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Cyclic voltammetry of KI at polyaniline-filmed Pt electrodes Part II: Effects of pH

H. TANG, A. KITANI, M. SHIOTANI

Department of Applied Chemistry, Faculty of Engineering, Hiroshima University, Kagamiyama 1-4-1, Higashihiroshima 739, Japan

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Effects of pH on the cyclic voltammetry of KI at high concentrations was studied at Pt and polyaniline-modified Pt electrodes. The mechanism of oxidation of iodide to iodine was almost identical at both bare and polyaniline-filmed Pt electrodes at pH ≤ 2. In cyclic voltammograms the redox peak currents increased, or new peaks occurred at polyaniline-filmed Pt electrodes, depending on the experimental conditions. The latter finding is due to the interactions of iodine species with the polyaniline main chains. At pH 4.7, the PAn film became electroinactive, the redox process proceeded at the Pt/PAn interface of the electrode. A change in the pH dependence of this kind was observed at a Pt electrode filmed with PAn modified by the presence of paraphenylenediamine in the growth solution.

1. Introduction

The successive oxidation of iodide to iodine via formation of an iodide–iodine complex has been observed by Yaraliyev [1] by cyclic voltammetry in neutral iodide solution. During the anodic oxidation of iodide at concentrations of 10 mM or more, a steady-state anodic current is observed due to the formation of a thick layer of iodine [2, 3], which is governed by a precipitation–dissolution mechanism of the iodine film [4, 5]. Recently, we have found that the anodic oxidation mechanism of iodide to iodine at polyaniline (PAn) electrodes is almost the same as that at a bare Pt electrode in 0.1 M $HClO_4$, and that the formation of PAn-iodine complexes leads to new redox peaks in the cyclic voltammograms [6].

The insulator-to-metal transition in PAn is affected by protonation. In brief, the conductivity of PAn is a function of protonation or the pH value [7]. The study of the effects of pH on the PAn switching reaction has demonstrated that electrical neutrality in PAn films is maintained at a pH below 1 by the egress of hydronium ions, whereas at pH above 2, neutrality is maintained by the insertion of anions into the film [8]. The electrochemical behaviour of PAn films has been studied in buffered solutions of wide pH range [9, 10]. Because the electroactivity of PAn depends on the pH [7–11] and the redox process of iodide at low concentrations becomes increasingly irreversible as solution pH increases [12], the present work was carried out to investigate the effects of pH on the cyclic voltammetry of KI at Pt electrodes filmed with PAn with and without the presence of para-phenylenediamine (PPDA) in the growth solution.

2. Experimental details

All chemicals used were special reagent grade or better and were used as received. The compositions of test solutions of various pH were as follows:

pH −0.7	5 M $HClO_4$
pH 0	1 M $HClO_4$
pH 1	0.1 M $HClO_4$
pH 2	0.01 M $HClO_4$ + 0.09 M $KClO_4$
pH 4.7	0.05 M HAc + 0.05 M NaAc + 0.05 M $KClO_4$

where the constant ionic strength is not kept for the first two cases of low pH. Only the KI concentration of 10 mM was used because the solubility of KI in 5 M $HClO_4$ is limited. After the background electrolyte solution had been bubbled with nitrogen for about 15 min, a specified amount of KI was dissolved into it. During the experiment the test solution was kept under nitrogen atmosphere.

A Pt disc electrode with a diameter of 1 mm, after being polished with 0.3 μm alumina and cleaned in acetone, was electrodeposited with a film of PAn at a current density of 1 mA cm^{-2} in solution of 1.3 M aniline and 2.3 M $HClO_4$, with or without the presence of 10 mM PPDA, until a given anodic oxidation charge, Q_a (mC cm^{-2}), had passed to achieve a required film thickness. The film electrode was accordingly denoted as Q_a-PAn/Pt or Q_a-PPDA–PAn/Pt, respectively, for the case with or without presence of PPDA in the growth solution. The electrode with $Q_a = 0$ mC cm^{-1} appearing in Figs 2 and 5 is a bare Pt electrode.

