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Electrochemical Peltier heat in the polypyrrole–electrolyte system¹

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Abstract

The simultaneous detection of electrochemical and thermal responses of polypyrrole in 1 M NaClO₄ aqueous solution (pH = 5) was carried out. Thermal measurement with cyclic voltammetry and galvanostatic electrolysis revealed exothermic and endothermic changes due to anodic and cathodic currents, respectively, on the surface of the polypyrrole electrode. The proportional relation between the heat due to electrolysis and electric quantity or current was confirmed in both the exothermic and endothermic processes. This electrochemical Peltier heat could be attributed to the entropy change in the electrochemical doping and dedoping of ClO₄⁻ ions. It suggested the occurrence of a decrease and an increase in entropy in the doping and dedoping processes, respectively. The value of the entropy change in the dedoping of ClO₄⁻ ions could be evaluated on the basis of the entropy change in the anodic oxidation of Fe(CN)₆⁴⁻ ions.

Keywords: Peltier heat; Polypyrrole; Electrolyte; Electrochemical doping; Entropy change

1. Introduction

Various kinds of conducting polymers have been synthesized and their physico-chemical properties studied and their applications carried out actively. Polypyrrole, one of the conducting polymers, has attracted attention as a functional materials, e.g. electrode for batteries. The electrochemical properties of polypyrrole have been reported by several authors [1–9]. We have reported on the preliminary results of the simultaneous detection of electrochemical and thermal responses of the polyaniline in aqueous solutions [10,11]. This technique may be useful for us to obtain knowledge on the electro-

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chemical process of conducting polymers from the viewpoint of entropy change. In the present work, we investigated the thermal behavior of the polypyrrole electrode in NaClO_4 aqueous solution to clarify electrochemical Peltier heat in this system.

2. Experimental

Polypyrrole was deposited on graphite (Toyo Tanso Company; size $10 \times 20 \times 0.6 \text{ mm}^3$) by electrochemical polymerization under potentiostated conditions (potential, 0.8 V versus saturated calomel electrode [SCE]; electrolysis time, 2 h) in 0.1 M ($M = \text{mol dm}^{-3}$) *p*-toluenesulfonic acid aqueous solution containing 0.1 M pyrrole. This was used as a polypyrrole working electrode. The counter and reference electrodes were a platinum wire and an SCE, respectively. The latter was connected to the electrolytic solution through a KCl salt bridge. The construction of the cell used here is shown in Fig. 1. Electrochemical measurements were based on cyclic voltammetry and galvanostatic electrolysis by a potentiogalvanostat (Hokuto Denko Company; Model HA-301) and a function generator (Hokuto Denko Company; Model HB-105). Thermal measurements were carried out as follows. One of two thermistors (Takara Thermistor; Model PXX-76; resistance, 7.326 and 7.328 $\text{K}\Omega$ at 20°C; thermistor constants, 3348 and 3337 K, respectively) was attached to the surface of the polypyrrole electrode and the other positioned in the bulk of the electrolytic solution. The temperature change of the electrode surface due to current was differentially detected by an AC bridge (Fuso Seisakusho Company;

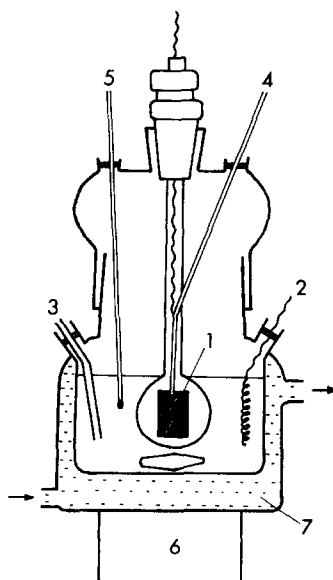


Fig. 1. Construction of the cell. 1, Polypyrrole working electrode; 2, platinum wire counter electrode; 3, KCl salt bridge connected with an SCE reference electrode; 4 and 5, thermistor; 6, magnetic stirrer; 7, thermostated water.

