Short communication

Influence of solvent species on the charge–discharge characteristics of a natural graphite electrode

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Abstract

The charge–discharge characteristics of a natural graphite electrode are examined in a mixed solvent composed of ethylene carbonate (EC) and propylene carbonate (PC). The characteristics are influenced largely by the solvent species. Natural graphite electrode displays good charge–discharge characteristics in an electrolyte containing EC with a high volume fraction. In an electrolyte containing PC, however, the electrode cannot be charged and the solvent is decomposed. X-ray photoelectron spectroscopy is used to obtain information about the surface of natural graphite. A thin LiF layer, the decomposition product of lithium hexafluorophosphate ($LiPF_6$), is formed on the surface of the natural graphite charged to 0.5 V (vs. Li/Li^+) in an electrolyte containing a high volume fraction of EC. On the other hand, LiF and a carbonate compound are formed in the bulk and on the surface of natural graphite when the volume fraction of PC is high. These results suggest that the thin LiF layer, which is produced at a potential higher than 0.5 V (vs. Li/Li^+) on the surface of natural graphite, enables the lithium ions to intercalate into the natural graphite without further decomposition of the electrolyte. © 1998 Elsevier Science S.A.

Keywords: Lithium; Carbon; Graphite; Electrolyte

1. Introduction

The intercalation of lithium into graphite by the vapour transport method was first reported by Guerard and Herold in 1975 [1]. Carbon electrodes have also been investigated by using electrochemical intercalation methods [2–6]. Recently, lithium secondary batteries with carbon negative electrodes have been actively studied because this type of battery is superior in terms of cycle performance to other types of lithium secondary batteries which use lithium metal or Li–Al alloy as a negative electrode. The capacity of the carbon negative electrode is smaller, however, than that of the lithium metal. Various kinds of carbon materials have been studied for the negative electrode of lithium secondary batteries, and the relationship between the physical properties of the carbon material and discharge characteristics have been investigated. We reported that natural graphite showed a high discharge capacity of 370 mAh g^{-1} and a good charge–discharge cycle performance in EC [7]. In other solvents, such as PC, natural graphite could not be charged, and the solvents decomposed. Dey and Sullivan [8] also reported that natural graphite could not be charged in PC.

In this study, the surface and crystal structure of the natural graphite after charging and discharging are investigated by using X-ray diffraction (XRD) and the X-ray photoelectron spectroscopy (XPS) in order to clarify the reason why natural graphite could not be charged in PC but could be charged and discharged in EC.

2. Experimental

Refined natural graphite with a purity of more than 99.9% was used as the negative electrode material. Natural graphite was mixed with polytetrafluoroethylene (PTFE) powder as a binding agent, and this mixture was pressed on to a Copper mesh to form a test electrode (20×20 mm, thickness 0.1 mm). Organic solvents (EC, PC, EC/PC) containing $LiPF_6$ (1 mol dm^{-3}) were used as the electrolyte solution.

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Charge–discharge tests and cyclic voltammetry were carried out on experimental cells with lithium metal used as a counter and as a reference electrode. In the charge–discharge tests, both the charge and discharge current density were 0.2 mA cm^{-2}. XPS was employed to identify the compounds on the surface of the natural graphite electrode. The XRD method gave a measure of the crystallinity of the natural graphite electrode.

3. Results and discussion

The charge–discharge curves of natural graphite electrodes in PC and in EC containing 1 mol dm^{-3} LiPF$_6$ are shown in Fig. 1. In EC, the natural graphite electrode could be charged and showed a large discharge capacity. In PC, on the other hand, the natural graphite electrode could not be charged and gas evolution occurred during charging. As propylene gas is detected during charging by gas chromatography analysis, the gas evolution is thought to be caused by the decomposition of the electrolyte. The charge–discharge characteristics of the natural graphite electrode were also investigated in a mixed solvent of EC and PC. Fig. 2 shows the influence of the electrolyte composition on the discharge capacity and initial efficiency of the natural graphite electrode in 1 mol dm^{-3} LiPF$_6$ PC/EC electrolytes. The natural graphite electrode can be charge and discharged when the volume fraction of EC is more than 30%.

