A.c. impedance analysis of electrochemical lithium intercalation into highly oriented pyrolytic graphite

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Abstract

Electrochemical lithium intercalation into graphite was studied by cyclic voltammetry and a.c. impedance spectroscopy. Highly oriented pyrolytic graphite was used as a model graphite material to distinguish the difference in electrochemical behavior between the basal and the edge planes at graphite. A comparison between cyclic voltammograms of the basal plane and the whole surface of highly oriented pyrolytic graphite revealed that electrochemical lithium intercalation proceeds predominantly at the edge plane/electrolyte interface. The charge-transfer resistance changed continuously with electrode potential, and no significant change was observed at stage transition potentials (210, 120, and 90 mV versus Li/Li^+). From the variations of the Warburg impedance of samples of different sizes, it was concluded that lithium diffuses from the edge plane to the interior in the direction parallel to the basal plane and that its diffusivity changes with the stage structure of the bulk lithium–graphite intercalation compound. © 1997 Elsevier Science S.A.

1. Introduction

Graphite has been extensively studied for use as the negative electrodes of rechargeable lithium batteries. Structural changes of graphite electrodes upon electrochemical lithium intercalation have been studied in detail by X-ray diffraction [1,2] and Raman spectroscopy [3].

Graphite is a layered compound with an anisotropic structure, and has two kinds of characteristic surfaces: normal and parallel to the *c*-axis, which are called basal and edge planes, respectively. While the basal plane, in general, is inert, the edge plane shows high reactivity in many electrochemical systems [4–6]. Hence, the interfacial processes for lithium intercalation at the two kinds of interface should differ greatly from each other, and be distinguished to be precisely understood. Highly oriented pyrolytic graphite (HOPG) is a graphite block and has a highly anisotropic structure with well-defined basal and edge planes. Thus, HOPG can be regarded as a typical model of highly graphitized carbonaceous materials. Tran and Kinoshita [7] conducted a cyclic voltammetry study of electrochemical lithium intercalation at the two different interfaces utilizing the anisotropy of HOPG. They showed that the electrochemical kinetics of

lithium intercalation is more facile at the edge plane/electrolyte interface.

A.c. impedance spectroscopy is one of potential tools to analyze electrochemical processes occurring at electrode/electrolyte interfaces, and has been recently applied to the analysis of the electrochemical lithium intercalation into carbonaceous materials including graphite [8–12]. In most of the works, however, the electrodes were made of carbon powder, and hence the contributions of both basal and edge planes could not be separated. It is also difficult to define the surface area of test electrodes. In this work, we studied electrochemical lithium intercalation into graphite by a.c. impedance spectroscopy to elucidate the interfacial processes in detail using HOPG as a model graphite material.

2. Experimental

Electrochemical measurements were carried out using conventional three-electrode cells. A block of HOPG (Le Carbone Lorrain, PGCCL, 1.0 cm × 1.0 cm × 0.2 cm) was cleaved with an adhesive tape, and only the basal plane (0.13 cm^2) was brought into contact with electrolyte solution using an O-ring. The electrolyte solution was 1 M $LiClO_4$ dissolved in a 1:1 (by volume) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (Mitsubishi Chemical, battery

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grade). Lithium metal was used as the reference and counter electrodes. Electrochemical behavior of the basal plane was examined by cyclic voltammetry at a low sweep rate of 0.1 mV/s using a PAR 273 A potentiostat. In another series of experiments, a small rectangular piece was cut from the as-received HOPG block, and the whole surface of the piece was immersed in the electrolyte solution using a stainless-steel clip. Cyclic voltammograms of the whole surface was obtained in a similar manner. The electrochemical behavior of the edge plane was deduced by comparing the results for both electrodes.

