ELSEVIER

Short communication

Suppressive effect of lithium phosphorous oxynitride at carbon anode on solvent decomposition in liquid electrolyte

Kwang-il Chung[a], Jong-Guen Park[a], Woo-Seong Kim[b],
Yung-Eun Sung[b], Yong-Kook Choi[a],*

[a]*Department of Chemistry & RRC/HECS, Chonnam National University, Kwangju 500-757, South Korea*
[b]*Department of Materials Science & Engineering, Kwangju Institute of Science and Technology, Kwangju 500-712 South Korea*

Abstract

The irreversible capacity during the first cycle is investigated at a carbon electrode in a Li-ion battery in 1 M $LiPF_6$/EC:DEC (ethylene carbonate:1,2 diethyl carbonate; 1:1 volume ratio). Solvent decomposition is one of main causes of the initial irreversible capacity. A lithium phosphorus oxynitride (LiPON) thin-film, which is a solid ionic conductor, is deposited on the surface of the carbon electrode by means of a radio frequency magnetron sputtering system. The effect of the LiPON layer is examined with chronopotentiometry and cyclic voltammetry, as well as with scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX), and X-ray diffraction (XRD). The deposition of LiPON on the surface of the carbon electrode results in a decrease in the initial irreversible capacity due to the suppression of solvent decomposition on the electrode surface.
© 2002 Elsevier Science B.V. All rights reserved.

Keywords: Lithium ion battery; Initial irreversible capacity; Lithium phosphorus oxynitride; Carbon anode; Sputtering deposition

1. Introduction

Since the 1980s, there has been increasing interest in lithium–carbon insertion compounds for use as materials in negative electrodes (anodes) in Li-ion batteries. Carbon has the advantages of low cost, low toxicity, and a high chemical stability, compared with other candidate electrode materials. Although it shows a highly reversible lithium insertion reaction, carbon has an initial irreversible capacity due to side reactions. Typically, these reactions involve: (i) solvent decomposition at the electrode surface; (ii) the irreversible reaction of lithium-ions with functional groups, such as carboxyl, hydroxyl and carbon hydride on the carbon surface; (iii) the irreversible insertion of lithium into carbon. In particular, (i) and (ii) lead to the formation of a passivation film or solid electrolyte interface (SEI) on the carbon electrode surface [1–7]. Solvent decomposition is not simply a reaction on the carbon surface, but a complex three-dimensional problem which involves solvent co-intercalation [8]. The carbon structure is destroyed due to solvent co-intercalation when solvent decomposition occurs on the electrode surface. A number of investigations have examined the mechanism by which the passivation film is formed on a carbon electrode [1–7,9].

The growth and properties of the SEI are dependent upon the electrolyte composition, the nature of the impurities present, and the additives employed. For example, the addition of SO_2 [10], CO_2 [11–13], or inorganic agents, such as Ni and Sn [14,15], has been found to favor the deposition of passivation films, and thus prevent the reduction of the majority of the components in the electrolyte. Our previous work [16] reported the use of Li_2CO_3 as an additive for the formation of a passivation film on the carbon surface to suppress the initial irreversible capacity associated with solvent decomposition.

In this work, the deposition of lithium phosphorus oxynitride (LiPON) using a sputtering method is examined to reduce the extent of solvent decomposition and solvent co-intercalation. LiPON is known to be a solid electrolyte since all-solid-state, thin-film, rechargeable lithium batteries have been fabricated at ORNL [17]. The stability of these batteries at high voltage and for long cycle times is attributed to the electrochemical stability of the LiPON films. Thus, LiPON might function as a stable, protective, solid electrolyte interphase film on the surface of a carbon electrode. The

---

* Corresponding author. Fax: +82-62-530-3389.
E-mail address: ykchoi@chonnam.chonnam.ac.kr (Y.-K. Choi).

effects of LiPON deposition on a carbon electrode surface are examined with chronopotentiometry, cyclic voltammetry, scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX), and X-ray diffraction (XRD).

2. Experimental

A Kawasaki mesophase fine carbon (KMFC) electrode was prepared by mixing KMFC powder with polyvinyldifluoride (PVDF) as a binder, followed by pressing or on to a copper foil. After vacuum drying at $120\ ^\circ C$ for 6 h, the electrode was placed in a three-electrode cell under an atmosphere of argon. A thin-film of lithium phosphorus oxynitride (LiPON) was then deposited on the KMFC electrode by r.f. sputtering (13.56 MHz)—this is the most popular solid electrolyte material for use in thin-film rechargeable batteries. A schematic illustration of the r.f. sputtering equipment used for the LiPON deposition is given in Fig. 1. The film was deposited from a Li_3PO_4 target (Pure Tech Chemistry) using N_2 process gas. The conditions involved a process pressure of 15 mTorr N_2 and a film deposition rate of 13 Å/min. Lithium metal was used as both the counter and the reference electrodes. The reference electrode was sandwiched between a square KMFC electrode (1 cm^2) and the Li counter electrode, and was separated with a Celgard polypropylene separator. The fabrication was performed under an atmosphere of argon.

