

# Electrochemical Lithium Insertion/Extraction for Carbonaceous Thin Film Electrodes in Propylene Carbonate Solution

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## Abstract

Carbonaceous thin films were prepared from acetylene and argon gases by plasma assisted chemical vapor deposition (Plasma CVD) at 873 K. The carbonaceous thin films were characterized by mainly Raman spectroscopy, and their electrochemical properties were studied by cyclic voltammetry and charge-discharge measurements in propylene carbonate (PC) solution. Raman spectra showed that crystallinity of carbonaceous thin films is correlated by the applied RF power. The difference of the applied RF power also affected on the results of cyclic voltammetry and charge-discharge measurements. In PC solution, intercalation and de-intercalation of lithium ion can occur as well as in the mixed solution of EC and DEC.

**Keywords :** Plasma Assisted Chemical Vapor Deposition, Carbonaceous Thin Film Electrode, Lithium Insertion and Extraction

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## 1. Introduction

Lithium ion batteries have been extensively studied because of their high performance and potentialities. Carbonaceous materials of  $sp^2$ -type structure have received much attention for use as negative electrodes of lithium ion batteries. Among them, highly crystallized graphite has been used in commercial market due to the flat potential as low as Li metal and acceptable high energy. However, various carbonaceous materials such as disordered carbon have been still extensively investigated for use as negative electrode materials to improve the performance of lithium ion batteries [1-9].

Since commercialized carbonaceous materials are generally obtained as powder form, binders such as PVdF and PTFE are essential for preparation of electrodes, which makes us difficult to elucidate the precise electrochemical properties of the carbonaceous materials themselves. For the study of carbonaceous negative electrodes, carbonaceous thin films are ideal, because the films can be used as electrodes without binders and it is easy to define their surface area of electrodes. However, few studies employing carbonaceous thin films as negative electrodes of lithium ion batteries have been made [10, 11]. This is because there are some difficulties to prepare thin film electrode of  $sp^2$ -type carbonaceous materials due to low adherence on a substrate, high heat treatment temperature, and others.

One of the good methods for preparation of thin films is plasma CVD. In glow discharge plasma, inorganic thin films can be synthesized at lower temperatures [12, 13]. Synthesis

of carbonaceous thin films using plasma CVD has been also carried out by many workers. However, most of these studies have been focused on the preparation of diamond films and/or diamond-like carbon films of  $sp^3$ -type structure [14, 15], and little attention has been paid to synthesis of  $sp^2$ -type carbonaceous thin films.

The preparation and characterization of  $sp^2$ -type carbonaceous thin films by plasma CVD have been already reported by the present authors [16-19]. In this work, electrochemical properties of carbonaceous thin film electrodes prepared by plasma CVD in propylene carbonate (PC) solution were studied by cyclic voltammetry (CV) and charge-discharge measurements.

## 2. Experimental

Fig. 1 shows a schematic diagram of plasma CVD apparatus used in this study. The starting materials were acetylene and argon. Acetylene and argon gases were used as a carbon source and a plasma assist gas, respectively. Substrates were placed on a ground electrode whose temperature was kept at 873 K. Carbonaceous thin films were deposited on substrates of nickel sheets. The detail procedure can be referred by our previous literature [16].

Resultant carbonaceous thin films were characterized by Raman spectroscopy. Raman spectra were excited by using a 514.5 nm line (50 mW) of an argon ion laser (NEC, GLG3260), and the scattered light was collected in a back-scattering geometry. All spectra were recorded using a spec-