Fig. 3 shows the XRD patterns of the natural graphite electrode discharged to 3.0 V (vs. Li/Li$^+$) in EC/PC after charging to 0.0 V (vs. Li/Li$^+$). When the volume fraction of PC is high, the full width at half maximum (FWHM) calculated from the XRD pattern of the natural graphite electrode is larger and the shape of the peaks which are due to the interlayer distance become broader. It is concluded that the crystal structure of the natural graphite is destroyed when the volume fraction of PC is high.

The XPS method is used to obtain information about the surface of the natural graphite electrode after charging and discharging. Fig. 4 shows the X-ray photoelectron spectrum of fluorine (1s) on natural graphite electrode
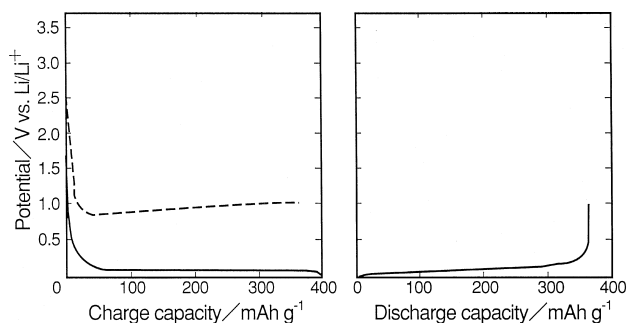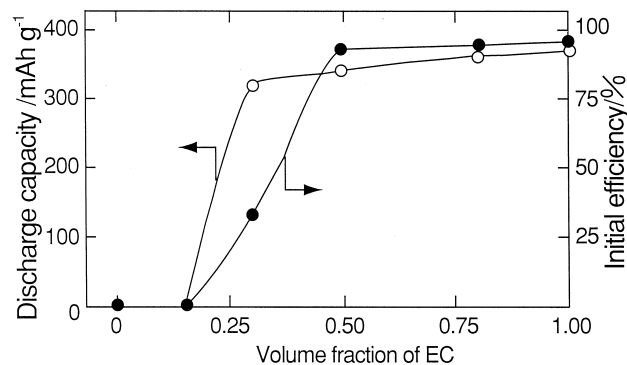
Fig. 2. Influence of composition of electrolyte on discharge capacity and initial efficiency of natural graphite electrode in 1 mol dm^{-3} LiPF$_6$ PC/EC electrolytes. (○) discharge capacity, (●) initial efficiency.

discharged to 3.0 V (vs. Li/Li$^+$) after charging to 0.0 V (vs. Li/Li$^+$) in EC/PC (50/50, 30/70). In PC, the natural graphite electrode was charged to 20 mAh g^{-1} and discharged to 3.0 V (vs. Li/Li$^+$) before XPS analysis, because the decomposition of PC occurred during charging. Peaks attributed to the binding energy of LiF are observed in these spectra [9]. When PC is used as a solvent, the peak intensity attributed to LiF is large in the bulk of the natural graphite. On the other hand, a thin LiF layer is formed when the volume fraction of EC is more than 30%. The X-ray photoelectron spectra of carbon (1s) on the natural graphite electrode are shown in Fig. 5. Two peaks can be observed when the volume fraction of PC is high. The lower peak corresponds to the binding energy of the C–C bonds of the natural graphite [9]. The higher peak
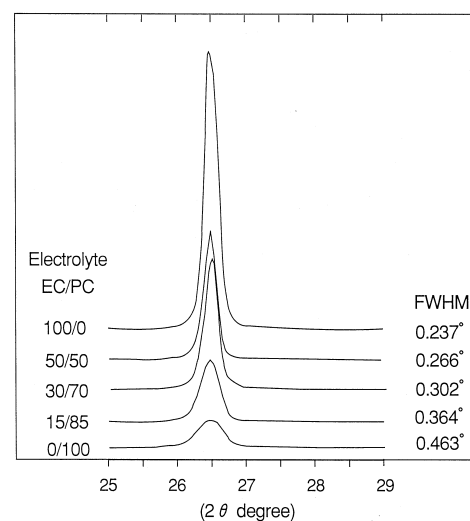
Fig. 3. X-ray diffraction patterns of natural graphite electrode after charge and discharge. Charge condition: EC/PC (50/50, 30/70): current density = 0.1 mA cm^{-2}, end voltage = 0.0 V (vs. Li/Li$^+$), EC/PC (0/100): current density = 0.1 mA cm^{-2}, charge capacity = 20 mAh g^{-1}. Discharge condition: current = 0.1 mA cm^{-2}, end voltage = 3.0 V (vs. Li/Li$^+$).