Cycling tests for the KMFC electrode were conducted with a WBCS3000 battery cycler system (Won-A Tech). The electrochemical properties of the passivation film on the KMFC were investigated using an organic electrolyte system. High-purity ethylene carbonate (EC, 99.99%) and 1,2-diethyl carbonate (DEC, >99.99%) (Mitsubishi Chemical, battery grade) were used as solvents for the electrolyte solution. Lithium hexafluoro phosphate, $LiPF_6$ (Morita Chemical Industry) was used as the electrolytic salt.

Chronopotentiometry and cyclic voltammetry were used to study the initial irreversible capacities and solvent decomposition. To study the morphology of the KMFC anode and the LiPON-deposited KMFC anode, SEM/EDX analyses were performed on samples through the use of a S-4700 HITACHI Scanning Microscope (NORAN Instruments). The working voltage was set at 20 kV, and the working distance of the lens at 27 md. XRD measurements (Rigaku D/max-1200) were used to investigate the LiPON structure. The measurements were carried out at room temperature.

3. Results and discussion

The surface morphologies of the KMFC electrode were observed by SEM. The original KMFC electrode surface was measured in order to compare with the LiPON-deposited KMFC electrode surface. The original KMFC electrode surface, on which carbon beads are distributed is shown in
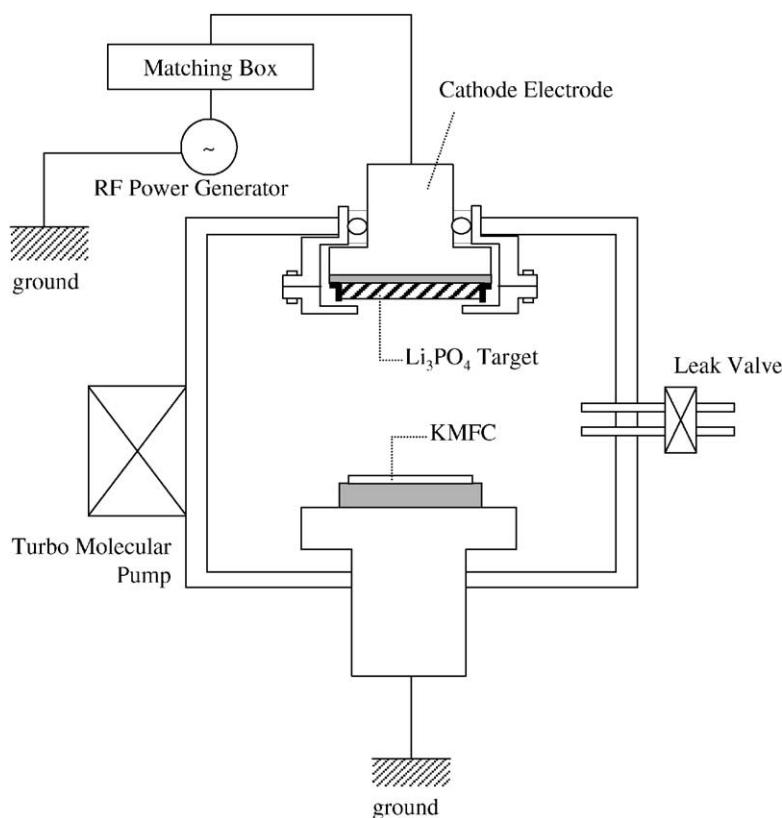