The resulting film electrode was washed by dipping in distilled water, transferred into the test solution, then subjected to potential cycling between −0.15 and 0.6 V at 50 mV s^{-1} for 10 min prior to the CV measurement. The steady-state CV responses of KI were recorded between −0.1 and 0.7 V at scan rates of 1–200 mV s^{-1}. The electrochemical measurement was carried out at 25 °C in a typical three-electrode

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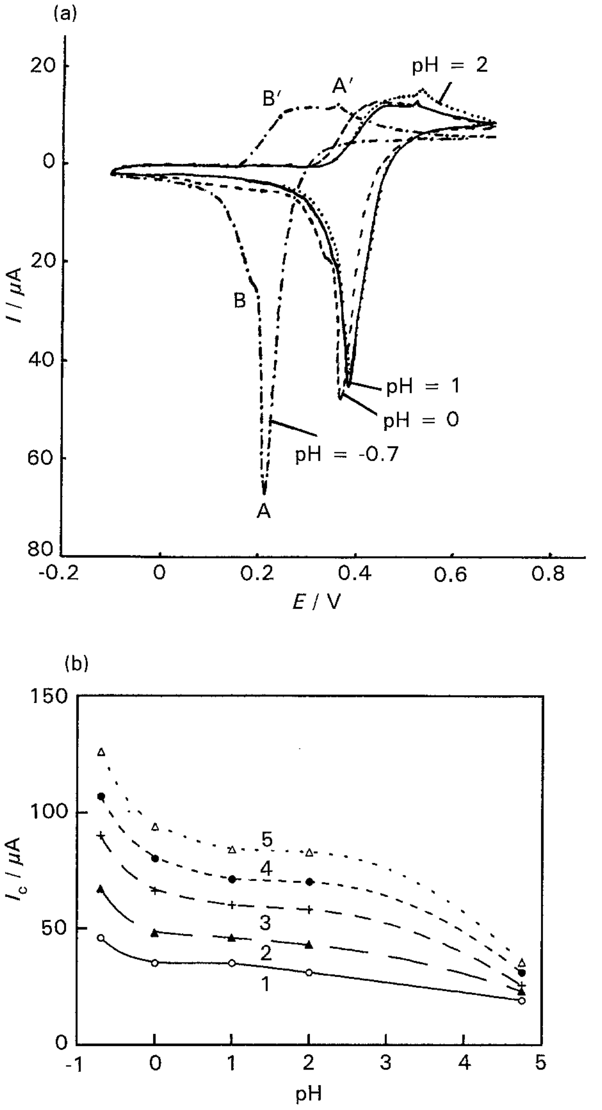

Fig. 1. (a) Steady-state voltammograms of KI on a Pt electrode in solutions of various pH values and (b) the pH dependence of the cathodic peak current. Scan rate: 20 mV s^{-1} for (a); 5, 20, 50, 100 and 200 mV s^{-1} for the curves 1 to 5 in (b).

cell with a wire Pt counter-electrode and a saturated calomel reference electrode (SCE). Further details can be found in the previous report [6].

3. Results and discussions

3.1. *On bare Pt electrode*

Figure 1(a) shows the cyclic voltammograms of KI at 20 mV s^{-1} at various pH values. (The voltammogram at pH 4.7 overlaps partially with that at pH 2, but with lower cathodic current. It is not given in Fig. 1(a) in order not to lose the detail of other voltammograms.) These voltammograms are similar to previous observation in 0.1 M $HClO_4$ (pH 1) [6] and those in 0.05 M Na_2SO_4 (pH ~7) reported by Yaraliyev [1]. It may be concluded that the mechanism of the oxidation of iodide to iodine is almost the same on a Pt electrode in the pH interval −0.7 to 4.7. In such concentrated solutions of iodides the following reactions may be involved in the oxidation process:

$$2I^- - 2e^- = I_2 \qquad (1)$$

$$3I^- - 2e^- = I_3^- \qquad (2)$$

$$2I_3^- - 2e^- = 3I_2 \qquad (3)$$

The successive oxidation of iodide ions by the steps (Equations 1–3) are clearly demonstrated in Fig. 1(a). In the oxidation process two waves appeared, an anodic peak A′ and a shoulder B′. The shoulder B′ may be ascribed to oxidation of I^- to I_3^-, that is, the formation process of the iodine–iodide complex via the second step (Equation 2). The peak A′ corresponds to the oxidation of iodide and/or triiodide ions, in which the iodine film is formed on the electrode surface. Once the iodine film is formed, the oxidation current decreases rapidly and at the end of peak A′ a quasi plateau is observed, which corresponds to the so-called steady-state current [1, 4, 5]. Correspondingly, in the reduction scan a peak A and a shoulder B are observed. Peaks A and B correspond to the reverse processes of peaks A′ and B′, respectively. Compared with the CV at pH 0 ~ 4.7, the case for pH −0.7 may be taken as an exception because all the redox peaks shifted negatively by about 180 mV, the reason for this is yet unknown. As shown in Fig. 1(b), the height of peak A decreases with increase in pH, with a quasi-plateau appearing in the pH interval 0 to 2.

3.2. *On PAn-filmed electrodes*

Recently, in Part I, we have reported that the oxidation mechanism of iodide to iodine at PAn-filmed electrodes is similar to that on a bare Pt electrode in 0.1 M $HClO_4$ [6]. In the cathodic scan, the peaks A and B at a Pt electrode usually emerge as a single peak AB at PAn electrodes. There are two cases for the reduction process on PAn electrodes. In the first case, the reduction peak increases in height without evident change of shape. In the second case, the peak current increases little or even decreases (but the total area of the whole peaks increases markedly), and new cathodic shoulders or peaks appear, which may grow and become the main peak, according to experimental conditions. The phenomenon of the increase in the number of reduction peaks and shoulders has been assigned to peak splitting, which is strongly dependent on the interaction of iodine species with the PAn chains on the inner surface of the PAn film [6]. From similar CVs and similar peak splitting observed in the present work, it may be concluded that the redox mechanism for iodide/iodine is the same regardless of the pH if pH ≤ 2 with an exception at pH 4.7

CV of the PAn film were measured (although not given here) in the background electrolyte solutions to distinguish the redox peaks of iodine/iodide from those of the polymer. As shown in Fig. 2(a) and (a′), redox peaks of iodide/iodine occur as well as the redox peaks of PAn itself. For faster scan rate and/or thicker film, the oxidation peaks of KI are masked by the