Fig. 1. Charge–discharge curves of the natural graphite electrodes. (—) EC, (---) PC, concentration of LiPF$_6$:1 mol dm^{-3}.
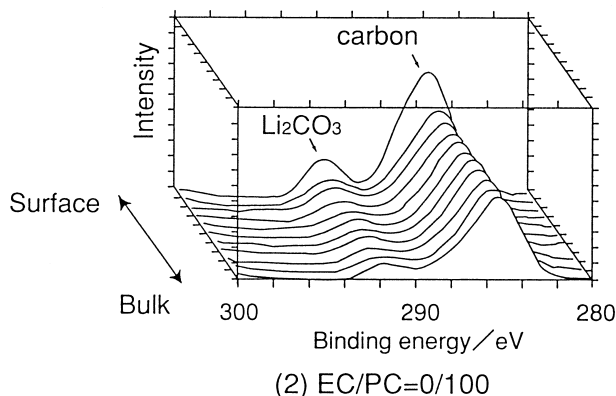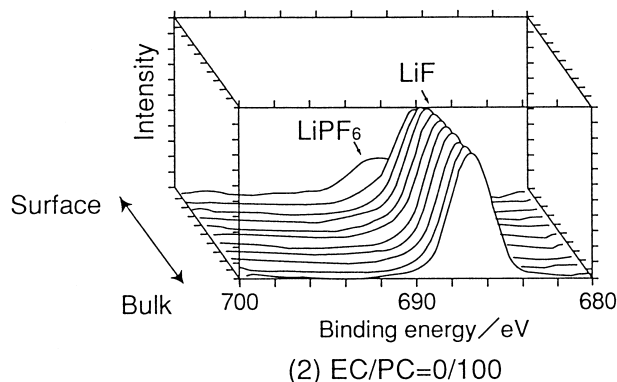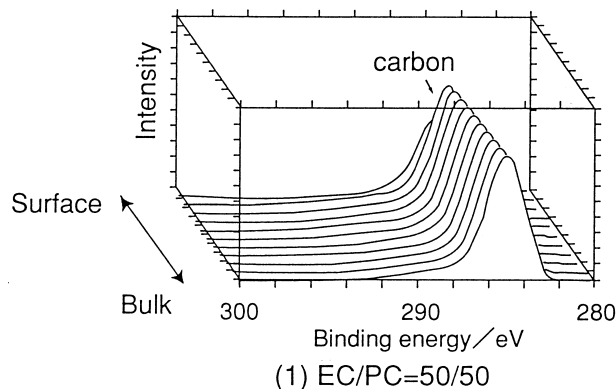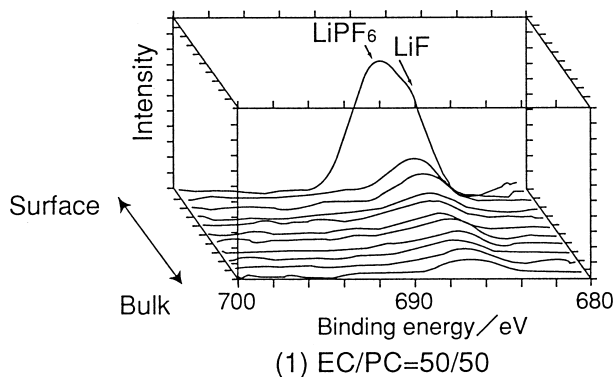
(1) EC/PC=50/50