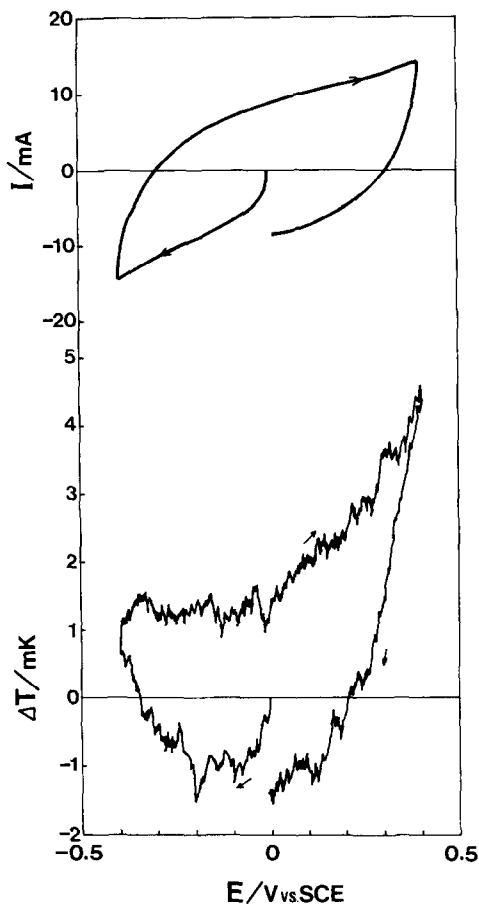


Fig. 2. Cyclic voltammogram and the relation between electrode potential and temperature change of the polypyrrole in 1 M NaClO_4 aqueous solution (pH = 5) Scan rate 10 mV s^{-1} .

Model 362B). The electrolytic solution (volume 0.1 dm^3), which was 1 M NaClO_4 aqueous solution (pH = 5), was stirred by a magnetic stirrer and its temperature was kept at 20°C by circulation of thermo-stated water.

3. Results and discussion

Fig. 2 shows the cyclic voltammogram (CV) and simultaneously measured relation between electrode potential and temperature change ($E-\Delta T$) of polypyrrole in the electrolytic solution. In the potential range of -0.4 – 0.4 V , exothermic change (corresponding to positive ΔT) due to the anodic current and endothermic change due to the cathodic current were observed.

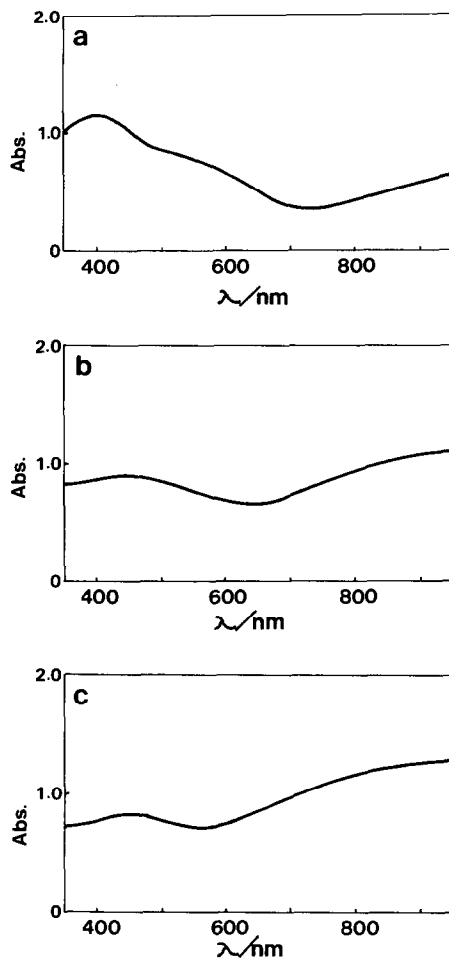
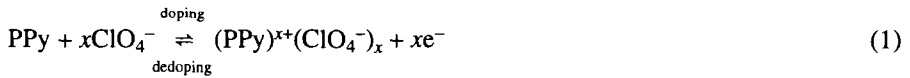


Fig. 3. Absorption spectra of the polypyrrole/ITO in 1 M NaClO₄ aqueous solution (pH = 5) at various potentials: (a) -0.3 V; (b) 0.0 V; (c) 0.3 V.