Fig. 1. Schematic illustration of r.f. sputtering equipment for preparation of LiPON thin-film on KMFC electrode.
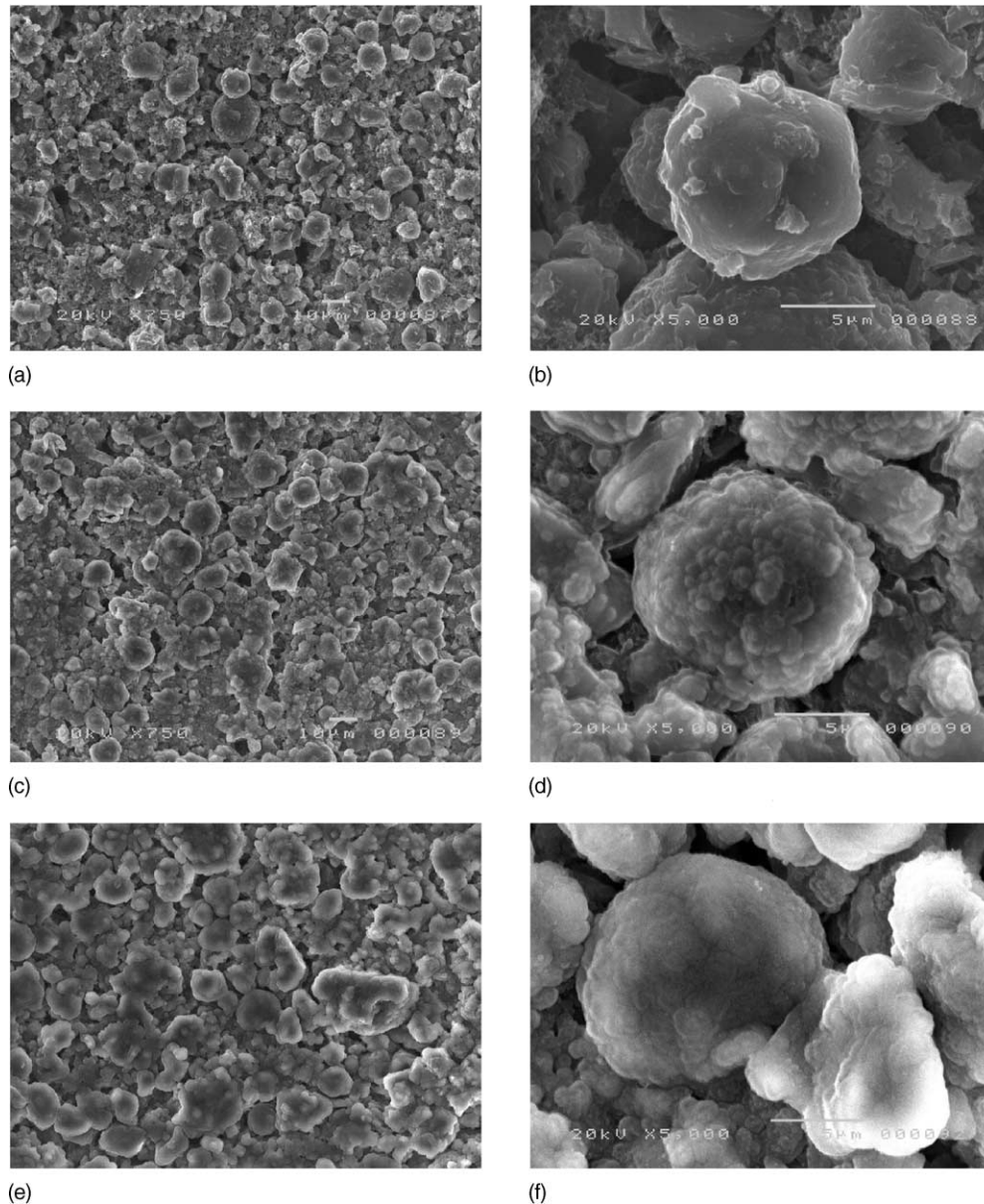
Fig. 2. Scanning electron micrographs of original KMFC electrode surface ((a) 750× and (b) 5000×), LiPON-deposited KMFC electrode surface deposited by sputtering ((c) 750× and (d) 5000×), and LiPON-deposited KMFC electrode surface after dipping in liquid electrolyte ((e) 750× and (f) 5000×).

Fig. 2a and b. The diameter of the KMFC is not regular for particle sizes under 20 μm. After r.f. magnetron sputtering of the Li_3PO_4 target in N_2 process gas, the deposited KMFC electrode surface was investigated. The results are shown in Fig. 2c and d. The surface of the LiPON-deposited KMFC electrode has a clearly different surface morphology from the original electrode one. As can be seen in Fig. 2c and d, fine deposits encapsulated the KMFC beads. Based on previous reports [18–20], particles that were sputtered from the Li_3PO_4 target were deposited on the surface of substrate, to form a lithium phosphorus oxynitride (LiPON) film. After dipping in the electrolyte for 24 h, the surface morphology of the LiPON deposited KMFC electrode was investigated. The results are shown in Fig. 2e and f. Compared with the

film deposited by r.f. sputtering on the KMFC beads, the film is both smoother and thicker. This can be attributed to the penetration of electrolyte into the LiPON deposited film of the KMFC electrode.