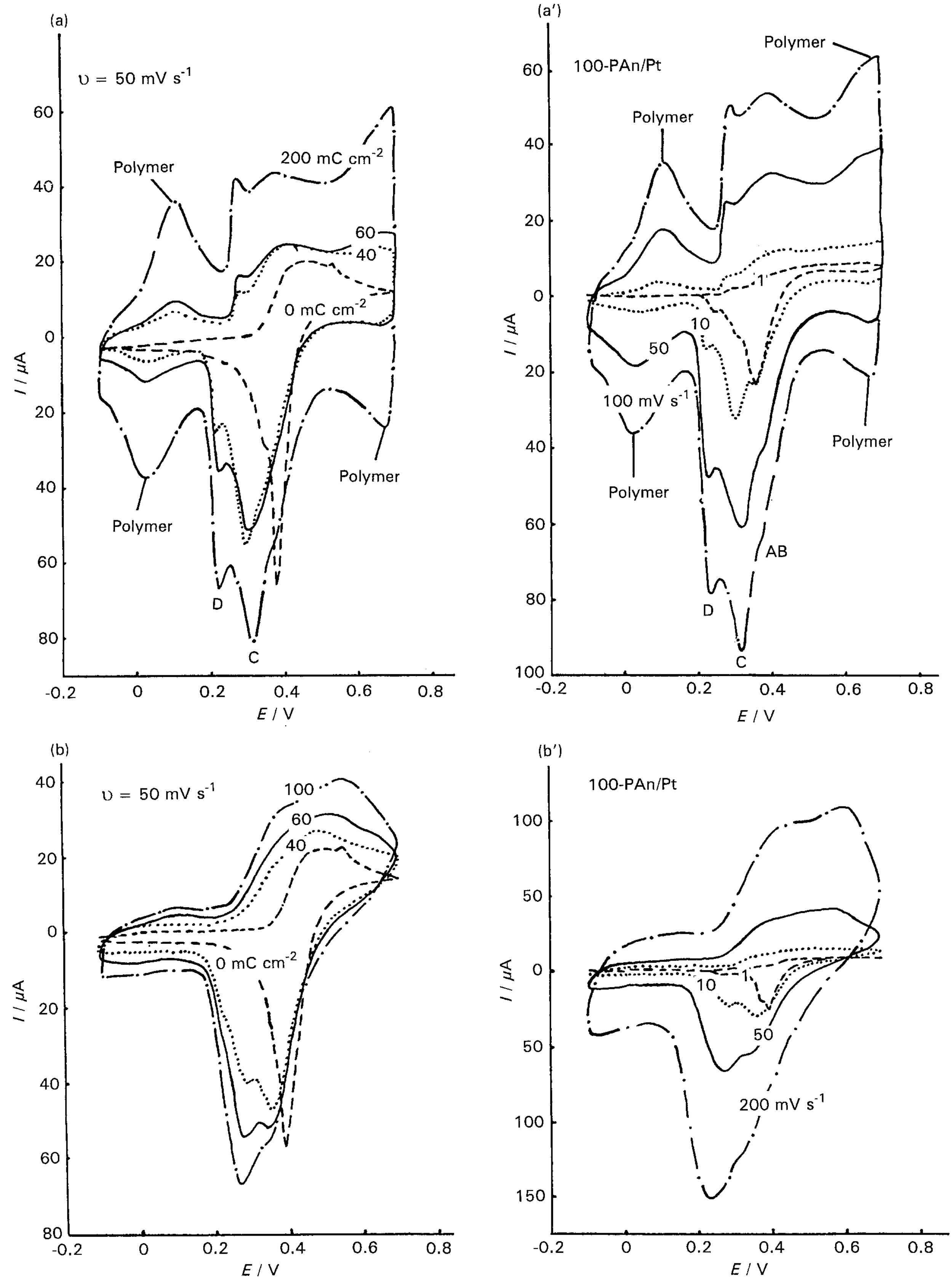

Fig. 2. Cyclic voltammograms of KI on PAn-filmed Pt electrodes at solutions of various pH values. (a) and (a′): pH 0; (b) and (b′): pH 2; (c) and (c′): pH 4.7.

polymer oxidation. In the cathodic scan, a new peak C appears, together with the intrinsic peak AB for the reduction of iodine, which has been denoted as peak splitting in our previous paper [6]. This kind of peak splitting is also observed at pH 0, 1 and 2, but it is the most evident at pH 0, where two new peaks, C and D, occur. If the relative height of peak C to peak AB is used to evaluate the extent of the peak splitting, from Fig. 3 it is found that the extent of peak splitting is highest at pH 0, which may be related