Impedance measurements were carried out only for the whole surface of HOPG pieces using a Solartron 1255 frequency response analyzer coupled with the potentiostat. A nickel mesh was used as a current collector to obtain a better electrical contact. The electrode potential was stepped at a given potential, and kept for a sufficient time until the current became negligible (typically < 1 μA). The impedance of the electrode/electrolyte interface was then measured by applying a sine wave of 5 mV rms amplitude over the frequency region of 100 kHz to 1 mHz. The potential of the sample was successively lowered from the open-circuit voltage (2.6 V) to less than 50 mV. The measured impedance data were analyzed using a non-linear least-squares fitting program (NLLS).

All measurements were performed at room temperature in an argon-filled glove box.

3. Results and discussions

3.1. Cyclic voltammetry

Fig. 1 shows cyclic voltammograms in the second cycle of the basal plane of the HOPG block (0.13 cm^2) and the whole surface of a piece (0.25 cm^2) in LiClO$_4$/EC + DEC. The geometrical surface areas of the basal and edge planes of the latter HOPG piece were 0.20 cm^2 and 0.05 cm^2, respectively. These voltammograms showed an obvious difference in electrochemical reactivity between both electrodes. The cathodic (lithium intercalation) and anodic (lithium de-intercalation) peaks of the whole surface were two orders of magnitude larger than those of the basal plane although the apparent surface area of the former sample was twice as large as that of the latter. The peak areas of the cathodic and anodic peaks are comparable in the case of the whole surface in Fig. 1(b), whereas the anodic peak area was much smaller than that of the corresponding cathodic peak in the case of the basal plane in Fig. 1(a). The latter fact means that electrochemical lithium intercalation did not take place effectively at the basal plane/electrolyte interface. Since the whole surface of the HOPG piece consisted of the basal and edge planes, it is reasonable to consider that lithium intercalation proceeded predominantly at the edge plane/electrolyte interface. This result is in agreement with that of Tran and Kinoshita [7].
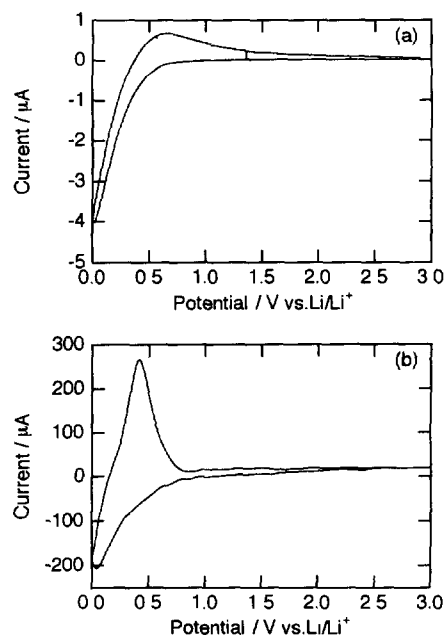

Fig. 1 Cyclic voltammograms in the second cycle of (a) the basal plane (0.13 cm^2) of a HOPG block and (b) the whole surface of a HOPG piece (0.25 cm^2) in 1 M LiClO$_4$/EC + DEC (1.1) $v = 0.1$ mV/s.

It should be noted that a small anodic peak corresponding to lithium de-intercalation was observed at around 0.6 V on the voltammogram of the basal plane shown in Fig. 1(a). Although cleaved HOPG has an atomically flat basal plane surface, some cleaving defects such as steps exist on it [13]. At such defects, edge plane was exposed to the electrolyte solution, and hence the small anodic peak in Fig. 1(a) is attributed to the de-intercalation of lithium occurring at the defects. Major part of the current on the cathodic sweep in Fig. 1(a) may have been consumed by some irreversible reactions such as solvent decomposition, etc.

3.2. A.c. impedance spectroscopy

From the results of the above cyclic voltammetry, it was shown that lithium intercalation from the basal plane is negligible compared with that from the edge plane. This result enables us to obtain selective information about the interfacial processes occurring at the edge plane/electrolyte interface even when we used the whole surface of the HOPG piece as a sample electrode.