In order to obtain knowledge on these anodic oxidation and cathodic reduction processes, the absorption characteristics of the polypyrrole at various potentials was checked. Fig. 3a–c shows the absorption spectra of the polypyrrole deposited on an indium–tin–oxide (ITO) optically transparent electrode at potentials of -0.3, 0.0 and 0.3 V in 1 M NaClO₄ aqueous solution (pH = 5), respectively. The absorption peak of ca. 400 nm observed at a potential of -0.3 V corresponds to the π - π^* absorption. This means the undoped state of the polypyrrole due to the cathodic reduction. The peak of ca. 450 nm observed at potentials of 0.0 and 0.3 V may be attributed to the bipolaron state formed in the anodic oxidation. Also an increase in absorption at wavelengths longer than 700 nm was observed at positive potentials. By consideration of the results of the absorption spectra, the anodic oxidation of polypyrrole in NaClO₄ aqueous solution could be re-

garded as the formation of the bipolaron state and simultaneous doping of ClO_4^- ions, and cathodic reduction dedoping as shown below.



where PPy is the undoped polypyrrole, x the moles of the doped ClO_4^- ions.

To determine the dependence of the thermal response upon the current, the temperature change due to constant current was examined. Fig. 4a,b shows the response of temperature change and electrode potential of the polypyrrole in the electrolytic solution to constant current (current value, ± 4 , ± 8 and ± 12 mA; period, 20 s) in the anodic and cathodic processes, respectively. The exothermic and endothermic changes were clearly due to the anodic and cathodic current, respectively. The area of the portion surrounded by the response curve of ΔT and the base line in Fig. 4, $\int \Delta T dt$, may be proportional to

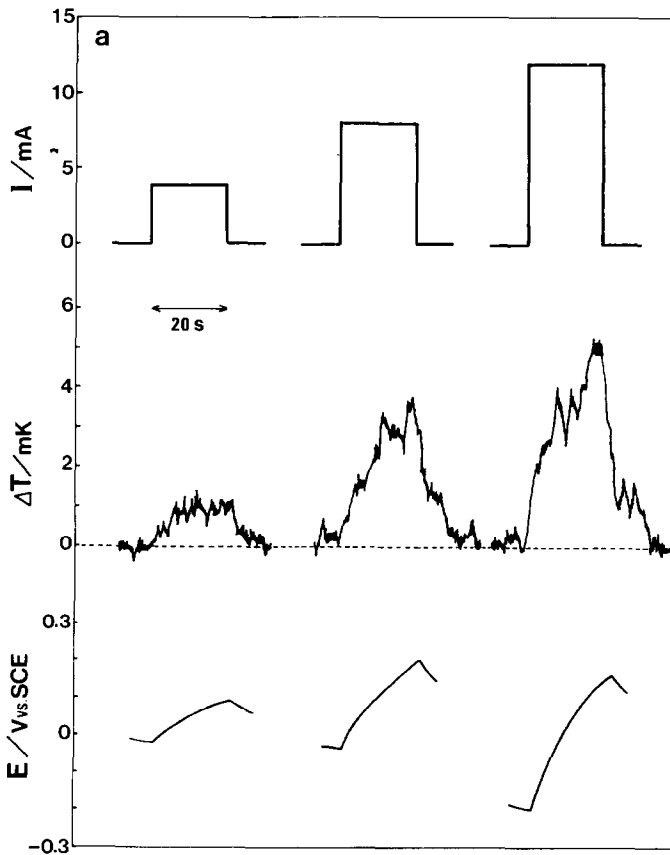


Fig. 4a.