EDX data for the original KMFC electrode and the LiPON-deposited KMFC electrode are given in Fig. 3. The original KMFC electrode (Fig. 3a) shows only peaks corresponding to C and Cu. The origin of the C peak is the carbon electrode, while that of the Cu peak is the Cu current collector. Additional N, O and P peaks are also present in the EDX data of the LiPON-deposited KMFC electrode (Fig. 3b). The origin of the N, O and P peaks are the film formed on the carbon electrode surface by sputtering. The O and P peaks arise from the Li_3PO_4 target, and the N peak is
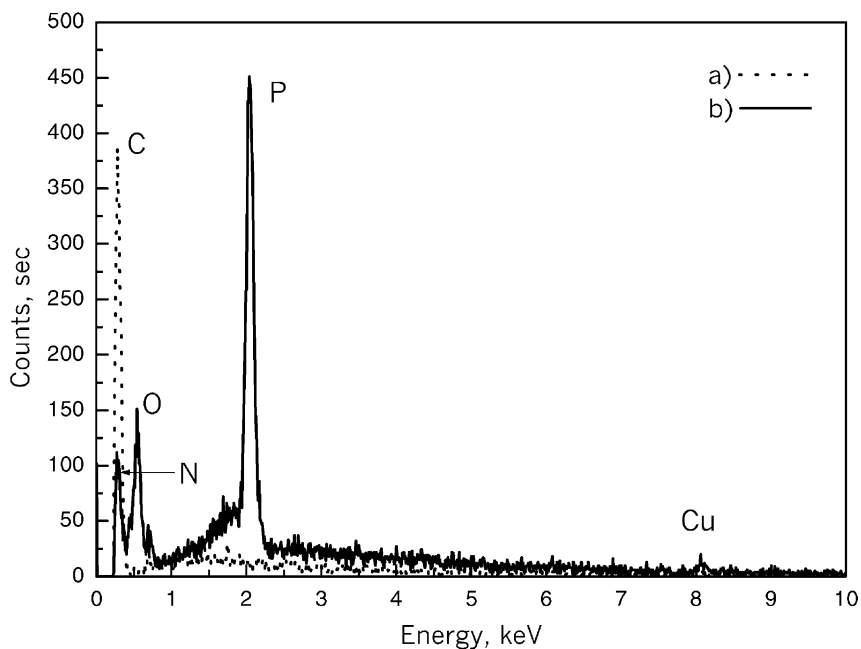
Fig. 3. EDX data for (a) original KMFC and (b) LiPON-deposited KMFC electrodes.

clearly derived from the process gas, N_2. Therefore, the film deposited using the above method is clearly LiPON, as reported in previous studies [18–20].

XRD analysis was performed for both the original KMFC and the LiPON-deposited KMFC electrode (Fig. 4). From the results, (0 0 2) peaks corresponding to graphitic carbon are present at about 26°. The broad region of enhanced X-ray intensity for the LiPON-deposited KMFC electrode is indicative of an amorphous phase, which is believed to be amorphous LiPON.

The voltage–capacity profile of an original KMFC electrode at a low rate of 0.5 mA cm^{-2} in 1 M LiPF$_6$/EC:DEC (1:1, volume ratio) is presented in Fig. 5a. The initial irreversible capacity is about 120 mAh g^{-1}, and is calculated by subtracting the initial de-intercalation capacity from the initial intercalation capacity. Voltage plateau are observed at about 2.2 and 0.8 V, as the result of solvent decomposition [21]. Below 0.5 V; lithium intercalation into the KMFC electrode is the predominant process. The voltage–capacity profile of the LiPON-deposited KMFC electrode is
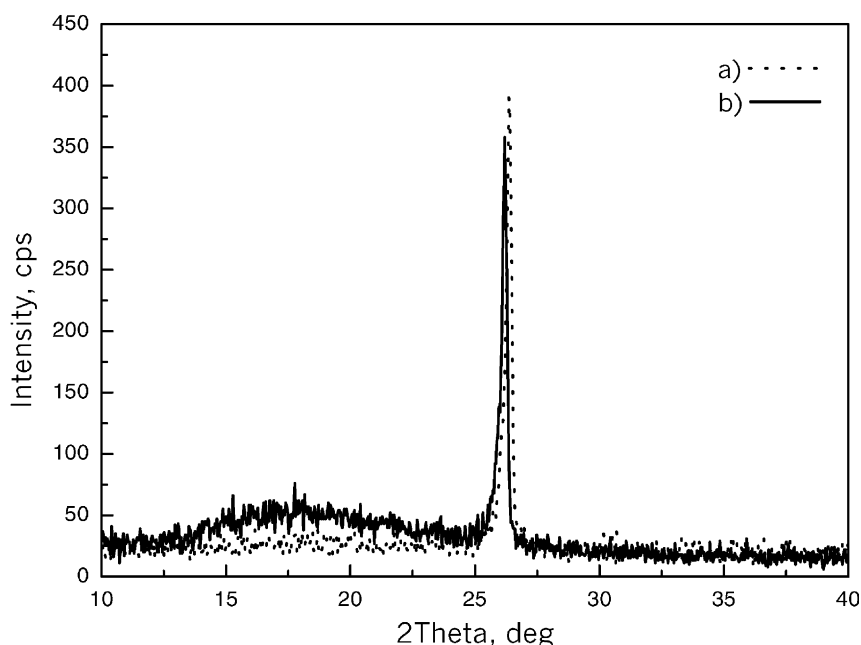