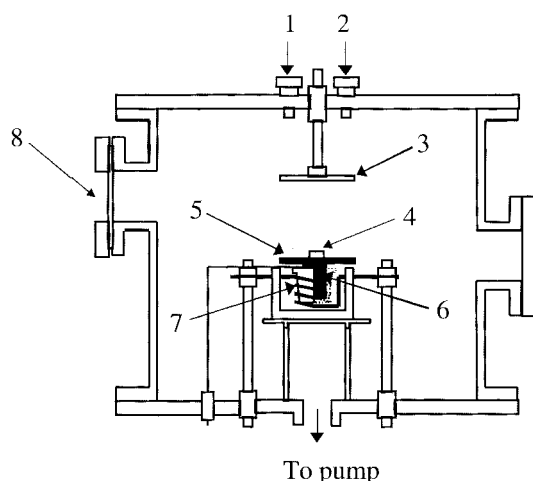


Fig. 1. Schematic diagram of RF reactor for the plasma CVD apparatus. 1: Ar inlet; 2:  $C_2H_2$  inlet; 3: RF electrode; 4: substrate; 5: thermocouple; 6: ground electrode; 7: tungsten heater; 8: view port.

trometer (Jobin-Yvon, T64000) equipped with a multi-channel CCD detector. Each measurement was carried out at room temperature with an integration time of 300 s.

Electrochemical measurements were performed by using a three-electrode electrochemical cell. Carbonaceous thin films were used as a working electrode, and lithium metal was used as counter and reference electrodes. The electrolyte solution was a propylene carbonate (PC) containing  $1 \text{ mol dm}^{-3}$   $LiClO_4$  (battery grade by Mitsubishi Petrochemical Company, Limited). The cell was assembled in an argon-filled glove box. Electrochemical properties were examined by cyclic voltammetry (VoltaLab 32) and charge-discharge measurements using a battery test system (Hokuto Denko, HJ101SM6).

### 3. Results and Discussion

The morphology of carbonaceous thin films was investigated by scanning electron microscopy (SEM) and surface of carbonaceous thin film was very flat and free from pin-hole. The film thickness was determined to be less than  $1 \mu\text{m}$  by cross section of SEM image [17, 19]. Carbonaceous thin films prepared using all RF powers also gave the similar morphologies. The electrical conductivity of carbonaceous thin films are 2-28 S/cm [16] and these values are as high as those of carbonaceous films prepared by thermal CVD method [20].

The Raman spectra of carbonaceous thin films are shown in Fig. 2. Mainly three peaks around  $1360$ ,  $1580$  and  $1620 \text{ cm}^{-1}$  were observed. The peak around  $1580 \text{ cm}^{-1}$  is well known to be related with crystallinity of carbonaceous materials, and is assigned to Raman active  $E_{2g}$  mode frequency (G band) [21]. The peak around  $1360 \text{ cm}^{-1}$  is Raman inactive  $A_{1g}$  mode frequency [21]. The peaks around  $1360$  and  $1620 \text{ cm}^{-1}$  appear in the case of finite crystal size and imperfection of carbonaceous materials [22], and the former is

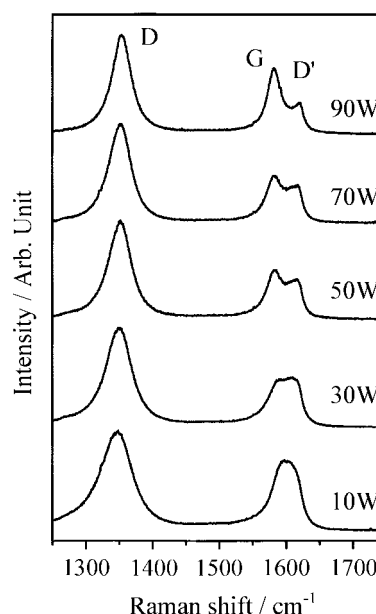


Fig. 2. Raman spectra of carbonaceous thin films prepared by plasma CVD. Reaction time: 6 h, substrate: Ni, applied RF power for preparation: 10, 30, 50, 70, 90 W. Integration time: 300 s.