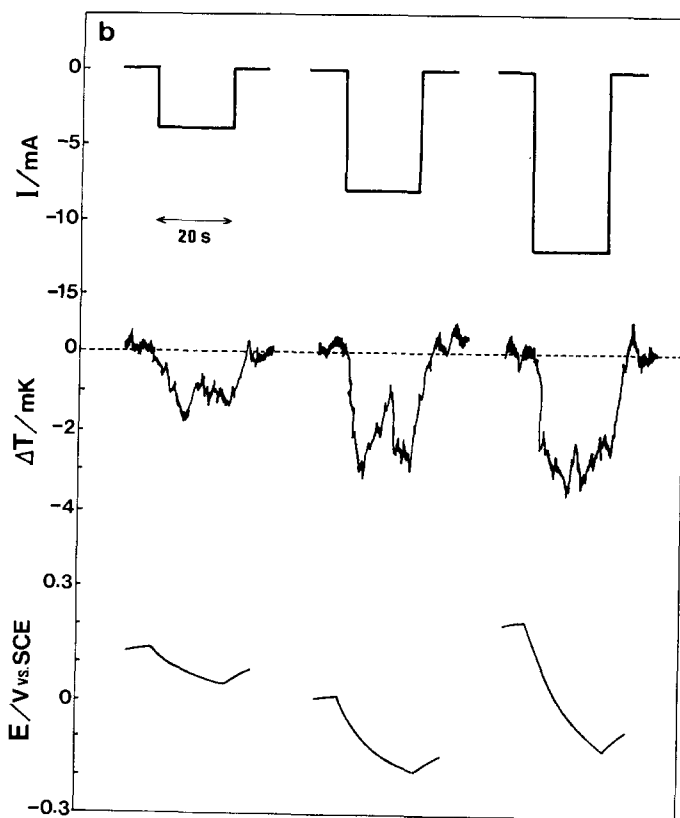


Fig. 4. Response of temperature change and electrode potential of the polypyrrole in 1 M NaClO_4 aqueous solution (pH = 5) to constant current: (a) anodic oxidation process; (b) cathodic reduction process.

Q , the total heat absorbed or generated at the electrode/electrolyte interface during electrolysis. This relation is expressed as follows:

$$Q = -k \int \Delta T dt \quad (2)$$

where k is a positive constant.

Fig. 5 shows the relation between $\int \Delta T dt$ and electric quantity (absolute value) in the exothermic (a) and endothermic (b) processes. The obvious proportional relation between $\int \Delta T dt$ and electric quantity in both processes means that the temperature change observed here was dominantly attributed to the electrochemical Peltier heat Q_{ecp} . Q_{ecp} is represented as follows:

$$Q_{\text{ecp}} = \frac{(T\Delta S + Q^*)|I|t}{nF} \quad (3)$$

where ΔS is the molar entropy change of the electrode reaction, Q^* the heat of transfer of

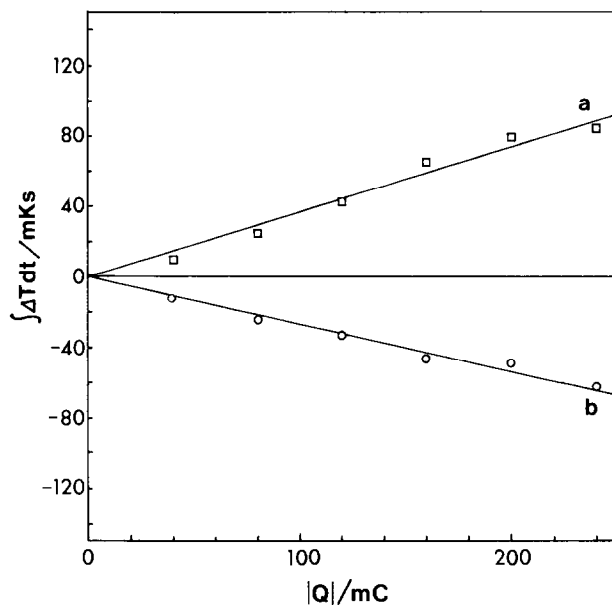


Fig. 5. Relation between $\int \Delta T dt$ and electric quantity (absolute value): (a) anodic oxidation process; (b) cathodic reduction process.

the ions, I the current and t the electrolysis period. Since Q^* is negligibly smaller than $T\Delta S$ except in strong acid and alkaline solutions, Q_{ecp} almost equals $T\Delta SIt/nF$. Therefore, the exothermic and endothermic changes in the processes of anodic doping and cathodic dedoping of ClO_4^- ions lead to the occurrence of a decrease and an increase in entropy, respectively. The proportional constants of the plots of $\int \Delta T dt$ against electric quantity, that is Peltier coefficients, were 0.369 K A^{-1} and -0.269 K A^{-1} in the exothermic and endothermic processes, respectively. From Eqs. (2) and (3),

$$\Delta S = -\frac{nFk}{T|I|t} \int \Delta T dt \quad (4)$$

Knowledge of k is necessary to obtain the values of ΔS from the thermal data.

Fig. 6 shows the CV and $E-\Delta T$ of polypyrrole in an electrolytic solution containing $0.01 \text{ M K}_4\text{Fe}(\text{CN})_6$.