(2) EC/PC=0/100

Fig. 4. X-ray photoelectron spectra of F (1s) of natural graphite electrode after charge and discharge. Solvent: (1) EC/PC (50/50), (2) EC/PC (30/70), (3) EC/PC (0/100). Charge condition: EC/PC (50/50, 30/70): current density = 0.1 mA cm^{-2}, end voltage = 0.0 V (vs. Li/Li$^+$), EC/PC (0/100): current density = 0.1 mA cm^{-2}, charge capacity = 20 mAh g^{-1}. Discharge condition: current density = 0.1 mA cm^{-2}, end voltage = 3.0 V (vs. Li/Li$^+$).

(1) EC/PC=50/50

(2) EC/PC=0/100

Fig. 5. X-ray photoelectron spectra of C (1s) of natural graphite electrode. Solvent: (1) EC/PC (50/50), (2) EC/PC (30/70), (3) EC/PC (0/100). Charge condition: EC/PC (50/50, 30/70): current = 0.1 mA cm^{-2}, end voltage = 0.0 V (vs. Li/Li$^+$), EC/PC (0/100): current density = 0.1 mA cm^{-2}, charge capacity = 20 mAh g^{-1}. Discharge condition: current density = 0.1 mA cm^{-2}, end voltage = 3.0 V (vs. Li/Li$^+$).

is attributed to the binding energy of carbonate [9]. In EC/PC (30/70, 50/50), no peaks attributed to carbonate can be observed. From these results, it is found that LiF and a carbonate compound are formed on the surface and in the bulk of natural graphite when the volume fraction of PC is high, and that a thin LiF layer is formed only on the surface when the volume fraction of EC is high.

The cyclic voltammetric method is used to investigate the process of layer formation on the surface of natural graphite in EC/PC (50/50, 0/100). Fig. 6 shows the cyclic voltammogram of the natural graphite electrode. A cathodic peak is observed at 0.6 V (vs. Li/Li$^+$) in EC/PC (50/50). In PC, a large cathodic current is observed at 0.8 V (vs. Li/Li$^+$).

The surface of a natural graphite electrode charged to 0.5 V (vs. Li/Li$^+$) was investigated by XPS to identify the reaction at a potential more noble than 0.5 V. Fig. 7 shows the X-ray photoelectron spectra of fluorine (1s) of a natural graphite electrode charged to 0.5 V (vs. Li/Li$^+$) in EC/PC (50/50) and those charged to 20 mAh g^{-1} in EC/PC (0/100). When EC/PC (50/50) is used as a solvent, a peak corresponding to the binding energy of LiF