called as D band and the latter is as D' band. As is shown in Fig. 2, the peak around  $1580 \text{ cm}^{-1}$  of G band became sharper and its position shifted toward  $1580 \text{ cm}^{-1}$  with increasing the applied RF power. Full width at half maximum (FWHM) of the peak around  $1580 \text{ cm}^{-1}$  was reported to be correlated with crystallinity of carbonaceous materials, and single crystal of graphite gives only one peak around  $1580 \text{ cm}^{-1}$  [22]. Therefore, the result in Fig. 2 indicates that crystallinity of the samples increased with increasing the applied RF power, which was also confirmed by the conductivity measurements. The important point of the spectra was that crystallinity of carbonaceous thin film was changed easily by changing the applied RF power at fixed temperature as low as  $873 \text{ K}$ .

In PC solution, the decomposition of electrolyte occurs at about  $1 \text{ V vs. Li/Li}^+$  with exfoliation of graphite layers, and lithium ion does not intercalate into graphite electrode [23]. In the case of the present carbonaceous thin film electrodes, insertion of lithium ion took place in PC solution. Fig. 3 shows cyclic voltammograms of thin film electrode prepared at 10W in PC solution (1st cycle and 2nd cycle). The cyclic voltammogram was measured with a sweep rate of  $1 \text{ mV/s}$  in the potential range of  $0$  to  $3 \text{ V vs. Li/Li}^+$ . For the first sweep, large irreversible reduction current appeared from the potential around  $1.0$  to  $0.5 \text{ V}$ . The reduction current almost disappeared after the second sweep, indicating that the decomposition of solvent and formation of solid electrolyte interface (SEI) [24, 25] on the surface of carbonaceous thin film effectively occurred in PC solution in the first sweep. For other thin film electrodes prepared at the other RF powers, large reduction currents at around  $1.0$  to  $0.5 \text{ V}$  also appeared in the first sweep of cyclic voltammograms. In the oxidation process, clear oxidation current is obtained at

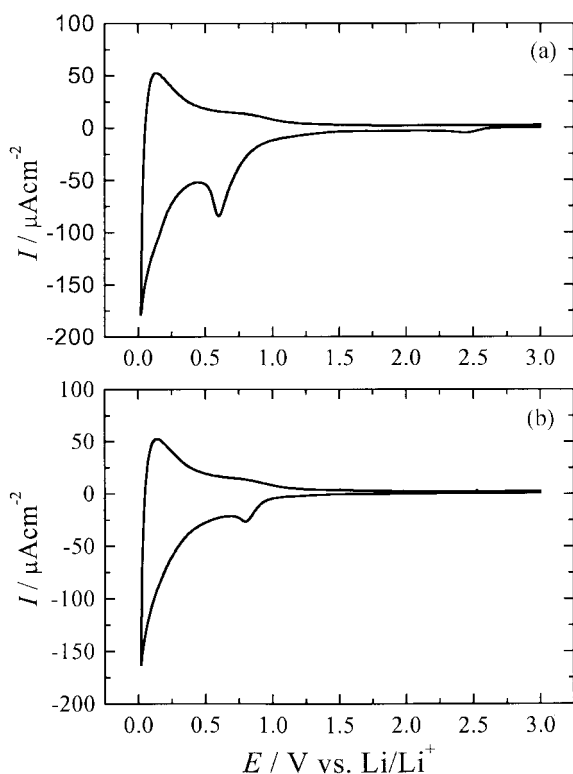


Fig. 3. Cyclic voltammograms of carbonaceous thin film electrode in  $1 \text{ mol dm}^{-3} \text{ LiClO}_4/\text{PC}$ . Sweep rate:  $1 \text{ mV/s}$ . Applied RF power for preparation:  $10 \text{ W}$ . (a) 1st cycle and (b) 2nd cycle.

around  $0.1 \text{ V}$  corresponding to the extraction of lithium ion. From above results, it is found that lithium ion can insert into carbonaceous thin films in PC solution as well as in EC based solution.