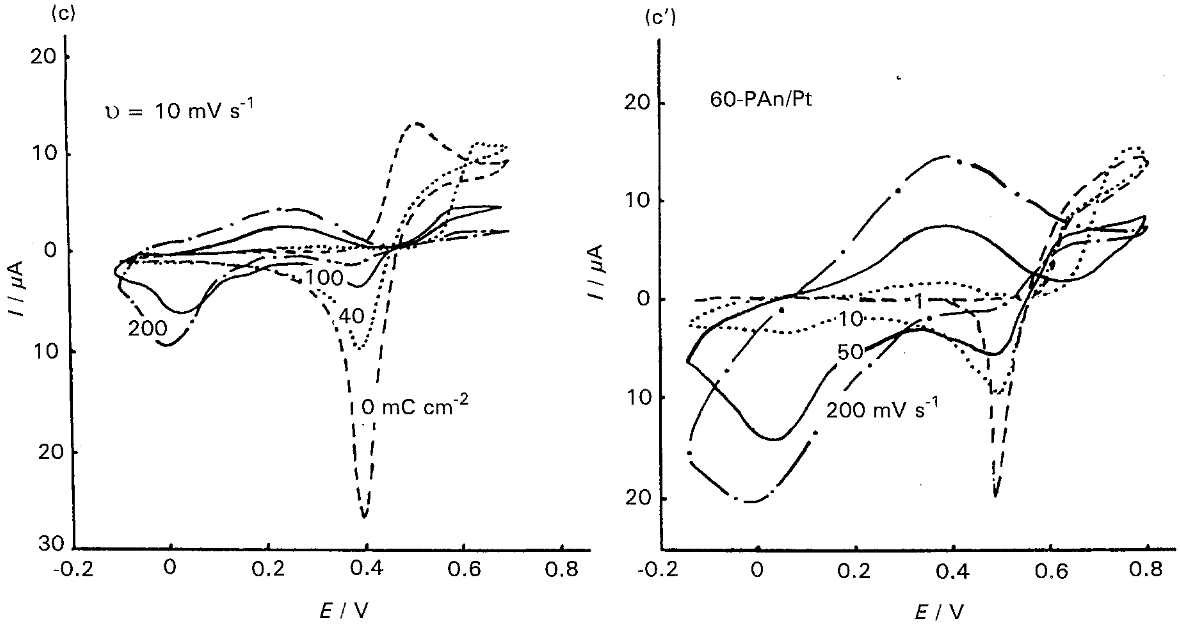

Fig. 2. (Continued).

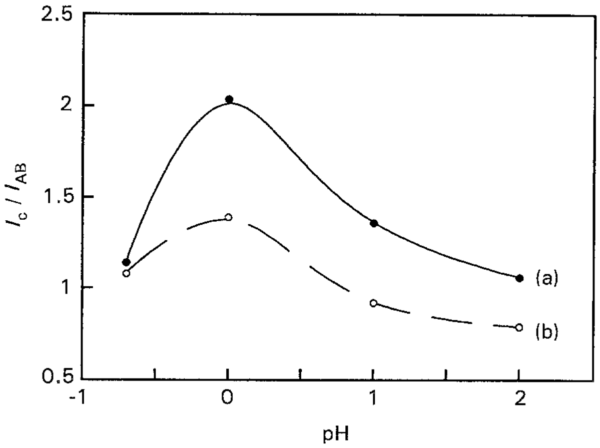

Fig. 3. Effects of pH on the relative height of peak C to peak AB in Fig. 2 on a 60-PAn/Pt electrode at 50 mV s^{-1} (a) and a 100-PAn/Pt electrode at 10 mV s^{-1} (b). ($I_C + I_D$)/I_{AB} is used instead of I_C/I_{AB} at pH 0 in curve (a).

to a competition between the effects of H^+ and anion ions. According to the model proposed previously [6], peak splitting depends on the interaction of I_2 and I_3^- with the N atoms of PAn main chains on the inner surface of the PAn film. For higher H^+ concentration (lower pH), more N atoms in the PAn main chains are protonated, hence the interaction between I_3^- and the N^+ is enhanced. In contrast, higher concentration of the anion (ClO_4^-) depress the interaction.

It has been reported that PAn forms a conductive amine-imine structure at pH < 4, and an insulating quinone–diimine structure at pH > 6 [11]. Recently, Miwa *et al.* [13] have reported that at a constant potential of 0.25 V, the pH-conductivity profile of the PAn is sigmoidal, with an apparent inflection point at 4.5. The conductivity of PAn changes by three orders of magnitude as the pH changes from 4 to 5.4. Thus, the PAn film is expected to become insulating rather than conducting at pH 4.7. This is demonstrated by the observation that the cyclic voltammograms at pH 4.74 (Fig. 2(c) and (c′) are

