

LETTERS

Ion- and Electron-Transport Properties of a Single Particle of Disordered Carbon during the Lithium Insertion Reaction

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The electrical dc conductance (S) and the solid-state diffusion coefficient of the lithium ion (D_{Li^+}) were evaluated for a single spherical particle of mesocarbon microbead (MCMB) heat-treated at 1000 °C. The measurements were conducted in situ during the electrochemical lithium insertion into the MCMB by using microelectrode-based techniques. The data obtained are discussed as functions of the electrode potential and of the amount of inserted lithium. Both parameters (S and D_{Li^+}) were found to depend on the lithium content, and their variation manner changed around 0.6 V vs Li/Li⁺ at which the inserted lithium amount was ca. 25% of the total insertion. The results would arise from the difference between the first and the second half of the lithium insertion reaction mechanisms.

Introduction

Lithium-ion batteries consisting of lithium insertion materials are the state-of-the-art rechargeable power sources for consumer electronics.^{1–4} Among the characteristics of insertion materials, the electrical conductivity and the solid-state diffusion coefficient of lithium ions are the most important in connection with the rate-performance of batteries. These parameters have been evaluated by using a composite film consisting of the powdery active material and organic polymer binders. Results obtained in such a way should be “practically” informative because the present battery manufacturers are using the composites in fact. However, from the electroanalytical standpoint, the composites will be treated as porous electrodes; furthermore, the results obtained should be an average of numerous particles having different sizes and shapes. To eliminate the uncertainties at the composite electrodes, the investigation of a single particle of active material alone should be an attractive approach.^{5–7}

In the present paper, we studied the conductance (S) and the diffusion coefficient of lithium ions (D_{Li^+}) in a single particle of mesocarbon microbead (MCMB, Osaka Gas Co.) heat-treated at 1000 °C. MCMB is one of the promising anode materials for lithium-ion batteries.^{8,9} The mesophase carbons heat-treated at temperatures below 2000 °C are known to contain many imperfections such as turbostratic disorder and unorganized parts, and therefore the lithium insertion reaction proceeds without the formation of any staging structure characteristic of graphite intercalation compounds (GICs).^{1–3,8–11} The reversible capacity of such low-temperature carbon is often beyond the theoretical limit for the graphite, the fact being one of the most attractive points concerning the carbonaceous anode material. In the previous paper,⁷ we presented the in situ conductance profile of an MCMB(1000 °C) particle just as a reference for analyzing the conductance behavior of its composite films. In the present work, we discuss the ion- and electron-transport properties of a MCMB(1000 °C) themselves in connection with the lithium insertion mechanism at the disordered carbon.

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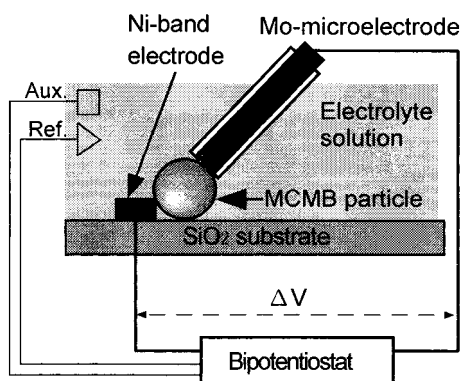


Figure 1. Schematic configuration of in situ conductance measurement for a single MCMB particle with a Mo electrode and a Ni-band electrode. Cyclic voltammetry and the potential-step chronoamperometry were conducted with only the Mo microelectrode. Both the reference electrode (Ref.) and the counter electrode (Aux.) were made of lithium foils.

Experimental Section

Mesocarbon microbeads (MCMB) heat-treated at 1000 °C was provided by Osaka Gas Co. The electrolyte solution used for the electrochemical measurements was 1 M LiClO₄/propylene carbonate (PC) + ethylene carbonate (EC) (1:1 in volume) (Li-ion battery grade, Mitsubishi Chemical Co.). The water content of the solution was less than 20 ppm. All measurements were performed in an airtight container filled with dry air (−70 °C dew point). A lithium foil of 1 cm² served as both the reference and the counter electrodes.

