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Temperature Change of Graphite Surface Due to Electrochemical Intercalation of ClO_4^- Ion

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Synopsis. Anodic intercalation and cathodic deintercalation of ClO_4^- ions were shown to cause exothermic and endothermic changes, respectively, on a graphite surface. This suggests the occurrence of an increase in entropy for the deintercalation process and a decrease for the case of intercalation.

Studies on the syntheses, structure, properties, and applications of graphite intercalation compounds have been actively carried out. There have been several reports concerning electrochemical intercalation on graphite.[1–10] This process is important because it may provide both kinetic and thermodynamic interpretations for intercalation behavior. It has been reported[11–13] that useful information concerning electrochemical reactions may be obtained by the detection of heat due to electrolysis. In the present study in-situ measurements of the temperature changes of graphite surfaces due to electrochemical intercalation were carried out in order to reveal heat behavior during the intercalation process.

Experimental

Measurements of the temperature change were based on the differential thermal method; two thermistors (Takara Industry Co., type: PXK-67) were used, the one of which was attached to the surface of the graphite electrode and the other placed in the bulk of the solution. The temperature difference between them was detected by a bridge (Fuso Seisakusho Co., model: 362A). The solution (volume: 0.1 dm^3) was stirred and N_2 gas bubbled during electrolysis. By circulating thermostated water outside the solution, its temperature was maintained at 20 °C. A graphite sheet (Toyo Tanso Co., size: 12×10×0.5 mm) was used as the working electrode. The counter electrode was a platinum wire, and the reference electrode was an oxidized silver wire galvanostatically (at 1 mA for 10 min) placed in 1 mol dm^{-3} hydrochloric acid. Electrolytic solutions were prepared by the dissolution of anhydrous $LiClO_4$ into distilled propylene carbonate (PC), acetonitrile (AN), and nitromethane (NM). The electrochemical intercalation of ClO_4^- ions was performed by cyclic voltammetry. Simultaneously, the temperature change of the graphite surface was measured during electrolysis.

Results and Discussion

It has been reported[1,2] that anodic oxidation of graphite in organic solutions containing perchlorate causes the intercalation of ClO_4^- ions, as follows:

$$n\mathrm{C} + \mathrm{ClO_4^-} \rightleftarrows \mathrm{C}_n^+\,\mathrm{ClO_4^-} + \mathrm{e}$$

In this case, the reaction on the left represents the cathodic deintercalation of ClO_4^- ions.

Figure 1 shows the cyclic voltammogram (CV) as well as the relation between the temperature change and the electrode potential (ΔT–E) of graphite in a 0.2 mol dm^{-3} $LiClO_4$-PC solution. Regarding the sign of ΔT, the positive and the negative signs represent a rise and a fall in temperature, that is, exothermic and endothermic changes, respectively. Concerning the CV in Fig. 1, the anodic current and the corresponding cathodic current peak were observed. The former indicates the intercalation process of the ClO_4^- ion and the latter its deintercalation. The ΔT–E relation showed a marked increase in temperature with the anodic current; also, the peak of the fall in temperature nearly fit the cathodic peak.

Figure 2 shows the CV and the ΔT–E relation of graphite in a 0.2 mol $dm^{-3}$$LiClO_4$–AN solution. The anodic current and the corresponding cathodic peak due to the intercalation and deintercalation of ClO_4^- ions, respectively, were observed. The ΔT–E relation showed an increase in temperature with the anodic current; also, the peak of the fall in temperature nearly fit the cathodic peak.

Figure 3 shows the CV and the ΔT–E relation of graphite in a 0.1 mol dm^{-3} $LiClO_4$-NM solution. In this case, a similar rise and a fall in temperature occurred during the processes of intercalation and deintercalation of ClO_4^- ions , respectively, though the fit of the fall in temperature with the cathodic peak

