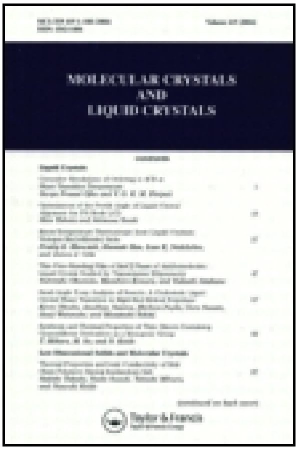

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Lithium Ion Transfer At Carbon Thin Film Electrode/Electrolyte Interface

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LITHIUM ION TRANSFER AT CARBON THIN FILM ELECTRODE/ELECTROLYTE INTERFACE

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Lithium ion transfer at an interface between carbonaceous thin film electrode prepared by plasma-assisted chemical vapor deposition and electrolyte was studied by AC impedance spectroscopy. In Nyquist plots, semi-circles assigned as charge (Li^+) transfer resistance were observed. The charge transfer resistance was dependent on the electrode potentials. Activation energy for the lithium ion transfer through the interface between electrode and electrolyte was also evaluated.

Keywords: carbon; thin film; lithium ion battery; ion transfer; charge transfer

INTRODUCTION

Much work has been done on carbonaceous materials as a negative electrode in Li^+ ion batteries. Among them, highly graphitized carbonaceous materials and non-graphitizable carbons have been commercialized [1,2]. Various carbonaceous materials are still in investigation for further improvement of the performance of lithium ion batteries.

In many works, capacities, ionic conductivity, and diffusion coefficients have been focused. Rate performance of Li^+ ion batteries should be influenced not only by diffusion coefficients in active materials and ionic conductivity but also by the interfacial resistances due to Li^+ ion transfer between electrode and electrolyte. However, the latter has been dismissed

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so far because structurally defined electrode/electrolyte interface including real active surface area should be required for precise studies on interfacial phenomena.

We have fabricated thin film negative and positive electrodes by plasma assisted chemical vapor deposition (plasma CVD) [3–6] and pulsed laser ablation [7,8]. The resultant thin film electrodes were very flat and homogeneous without any pin-hole. Hence, it becomes easy to fabricate well structurally ordered electrode and electrolyte interfaces.

This work reports lithium ion transfer through an interface between electrolyte and electrode composed of carbonaceous thin films prepared by plasma CVD.

EXPERIMENTAL

Carbonaceous thin films were deposited on substrates of nickel sheets from acetylene and argon. Substrates were placed on a ground electrode whose temperature was kept at 873 K and the applied RF power was set at 10 W. The detailed procedure is shown in the previous paper [3,6].

Lithium ion transfer through the interface between resultant carbonaceous thin film electrode and electrolyte (a mixture (1:1 by volume) of ethylene carbonate (EC) and diethyl carbonate (DEC) containing 1 mol dm^{-3} $LiC1O_4$) was studied by electrochemical impedance analysis using Sorlatron 1255 in the frequency range of 100 KHz–1 mHz with a three-electrode cell. Li metal was used as counter and reference electrodes. Unless otherwise stated, potential is referred against Li^+/Li. Measurements of AC impedance spectra were carried out from 3.0 to 0.02 V. Each potential was held at 1 h to attain the condition of sufficiently low residual current. Prior to AC impedance measurements, cyclic voltammetry was conducted at a scan rate of 1 mV/s over 3.0–0.0 V, leading to the formation of passivation film on carbonaceous thin film electrodes.

RESULTS AND DISCUSSION

Electrochemical properties of the resultant thin film electrodes were reported elsewhere [6]. Figure 1 shows Nyquist plots for carbonaceous thin film electrode for Li^+ ion insertion. Above the potential of 0.8 V, no semicircle appeared and only capacitive behaviors were observed. This result suggests that no lithium insertion into the carbonaceous thin film occurred at this potential, which is in good agreement with the previous results [6]. In contrast, one semi-circle in the higher frequency region was observed below the potential of 0.5 V, and the resistances of the semi-circles decreased with decreasing the electrode potentials. In our previous studies,

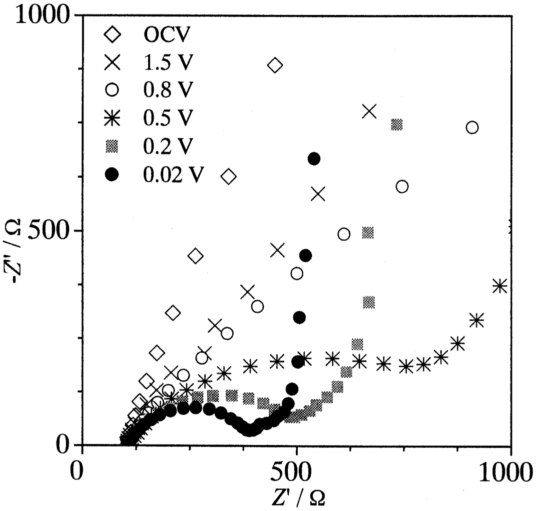

FIGURE 1 Nyquist plots of carbonaceous thin film electrodes for lithium insertion at various electrode potentials.

the electrical conductivities of the carbonaceous films were evaluated to be 1–100 S/cm [3]. Since the thickness of the present films is around 0.3–0.5 μm, the resistances of the semi-circles should not be ascribed to the electrical resistances. In addition, electrolyte salt concentration dependency on the semi-circle was studied. In Figure 2 are shown the Nyquist plots of carbonaceous thin film electrode in different salt concentration of electrolytes. Electrode potential was kept at 0.02 V. As is clear from Figure 2, the resistances increased linearly with decreasing the salt concentration. This result indicates that the relaxation process for the semi-circles should be related with Li^+ ion. It is now clear that the semi-circles in Figure 1 are due to the lithium-ion-transfer resistances.

