

Lithium-ion transfer at interface between carbonaceous thin film electrode/electrolyte

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Abstract

A carbonaceous thin film electrode was prepared by plasma-assisted chemical vapor deposition, and lithium-ion transfer at the interface between the resultant thin film electrode and the electrolyte was studied by AC impedance spectroscopy. On the Nyquist plots, semi-circles assigned as charge (Li^+ ion) transfer resistance were observed in the intermediate frequency region. The charge-transfer resistance was dependent on electrode potential. The activation energy for lithium-ion transfer through interface between the electrode and the electrolyte was evaluated, and the value was very large. Hence, it is concluded that a high-energy barrier of activation exists at the interface between the electrode and the electrolyte.

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1. Introduction

Since graphite and non-graphitizable carbons have been used as negative electrode materials in lithium-ion batteries, various other kinds of carbonaceous materials have been extensively studied as negative electrodes for further improvement of lithium-ion batteries [1,2].

Lithium-ion batteries have expanded their application area such as portable electronic devices and their production amount, and recently lithium-ion batteries are expected as an essential power source for electric and hybrid vehicles due to their high performance. The rate performance of lithium-ion batteries should be improved because high power density is required for use in electric and hybrid vehicles.

The rate performance of lithium-ion batteries should be influenced by diffusion coefficients of lithium ion through active materials and by lithium ion transport in electrolytes. In addition, we reported that the interfacial lithium-ion transfer between electrode and electrolyte is a slow process [3,4], and the lithium-ion transfer at the electrode/electrolyte interface should also affect the rate performance of lithium-ion batteries. However, the latter process has been ignored so far because structurally defined electrode/electrolyte interface including real active surface area was not easily attain-

able, while that is essential for precise studies on interfacial phenomena.

A thin film electrode is preferable for the fabrication of structurally defined electrode/electrolyte interface. Various methods such as sputtering, pulsed laser deposition, chemical vapor deposition can give a thin film of various materials. Among these methods, we have employed pulsed laser deposition for preparation of positive thin film electrodes [5–8] and plasma-assisted chemical vapor deposition (plasma CVD) for negative thin film electrode of carbonaceous thin films [9–12]. Electrochemical properties of fabricated thin films have been examined and electrochemical properties of the thin film electrodes are identical to those of bulk positive and negative active materials. These results inspire us to investigate the interfacial phenomena, namely, ion transfer at the interface employing the thin films of positive and negative electrodes.

In the present paper, we report lithium-ion transfer at the interface between the carbonaceous negative thin film electrode and the electrolyte and discuss the high activation barrier at the interface for lithium-ion transfer.

2. Experimental

Carbonaceous thin films were deposited on substrates of nickel sheets from acetylene and argon by plasma CVD.

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Substrates were placed on a ground electrode whose temperature was kept at 873 K and the applied RF power was set at 10 and 90 W. The detailed procedure was shown in the previous papers [9–12]. The resultant thin film electrode was characterized by X-ray diffraction (XRD) (Rigaku, Rint2500), Raman spectroscopy (Jovin-Yvon), and transmission electron microscopy (TEM, Hitachi-9000).

Lithium-ion transfer through the interface between the resultant carbonaceous thin film electrode and the electrolyte (a mixture (1:1 by volume) of ethylene carbonate (EC) and diethyl carbonate (DEC) containing $1 \text{ mol dm}^{-3} \text{ LiClO}_4$) was studied by electrochemical impedance analysis using Sorlatron 1255 in the frequency range of 100 kHz to 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. The electrode was held at each potential for 1 h to attain the condition of sufficiently low residual current after potential change. 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 a passivating film on the carbonaceous thin film electrodes.

3. Results and discussion

Fig. 1 shows XRD patterns of the resultant carbonaceous thin films prepared at applied RF powers of 10 and 90 W. As is obvious from Fig. 1, broad peaks are observed at around 26° in 2θ . This diffraction angle gives a value of d_{002} of ca. 0.342 nm, and therefore the crystallinity of these carbonaceous films is low. No obvious difference in crystallinity was obtained from XRD patterns between two thin carbonaceous films prepared at different RF powers.

