February, 1994] © *1994 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn., **67**, 575—577(1994)* 575

Thermal Behavior of Polyaniline Due to Anodic Oxidation in Various Aqueous Solutions

Yasuhisa MAEDA* and Ai KATSUTA
Department of Materials Science, Toyohashi University of Technology, Tempaku-cho, Toyohashi 441

(Received August 27, 1993)

Synopsis. The anodic oxidation of polyaniline in aqueous solutions containing $SO_4{}^{2-}$ and $PO_4{}^{3-}$ ions caused an exothermic change at lower potential and an endothermic change at higher potential, but only the exothermic change was observed in the anodic process of polyaniline in a solution containing $ClO_4{}^-$ ions.

Polyaniline, a conducting polymer, has attracted attention because of the appearance of functional characteristics due to electrochemical doping of anions. There have been various reports concerning electrochemical properties of polyaniline.[1—12] It is important to make clear the doping process to use polyaniline as an electrode material effectively. It has been pointed out that anodic oxidation of polyaniline in aqueous solutions may cause not only anion doping but also proton elimination. In-situ measurements of absorption spectra[6—9] and weight changes[4,10—12] of polyaniline during electrolysis have been done to get a knowledge of the doping process. We have reported the thermal behavior of polyaniline and its derivative electrodes in $ZnSO_4$ aqueous solution.[13,14] This thermal measurement could provide information on aspects of entropy changes for the electrochemical process of polyaniline. In this paper, we did in-situ thermal measurement of a polyaniline electrode in aqueous solutions containing $ClO_4{}^-$, $SO_4{}^{2-}$, and $PO_4{}^{3-}$ ions to compare the behavior due to electrochemical doping of anions.

Experimental

Polyaniline was deposited on a graphite sheet electrode (Toyo Tanso Company; size: $10\times20\times0.6$ mm^3) by electrochemical polymerization using the potential sweep method in 1 M (M=mol dm^{-3}) acid solutions of $HClO_4$, H_2SO_4, and H_3PO_4 containing 0.1 M aniline. The potential range was from 0.0 to 0.8 V versus a saturated calomel electrode (SCE) and the potential scan rate was 10 mV s^{-1}. The numbers of times of scan repetition were 90, 57, and 90 in $HClO_4$, H_2SO_4, and H_3PO_4 solutions, respectively. The polyaniline thus prepared was used as a working electrode. A platinum wire and an SCE were the counter and reference electrodes, respectively. The thermal measurement was done by the differential method using a bridge (Fuso Seisakusho Company; Model 362B) and two thermistors (Takara Industry Company; Model PXK-67; resistance: 7.326 and 7.328 kΩ at 20 °C; thermistor constants: 3348 and 3337 K, respectively). One thermistor was attached to the surface of the polyaniline electrode and the other was positioned in the bulk of electrolytic solution. The in-situ measurement of the temperature change on the polyaniline electrode in various aqueous solutions was done during electrolysis by cyclic voltammetry and potential step methods. The electrolytic solution (volume: 0.1 dm^3) was stirred by a magnetic stirrer. The temperature of the solution was kept at 20 °C by circulation of thermostated water.

Results and Discussion

Figures 1a, 1b, and 1c show the voltammograms and simultaneously measured relation between electrode potential and temperature change ($E-\Delta T$) on polyaniline in 1 M $Zn(ClO_4)_2$, -$ZnSO_4$, and -Na_3PO_4 aqueous solutions (pH=3.5). The positive value of temperature change represents a rise in temperature (exothermic change) and the negative value a fall in temperature (endothermic change). In the anodic process of polyaniline in both $ZnSO_4$ and Na_3PO_4 solutions, two anodic current peaks appeared at 0.30 and 0.65 V in the former and at 0.20 and 0.45 V in the latter solution and the two peaks could be distinguished by the different thermal response, the exothermic change on the first peak and the endothermic change on the second peak as shown in Figs. 1b and 1c. In the cathodic process in $ZnSO_4$ solution, the exothermic change peak at 0.50 V and the endothermic change at lower potential than 0.05 V were observed. In Na_3PO_4 solution, a distinct exothermic change on the cathodic peak at 0.25 V was observed. In the anodic process of polyaniline in $Zn(ClO_4)_2$ solution, only the exothermic change occurred. The endothermic change appearing at a higher potential in $ZnSO_4$ and Na_3PO_4 solutions was not observed in this solution (Fig. 1a).