The electrochemical apparatus was the same as that described previously,⁷ which was designed to permit electrochemical characterization of a single particle, as illustrated in Figure 1. Briefly, a Ni-band electrode was prepared previously by sputtering on a SiO₂ substrate, and then an MCMB particle was pressed against the band electrode by a molybdenum filament microelectrode using an *x*–*y*–*z* axis micromanipulator. By means of a bipotentiostat, the potentials of the two working electrodes (Ni-band and Mo-filament) were scanned at 0.2 mV s^{−1} with maintaining 7 mV potential difference between them, and the electrical conductance ($S = i_{\Omega} \Delta V^{-1}$) of the particle was evaluated from the derived ohmic current. Cyclic voltammetry (at 0.2 mV s^{−1}) and the potential-step experiments were conducted with only the Mo microelectrode. The apparent diffusion coefficient (D_{app}) of lithium ions was calculated from the potential-step chronoamperograms considering the spherical diffusion model, as we did for a graphitized MCMB.⁶ For the spherical diffusion process in which the reaction promotes from the surface of a sphere to its center, the current response upon a potential step will follow the equation:¹²

$$\ln(i) = (-\pi^2 D_{app}/a^2)t + \ln(2nFAD_{app}\Delta C/a) \quad (t \gg a^2/\pi^2 D_{app}) \quad (1)$$

where a is the radius of the particle, A is the surface area of the particle, and ΔC is the change in concentration of lithium induced by the potential step. For the MCMB(1000 °C), we obtained an excellent linear relationship between $\ln(i)$ and t , ensuring that the reaction would kinetically be limited by spherical diffusion of lithium ions in the MCMB particle. According to eq 1, the D_{app} values can be easily calculated from the slope of the plot ($\ln(i)$ vs t) without information about ΔC .

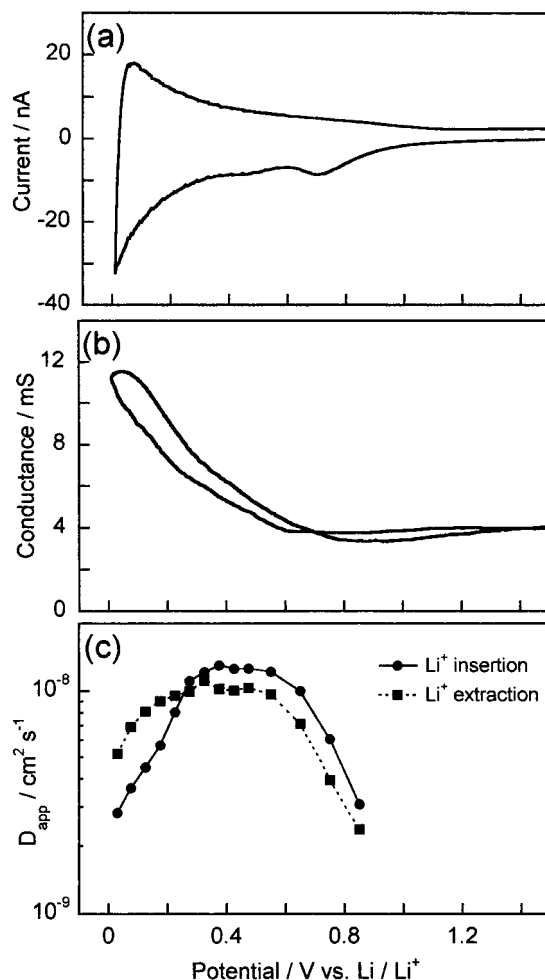


Figure 2. (a) Cyclic voltammogram, (b) conductance–potential profile, and (c) D_{app} –potential profile obtained for an MCMB (45 μ m diameter) heat-treated at 1000 °C. Measurements were conducted using 1 M LiClO₄/PC + EC as an electrolyte solution. The scan rate of 0.2 mV s^{−1} was used for both voltammogram and conductance measurements. Width of potential steps for chronoamperometry was 50 or 100 mV.

Results and Discussion

Figure 2 shows (a) the cyclic voltammogram (CV), (b) the conductance–potential profile, and (c) the D_{app} –potential profile, obtained for an MCMB (45 μ m diameter) treated at 1000 °C. Since all data shown in Figure 2 were obtained after a few pre-cyclings of the electrode potential, the effect of the surface-film formation is negligible.¹³ The CV profile is characteristic of soft carbons heat-treated at low temperatures; the lithium insertion/extraction reaction takes place continuously in a wide region of potential within 1.0 and 0 V vs Li/Li⁺, being in contrast to the stepwise reaction process at the graphitized MCMB accompanying the stage formation.^{6,14,15} We obtained the lithium insertion capacity of ca. 327 m Ah g^{−1} from the amount of charge consumed during the cathodic potential scan. Although the cathodic CV current due to the lithium insertion reaction was observed even at 1 V, the change in conductance started around 0.6 V. This discrepancy indicates that there are at least two different lithium insertion mechanisms for the MCMB(1000 °C), as already proposed by other analyses such as XRD.^{1–3,8,9} Furthermore, it is also indicated here that the reaction taking place at potential more positive than 0.6 V would be of a type which brings no change in conductance. The D_{app} value of lithium within the MCMB(1000 °C) varied between