Fig. 2 shows impedance spectra of the whole surface of a HOPG rectangular piece (0.50 cm × 0.18 cm × 0.02 cm) obtained at various potentials. At open-circuit potential (2.6 V), the eletrode exhibited an impedance spectrum typical of the behavior of a blocking electrode, with a linear line approaching an angle of 90° to the Z'-axis, which indicated that detectable lithium intercalation did not occur at this potential. At potentials below 0.6 V, two depressed semicircles and a inclined line appeared. For comparison, we measured the impedance spectra of the nickel mesh current collector in a similar manner, and observed a semicircle sim-
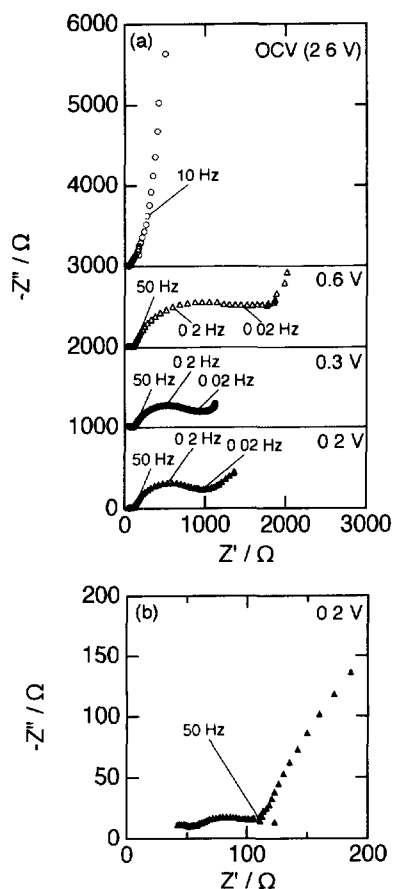
Fig. 2. (a) Variations of impedance spectra of the whole surface of a HOPG piece (0.50 cm×0.18 cm×0.02 cm) with electrode potential in 1 M LiClO₄/EC + DEC (1:1). (b) An expanded spectrum of the high frequency region obtained at 0 2 V.

dance spectra in the vicinity of these phase transition potentials. In each panel, the size of the semicircle in the middle frequency region hardly changed, whereas the impedance in the low frequency region changed greatly in the vicinity of the stage transition potentials.

3.3. Equivalent circuit

We used an equivalent circuit shown in Fig. 4 to analyze the measured impedance data. The equivalent circuit is a
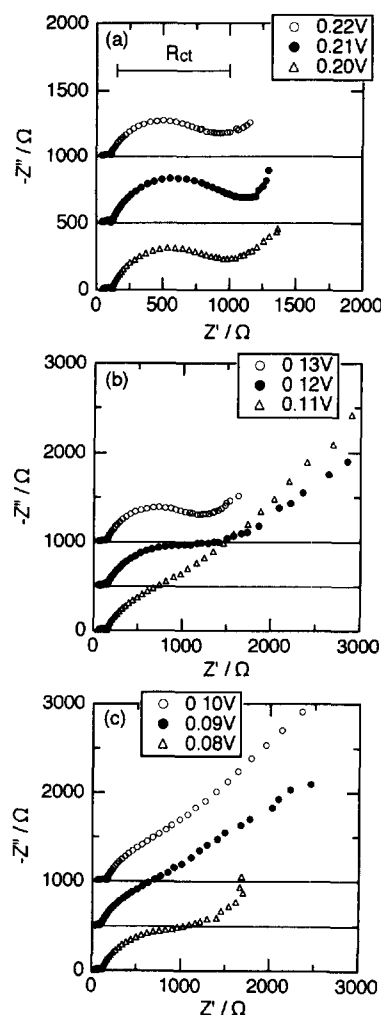