In Fig. 2 are shown Raman spectra for thin films prepared at different RF powers of 10 and 90 W. The spectra

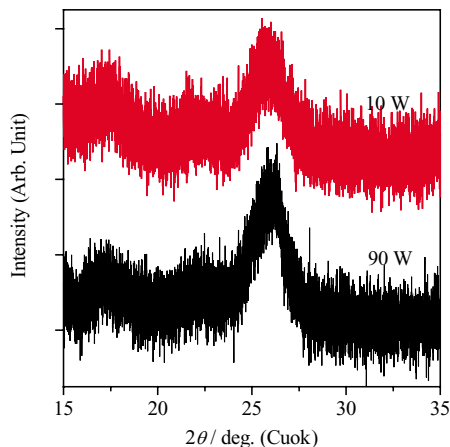


Fig. 1. XRD patterns of carbonaceous thin films prepared at applied RF powers of 10 and 90 W. Substrate was Ni sheet kept at 873 K.

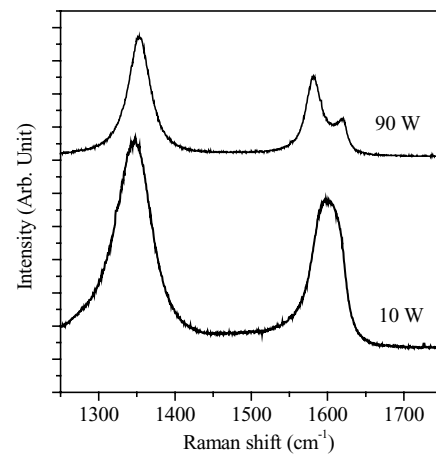


Fig. 2. Raman spectra of carbonaceous thin films prepared at applied RF powers of 10 and 90 W.

differ from each other in Raman active E_{1g} mode frequencies around 1600 cm^{-1} . For the film prepared at 10 W, only one broad peak appeared at 1600 cm^{-1} , while two peaks at 1580 and 1620 cm^{-1} were observed for films prepared at 90 W. Full width at half maximum of peak for the E_{1g} mode is well known to be correlated with the crystallinity of carbonaceous materials [13], and hence the crystallinity of the films prepared at 90 W is somewhat higher than that at 10 W. This is supported by the TEM results; many lamellar structures were observed in the TEM image for films prepared at 90 W while only a few lamellar structures appeared for films prepared at 10 W.

The above facts given by XRD and TEM indicate that the bulk crystallinity of the carbonaceous thin films is not influenced significantly by the applied RF powers. On the other hand the crystallinity is lower at the surface zone than that at the bulk and the crystallinity at the surface zone is dependent on the applied RF powers.

Cyclic voltammograms for carbonaceous thin films showed lithium ion insertion and extraction mainly take place at potentials below 0.5 V, which agrees with the previous work [10]. Fig. 3 shows Nyquist plots for carbonaceous thin film electrode prepared at applied RF power of 10 W. At potentials over 0.8 V, no semi-circle appeared and only capacitive behavior was observed. This fact indicates that no lithium insertion into the carbonaceous thin film should occur at this potential, which is in good agreement with the previous results [10]. In contrast, one semi-circle in the higher frequency region was observed at potential below 0.5 V, and the resistances of the semi-circles decreased with decreasing the electrode potential. In our previous studies, the electrical conductivities of the carbonaceous thin films were evaluated to be 1–100 S/cm [9]. Since the thickness of the present films is around $0.3\text{--}0.5 \mu\text{m}$, the resistances of the semi-circles should not be ascribed to the electrical resistances. In addition, the semi-circle was dependent on the salt concentration of the electrolytes. Hence, the semi-circles should be ascribed to a relaxation process related to the