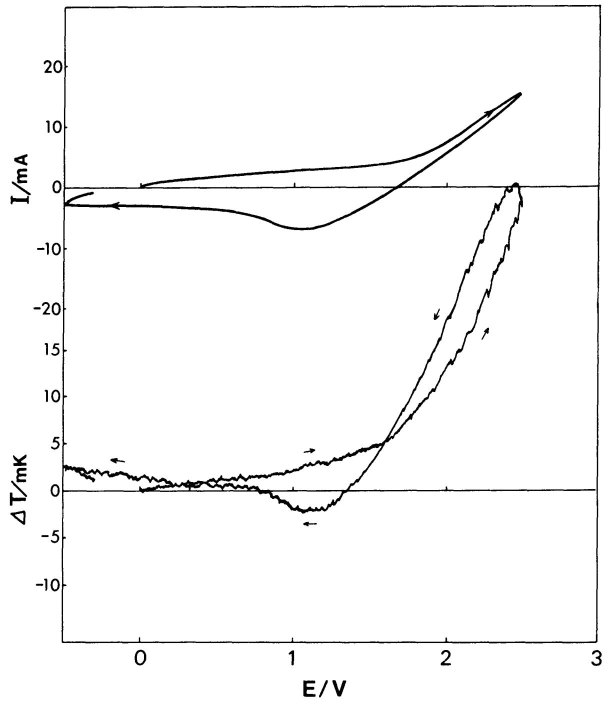

Fig. 1. The CV and the ΔT-E relation of the graphite in a 0.2 mol dm^{-3} $LiClO_4$-PC solution. Scan rate: 10 mV s^{-1}.

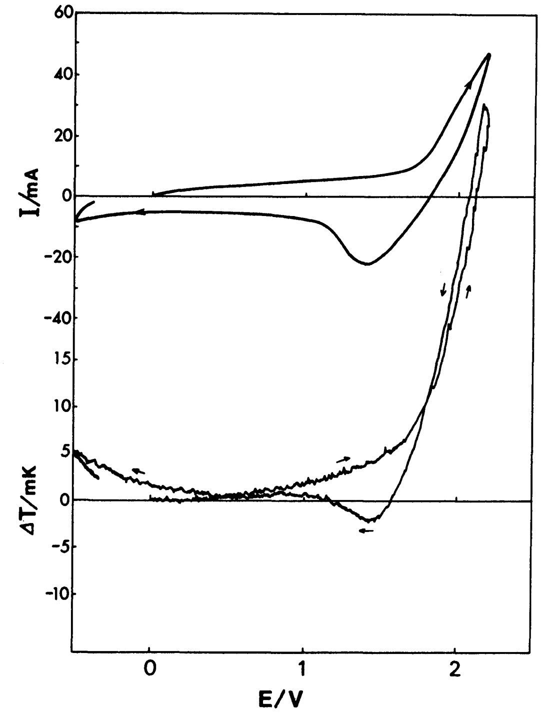

Fig. 2. The CV and the ΔT-E relation of the graphite in a 0.2 mol dm^{-3} $LiClO_4$-AN solution. Scan rate: 10 mV s^{-1}.

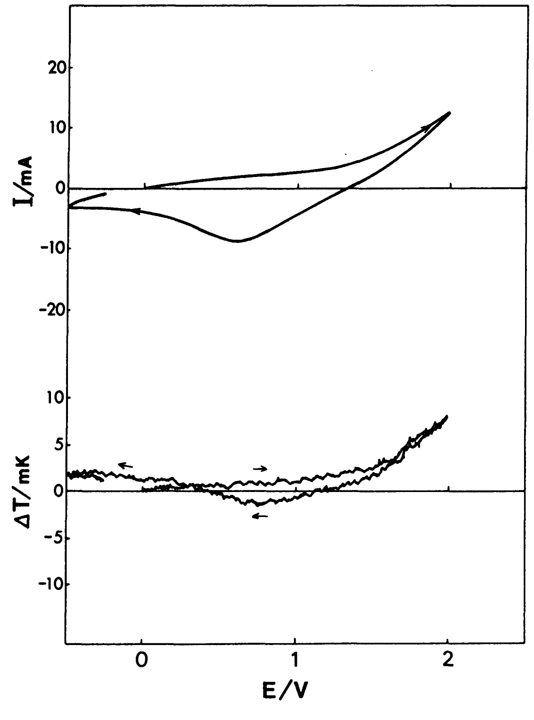

Fig. 3. The CV and the ΔT-E relation of the graphite in a 0.1 mol dm^{-3} $LiClO_4$-NM solution. Scan rate: 10 mV s^{-1}.

was not clear.

At the electrode/electrolyte interphase, the absorbed heat dQ during the electrolysis period dt can be expressed as

$$dQ = \frac{(T\Delta S + Q^*)|I|dt}{nF} - |I|\,\eta\,dt - I^2 R\,dt, \qquad (1)$$

where ΔS is the molar entropy change of electrode reaction, Q^* the heat of transfer, I the current, η the overpotential and R the electric resistance. The relation between the temperature change and the absorbed heat at the interphase is given by

$$\Delta T = -K\frac{dQ}{dT}, \qquad (2)$$

where K is a positive constant. In Eq. 1, the first term is called the electrochemical Peltier heat. Q^* equals $T\Delta S^*$, where ΔS^* is the molar entropy change of transfer of ions. Since the value of $\Delta S^*/nF$ (except the case of H^+ or OH^- participating) is within +0.08—−0.08 mV deg^{-1} (much smaller than that of $\Delta S/nF$14)), virtually the first term could be regarded as being the heat due to the entropy change of electrode reaction. The second term represents the heat due to polarization, and the third is the Joule heat. Both the second and third terms are always exothermic, though the first one depends on the sign of ΔS: an increase or decrease in entropy leads to an endothermic or exothermic change, respectively.