Fig. 3. Variations of impedance spectra of the whole surface of a HOPG piece (0.50 cm×0.18 cm×0.02 cm) in 1 M LiClO₄/EC + DEC (1:1) in the vicinity of (a) 210, (b) 120, and (c) 90 mV.
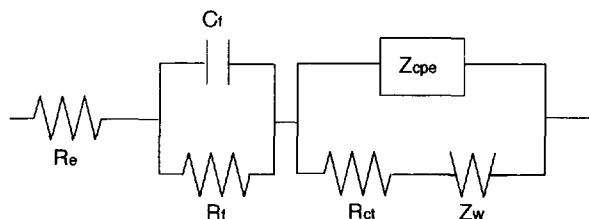
ilar to that of the HOPG piece in the frequency region of 50 Hz to 100 kHz. In addition, Aurbach and Zaban [14] reported in their infrared study that the surface film formed on the nickel electrode has a composition similar to that formed on the graphite. Therefore, the semicircle in the high frequency region is attributed to the impedance of the surface films formed on the graphite and nickel mesh current collector. These facts permit us to assign the semicircle in the middle frequency region of 0.02 to 50 Hz and the inclined line at lower frequencies below 0.02 Hz to the impedance of charge transfer at the graphite/electrolyte interface and lithium diffusion within the graphite, respectively.

It is well known that graphite intercalation compounds (GICs) are formed by charging of highly graphitized carbonaceous materials and that three distinct potential plateaus are observed at about 210, 120, and 90 mV on their charge and discharge curves. From in situ X-ray diffraction [1] and Raman spectroscopy [3], the plateaus at about 210, 120, and 90 mV have been assigned to stage transitions from dilute stage-1 to stage-4, from stage-2L to stage-2, and stage-2 to stage-1, respectively. These structural changes are expected to affect the interfacial processes of lithium intercalation. Panels (a)–(c) in Fig. 3 show the variations of the impe-

Fig. 4. Equivalent circuit used for the analysis of impedance data in this study. R_e electrical resistance of the electrolyte; C_f and R_f capacitance and resistance, respectively, of surface films formed on the sample and current collector; Z_{cpe} constant phase element, R_{ct} charge-transfer resistance; Z_w, Warburg impedance.
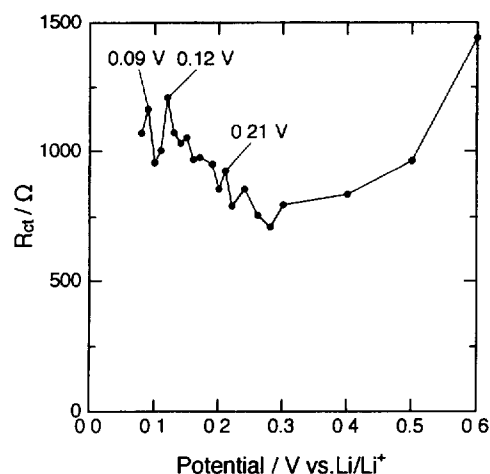
Fig. 5. Variation of R_{ct} with electrode potential.

Fig. 6. Variations of σA_{edge} of two samples of different A_{edge}'s with electrode potential.

modified Randles circuit, where R_e is the electrolyte resistance, C_f and R_f the capacitance and resistance, respectively, of surface films formed on the sample and current collector, Z_{cpe} the constant phase element, R_{ct} the charge-transfer resistance, and Z_w the Warburg impedance. We introduced the constant phase element representing the depressed semicircle in the middle frequency region. The constant phase element has been interpreted in terms of phenomena resulting from a porous electrode structure, overlapping of several semicircles of different relaxation times, etc. [15,16]. An origin of the presence of a constant phase element in the present electrochemical system may be attributed to the irregular morphology of the edge plane. However, detailed interpretation of the Z_{cpe} is beyond our scope of this work and is not discussed here.

3.4. Analysis of the impedance in the middle frequency region

Fig. 5 shows the variation of the charge transfer resistance, R_{ct}, with electrode potential. With a drop of potential, the charge-transfer resistance decreased, showed the minimum value at about 300 mV, and then increased. As mentioned above, lithium intercalation into graphite is accompanied with stage transitions occurring at about 210, 120, and 90 mV [1,2]. In Fig. 5, nevertheless, no significant change in R_{ct} was observed at these potentials. This indicates that the kinetics of the charge-transfer process is not affected by a change in the stage structure of Li–GIC bulk.