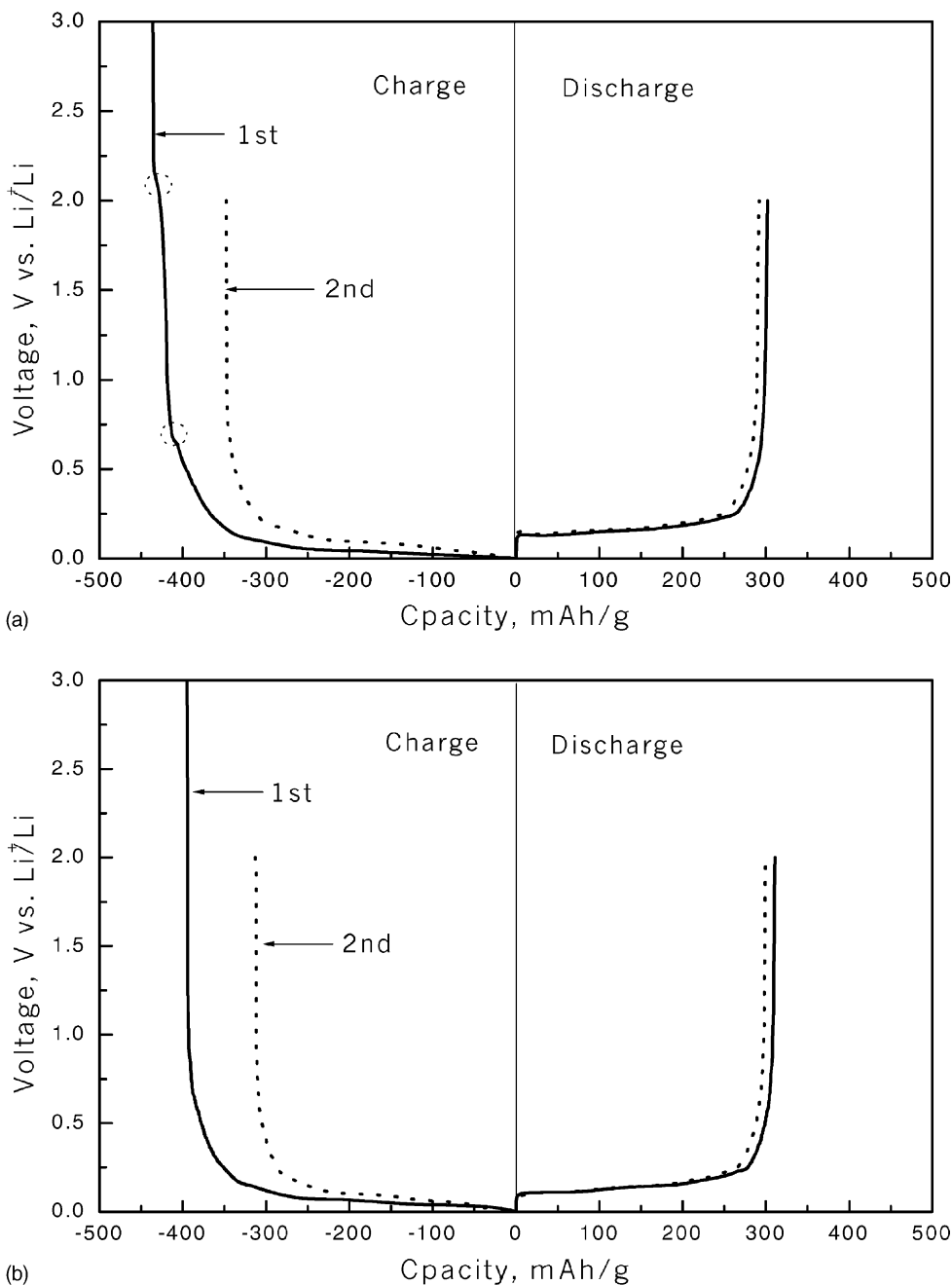Fig. 4. XRD results for (a) original KMFC and (b) LiPON-deposited KMFC electrodes.

Fig. 5. Voltage–capacity profiles for (a) original KMFC and (b) LiPON-deposited KMFC electrodes in 1 M LiPF$_6$/EC:DEC (1:1).

given in Fig. 5b. Its initial irreversible capacity is decreased to about 90 mAh g^{-1}. The profile of the LiPON-deposited KMFC electrode is clearly different from that of the original KMFC electrode. To investigate this in more detail, the profile is compared with the initial charge curve shown in Fig. 6. The initial charge curve of the original KMFC electrode decreases at a slower rate from the open-circuit voltage to the voltage of Li$^+$ intercalation into KMFC (under 0.5 V) compared with that for the LiPON-deposited KMFC electrode. This indicates that side reactions, such as solvent decomposition are suppressed on the LiPON-deposited KMFC electrode.