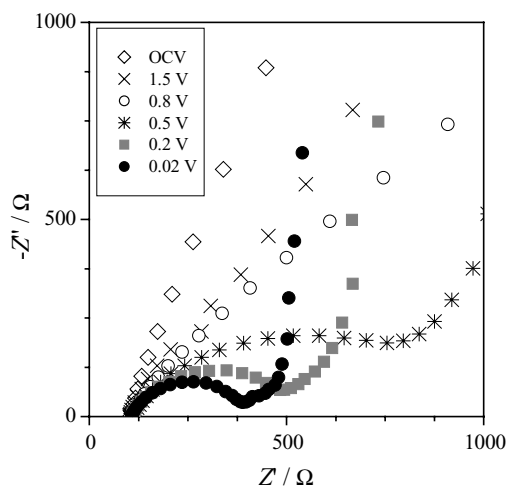


Fig. 3. Nyquist plots of carbonaceous thin film electrodes prepared at applied RF power of 10 W for lithium insertion at various electrode potentials at ambient temperature. Super-imposed AC voltage for impedance measurement was set at 5 mV.

lithium ion. Consequently, the semi-circles given in Fig. 3 can be assigned as charge (lithium ion) transfer resistances.

In Fig. 4 are shown Nyquist plots for the carbonaceous thin film electrode prepared at an applied RF power of 90 W. Similarly to the results in Fig. 3, the semi-circles are observed at potential below 0.5 V, and the resistances decrease with decreasing the electrode potentials. In a similar manner, the semi-circles can be assigned again as the charge-transfer resistance. Two features should be pointed out for the comparison of the results as given in Figs. 3 and 4. One is the value of charge-transfer resistances. The carbonaceous thin film electrode prepared at applied RF power of 90 W showed the charge-transfer resistance of half the value of

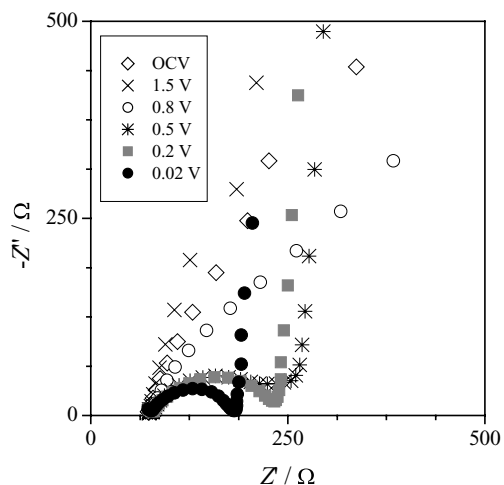


Fig. 4. Nyquist plots of carbonaceous thin film electrodes prepared at applied RF power of 90 W for lithium insertion at various electrode potentials at ambient temperature. Super-imposed AC voltage for impedance measurement was set at 5 mV.

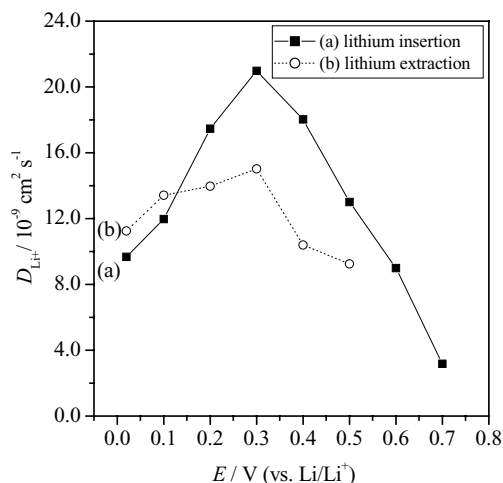


Fig. 5. Potential dependence of apparent diffusion coefficient $D(\text{Li}^+)$ through carbonaceous thin film prepared at applied RF power of 10 W.

that at 10 W. The charge-transfer resistances are correlated with reaction areas. Comparing the values of charge-transfer resistance, the reaction sites for lithium insertion and extraction at the carbonaceous thin film electrode prepared at RF power of 90 W is larger than those of thin film by RF power of 10 W, which is in good agreement with the TEM observation as mentioned above. The other point is the existence of Warburg impedance. In the intermediate frequency region in Fig. 3 at electrode potentials below 0.5 V, the Warburg impedances can be observed in the narrow region, and then capacitive behavior appeared. On the contrary, no Warburg impedances can be seen in Fig. 4. That should be due to the film thickness. It is generally known that the larger RF power decreases the rate of thin film deposition in plasma CVD such as plasma polymerization because of accelerated ablation [14], and therefore, the carbonaceous thin film electrode prepared at an RF power of 90 W was too thin to give Warburg impedances while the thickness was too low to be precisely estimated by weight increase.