is observed at 685 eV only on the surface of the natural graphite electrode. On the other hand, a thick LiF layer is observed when PC is used as a solvent. Fig. 8 shows the X-ray photoelectron spectra of carbon (1s) on a natural graphite electrode charged to 0.5 V (vs. Li/Li$^+$) in EC/PC (50/50) and those charged to 20 mAh g^{-1} in EC/PC
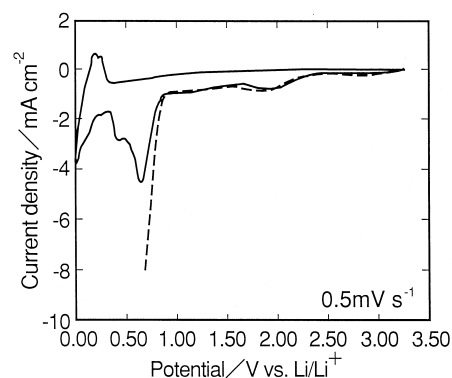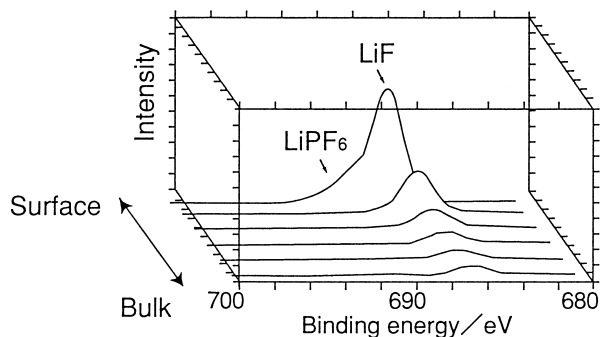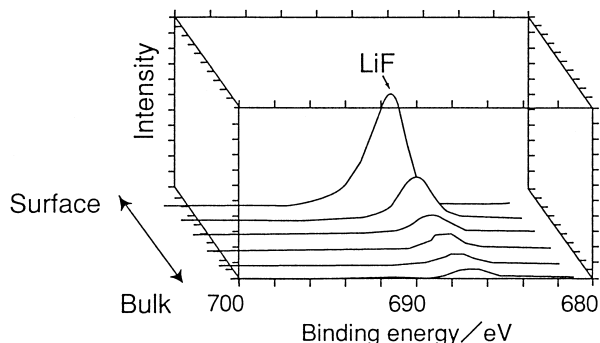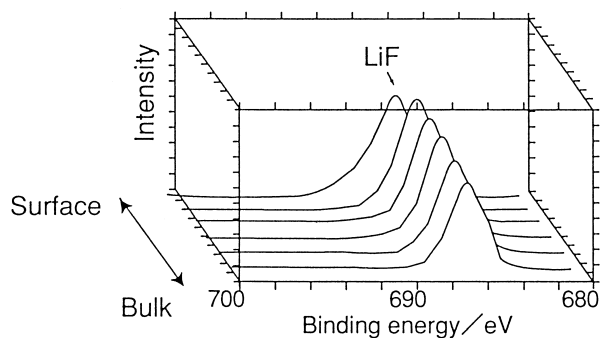

Fig. 6. Cyclic voltammogram of natural graphite electrodes in EC/PC electrolytes. (—) EC/PC (50/50), (—) EC/PC (0/100), concentration of LiPF$_6$ 1 mol dm^{-3}. Sweep rate: 0.5 mV s^{-1}.
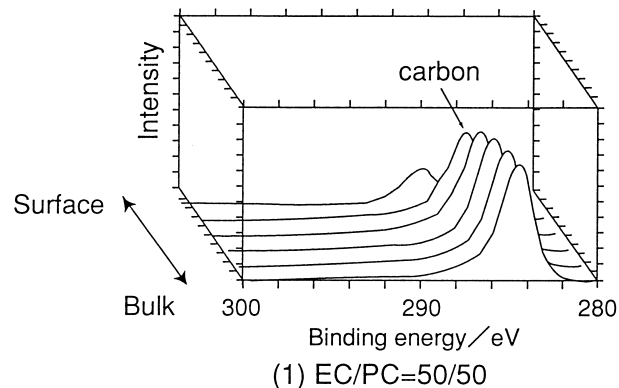
(1) EC/PC=50/50

(2) EC/PC=30/70

(3) EC/PC=0/100

Fig. 7. X-ray photoelectron spectra of F (1s) of natural graphite electrode. Solvent: (1) EC/PC (50/50), (2) EC/PC (0/100). Charge condition: EC/PC (50/50, 30/70): current density = 0.1 mA cm^{-2}, end voltage = 0.5 V (vs. Li/Li^{+}), EC/PC (0/100): current density = 0.1 mA cm^{-2}, charge capacity = 20 mAh g^{-1}.

