J. Electrochem. Soc.* **1995**, 142, 1041.
- (8) (a) Ohzuku, T.; Iwakoshi, Y.; Sawai, K. *J. Electrochem. Soc.* **1993**, 140, 2490. (b) Sawai, K.; Iwakoshi, Y.; Ohzuku, T. *Solid State Ionics* **1994**, 67, 273.
- (9) (a) Ogumi, Z.; Inaba, M. *Bull. Chem. Soc. Jpn.* **1998**, 71, 521. (b) Inaba, M.; Yoshida, H.; Ogumi, Z. *J. Electrochem. Soc.* **1996**, 143, 2572.
- (10) (a) Nishizawa, M.; Shibuya, M.; Sawaguchi, T.; Matsue, T.; Uchida, I. *J. Phys. Chem.* **1991**, 95, 9042. (b) Matsue, T.; Nishizawa, M.; Sawaguchi, T.; Uchida, I. *J. Chem. Soc., Chem. Commun.* **1991**, 1029. (c) Nishizawa, M.; Matsue, T.; Uchida, I. *Anal. Chem.* **1992**, 64, 2642. (d) Nishizawa, M.; Miwa, Y.; Matsue, T.; Uchida, I. *J. Electrochem. Soc.* **1993**, 140, 1650. (e) Nishizawa, M.; Miwa, Y.; Matsue, T.; Uchida, I. *J. Electroanal. Chem.* **1994**, 371, 273.
- (11) (a) Nishizawa, M.; Matsue, T.; Uchida, I. *J. Electroanal. Chem.* **1993**, 353, 329. (b) Nishizawa, M.; Tomura, K.; Matsue, T.; Uchida, I. *J. Electroanal. Chem.* **1994**, 379, 233.
- (12) (a) Shibuya, M.; Nishina, T.; Matsue, T.; Uchida, I. *J. Electrochem. Soc.* **1996**, 143, 3157. (b) Yamamura, S.; Koshika, H.; Nishizawa, M.; Matsue, T.; Uchida, I. *J. Solid State Electrochem.* **1998**, 2, 211. (c) Nishizawa, M.; Yamamura, S.; Itoh, T.; Uchida, I. *Chem. Commun.* **1998**, 1631.
- (13) (a) White, H. S.; Kittleson, G. P.; Wrighton, M. S. *J. Am. Chem. Soc.* **1984**, 106, 5375. (b) Natan, M. J.; Wrighton, M. S. In *Progress in Inorganic Chemistry*; Lippard, S. J., Ed.; Wiley: New York, 1989; Vol. 37.
- (14) (a) Uchida, I.; Fujiyoshi, H.; Waki, S. *J. Power Sources* **1997**, 68, 139. (b) Waki, S.; Dokko, K.; Matsue, T.; Uchida, I. *Denki Kagaku* **1997**, 65, 954. (c) Nishina, T.; Ura, H.; Uchida, I. *J. Electrochem. Soc.* **1997**, 144, 1273.
- (15) Nishizawa, M.; Hashitani, R.; Itoh, T.; Matsue, T.; Uchida, I. *Electrochem. Solid State Lett.* **1998**, 1, 10.
- (16) A manuscript describing the effect of heat-treatment temperature on crystallographic character of MCMB and on the diffusion coefficient of lithium is in preparation.
- (17) Peled, E. *J. Electrochem. Soc.* **1979**, 126, 2047.
- (18) (a) Aurbach, D.; Ein-Eli, Y.; Chusid, O.; Carmeli, Y.; Babai, M.; Yamin, H. *J. Electrochem. Soc.* **1994**, 141, 603. (b) Aurbach, D.; Ein-Eli, Y.; Markovsky, B.; Zaban, A.; Lusk, S.; Carmeli, Y.; Yamin, H. *J. Electrochem. Soc.* **1995**, 142, 2882. (c) Aurbach, D.; Ein-Eli, Y. *J. Electrochem. Soc.* **1995**, 142, 1746.
- (19) Fong, R.; Sacken, U. V.; Dahn, J. R. *J. Electrochem. Soc.* **1990**, 137, 2009.
- (20) (a) Zheng, T.; Liu, Y.; Fuller, E. W.; Tseng, S.; Sacken, U. V.; Dahn, J. R. *J. Electrochem. Soc.* **1995**, 142, 2581. (b) Zheng, T.; McKinnon, W. R.; Dahn, J. R. *J. Electrochem. Soc.* **1996**, 143, 2137. (c) Zheng, T.; Xue, J. S.; Dahn, J. R. *Chem. Mater.* **1996**, 8, 389.