Fig. 4 shows cyclic voltammograms at the second sweep for thin film electrodes prepared by RF powers of  $10 \text{ W}$  and  $90 \text{ W}$ . The difference in the magnitude of the value of currents is probably due to the thickness of film, that is, film thickness of the thin film electrode prepared at  $10 \text{ W}$  is

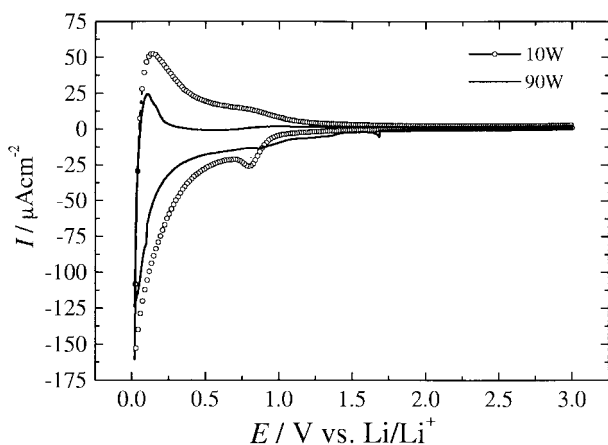


Fig. 4. Cyclic voltammograms (2nd cycle) of carbonaceous thin film electrodes in  $1 \text{ mol dm}^{-3} \text{ LiClO}_4/\text{PC}$ . Sweep rate:  $1 \text{ mV/s}$ , applied RF power for preparation:  $10 \text{ W}$  and  $90 \text{ W}$ .

thicker than that of prepared at  $90 \text{ W}$ . The shape of cyclic voltammogram is affected by RF powers of  $10 \text{ W}$  and  $90 \text{ W}$  as shown in Fig. 4. In the oxidation process, the peak at around  $0.1 \text{ V}$  of thin film electrode prepared at  $90 \text{ W}$  was sharper than that of prepared at  $10 \text{ W}$ . For the thin film electrode prepared at  $90 \text{ W}$ , small shoulder was shown at large oxidation peak at  $0.1 \text{ V}$  probably due to the existence of another successive oxidation. These results were correlated with the formation of stage structures of Li-GIC [26]. The difference of the shape of cyclic voltammograms was also related with Raman spectra shown in Fig. 2, that is, crystallinity of the thin film prepared at  $90 \text{ W}$  was higher than that of the thin film prepared at  $10 \text{ W}$ . In other words, the degree of crystallinity of the carbonaceous thin films affected the shapes of cyclic voltammograms.

Fig. 5a shows the second cycle of charge and discharge characteristics for carbonaceous thin film electrode prepared at  $10 \text{ W}$  in PC solution. Current density was set at  $26 \text{ mA/g}$ . In this paper, carbonaceous thin film electrodes act as positive electrodes against counter electrode of lithium metal, therefore insertion of lithium is expressed as discharge and extraction of lithium ion as charge. At the first cycle, very large irreversible capacity above  $0.5 \text{ V}$  appeared. In the mixed solution of EC and DEC, the large irreversible capacity also appeared [19]. This irreversible capacity decreased dramatically after the second cycle. At the second cycle, insertion curve of thin film electrode prepared at  $10 \text{ W}$  showed about  $300 \text{ mAh/g}$  of capacity and extraction curve showed about  $200 \text{ mAh/g}$ . These discharge and charge capacity were smaller than those of thin film electrodes in mixed solution of EC and DEC [19]. Similar tendency is also observed for the thin film electrode prepared at  $90 \text{ W}$  (Fig. 5b). From this result, it is considered that insertion and extraction of lithium ion for carbonaceous thin film electrodes in PC solution are not as easy as those in the mixed solution of EC and DEC. In the extraction curves, a comparatively large potential plateau appeared at approximately  $1 \text{ V}$ . These results indicated that the electrochemical properties of thin film electrode prepared at  $10 \text{ W}$  were very similar to those for graphitizable carbon heat-treated at low temperatures [27]. Fig. 5b shows charge and discharge characteristics of thin film electrode prepared at  $90 \text{ W}$ . Insertion curve of sample prepared at  $90 \text{ W}$  showed about  $230 \text{ mAh/g}$  of capacity at the second cycle and extraction curve showed about  $160 \text{ mAh/g}$ . On extraction curves, relatively small potential plateau appeared at approximately  $1 \text{ V}$ . In the case of graphite, de-intercalation of lithium ion from Li-GIC is known to take place below  $0.25 \text{ V}$  [28]. The proportion of discharge capacity below  $0.25 \text{ V}$  to whole discharge capacity of thin film electrode prepared at  $90 \text{ W}$  is larger than that of thin film electrode prepared at  $10 \text{ W}$ . Tatsumi *et al.* reported that this proportion became large with increasing in crystallinity of MCMBs [29]. Hence, the present results of charge-discharge measurements support that the high RF power gave a thin film of high crystallinity. From these results, charge and discharge characteristics showed similar tendency to the results of cyclic voltammograms for carbon-