(0/100). In EC/PC (50/50), a peak corresponding to the binding energy of the C–C bonds is observed at 285 eV and there are no peaks corresponding to carbonate. When PC is used as a solvent, a peak corresponding to carbonate can be observed at 290 eV. From the results of these XPS measurements and the cyclic voltammogram, it is confirmed that layer formation occurs at a potential more noble than 0.5 V (vs. Li/Li^{+}) and that it occurs at 0.6 V (vs. Li/Li^{+}) in EC/PC (50/50).

Because a carbonate compound could be observed on the surface and in the bulk of the natural graphite elec-

trode, and the crystallinity of the natural graphite became lower in the electrolyte containing PC with a high volume fraction, the process of LiF and a carbonate compound formation can possibly be explained as follows. PC was decomposed on the edge of the natural graphite crystal and propylene was produced. As a result of decomposition, LiF and carbonate compound were formed and the crystal structure of the natural graphite was destroyed. On the other hand, when the volume fraction of EC was high LiPF$_6$ decomposed on the surface of the natural graphite

(1) EC/PC=50/50
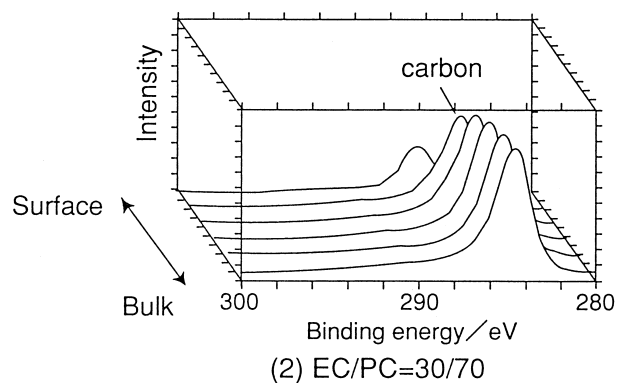
(2) EC/PC=30/70
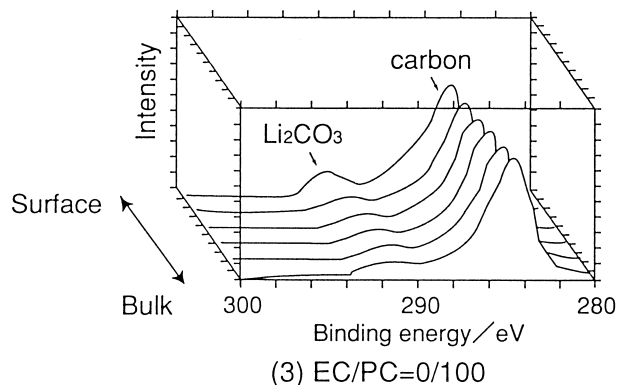
(3) EC/PC=0/100

Fig. 8. X-ray photoelectron spectra of C (1s) of natural graphite electrode. Solvent: (1) EC/PC (50/50), (2) EC/PC (0/100). Charge condition: EC/PC (50/50, 30/70): current density = 0.1 mA cm^{-2}, end voltage = 0.5 V (vs. Li/Li^{+}), EC/PC (0/100): current density = 0.1 mA cm^{-2}, charge capacity = 20 mAh g^{-1}.

and a thin LiF layer was formed. Lithium ions are thought to be able to go through this thin LiF layer and intercalate into the natural graphite.

4. Conclusions

In a mixed solvent of EC and PC containing EC with a high volume fraction, a natural graphite electrode can be charged and discharged, and it is observed that a LiF layer is formed only on the surface of the natural graphite. On the other hand, the natural graphite cannot be charged in electrolyte containing PC with a high volume fraction, and LiF and a carbonate compound as the decomposition products of PC are formed in the bulk and on the surface of the natural graphite. It is suggested that the natural graphite can be charged and discharged because a thin LiF layer which is formed on the natural graphite surface enables the lithium ions to intercalate into the natural graphite without

further decomposing the electrolyte when the volume fraction of EC is high.

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