Interpretation of voltammograms of lithium ion at pyrolytic graphite electrode

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Abstract

Peak currents and potentials of voltammograms of lithium ion at the pyrolytic graphite electrode were obtained under the conventionally voltammetric conditions except for addition of supporting electrolyte. They were interpreted on the basis of the voltammetric concept in order to estimate rate-determining steps and redox potentials at zero current. The cathodic wave at concentrations less than 10 mM was controlled by diffusion and migration of lithium ion in the solution, whereas that at higher concentrations was by the intercalation kinetics. The anodic wave was caused by the deintercalation, and behaved like an adsorption wave. The cathodic charge evaluated from the integration of the voltammogram was larger by 30% than the anodic one because of side reaction of acetonitrile or impurities. The anodic and the cathodic peak potentials extrapolated to zero current were, respectively, $-1.58$ and $-2.11$ V vs. Ag|AgCl, which can be regarded as universal values. The crystallinity of graphite electrode was investigated by Raman spectroscopy.

Keywords: Intercalation of lithium ions; Pyrolytic graphite electrode; Charge balance; Voltammetry; Migration

1. Introduction

The principle of lithium rechargeable batteries at graphite anodes lies in the intercalation of lithium ion into graphite layers and the deintercalation of the intercalated lithium to the solution [1–8]. The former is caused by the cathodic reaction of Li⁺ at less negative potential than the standard potential of Li⁺|Li owing to the stabilization of Li into several graphite stages by the intercalation [3,4,9]. The latter is the anodic dissolution of the intercalated lithium at more positive potential by 0.5–1.3 V than the intercalation potential [10–12]. Although the lithium batteries have practically reversible with good cycleability, the potential difference between the intercalation and the deintercalation is much larger than that of voltammetrically reversible reaction. The irreversibility is also found in the cathodic charge larger than the anodic charge [10,12–14]. These complications obviously degrade the efficiency and the life of lithium batteries.

The intercalation and the deintercalation have frequently been observed under kinetic conditions rather than static conditions like potentiometry. Even basic experiments of graphite anodes have been made at large current, high concentration of lithium ions and a large electrode area without adding supporting electrolyte. Consequently, experimental values depend so strongly on conditions and techniques that they vary from laboratory to laboratory. A strategy of minimizing of the complications is to decrease concentrations of lithium ion. However, charge interaction among lithium ions cannot be prevented from voltammograms because there exists, in principle, no supporting electrolyte for the lithium ion systems.

This paper aims at analyzing voltammetric peaks of lithium ion at graphite electrodes and determining peak potentials almost independent of techniques and experimental
There is a sharp band at 1580 cm\(^{-1}\) immediately after polishing (curve (a)) and after 15 potentiodynamic intercalation–deintercalation cycles (curve (b)).

2. Experimental

All the chemicals were of analytical grade. Acetonitrile was treated with molecular sieves 4A1/8 (Wako, Tokyo) in order to remove moisture. All the solutions were bubbled with highly purified nitrogen before voltammetric run.

Cyclic voltammetry was performed with a Potentio/Galvanostat (Model 1112, Huso, Kawasaki) under the control of a computer at room temperature in a three-electrode cell. The pyrolytic graphite electrode (PGE) (BAS Inc, Tokyo) and the glassy carbon electrode (GCE) (BAS Inc, Tokyo) 3 mm in diameter were used as working electrodes. A platinum coil and a Ag|Ag\(_x\)O were used as the counter and the reference electrodes, respectively. The potential at the Ag|Ag\(_x\)O was by 0.054 V lower than that at Ag|AgCl. The working electrode was polished with 0.05 µm alumina paste on wetted cotton and rinsed with acetonitrile in the ultrasonic bath for 1 min before each voltammetric run. The crystallinity of graphite electrode was investigated by Raman spectroscopy (JASCO, NRS-1000) with an Ar-ion laser (excitation line 514.5 nm, 0.2 mW), objective 50\(\times\) (numerical aperture 0.75).