In the potential range of -0.4 – 0.1 V , the exothermic and endothermic changes due to electrochemical doping and dedoping of ClO_4^- ions, respectively, were observed, and also the endothermic change with a distinct anodic current appeared at higher potential than 0.15 V . The latter endothermic change could be attributed to the entropy change of the anodic oxidation of $\text{Fe}(\text{CN})_6^{4-}$ ions as follows:



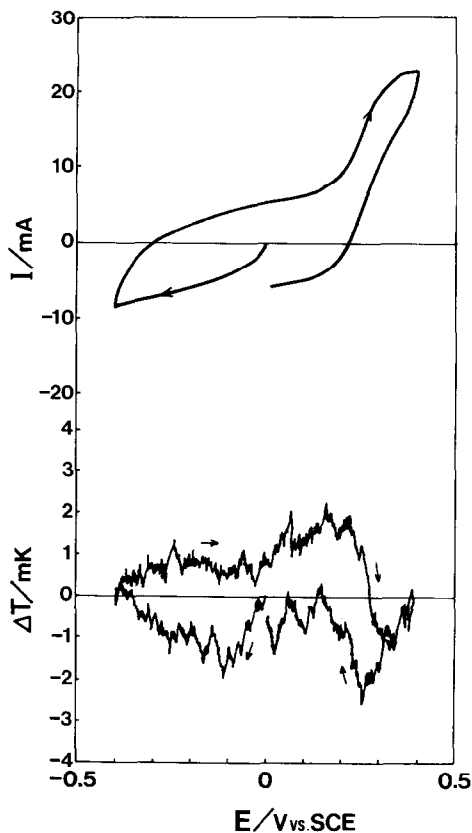


Fig. 6. Cyclic voltammogram and the relation between electrode potential and temperature change of the polypyrrole in 1 M NaClO₄ aqueous solution (pH = 5) containing 0.01 M K₄Fe(CN)₆. Scan rate 10 mV s⁻¹.

The entropy change in this process can be evaluated according to de Bethune et al. [12] as shown below.

$$\begin{aligned}
 \Delta S &= S[\text{Fe}(\text{CN})_6^{3-}] + S[\text{e}^-] - S[\text{Fe}(\text{CN})_6^{4-}] \\
 &= \{S[\text{Fe}(\text{CN})_6^{3-}] - 3S[\text{e}^-]\} - \{S[\text{Fe}(\text{CN})_6^{4-}] - 4S[\text{e}^-]\} \\
 &= S^*[\text{Fe}(\text{CN})_6^{3-}] - S^*[\text{Fe}(\text{CN})_6^{4-}] \\
 S^*[\text{Fe}(\text{CN})_6^{3-}] &= S[\text{Fe}(\text{CN})_6^{3-}] - 3S[\text{e}^-] \\
 S^*[\text{Fe}(\text{CN})_6^{4-}] &= S[\text{Fe}(\text{CN})_6^{4-}] - 4S[\text{e}^-] \tag{6}
 \end{aligned}$$

where $S^*[\text{Fe}(\text{CN})_6^{3-}]$ and $S^*[\text{Fe}(\text{CN})_6^{4-}]$ are the entropies of electrochemical transport. These values can be computed by the following equation:

$$S^*[i] = S^\circ[i] + Z_i(-18.75 \text{ J K}^{-1} \text{ mol}^{-1}) \quad (7)$$

where $S^\circ[i]$ is the standard entropy of ions referred to $S^\circ[\text{H}^+] = 0$ at all temperatures and Z_i the ionic charge with sign. By using the values of $270.3 \text{ J K}^{-1} \text{ mol}^{-1}$ and $95.0 \text{ J K}^{-1} \text{ mol}^{-1}$ as the standard entropies of $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Fe}(\text{CN})_6^{4-}$ ions, respectively [13],

$$S^*[\text{Fe}(\text{CN})_6^{3-}] = 270.3 + (-3)(-18.75) = 326.6 \text{ J K}^{-1} \text{ mol}^{-1} \quad (8)$$

$$S^*[\text{Fe}(\text{CN})_6^{4-}] = 95.0 + (-4)(-18.75) = 170.0 \text{ J K}^{-1} \text{ mol}^{-1} \quad (9)$$

Therefore $\Delta S = 156.6 \text{ J K}^{-1} \text{ mol}^{-1}$. This means the occurrence of an increase in entropy and the appearance of the endothermic change in the anodic oxidation from $\text{Fe}(\text{CN})_6^{4-}$ to $\text{Fe}(\text{CN})_6^{3-}$ ions.