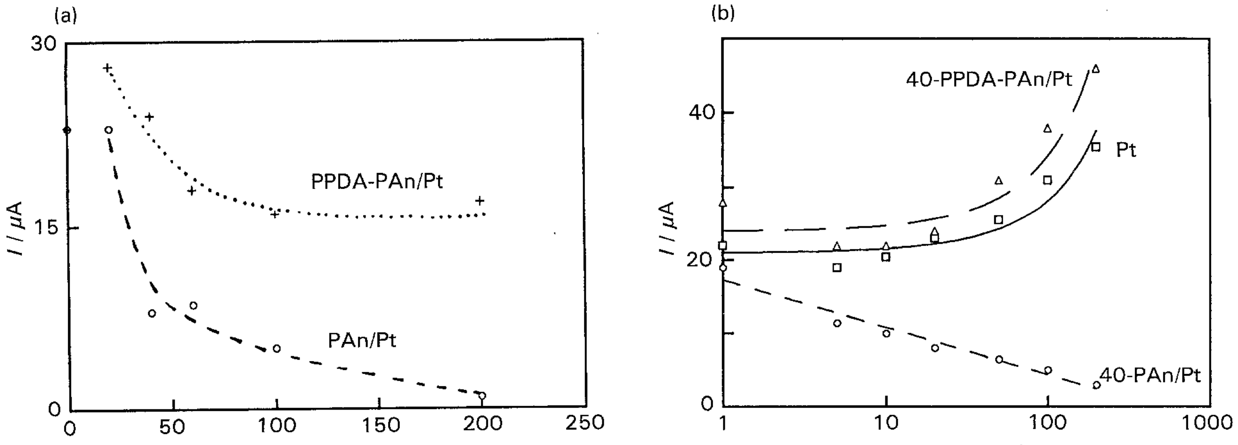

Fig. 4. Effects of the film thickness at 20 mV s^{-1} (a) and the scan rate (b) on the cathodic peak current on PAn-Pt and PPDA–PAn/Pt electrodes at pH 4.7.