3. Results and discussion

Fig. 1 shows the Raman spectra of the PGE electrode immediately after polishing (curve (a)) and after 15 potentiodynamic intercalation–deintercalation cycles (curve (b)). There is a sharp band at 1580 cm\(^{-1}\) and a faint band at about 1350 cm\(^{-1}\) on curve (a). The sharp band at 1580 cm\(^{-1}\) has been assigned to Raman active E\(_{2g}\) mode frequency [40], known as the G band, associated with in-plane symmetric C–C stretches. Carbonaceous materials with high degree of graphitization usually give a strong peak at 1580 cm\(^{-1}\). Polycrystalline graphite and disordered carbons have exhibited a band at about 1350 cm\(^{-1}\) (A\(_{1g}\) mode, D band) due to finite crystalline sizes and imperfection of carbonaceous materials [41]. From curve (a) we can conclude that the structure of the electrode is not destroyed with the polishing but does keep good crystallinity. The decrease in the band at 1580 cm\(^{-1}\) indicates that the crystallinity was lost after the lithium ions intercalation.

Fig. 2 shows the voltammogram of 0.76 mM LiClO\(_4\) at the PGE (curve (a)) in acetonitrile after removing oxygen and moisture. The voltammogram did not vary with the number of potential cycles. The cathodic wave appeared at ca. −2.4 V. The GCE instead of the PGE showed no wave at this potential (curve (b)). The cathodic wave, being specific to the PGE, can be attributed to the intercalation of lithium ions into the graphite. The shoulder of the cathodic wave at −3.0 V can be attributed either to the ordinary reduction of Li\(^+\) to Li or to the reduction of acetonitrile. Since the concentration of lithium ion on the PGE surface at \(E < −2.5\) V is actually zero owing to the limiting current, the further reduction of lithium ion is not be predicted. Therefore, the shoulder is ascribed to the reduction of acetonitrile at the intercalated PGE surface, as will be described in the latter section.

The anodic wave with a peak at −0.8 V is caused by the deintercalation, because it cannot be observed at the GCE which exhibited no intercalation [17,42–45]. The anodic peak potential reported varied largely with the current from −1.7 to −0.8 V [12,15], owing to large electric resistance of the solution. The disappearance of the anodic current at \(E > −0.5\) V indicates the exhaustive dissolution of the intercalated lithium to the solution bulk.

When the solution was not deaerated and not dried, the voltammogram at the PGE showed (curve (c)) two cathodic waves at −0.9 and −2.8 V and the broad anodic wave at −2.0 V. Since the cathodic wave at −0.9 V disappeared by deaeration of the solution, it is caused by the reduction of oxygen or oxygen-containing surface groups at the electrode [16,17]. Oxygen and water suppressed the intercalation effects from the currents and the solution resistance from the observed potentials.

![Fig. 1. Raman spectra of a PGE: (a) immediately after polishing and (b) after 15 potentiodynamic intercalation–deintercalation cycles in 3 mM LiClO\(_4\) in acetonitrile at room temperature.](image1)

![Fig. 2. Cyclic voltammograms of 0.76 mM LiClO\(_4\) at \(v = 50\) mV s\(^{-1}\) in acetonitrile at the PGE without (a) and with (c) oxygen and moisture, and at the GCE without (b) oxygen and moisture.](image2)
tion and the deintercalation currents [18], and shifted the intercalation potential in the negative direction.

Fig. 3 shows the dependence of cathodic peak current, $I_{p,c}$, on the concentration, $c$, of LiClO$_4$. The current for $c > 25$ mM was almost independent of $c$. It should be controlled by slower processes than the supply of lithium ion. The slower processes are possibly the charge transfer step of Li$^+$ in the graphite [8–30] and mass transport of the reaction product (Li) into the graphite [19,23–32]. In contrast, the proportionality at low concentrations indicates that the current should be controlled by diffusion of Li$^+$ or the first-order kinetics with respect to $c$. The behavior in this domain can be analyzed by means of usual voltammetric techniques, and hence our concern is directed to the proportional domain.