The fit of a peak of a fall in temperature with the cathodic peak in Figs. 1 and 2 suggests that the heat in the cathodic process may be mainly due to an entropy change for the deintercalation of ClO_4^- ions in $LiClO_4$-PC and $LiClO_4$-AN solutions. The obscure fit of the fall in temperature with the cathodic peak in an $LiClO_4$-NM solution could be explained by the contribution of not only the first, but also the second and third terms. The endothermic change in the cathodic deintercalation of ClO_4^- ions suggests the occurrence of an increase in entropy and may also lead to a decrease due to intercalation.

It is possible to obtain information concerning the entropy change of the electrode reaction by measuring the temperature-dependence of the electrode potential.14) The thermal temperature coefficient of the electrode potential $(dE/dT)_{th}$ is expressed as

$$(dE/dT)_{th} = \frac{\Delta S}{nF} + \frac{\Delta S^*}{nF}. \qquad (3)$$

Thus, the value of $(dE/dT)_{th}$ for the graphite oxidized anodically in these solutions (that is, after the intercalation of ClO_4^- ions) was checked while changing the temperature of only the graphite electrode. Figures 4 and 5 show the temperature-dependence of the electrode potential of the graphite after anodic oxidation in $LiClO_4$-PC and $LiClO_4$-NM solutions, respectively. In this case, the potential was measured versus a saturated calomel electrode (at room temperature) separated from the compartment of the working electrode by a vessel filled with the electrolyte using a Luggin cappillary and a KCl salt bridge. From the slope of the linear relation by the method of least squares, the values of $(dE/dT)_{th}$ were +1.30 mV deg^{-1} and +3.55 mV deg^{-1} for $LiClO_4$-PC and $LiClO_4$-NM solutions, respectively. Thus, the estimated values of ΔS were +125 J mol^{-1} K^{-1} and +343 J mol^{-1}

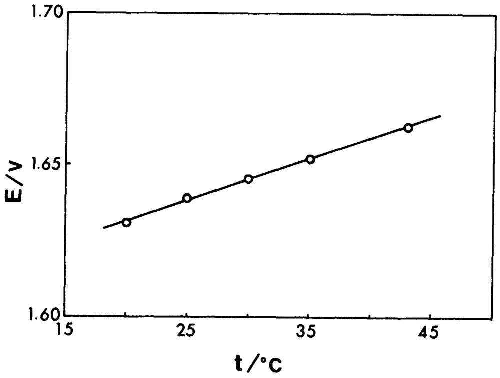

Fig. 4. The temperature-dependence of the electrode potential of the graphite after anodic oxidation (at +2.0 V for 1 h) in a 0.2 mol dm^{-3} $LiClO_4$–PC solution.

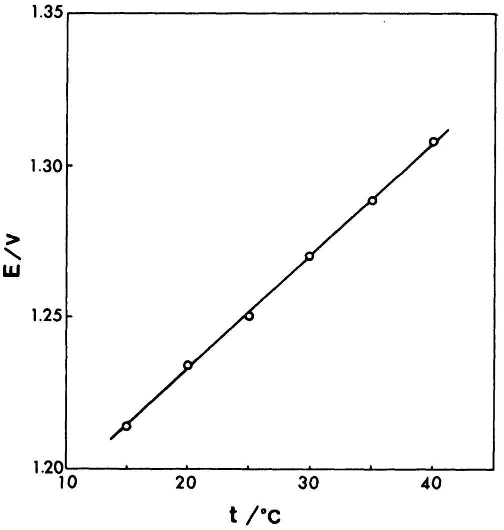

Fig. 5. The temperature-dependence of the electrode potential of the graphite after anodic oxidation (at +2.0 V for 1 h) in a 0.1 mol dm^{-3} $LiClO_4$–NM solution.

K^{-1}, respectively, by supposing that ΔS^* might be negligible. The positive value obtained in $LiClO_4$–PC and $LiClO_4$–NM solutions suggests an increase in entropy due to the deintercalation of ClO_4^- ions. The measurement of $(dE/dT)_{th}$ for graphite oxidized anodically in an $LiClO_4$–AN solution was impossible because of the unstable electrode potential. Nevertheless, also in this case, the occurrence of an increase in entropy could be supported by the thermal result, as mentioned above. This thermal method has the advantage of providing information concerning entropy change directly and promptly by the detection of the heat due to electrolysis.

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