Most of the initial irreversible capacity is caused by solvent decomposition on the carbon electrode surface and irreversible insertion into the carbon electrode. The irreversible reaction of lithium-ions with functional groups on the carbon surface also plays a role. As can be seen in Fig. 6, the main differences between the original KMFC electrode and the LiPON-deposited KMFC electrode are the profile at the voltage range from the open-circuit voltage to 0.5 V (versus Li/Li$^+$), as is obvious from the initial inter-calation curve. According to our previous work [16], the irreversible capacity that occurs at these voltage regions is the result of solvent decomposition. The irreversible
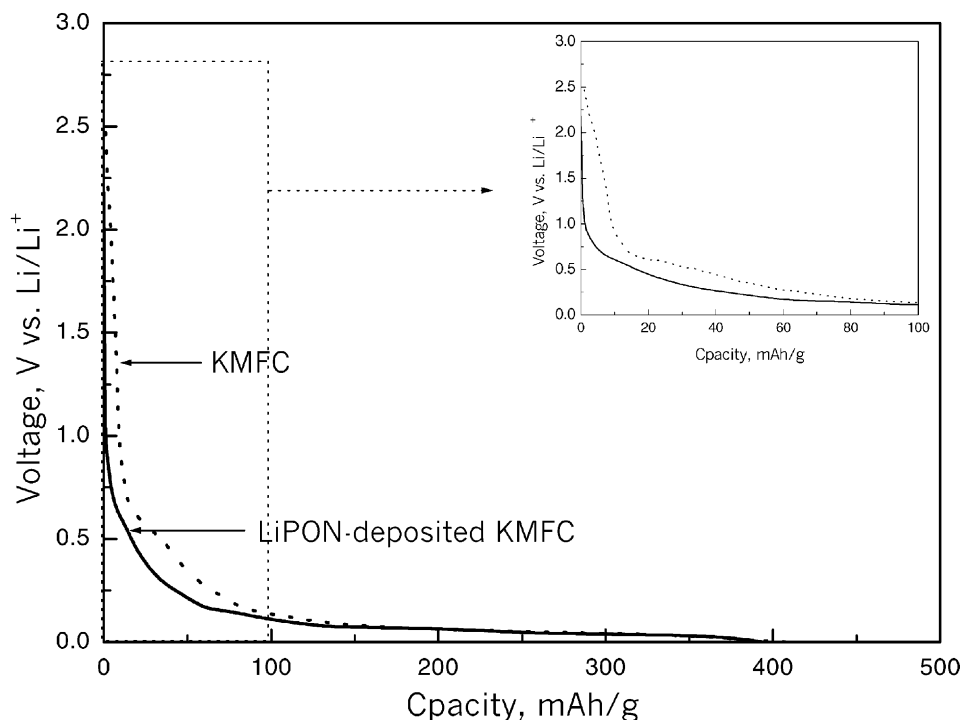
Fig. 6. Initial charge curves for original KMFC and LiPON-deposited KMFC electrodes in 1 M LiPF$_6$/EC:DEC (1:1).

capacity of the original KMFC electrode is about 30 mAh g^{-1} in this region. The irreversible capacity of the LiPON-deposited KMFC electrode is largely decreased because the KMFC electrode surface is deposited so as not to be in direct contact with the electrolyte.

Cyclic voltammograms for the original KMFC electrode and the LiPON-deposited KMFC electrode in 1 M LiPF$_6$/ EC:DEC (1:1) are shown in Fig. 7. The scan rate is 1 mV s^{-1}

and the voltage range is 3–0 V (versus Li/Li$^+$). Solvent decomposition is identified as irreversible cathodic peaks at about 2.2, 2.0 and 0.7 V for the initial intercalation process (Fig. 7a). The reduction of solvent is irreversible, and the decomposition of DEC and EC occurs at different potentials. In our previous work [18], cyclic voltammograms were measured in pure DEC and pure EC dissolved with LiPF$_6$ to obtain precise decomposition potentials for DEC and EC.
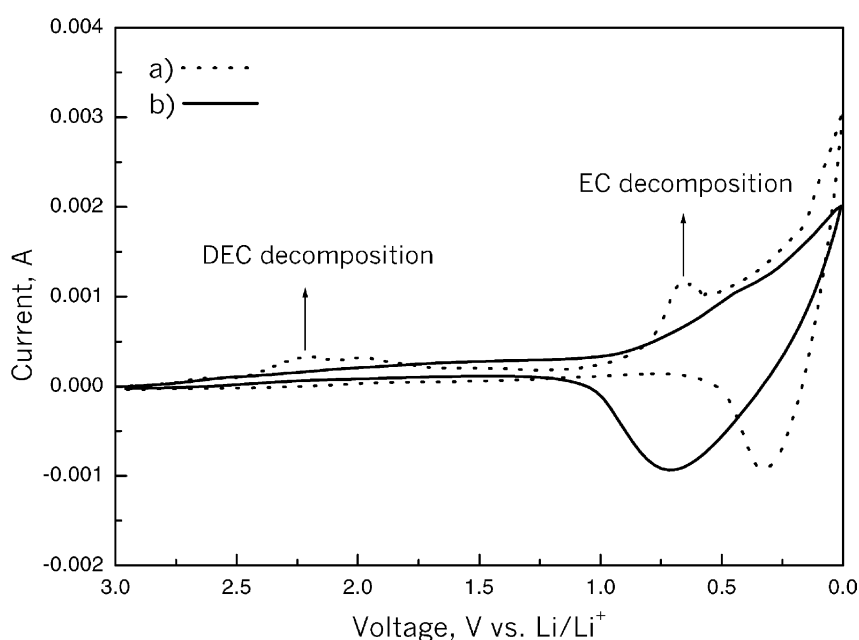