In order to find the rate-determining step in the proportional domain of the $I_{p,c}$ vs. $c$ variation, we examined dependence of the peak current on the potential scan rate, $v$. The increase in $v$ enhanced $I_{p,c}$, and shifted the cathodic peak potential in the negative direction. Fig. 4 shows the dependence of the cathodic peak current, $I_{p,c}$, on $v^{1/2}$, exhibiting the approximate proportionality. Proportionality implies a diffusion-controlled process of a reactant in solution. Since the solution contains only LiClO$_4$ without supporting electrolyte, the approximate proportionality infers that the current is controlled not only by diffusion but also by electric migration. The theory of the current controlled by both diffusion and migration has been developed in detail for the steady-state voltammogram at a microelectrode [33–35]. However, the assumptions in the theory are not realized in usual experiments because of a leak of ions from a reference electrode, formation of ions at a counter electrode, and difficulty of realizing the model of cell geometry and electrode geometry. Therefore, analysis of the migration current becomes necessarily semi-quantitative. When a reactant has single charge and a product has no charge, the limiting current value is reported to be twice the value without migration [34]. Applying this concept to the cathodic peak current without supporting electrolyte, we get approximately,

$$I_p = (0.446 \times 2)FcA(FDv/RT)^{1/2},$$

where $A$ is the area of the PGE, $D$ is the diffusion coefficient of Li$^+$ in the solution, and $F$, $R$, and $T$ have the conventional meanings. From the known values of $c$, $A$ and $I_{p,c}v^{-1/2}$ we estimated the diffusion coefficient to be $3 \times 10^{-5}$ cm$^2$ s$^{-1}$. It is close to the value $2.4 \times 10^{-5}$ cm$^2$ s$^{-1}$ for ferrocene in acetonitrile. Therefore, the cathodic peak current is controlled both by diffusion and migration of Li$^+$ in the solution rather than the kinetics of the intercalation. The value of $D$ is not so accurate that one digit may be allowed, not only because of involvement of approximation in Eq. (1) with respect to migration but also because of the assumption of the reversible reaction. We attempted to obtain a diffusion-controlled cathodic peak current at the platinum electrode and the GCE, but failed owing to exponentially rising current. Reported values of $D$ for lithium batteries are $4.7 \times 10^{-6}$ cm$^2$ s$^{-1}$ in the mixture of ethylene carbonate and ethylene methylene carbonate [36] and $3 \times 10^{-6}$ cm$^2$ s$^{-1}$ in propylene carbonate [37].

The anodic wave, which can be attributed to the deintercalation, may behave as an adsorption wave because the process of the intercalation and the deintercalation resembles mechanistically that of pre-electrolysis and dissolution in stripping voltammetry. In order to confirm the properties of a surface wave for the anodic peak current, we applied $-2.7$ V for 20 s and then scanned the potential in the positive direction at various scan rates. The peak current was unexpectedly not proportional to the scan rate although the voltammogram exhibited no diffusion tail at $E > -0.2$ V after the peak. The deviation from the proportionality is ascribed to the deformation of the anodic wave, associated with positive potential shift with an increase in the current. A strategy of confirming the anodic wave to be a surface wave is to compare the anodic charge with the cathodic one.

We evaluated the two kinds of the charge by integrating the current with respect to the electrolysis time after the voltammogram was redrawn to the current–time curve, as is shown in Fig. 5. Both the cathodic charge, $Q_c$, and the anodic one, $Q_a$, were increased proportionally with an increase in the concentration of lithium ion, whereas they decreased with an increase in the scan rate. $Q_a$ was

![Fig. 3. Variation of the cathodic peak current, $I_{p,c}$, with the concentration of the LiClO$_4$ in deaerated and dried acetonitrile at $v = 50$ mV s$^{-1}$.](image-url)
proportional to $Q_c$ for $v > 20 \text{ mV s}^{-1}$ and for various values of $c < 5 \text{ mM}$, as is shown in Fig. 6. The proportionality implies that the degree of the charge compensation is independent of $c$ and $v$. However, the compensation is not maintained, demonstrated quantitatively by $Q_c = 1.24Q_a$. Since $Q_a$ means the accumulated charge, the amount of 24% cathodic charge turns to be lost. The charge loss has been reported to be 67%, 130% and 160% in dimethyl sulfoxide, propylene carbonate and dimethyl formamide at the polypropylene–graphite composite electrode [10]. It has varied complicatedly with mixture of solvents [14].