3.5. Analysis of the impedance in the low frequency region

To estimate the diffusivity of lithium within graphite, the Warburg impedance was analyzed from the impedance in the low frequency region using the equivalent circuit shown in Fig. 4. The Warburg impedance, Z_w, and Warburg prefactor, σ, are expressed as [17]

$$Z_w = \sigma \omega^{-1/2}(1 - j) \tag{1}$$
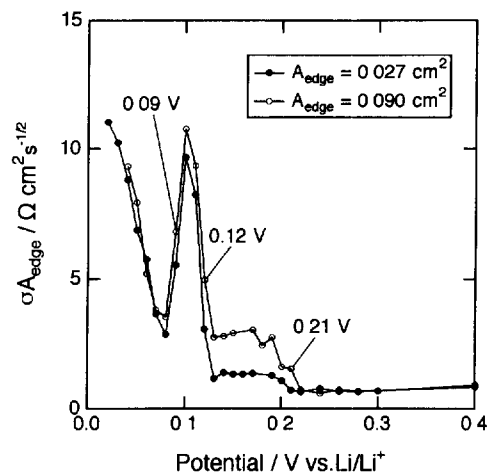
$$\sigma = V_m(dV_{OC}/dx)/zFA(2D)^{1/2} \tag{2}$$

where ω is the angular frequency, V_m the molar volume of the electrode, dV_{OC}/dx the slope of the open-circuit potential with the composition, z the valence of the diffusion species, F the Faraday constant, A the geometric surface area of the electrode, and D the chemical diffusion coefficient. As predicted from Eq. (2), the product, σA, is a constant at a given potential and independent of A if the other parameters in Eq. (2) remain unchanged; that is, the value of σA is regarded as a characteristic parameter that represents lithium diffusivity in highly graphitized samples. We measured and analyzed the impedance of two samples of different sizes. One sample was a HOPG piece of 0.50 cm×0.18 cm×0.02 cm with geometrical surface areas of the edge plane (A_{edge}) and of the whole surface (A_{whole}), equal to 0.027 and 0.207 cm^2, respectively. The size of the other sample was 0.38 cm×0.22 cm×0.075 cm with $A_{edge} = 0.090$ cm^2 and $A_{whole} = 0.257$ cm^2. Fig. 6 shows the variations of σA_{edge} of the two samples with electrode potential. In Fig. 6, the variations of σA_{edge} were well fitted with each other, indicating that σA_{edge} is independent of A_{edge}. On the other hand, such correlation was not obtained when A_{whole} was used as the surface area. These facts indicate that the geometrical area of the edge plane, A_{edge}, satisfies the conditions required for A in Eq. (2); that is, lithium diffuses from the edge surface to the interior in the direction parallel to the basal plane.

Furthermore, σA_{edge} was drastically changed in the vicinity of the stage transition potentials (210, 120, and 90 mV) in Fig. 6. This behavior is attributed to abrupt changes in the diffusivity of lithium by the stage transition of the bulk of Li–GIC. Unfortunately, we could not determine the chemical diffusion coefficient of lithium within graphite in this study.

4. Conclusions

The difference in electrochemical behavior for lithium intercalation between the basal and edge planes of graphite was clearly distinguished by using a HOPG as a model graph-

ite material. From the comparison between the cyclic voltamograms of the basal plane and the whole surface of HOPG, it was shown that electrochemical lithium intercalation occurs predominantly at the edge plane/electrolyte interface. Interfacial processes at the edge plane/electrolyte interface such as charge transfer and diffusion were then analyzed by a.c. impedance spectroscopy. The charge-transfer resistance changed continuously with electrode potential, which indicated that the kinetics of the charge transfer is not significantly affected by a change in the stage structure of Li–GIC bulk. On the other hand, the variation of σA_{edge} with electrode potential was independent of A_{edge}. It was concluded that lithium is intercalated from the edge surface and diffuses to the interior in the direction parallel to the basal plane.

Acknowledgements

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