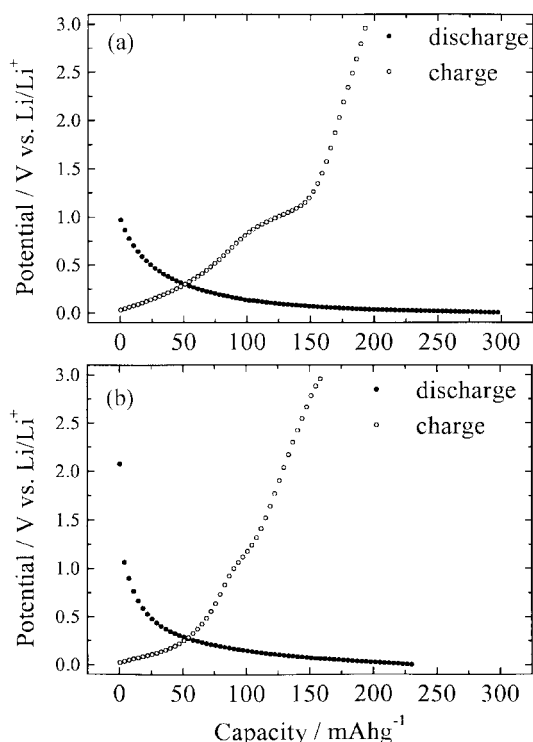


Fig. 5. Charge and discharge characteristics (2nd cycle) of carbonaceous thin film electrodes in 1 mol dm<sup>-3</sup> LiClO<sub>4</sub>/PC. Current density: 26 mA/g. Applied RF power for preparation: (a) 10 W and (b) 90 W.

aceous thin film electrodes in this study.

#### 4. Summary

Sp<sup>2</sup>-type carbonaceous thin films were prepared by C<sub>2</sub>H<sub>2</sub>/Ar glow discharge plasma at 873 K. Carbonaceous thin films in this study were homogeneous and pin-hole free. Applied RF power of plasma was found to influence on the crystallinity of carbonaceous thin films. In PC solution, insertion and extraction of lithium ion can occur for carbonaceous thin film, but reversible capacity was smaller than in EC based solution. This is probably because that the passivation film formed in PC solution was not so satisfactory as those in EC based solution.