The cathodic decomposition of solvents seems to decrease the charge compensation. In order to confirm the participation in the decomposition of acetonitrile, we obtained the cathodic charge at the PGE and the GCE from the integration of voltammograms by altering negative potentials, $E_p$, as is shown in Fig. 7. The cathodic charge increased with the negative shift of $E_p$, as is shown in Table 1. The ratio of the charge at the GCE to that at the PGE was almost 0.30, independent of $E_p$. Since the GCE does not provide intercalation, the cathodic charge at the GCE is ascribed to reduction of impurities included in acetonitrile or of acetonitrile itself. The ratio is close to the charge loss (24%) in Fig. 6. Therefore, the charge loss is not caused by reaction of lithium but is attributed to the decomposition of impurities or acetonitrile.

Although the voltammetric current and charge have been now interpreted approximately, a serious problem still lies in large variations of peak potentials with experimental conditions. Actually, characteristic potentials vary from laboratory to laboratory. We consider that the main reason is due to electric resistance ($IR$-drop) of the solution because of including no supporting electrolyte. Since a potential shift by the $IR$-drop should have a linear variation of the current, we plotted $E_{p,a}$ and $E_{p,c}$ against $I_{p,a}$ and $I_{p,c}$ in Fig. 8 for various values of $v$ at a given concentration, where $E_{p,a}$ stands for $E_{p,a}$ or $E_{p,c}$, and $I_p$ stands for $I_{p,a}$ or $I_{p,c}$. Data of $(E_p, I_p)$ at each concentration fall on a straight line, suggesting the potential shift by the $IR$-drop. The values of $E_p$ extrapolated to $I_p = 0$ for different concentrations merge in $(E_{p,a})_{t=0} = -1.53 \pm 0.05 \text{ V}$ or $-1.58 \text{ V}$ vs. Ag/AgCl and $(E_{p,c})_{t=0} = -2.06 \pm 0.05 \text{ V}$ or $-2.11 \text{ V}$ vs. Ag/AgCl. These values are peak potentials without including the $IR$-drop. The difference in the peak potentials, $(E_{p,a})_{t=0} - (E_{p,c})_{t=0}$, is 0.53 V, equivalent to 51 kJ mol$^{-1}$. This energy is an interfacial kinetic contribution of the intercalation and/or the deintercalation, and hence is lost at a cycle of the charge/discharge. A technique of reducing this voltage should be an important subject of improving energetic efficiency of lithium batteries.

![Fig. 5. Current–time curve converted from the cyclic voltammogram of 1.45 mM LiClO$_4$ acetonitrile solution at $v = 50 \text{ mV s}^{-1}$.](image)

![Fig. 6. Dependence of the anodic charge, $Q_a$, on the cathodic charge, $Q_c$, at different scan rates ($10 < v < 100 \text{ mV s}^{-1}$) in 0.48 (squares), 2.56 (circles), 3.8 (upper triangles), and 4.9 mM (lower triangles) LiClO$_4$ solutions in acetonitrile.](image)

![Fig. 7. Cyclic voltammograms at the (A,A’) PGE and at the (B) GCE when the potential was reversed at $-2.3$, $-2.5$ and $-2.8 \text{ V}$ in 4.9 mM LiClO$_4$ acetonitrile solution at $v = 50 \text{ mV s}^{-1}$.](image)