To discover the correspondence between the anodic and cathodic processes, the thermal response of polyaniline to a potential step change with an interval of 0.2 V (potential range: −0.2→0.8→−0.2 V) was examined. Figures 2a, 2b, and 2c show the response of the current and the temperature change of polyaniline to the anodic potential step in 1 M $NaClO_4$, $ZnSO_4$, and Na_3PO_4 aqueous solutions (pH=3.5), respectively. The upper portion of the figures was from 0.0 to 0.2 V (step 1) and the lower from 0.4 to 0.6 V (step 2). It is apparent that the exothermic and the endothermic changes occurred in the anodic oxidation of polyaniline by step 1 and step 2, respectively, in both $ZnSO_4$ and Na_3PO_4 solutions (Figs. 2b and 2c). The reverse of these thermal responses was confirmed by the cathodic potential step, that is, the occurrence of the endothermic change in the potential change from 0.0 to −0.2 V and of the exothermic change from 0.4 to 0.2 V in these solutions. In the anodic oxidation of polyaniline in $NaClO_4$ solu-

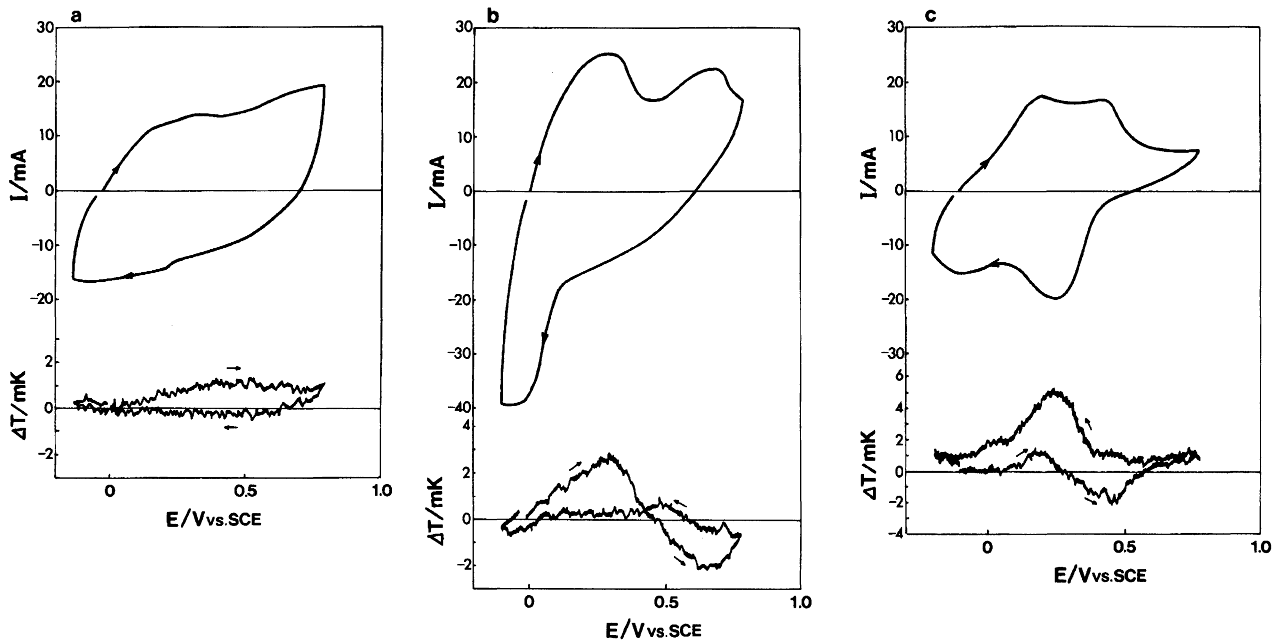

Fig. 1. Voltammograms and the relation between electrode potential and temperature change of polyaniline in various aqueous solutions (pH=3.5). (a) 1 M $Zn(ClO_4)_2$; (b) 1 M $ZnSO_4$; (c) 1 M Na_3PO_4. Scan rate: 10 $mV s^{-1}$.

