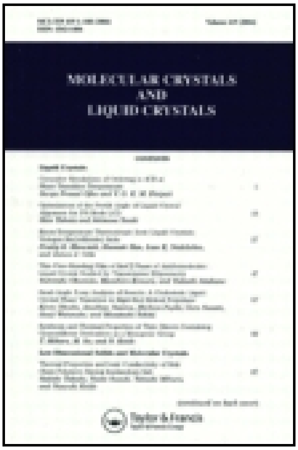

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Electrochemical Intercalation of Li into Carbon Thin Films Prepared by Plasma CVD

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Electrochemical Intercalation of Li into Carbon Thin Films Prepared by Plasma CVD

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Carbonaceous thin films were prepared from acetylene and argon by plasma CVD. The carbon thin films were characterized by Raman spectroscopy and then their electrochemical properties were studied by cyclic voltammetry and charge-discharge measurements. Crystallinity of the films prepared at 90W was much higher than that at 10W. The difference of the applied RF power also effected on the results of cyclic voltammetry and charge-discharge measurements. Correlation of applied RF power and the electrochemical properties of carbon thin films was discussed.

Keywords: carbon thin film; lithium intercalation; plasma CVD

INTRODUCTION

Rechargeable lithium ion batteries have been extensively studied because of their small size and high energy density. Various carbonaceous materials have been investigated as an anode material of secondary lithium battery[1-8]. Because carbonaceous materials are generally powders, binders are necessary for preparation of electrodes. For the study of carbonaceous negative electrodes, carbon thin films are very useful because films can be used as electrode without binders, which enable us to study the electrochemical properties of the carbon itself.

Plasma assisted chemical vapor deposition (CVD) is one of the best methods to prepare carbon thin films, however, most studies have been focused on the preparation of diamond films or diamond like carbon films[9-11]. Dense and pin-hole free thin films can be obtained by use of plasma CVD. Hence, such films are suitable for electrode because their surface area can be precisely determined and the films are electronically conductive.

The preparation and characterization of sp^2-type carbon thin films by glow discharge plasma have been already reported[12]. In this work, carbon thin film electrodes were prepared by plasma CVD, and the electrochemical intercalation of lithium into the resultant carbonaceous thin film electrodes were studied by cyclic voltammetry and charge-discharge measurements.

EXPERIMENTAL

Carbonaceous thin films were prepared by plasma CVD from acetylene as a carbon source and argon as a plasma assist gas. Films were deposited on substrate of nickel sheet whose temperature was kept at 873 K. Applied RF power was 10 and 90W induced by RF 13.56 MHz power supply unit. Details about preparation and characterization of carbonaceous thin films were reported elsewhere[12]. Intercalation of lithium into the carbonaceous thin films was performed by electrochemical methods of cyclic voltammetry and charge-discharge measurements. Lithium metal was used as counter and reference electrodes, and the electrolyte solution was 1 : 1 by volume mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) containing 1 mol dm^{-3} $LiClO_4$ (battery grade by Mitsubishi Petrochemical Company, Limited). The cell was assembled in an argon-filled glove box.

RESULTS AND DISCUSSION

Raman Spectra

The Raman spectra of carbonaceous thin films are shown in Figure 1. Mainly two peaks around 1350 and 1600 cm^{-1} were observed. These peaks have been known as Raman active A_{1g} (due to finite crystal size) and E_{2g} (due to infinite crystal size) mode frequencies, respectively[13]. The peak around 1620 cm^{-1} is also derived from imperfectness of graphite crystal[14]. As is shown in Figure 1, peaks around 1600 cm^{-1} of E_{2g} mode frequency become sharper and this peak position shifts toward 1580 cm^{-1} with increasing the applied RF power. Full width at half maximum (FWHM) of the peak around 1600 cm^{-1} is reported to be correlated with crystallinity of carbonaceous materials[14], and single crystal of graphite gives only one peak around 1580 cm^{-1}. These results may indicate that crystallinity of the samples increased with increasing the applied RF power, which is also confirmed by the conductivity results[12]. These Raman spectra are similar to that of non-graphitizable carbon in that intensities of around 1360 cm^{-1} peaks are higher than those of around 1580 cm^{-1} [15]. From these results, carbonaceous thin films in this study have partly non-graphitizable structures.

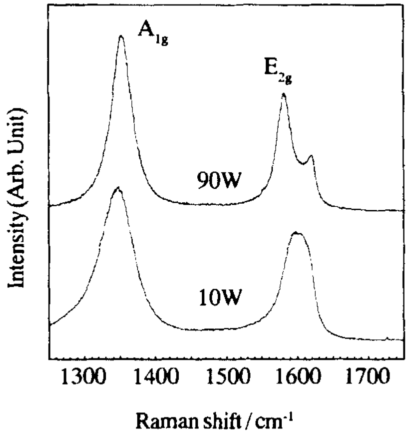

FIGURE 1 Raman spectra of carbon thin films prepared by plasma CVD.