<table>
<thead>
<tr>
<th>$E_p$, V</th>
<th>$Q_a$ (GCE), mC</th>
<th>$Q_a$ (GCE)/$Q_c$ (PGE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-2.1$</td>
<td>$0.028$</td>
<td>$0.30$</td>
</tr>
<tr>
<td>$-2.2$</td>
<td>$0.077$</td>
<td>$0.30$</td>
</tr>
<tr>
<td>$-2.3$</td>
<td>$0.153$</td>
<td>$0.29$</td>
</tr>
<tr>
<td>$-2.4$</td>
<td>$0.265$</td>
<td>$0.30$</td>
</tr>
<tr>
<td>$-2.5$</td>
<td>$0.392$</td>
<td>$0.30$</td>
</tr>
<tr>
<td>$-2.6$</td>
<td>$0.480$</td>
<td>$0.28$</td>
</tr>
<tr>
<td>$-2.7$</td>
<td>$0.520$</td>
<td>$0.25$</td>
</tr>
<tr>
<td>$-2.8$</td>
<td>$0.600$</td>
<td>$0.23$</td>
</tr>
</tbody>
</table>

Table 1 Dependence of ratios of $Q_a$ at the GCE to $Q_c$ at the PGE on reverse potentials, $E_p$.
Slopes of the lines in Fig. 8 have dimension of electric resistance, \( r \). The absolute values of the slopes increased with a decrease in the concentration. Since they may correspond to solution resistance, we plotted them against the inverse concentration of LiClO\(_4\) in Fig. 9. Although the plots are rather scattered, they show a proportional relation, common to the anodic waves and the cathodic waves. Therefore \( r \) means the solution resistance. The slope is \( 6 \, \Omega \text{M} \). We consider an electric resistance model (inset of Fig. 9) in the cell at which a disk electrode \( a \) in radius is located flush on a large planar insulator in a medium with the molar conductivity, \( \kappa_m \). The medium is covered with a large dome of a counter electrode, the resistance between the counter electrode and the disk electrode is given by \([38]\):

\[
r = \frac{1}{4c\kappa_m a_0},
\]

where \( \kappa_m \) is the sum of limiting ionic conductivity of Li\(^+\) and ClO\(_4^−\). Since no data of the conductivity in acetonitrile are available unfortunately, we use values in water, \( \kappa_m = (3.84 + 6.73) \times 10^{-3} \text{ S m}^2 \text{ mol}^{-1} \) \([39]\). If we take \( c \) to be the bulk concentration of LiClO\(_4\), the value of \( rc \) is 16 \( \Omega \text{M} \). This value is three-times larger than the experimental one (6 \( \Omega \text{M} \)). We have to be satisfied with only the agreement of the order of magnitude partly because of the rough model in cell geometry, partly because of the use of the \( \kappa_m \) values for water, and partly because of the disregard of mass transport of Li\(^+\) and ClO\(_4^−\) associated with the charge transfer. The practical method of subtracting the IR-drop contribution is to plot \( E \) against \( I \) and to extrapolate \( I \) to zero.

4. Conclusion

Voltammograms of LiClO\(_4\) in dried and deaerated acetonitrile showed the diffusion–migration controlled cathodic peak current and the adsorption-controlled anodic current when the concentration was less than 20 mM. The former is caused by the intercalation of Li\(^+\) into the PGE, but the current is controlled by the mass transport of Li\(^+\) in acetonitrile. It is not easy to evaluate the current accurately enough for in conventional voltammetry, because of complicated analysis of the migration current, involvement of impurity of salt, insufficient data of the diffusion coefficient and the conductivity, the irreversible reaction, and reduction of solvent. The cathodic charge was larger by 30% than the anodic one owing to the reduction current of acetonitrile or impurities in the solvent. The reduction of solvent is responsible for the charge loss in the charge–discharge cycle. The potential shift caused by the IR-drop was corrected with the extrapolation of \( I \) to zero in the plot of \( E \) vs. \( I \). Then there was 0.53 V potential difference between the intercalation and the deintercalation. This value, corresponding to 51 kJ mol\(^{-1}\), is the energy lost inevitably at each charge/discharge cycle.

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