Fig. 7. Cyclic voltammograms for (a) original KMFC and (b) LiPON-deposited KMFC electrodes in 1 M LiPF$_6$/EC:DEC (1:1).
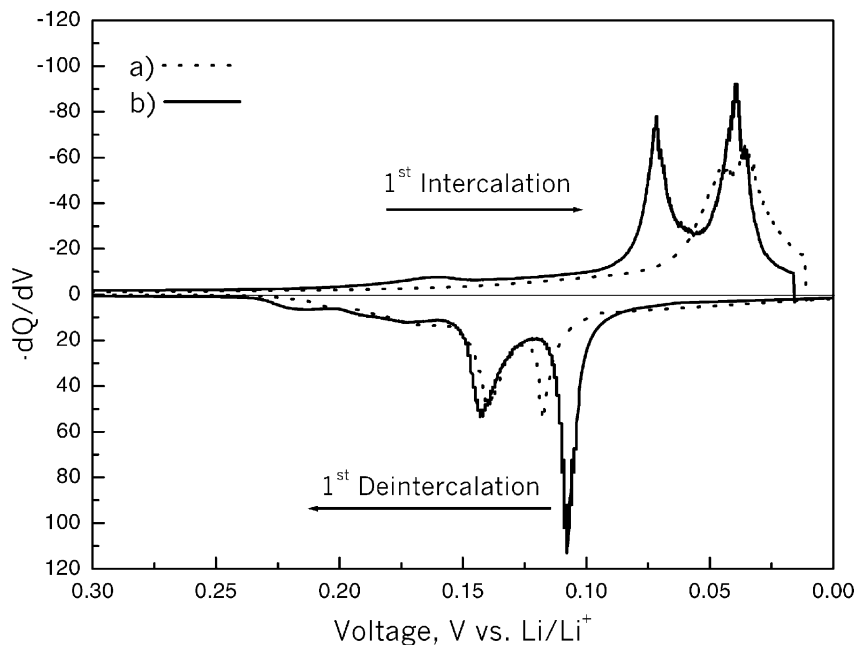
Fig. 8. Plots of $-dQ/dV$ vs. V for (a) original KMFC and (b) LiPON-deposited KMFC electrodes.

Based upon those results, the decomposition of pure DEC occurs at 2.2 and 2.0 V (versus Li/Li$^+$) and the decomposition of pure EC at 0.7 V (versus Li/Li$^+$). It is reasonable that the decomposition of DEC occurs at higher potential than that of EC since a linear carbonate solvent is known to be less stable than a cyclic carbonate, such as EC. In addition, the peak at about 2.7 V may be due to the irreversible reaction of lithium ions with functional groups on the carbon surface, or the effect of traces of water.

The suppression of solvent decomposition on the LiPON-deposited KMFC electrode is clearly evident in the cyclic voltammogram, as shown in Fig. 7b. The reduction peaks due to EC and DEC decomposition nearly disappear. The LiPON-deposited KMFC electrode was prepared so as not to be in direct contact with the electrolyte by forming an SEI film on the electrode surface. This film prevents solvent decomposition and co-intercalation, and also permits the intercalation of Li$^+$ into the KMFC electrode as an ionic conductor.

Plots of $-dQ/dV$ versus V for the original KMFC electrode and the LiPON-deposited KMFC electrode are given in Fig. 8 and demonstrate the difference in the initial intercalation/de-intercalation between the two electrodes. The initial intercalation peaks appear at about 0.04 and 0.03 V (versus Li/Li$^+$), and the de-intercalation peaks at about 0.12 and 0.14 V (versus Li/Li$^+$). These peaks are indicative of the transition of carbon when Li$^+$ ions are intercalated and de-intercalated. The two peaks on the de-intercalation curve are well separated, unlike the two peaks on the intercalation curve. This suggests that the transition of Li$^+$ intercalation into the KMFC electrode is affected by solvent co-intercalation, which results from solvent decomposition occurs. According to a previous report [8], solvent