Electrochemical Properties

Figure 2 shows cyclic voltammograms of carbonaceous thin films. Cyclic voltammogram was measured with a sweep rate of 1 mV / sec. For the first sweep, irreversible reduction current was observed from the potential around 0.6 to 0.5V vs. Li/Li^+, however, it almost disappeared for the second sweep, irrespective of applied RF power. These results indicate the decomposition of solvent and formation of solid electrolyte interface (SEI) on the surface of carbonaceous thin films[16,17]. The shapes of cathodic and anodic peaks around 0V are very different between Figures 2 (a) and (b). In Figure 2 (b), clear shoulders around 0V as shown by two arrows appeared, which may be correlated with the formation of stage structures[18,19]. From Raman spectrum of carbon thin film prepared at 90W, the FWHM of the peak at 1600 cm^{-1} was determined to be 27 cm^{-1}. This value corresponds to that obtained for carbon heat treated at above 2273 K[20]. Hence, stage structures can be formed for this carbon thin films. From the above results, the intercalation and de-intercalation behavior of carbon thin films was dependent on the applied RF power. In-situ Raman spectroscopy will be useful for the detail discussion of the stage sturcture[7,8].

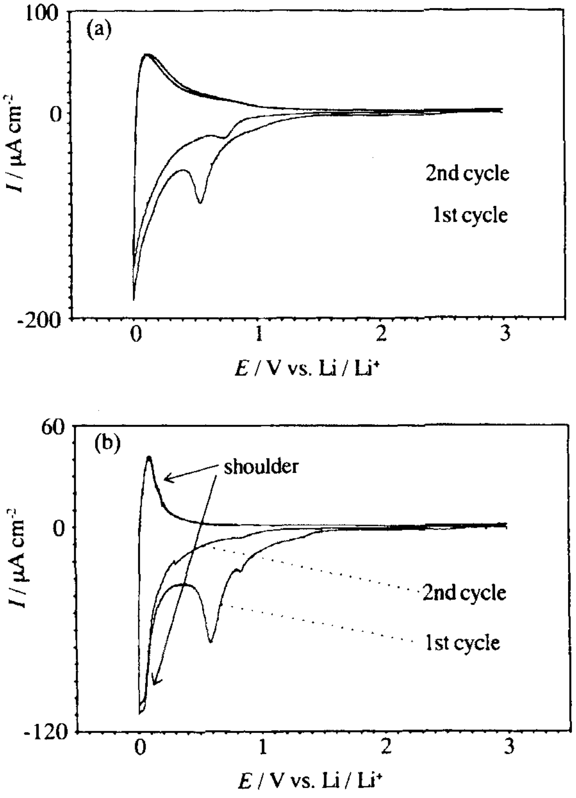

FIGURE 2 Cyclic voltammograms of carbon thin film in 1 mol dm^{-3} $LiClO_4$ / EC+DEC (1:1). Sweep rate : 1 mV / sec, applied RF power (a) 10W and (b) 90 W.

Figure 3 shows variation of potential intercalation and de-intercalation of lithium into carbon thin film. At 1st cycle, very large irreversible capacity around 1.0 to 0.8V appeared. This irreversible capacity is very similar to that reported by Mochida *et al*[21]. The irreversible capacity disappeared after 2nd cycle, but, another irreversible capacity appeared. De-intercalation curve of sample prepared at 10W showed about 550 $mAhg^{-1}$ of capacity at 2nd cycle and a comparatively large potential plateau appeared at approximately 1V. These results indicated that the electrochemical properties of carbon thin films prepared at 10W are very similar to those for low graphtized carbon such as low heat-treated mesocarbon microbeads (MCMB)[22]. De-intercalation curve of sample prepared at 90W gave c.a. 180 $mAhg^{-1}$ of capacity at 2nd cycle, and the ratio of capacity in the potential range 0 to 0.25V to that in the range 0.25 to 3 V was large in comparison with the ratio of sample prepared at 10W. It has been reported that the de-intercalation capacity in the potential range 0 to 0.25V becomes large with increasing of crystallinity of MCMB[23]. Hence, the present results of charge-discharge measurements are quite reasonable.

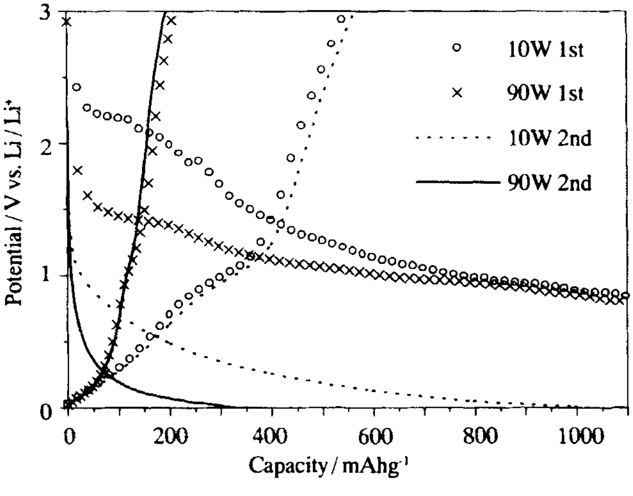

FIGURE 3 Variation of potential intercalation and de-intercalation of Li into carbon thin film in 1 mol dm^{-3} $LiClO_4$ / EC+DEC (1:1). Current : 24 mA/g.

CONCLUSION

Carbon thin films are prepared from acetylene and argon by using glow discharge plasma. Crystallinity of these films increase with increasing applied RF power. Only the difference of applied RF power affects on crystallinity and electrochemical properties of the resultant carbon thin films. Carbon thin films in this study are very useful as binder free negative electrode of lithium ion battery.

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