The Nyquist plots in Fig. 3 should be interpreted by Voigt-Frumkin and Melik-Gaykazyan impedance as suggested by Levi et al. [15].

As mentioned above, the present film electrode is sufficiently thin that one can obtain apparent Li^+ ion diffusion coefficients using the following equation [16]:

$$D(\text{Li}^+) = \frac{h^2}{3R_{\text{LF}}C_{\text{LF}}} \quad (1)$$

where C_{LF} is the limiting low frequency capacitance, R_{LF} the limiting low frequency resistance, and h denotes the film thickness. Fig. 5 shows the “apparent” Li^+ ion diffusion coefficients evaluated by the above Eq. (1). The diffusion coefficients gave the maximum value at a potential around 0.3 V for both lithium insertion and extraction. Nishizawa et al. [17] reported the electron and ion-transport properties for a single particle of mesocarbon microbeads heat-treated at 1273 K (MCMB1000). The electrical conductance and

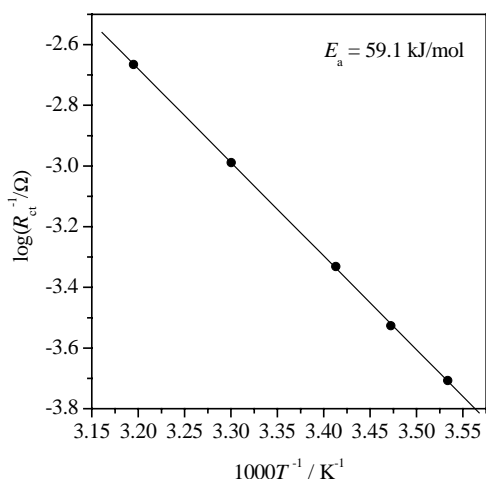


Fig. 6. Temperature dependence of charge-transfer resistance at the interface between carbonaceous thin film electrode (prepared by applied RF power of 10 W) and electrolyte against reciprocal temperatures. The activation energy was evaluated by the least-square fitting.

diffusion coefficient 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 [17]. Our results are in good agreement with those reported by Nishizawa et al., although the potential at which the dependence of diffusion coefficients changes (0.3 V) is different.

It is well known that lithium intercalation of graphite occurs below the potential of around 0.25 V (versus Li/Li^+) [18]. Raman spectroscopy and transmission 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 Fig. 5 should be related to the change in the lithium insertion mechanism; namely “lithium insertion into graphitized structures” or “lithium insertion into non-graphitized structures”.

The activation energy for interfacial Li^+ ion transfer at a potential of 0.1 V was evaluated from the temperature dependence of the charge-transfer resistances as is shown in Fig. 6. As a result, a value of 59.1 kJ/mol was obtained for the carbonaceous thin film electrode prepared at applied an RF power of 10 W. Almost the same activation energies were obtained for a thin film electrode prepared at RF power of 90 W. This value of activation energy is very large in comparison with the activation energy for lithium ion conduction through crystalline solids of fast-lithium-ion transfer (For example [19]) and through positive active material of LiCoO_2 [20]. Therefore, high barriers of activation for lithium-ion transfer exist at the interface between the solid insertion electrode and electrolyte. Thus the lithium-ion transfer through the interface between electrode and electrolyte gives a significant influence on the rate performance of lithium-ion batteries.

4. Conclusion

Carbonaceous thin films have been prepared by plasma CVD to obtain a structurally defined electrode/electrolyte interface. Lithium-ion transfer at the interface between the thin film electrode and the electrolyte were investigated by AC impedance spectroscopy. In the Nyquist plots, one semi-circle due to charge-transfer resistances appeared, and the values were dependent on electrode potentials. Lithium-ion diffusion coefficients were also evaluated by the finite diffusion model. The diffusion coefficient was dependent on the electrode potential. A high activation barrier was shown for interfacial lithium-ion transfer through the interface between carbonaceous electrode and electrolyte.

Acknowledgements

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