decomposition is not a simple reaction on the carbon surface, but is a complex three-dimensional problem that involves solvent co-intercalation. Therefore, the stage transition of the carbon phase is affected by the structural destruction of carbon due to solvent co-intercalation. In the case of the LiPON-deposited KMFC electrode (Fig. 8b), the initial intercalation peaks we are located at about 0.07 and 0.04 V (versus Li/Li$^+$), and the de-intercalation peaks are at about 0.11 and 0.14 V. The two peaks on the intercalation curve are well separated and shifted positively. The initial de-intercalation peaks are shifted negatively. In other words, the intercalation/de-intercalation of the LiPON-deposited KMFC electrode is easier than that of the original KMFC electrode. These results can be explained by assuming that the SEI film formed by r.f. sputtering has properties that are superior to a SEI film formed by solvent decomposition. The pre-deposited LiPON film on the KMFC electrode suppresses solvent co-intercalation.

4. Conclusions

The initial irreversible capacity is decreased by the deposition of an ionic conducting LiPON on an KMFC electrode surface. The irreversible capacity that occurs between the open-circuit voltage and 0.5 V (versus Li/Li$^+$) is caused mainly by the decomposition of solvent on the original KMFC electrode surface. By contrast, the irreversible capacity of the LiPON-deposited KMFC electrode is largely decreased since the electrode surface has an ionic conducting layer and is therefore not in direct contact with the electrolyte but still permits the intercalation of Li$^+$ into the KMFC electrode. The decrease in

irreversible capacity is caused by the suppression of solvent decomposition, as confirmed by cyclic voltammetry. Thus, the LiPON film deposited by sputtering can inhibit solvent decomposition in a Li-ion battery. More experiments are underway to evaluate the role of LiPON layer in detail.

Acknowledgements

References

[1] R. Fong, U.V. Sacken, J.R. Dahn, J. Electrochem. Soc. 137 (1990) 2009.
[2] E. Peled, C. Menachem, D. Bar-Tow, A. Melman, J. Electrochem. Soc. 143 (1996) L4.
[3] K. Suzuki, T. Hamada, T. Sugiura, J. Electrochem. Soc. 146 (1999) 890.
[4] G. Chung, S. Jun, K. Lee, M. Kim, J. Electrochem. Soc. 146 (1999) 1664.
[5] R. Yazami, Electrochim. Acta 45 (1999) 87.
[6] M. Inaba, Y. Kawatate, A. Funabiki, S. Jeong, T. Abe, Z. Ogumi, Electrochim. Acta 45 (1999) 99.
[7] Y.-K. Choi, J.-G. Park, K.-I. Chung, S.-K. Kim, W.-S. Kim, Microchem. J. 64 (2000) 227.
[8] J.O. Besenhard, M. Winter, J. Yang, W. Biberacher, J. Power Sources 54 (1995) 228.
[9] P. Arora, R.E. White, J. Electrochem. Soc. 145 (1998) 3647.
[10] Y. Ein-Eli, S.R. Thomas, V.R. Koch, J. Electrochem. Soc. 144 (1997) 1159.
[11] T. Osaka, T. Momma, Y. Matsumoto, Y. Uchida, J. Electrochem. Soc. 144 (1997) 1709.
[12] T. Osaka, T. Momma, T. Tajima, Y. Matsumeto, J. Electrochem. Soc. 142 (1995) 1057.
[13] M. Winter, R. Imhof, F. Joho, P. Novak, J. Power Sources 81 (1999) 818.
[14] O. Mao, R.A. Dunlap, J.R. Dahn, J. Electrochem. Soc. 146 (1999) 405.
[15] P. Yu, J.A. Ritter, R.E. White, B.N. Popov, J. Electrochem. Soc. 147 (2000) 1280.
[16] Y.-K. Choi, K.-i. Chung, W.-S. Kim, Y.-E. Sung, S.-M. Park, J. Power Sources 104 (2002) 132.
[17] N.J. Dudney, J. Power Sources 89 (2000) 176.
[18] X. Yu, J.B. Bates, G.E. Jellison Jr., F.X. Hart, J. Electrochem. Soc. 144 (1997) 524.
[19] J.B. Bates, N.J. Dudney, B.J. Neudecker, B. Wang, Thin-film lithium batteries, in: T. Osaka, M. Datta (Eds.), New Trends in Electrochemical Technology: Energy Storage Systems in Electronics, Gordon & Breach, Newark, NJ, 2000, pp. 453–485.
[20] J.B. Bates, N.J. Dudney, D.C. Lubben, G.R. Gruzalski, B.S. Kwak, X. Yu, R.A. Zuhr, J. Power Sources 54 (1995) 58.
[21] Y.-K. Choi, K.-i. Chung, W.-S. Kim, Y.-E. Sung, Microchem. J. 68 (2001) 61.