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#### References

[1] Imanishi, N.; Kashiwagi, H.; Ichikawa, T.; Takeda, Y.;

- Yamamoto, O.; Inagaki, M. *J. Electrochem. Soc.* **1993**, *140*, 315.
- [2] Sato, K.; Noguchi, M.; Demachi, A.; Oki, N.; Endo, M. *Science* **1994**, *264*, 556.
- [3] Yata, S.; Kinoshita, H.; Komori, M.; Ando, N.; Kashiwamura, T.; Harada, T.; Tanaka, K.; Yamabe, T. *Synth. Met.* **1994**, *62*, 153.
- [4] Dahn, J. R.; Zheng, T.; Liu, Y.; Xue, J. S. *Science* **1995**, *270*, 590.
- [5] Inaba, M.; Yoshida, H.; Ogumi, Z.; Abe, T.; Mizutani, Y.; Asano, M. *J. Electrochem. Soc.* **1995**, *142*, 20.
- [6] Zheng, T.; McKinnon, W. R.; Dahn, J. R. *J. Electrochem. Soc.* **1996**, *143*, 2137.
- [7] Inaba, M.; Shiroma, Z.; Funabiki, A.; Ogumi, Z. *Langmuir* **1996**, *12*, 1535.
- [8] Inaba, M.; Fujikawa, M.; Abe, T.; Ogumi, Z. *J. Electrochem. Soc.* **2000**, *147*, 4008.
- [9] Park, C.W.; Yoon, S.-H.; Lee, S. I.; Oh, S. M. *Carbon* **2000**, *38*, 995.
- [10] Levi, M. D.; Aurbach, D. *J. Phys. Chem. B* **1997**, *101*, 4630.
- [11] Lee, S.-J.; Nishizawa, M.; Uchida, I. *Electrochim. Acta* **1999**, *44*, 2379.
- [12] Awaya, N.; Arita, Y. *Jpn. J. App. Phys.* **1991**, *30*, 1813.
- [13] Kny, E.; Levenson, L. L.; James, W. J.; Auerbach, R. A. *Thin Solid Films* **1981**, *85*, 23.
- [14] Matsumoto, S. *J. Mater. Sci. Lett.* **1985**, *4*, 600.
- [15] Angus, J. C.; Hayman, C. C. *Science* **1988**, *241*, 913.
- [16] Abe, T.; Fukutsuka, T.; Inaba, M.; Ogumi, Z. *Carbon* **1999**, *37*, 1165.
- [17] Fukutsuka, T.; Abe, T.; Inaba, M.; Ogumi, Z. *Tanso* **1999**, *190*, 252.
- [18] Fukutsuka, T.; Abe, T.; Inaba, M.; Ogumi, Z. *Mol. Cryst. Liq. Cryst.* **2000**, *340*, 517.
- [19] Fukutsuka, T.; Abe, T.; Inaba, M.; Ogumi, Z. *J. Electrochem. Soc.* Submitted.
- [20] Yu, H. A.; Kaneko, T.; Otani, S.; Sasaki, Y.; Yoshimura, S. *Carbon* **1998**, *36*, 137.
- [21] Tuinstra, F.; Koenig, J. L. *J. Chem. Phys.* **1970**, *53*, 1126.
- [22] Katagiri, G. *Tanso* **1996**, *175*, 304 (in Japanese).
- [23] Dey, A. N.; Sullivan, B. P. *J. Electrochem. Soc.* **1970**, *117*, 222.
- [24] Peled, E. *J. Electrochem. Soc.* **1979**, *126*, 2047.
- [25] Besenhard, J. O.; Winter, M.; Yang, J.; Biberacher, W. *J. Power Sources* **1995**, *51*, 228.
- [26] Takagi, R.; Okubo, T.; Sekine, K.; Takamura, T. *Denki Kagaku* (presently *Electrochemistry*), **1997**, *65*, 333 (in Japanese).
- [27] Mabuchi, A.; Tokumitsu, K.; Fujimoto, H.; Kasuh, T. *J. Electrochem. Soc.* **1995**, *142*, 1041.
- [28] Ohzuku, T.; Iwakoshi, Y.; Sawai, K. *J. Electrochem. Soc.* **1993**, *140*, 2490.
- [29] Tatsumi, K.; Iwashita, N.; Sakaebe, H.; Shioyama, H.; Higuchi, S.; Mabuchi, A.; Fujimoto, H. *J. Electrochem. Soc.* **1995**, *142*, 716.