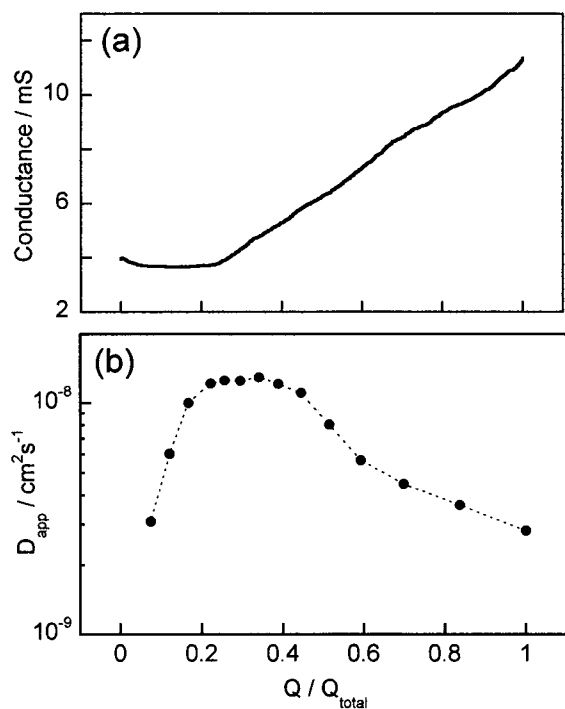


Figure 3. (a) Conductance and (b) D_{app} , plotted against the lithium insertion ratio.

10^{-9} and 10^{-8} $\text{cm}^2 \text{s}^{-1}$ over the course of lithium insertion/extraction. It was found that the potential-dependency of D_{app} inverted around 0.6 V, also. As for the potential region more positive than 0.6 V, the lithium mobility increased with proceeding of lithium insertion. In contrast, at more negative potential, the lithium insertion brought a decrease in lithium mobility. From these results, it can be suggested that the lithium insertion mechanism changes around 0.6 V, reflecting to the variation manners of both conductance and diffusion coefficient.

The lithium insertion mechanism depends on the carbon's structure which is sensitive to the heat-treatment temperatures.^{1-3,8-11} For example, Dahn et al.^{1,10} have successfully proved that lithium ions can bind on the hydrogen-terminated edges of graphene sheets, for the case of the carbons pyrolyzed at temperatures near 700 °C. Although the MCMB(1000 °C) would not contain such residual hydrogen atoms,^{10a} its structure is still essentially different from that of graphite obtained at temperatures around 3000 °C. The crystallite sizes of the MCMB(1000 °C) are small (11.3 Å for *c*-axis and 30.1 Å for *a*-axis); moreover the stacking of the hexagonal graphene layers in the crystallite is random.¹⁻³ Mabuchi et al.⁸ reported evidence that lithium ions insert not only into the layered structure but also into the unorganized intercrystallite spaces named "cavity", and they proposed the formation of lithium-ion clusters in the cavities.

Figure 3a represents the plot of conductance as a function of the insertion ratio, which is the reaction charge normalized by the total one. It is plainly seen that during the 25% initial lithium insertion, no conductance change occurred to the MCMB. It should be noticed that Mabuchi et al.⁸ estimated the ratio of the insertion at cavities as 27% from a point of inflection in the discharge-curve of a composite film of MCMB(1000 °C). If the reaction in this region occurs at the cavities isolated from each other, such type of lithium insertion may not influence significantly the total conductance determined originally by the network of carbon crystallites. The further lithium insertion beyond 25% would be identified to that into the interlayer structure of the carbon. The conductance rose linearly against

the insertion ratio, which corresponds directly to the increase in the amount of mobile carrier (electron) introduced to the π -band of graphene sheets. The linear increase in conductance may indicate that the mobility of the carrier is constant. Such property is somewhat different from that of the chemically synthesized GICs, which show conductance values peculiar to each staging level.¹⁶

Figure 3b represents the variation of D_{app} as a function of the insertion ratio. A decrease in D_{app} was observed in the region of high insertion ratio. This tendency has already been reported on composite films of graphite and other carbonaceous materials.¹⁷⁻²⁰ In most of these works, this tendency was attributed to the repulsive force between lithium ions inserted in layered carbon. On the other hand, the increasing property observed during the initial 25% insertion is reported here for the first time. This opposite tendency would indicate that the lithium insertion process in this region may contain some attractive force between lithium ions. For example, the formation of lithium-ion clusters in cavities⁸ is likely to explain our observation, while further works should be needed to determine the exact reaction mechanism.

Conclusion

By means of the novel microelectrode techniques, we showed that the profiles of both electrical conductance and lithium diffusion coefficient changed their variation manner around 0.6 V vs Li/Li^+ , potential corresponding to ca. 25% lithium insertion. These results prove that the lithium insertion mechanism changes drastically at this condition. The cavity model seems to explain our results, though the validity of the model itself is still controversial. Detailed investigation of the lithium insertion mechanism should be a next stage of our research. For this purpose, we are planning a systematic study with MCMBs heat-treated at various temperatures.

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