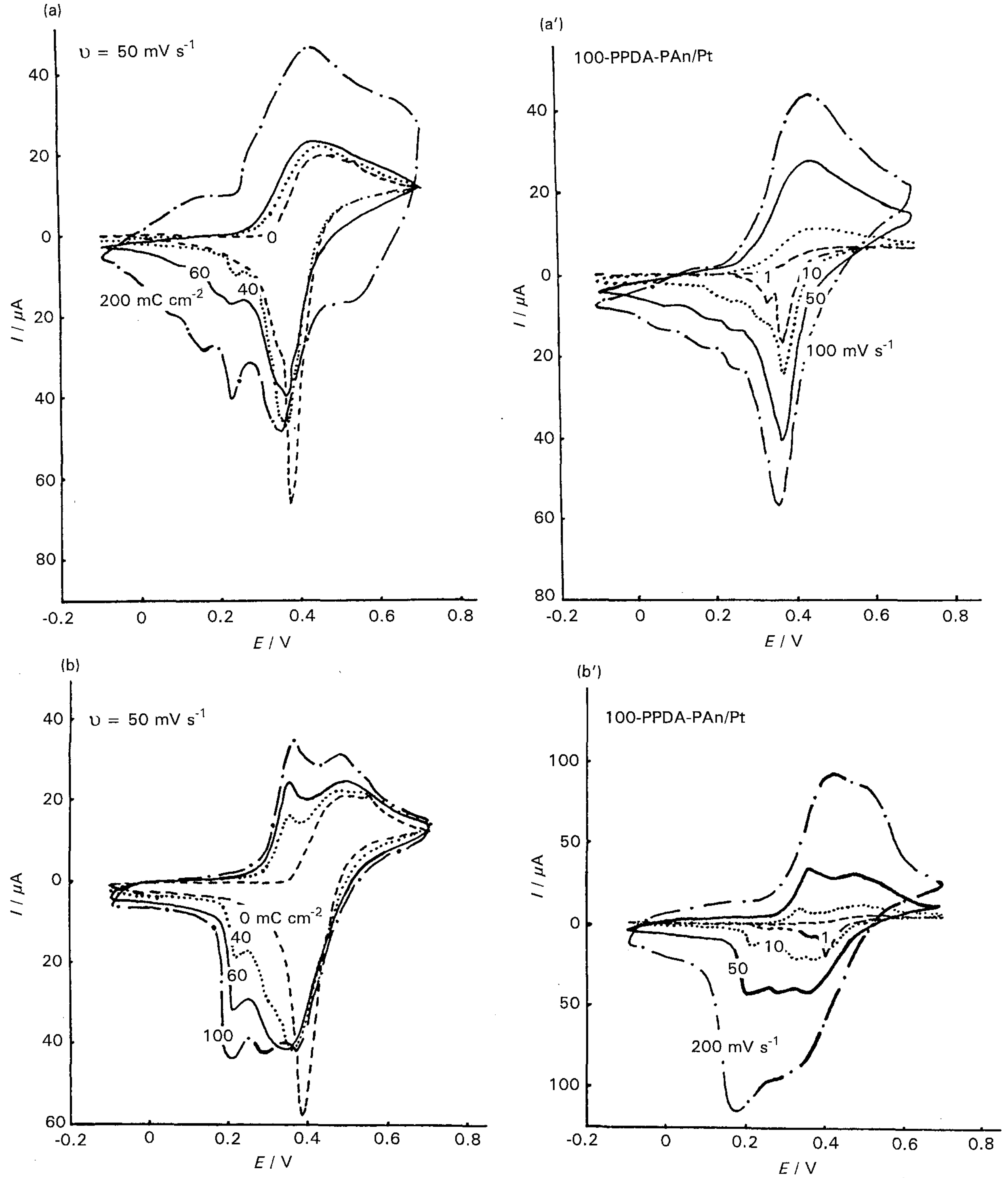

Fig. 5. Cyclic voltammograms of KI on PPDA–PAn/Pt electrodes at solutions of various pH values. (a) and (a′): pH 0; (b) and (b′): pH 2; (c) and (c′): pH 4.7.

markedly different from those for pH ≤ 2. At solutions of pH ≤ 2, the redox reaction of the iodine/iodide couple takes place through the PAn film rather than at the Pt/PAn interface. At solutions of pH > 4, however, the iodide ions have to penetrate through the polymer film, and are oxidized at the metal/polymer interface due to the electrochemical inactivity of the PAn film to the redox reaction of iodine species. At this point, the presence of the PAn film on the Pt electrode hinders the diffusion of iodide ions from the bulk of solution to the uncovered Pt surface, where iodide ions are oxidized. Therefore, the cathodic peak current in the following scan is strongly depressed with increase in film thickness and/or scan rate (Fig. 2(c) and (c′), and Fig. 4).

3.3. *On PPDA–PAn-filmed electrodes*

When the PAn film is modified by the presence of 10 mM PPDA in the growth solution, new middle peaks occur in the cyclic voltammogram of the resulting polymer in 0.1 M H_2SO_4 [14]. The redox processes of the modified PAn (PPDA–PAn) interfere with the iodine/iodide redox processes. Figure 5 shows the cyclic voltammograms of KI on PPDA–PAn/Pt electrodes at various pH.