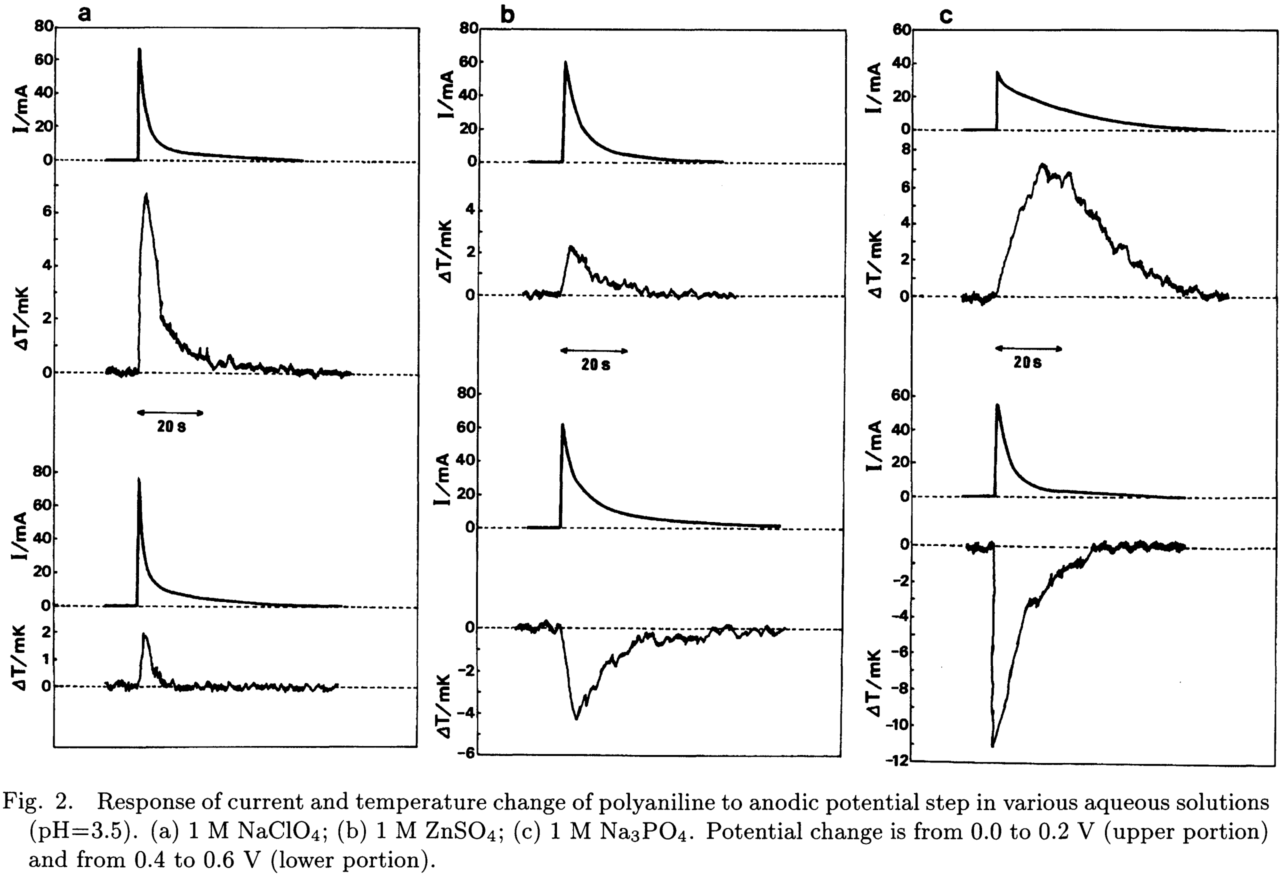

Fig. 2. Response of current and temperature change of polyaniline to anodic potential step in various aqueous solutions (pH=3.5). (a) 1 M $NaClO_4$; (b) 1 M $ZnSO_4$; (c) 1 M Na_3PO_4. Potential change is from 0.0 to 0.2 V (upper portion) and from 0.4 to 0.6 V (lower portion).

tion, the exothermic change occurred by step 2 although the magnitude of temperature change was smaller than that obtained by step 1 (Fig. 2a). The cathodic potential steps from 0.4 to 0.2 V and from 0.0 to −0.2 V in $NaClO_4$ solution both caused the endothermic changes corresponding to the reverse of the exothermic changes shown in Fig. 2a.

Thermal behavior due to electrolysis can be interpreted by the following equation. The heat $\mathrm{d}Q$ absorbed at the electrode/electrolyte interphase during electrolysis (period: $\mathrm{d}t$) is represented as

$$\mathrm{d}Q = \frac{(T\Delta S + Q^*)|I|\mathrm{d}t}{nF} - |I|\eta\mathrm{d}t - I^2R\mathrm{d}t \tag{1}$$

where ΔS is the molar entropy change of the electrode reaction, Q^* the heat of transfer of ions, I the current, η the overpotential and R the electric resistance. Temperature change ΔT is

$$\Delta T = -K\frac{\mathrm{d}Q}{\mathrm{d}t}, \tag{2}$$

where K is a positive constant. The first term in Eq. 1 is almost the heat due to the entropy change of electrode reaction because Q^* is negligibly smaller than $T\Delta S$ except in strong acid and alkali solutions.[15] Thus an increase in entropy leads to an endothermic change and a decrease in entropy to an exothermic change. The second and third terms in Eq. 1 represent the heat due to electrolytic polarization and Joule heat, respectively. These terms are exothermic changes. When the first term mostly contributes the heat, the sign of temperature change may appear in reverse for the corresponding anodic and cathodic processes.

The temperature change observed in this experiment could be ascribed to the heat due to the entropy change of electrode reaction. The anodic oxidation of polyaniline in aqueous solutions containing $SO_4{}^{2-}$ and $PO_4{}^{3-}$ ions caused the exothermic change at lower potential and the endothermic change at higher potential. The exothermic change suggests the occurrence of a decrease in entropy in the process of formation of polaron and bipolaron states and simultaneous doping of anions. The endothermic change suggests the occurrence of an increase in entropy in the process of proton elimination. In aqueous solutions containing multivalent anions, these processes could be distinguished clearly. This might be attributed mainly to facility in formation of bipolaron state in the anodic oxidation of polyaniline in these solutions. The anodic oxidation of polyaniline in the solution containing $ClO_4{}^-$ ions caused only the exothermic change. Similar results were obtained in the aqueous solutions containing $BF_4{}^-$ and $NO_3{}^-$ ions. This seems to imply that in the case of monovalent anions both the anodic reactions of anion doping and proton elimination might proceed at higher potential and the exothermic change due to the former process might exceed the endothermic change due to the latter process. The thermal results could show that there is a distinction between monovalent and multivalent anions in the anodic process of polyaniline in aqueous solution.

A part of this work was supported by the Tokyo Ohka Foundation for the Promotion of Science and Technology.

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