In the intermediate frequency region in Figure 1 for the electrode potentials below 0.5 V, the Warburg impedances can be observed in the narrow region, and then capacitive behaviors appeared. These Nyquist plots should be interpreted by Voigt-Frumkin and Melik-Gaykazyan impedance as suggested by Levi *et al.* [9].

As mentioned above, the present film electrode is sufficiently thin that one can obtain apparent Li^+ ion diffusion coefficients using the following Eq. [10]:

$$D(\mathrm{Li}^+) = h^2/3R_{\mathrm{LF}}C_{\mathrm{LF}} \tag{1}$$

where C_{LF} is the limiting low frequency capacitance, R_{LF} the limiting low frequency resistance, and h denotes the film thickness. Figure 3 shows

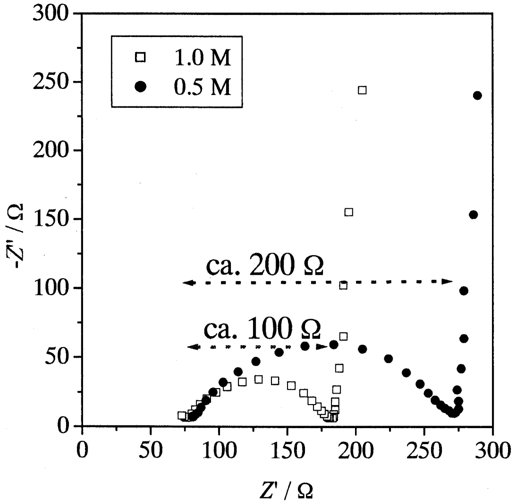

FIGURE 2 Nyquist plots of carbonaceous thin film electrodes in different salt concentration of electrolyte. Electrode potential was kept at 0.02 V.

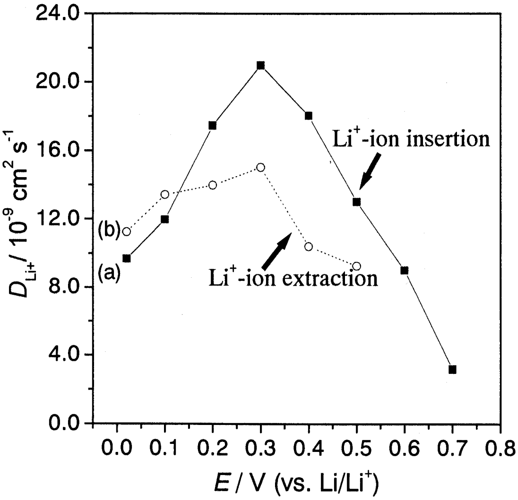

FIGURE 3 Potential dependence of apparent diffusion coefficient D^{Li^+} through carbonaceous thin film.

the apparent Li^+ ion diffusion coefficients evaluated by the above Eq. (1). The diffusion coefficients gave the maximum value at potential around 0.3 V for both lithium insertion and extraction. Nishizawa *et al.* reported the electron and ion transport properties for a single particle of mesocarbon microbeads heat-treated at 1273 K (MCMB1000) [11]. The electrical conductance and diffusion coefficients of Li^+ ion for MCMB1000 were dependent on the lithium content, and the dependency changed around 0.6 V, at which potential lithium insertion mechanism should change [11]. Our results are in good agreement with those reported by Nishizawa *et al.*, although the potential at which the dependency of diffusion coefficients changes (0.3V) is different.

It is well known that lithium intercalation of graphite occurs below the potential of around 0.25 V (vs. Li/Li^+) [12]. Raman spectroscopy and tunneling electron microscopy revealed that the thin film electrodes in this work possess graphitized and non-graphitized structures. Hence, the variation of diffusion coefficients given in Figure 3 should be related to the change in lithium insertion mechanism; “lithium insertion into graphitized structures” and “lithium insertion into non-graphitized structures”.

The activation energy for Li^+ ion transfer at a potential of 0.02 V was evaluated from the temperature dependence of charge transfer resistances. As a result, a value of 70.3 kJ/mol was obtained. This value seems large as compared with the lithium ion conduction in fast lithium ion conductive crystalline solids [13] and in positive active material of $LiCoO_2$ [14]. These results of the present work indicate that the lithium ion transfer through the interface between electrode and electrolyte should play an important role on rate performance of lithium ion batteries.

CONCLUSION

Carbonaceous thin films prepared by plasma CVD, and Li^+ ion transfer at the thin film electrode and electrolyte were investigated by AC impedance spectroscopy. In the Nyquist plots, one semi-circle due to charge transfer resistance appeared, and the values were dependent on electrode potentials. Li^+ ion diffusion coefficients were also evaluated by the finite diffusion model. The variation of the diffusion coefficients was dependent on the electrode potentials.

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