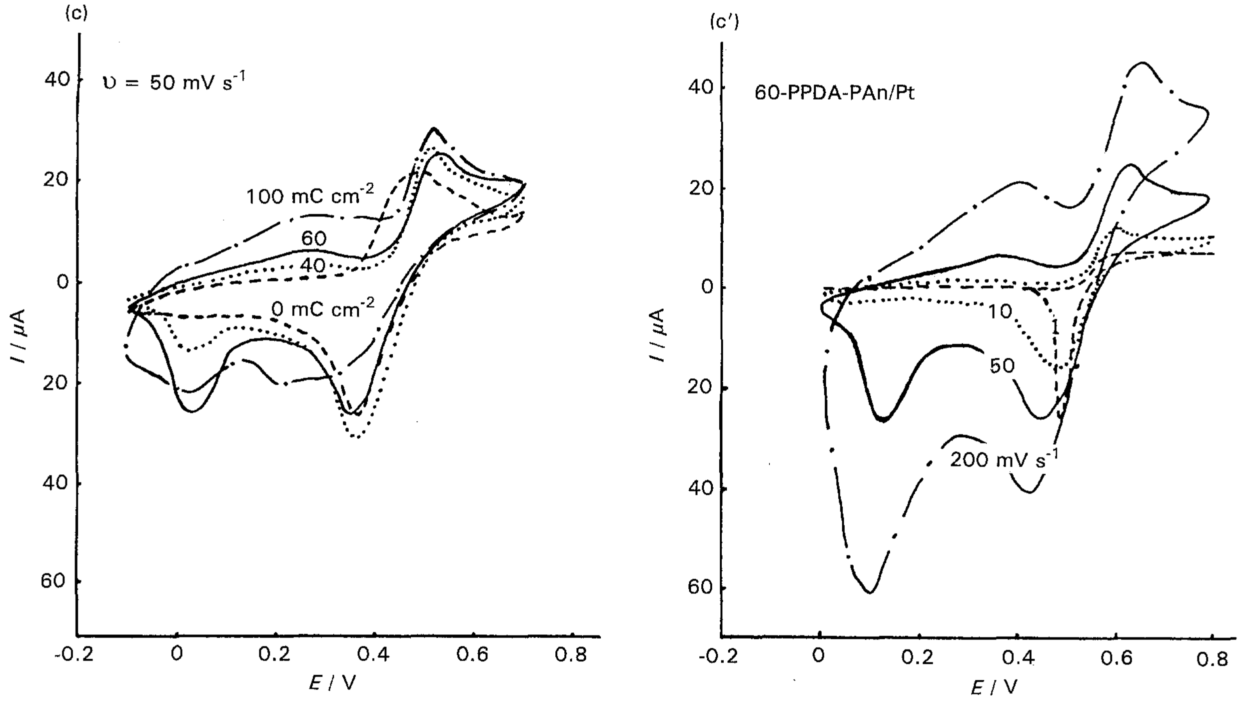

Fig. 5. (Continued).

Comparison of the voltammograms of Fig. 5 with those of Fig. 2, suggest that, except for the case of pH 4.7, the redox peaks of iodide/iodine at PPDA–PAn/Pt electrodes are lower than those at PAn electrodes, even taking into consideration that less polymer has been deposited when 10 mM PPDA is added to the growth solution. Figure 5 suggests that the peak splitting at PPDA–PAn/Pt electrodes is weaker than at PAn/Pt electrodes. Unlike the case for PAn/Pt electrodes, the CV of KI on PPDA–PAn/Pt electrodes at pH 4.7 is similar to those at pH ≤ 2, with impressed peak and no peak splitting. This hints that the PPDA–PAn film is sufficiently electroactive, even at pH 4.7. With a wide pH range microelectrode study of the electrochemical behaviour of PAn films in buffered solutions, Nyholm and Peter have suggested that the loss of electroactivity often reported for pH values above 3–4 is likely due to slow reduction of the fully oxidized PAn (pernigraniline), rather than because of a deprotonation of the emeraldine salt [10]. It is possible that the modification in the polymer structure with the presence of PPDA in the growth solution is beneficial to the reduction of the fully oxidized PAn, hence the PPDA–PAn film is more electroactive than the PAn film at higher pH. Thus, the redox peak on PPDA–PAn/Pt electrodes is higher than that on PAn/Pt electrodes at pH 4.7 (Fig. 4).

4. Conclusions

Cyclic voltammetry of KI at PAns films is dependent on the solution pH, which is at least partially due to the pH dependency of the electroactivity of the polymer film. At pH < 3–4, new redox peaks, other than those of the polymer itself, are observed, the showing peak splitting observed in [6]. The peak splitting results from the formation of PAn-iodine charge transfer complexes. The magnitude of the peak splitting increases at lower pH because more protonated N^+ species make their contribution to the interaction of iodine species with the PAn chains. At pH > 3–4, the electroactive response of the PAn film to the redox reaction of the iodine/iodide pair is greatly depressed, or lost completely, mainly due to the loss of conductivity of the polymer film. The modification of the electrosynthesis of PAn with the presence of PPDA in the growth solution may improve the electroactivity of the polymer film at higher pH. Therefore, unlike at a PAn/Pt electrode, the redox behaviours of KI at pH 4.7 are almost the same as those at pH < 3–4 at a PPDA–PAn/Pt electrode.

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