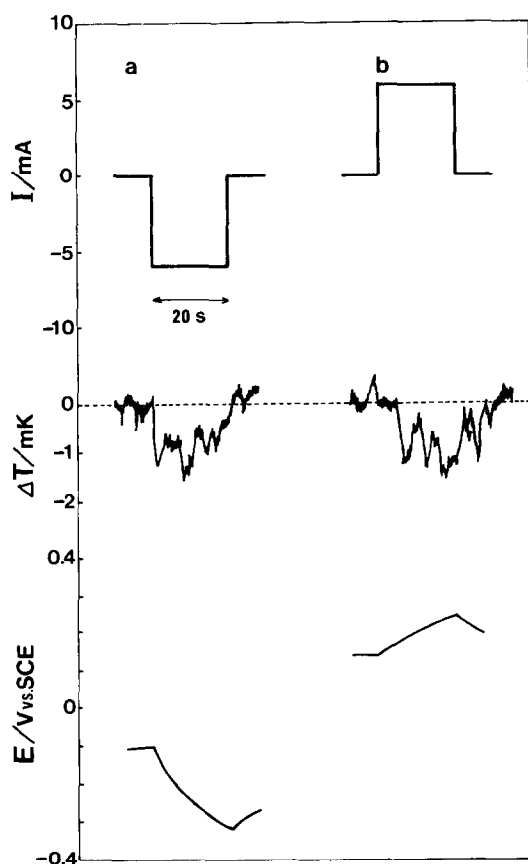


Fig. 7. Response of temperature change and electrode potential of the polypyrrole in 1 M NaClO_4 aqueous solution ($\text{pH} = 5$) containing 0.01 M $\text{K}_4\text{Fe}(\text{CN})_6$ to constant current: (a) cathodic reduction process; (b) anodic oxidation process.

Fig. 7 shows the responses of the temperature change and electrode potential of polypyrrole to constant current (current value, ± 6 mA; period, 20 s) in the electrolytic solution containing 0.01 M $\text{K}_4\text{Fe}(\text{CN})_6$. The two endothermic changes due to the cathodic and anodic currents could be attributed to the entropy change of the cathodic dedoping of ClO_4^- ions (a) and of the anodic oxidation of $\text{Fe}(\text{CN})_6^{4-}$ ions (b), respectively, by consideration of the range of the potential change. Since the value of k and the electric quantity (absolute value) are the same in these processes, the entropy change in process (a), $\Delta S(a)$, can be evaluated on the basis of the entropy change in process (b), $\Delta S(b)$, by comparison with the magnitude of $\int \Delta T dt$.

$$\Delta S(a) = \Delta S(b) \times \frac{\int \Delta T dt(a)}{\int \Delta T dt(b)} \quad (10)$$

As $\Delta S(b)$ is $156.6 \text{ J K}^{-1} \text{ mol}^{-1}$, $\int \Delta T dt(a) -19.34 \text{ mK s}$ and $\int \Delta T dt(b) -27.31 \text{ mK s}$, $\Delta S(a) = 110.9 \text{ J K}^{-1} \text{ mol}^{-1}$. Thus the entropy change in the cathodic dedoping of x moles of ClO_4^- ions (left direction in Eq. (1)) equals $110.9x \text{ J K}^{-1}$.

4. Conclusion

The electrochemical Peltier heat in a polypyrrole– NaClO_4 aqueous solution system was investigated by simultaneous detection of the electrochemical and thermal responses of the polypyrrole electrode. The observed heat could be attributed to the entropy change in the electrochemical doping and dedoping of ClO_4^- ions. The value of the entropy change in the cathodic dedoping could be evaluated at $110.9x \text{ J K}^{-1}$ (x is the moles of the doped ClO_4^- ions) on the basis of the entropy change in the anodic oxidation of $\text{Fe}(\text{CN})_6^{4-}$ ions. The thermal measurement of the conducting polymers in electrolytic solutions is useful to understand their electrochemical processes from the viewpoint of the entropy change.

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