

Short Communication

## Electrochemical Response to Dissolved Hydroquinone on Insulating Polyaniline-modified Electrode in Less Acidic Solution and Enhancement of the Conductivity of Polyaniline

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**Abstract:** A conductive polymer, polyaniline (PANI), was easily prepared on an electrode surface as a stable film by the electropolymerization of aniline in acidic solution. In McIlvain's buffer solution with a pH that exceeded 4, no redox current by the dissolved species was observed on the PANI-modified electrode because PANI acted as an electric insulator. However, in a less acidic solution, the redox current of the dissolved hydroquinone was evident because hydroquinone selectively permeates through the PANI film to reach the electrode substrate. The results of steady-state current-potential curves for the oxidation of hydroquinone using a PANI pellet electrode revealed that hydroquinone was concentrated in the PANI during the electro-oxidation. Furthermore, the concentration of hydroquinone increased the electric conductivity of the PANI from  $6.50 \times 10^{-7}$  S/cm to  $2.73 \times 10^{-3}$  S/cm.

**Keywords:** Electrodeposition; less acidic solution; polyaniline; hydroquinone; conductivity.

### 1. INTRODUCTION

A typical conductive polymer, polyaniline (PANI), has an acid-base equilibrium in aqueous solution because the polymeric backbone contains amine and imine nitrogen atoms [1]. Due to this acid-base equilibrium, the electric conductivity of the PANI significantly depends on the solution pH. In acidic solution, the PANI acts as an electric conductor because most of the amine and imine nitrogen atoms are positively charged, and cation radical species (polaron species) as charge carriers can continuously exist [2]. Unfortunately, however, the positively charged amine and imine nitrogen atoms decrease in solution pH and the PANI acts as an electric insulator in a less acidic solution whose pH exceeds 3.5, which is the  $pK_a$  value of the PANI [3]. This characteristic results in negating several useful functions of the PANI. If the PANI was transformed into an electric conductor in a less acidic solution, PANI would be applicable in more fields such as biosensors than has already been applied. Despite this possibility, little attention has been paid to such a transformation.

In a less acidic solution, most of the electrode reactions of the dissolved species do not occur on a PANI film-modified electrode

because the PANI film acts as an electric insulator [1]. Interestingly, however, we found that only a few hydroquinones selectively permeate through the PANI film and reach the electrode substrate, and the redox current is evident even using a PANI film-modified electrode [4]. If the selective permeation is due to an electronic affinity between the PANI and hydroquinones, the electric conductivity might be improved. In this paper, we report what happens in the PANI during the electro-oxidation and how the conductivity changes after the electro-oxidation. The analyses of the steady-state polarization curves for the electro-oxidation revealed that hydroquinone is concentrated in the PANI film. Furthermore, the conductivity of the PANI during the electro-oxidation was significantly enhanced up to  $2.8 \times 10^{-5}$  S/cm.

### 2. EXPERIMENTAL

Aniline (Sigma-Aldrich Co.) used as a monomer was distilled under reduced pressure. Hydroquinone and catechol (Tokyo Chemical Industry Co.) were used after recrystallization from ethanol. All the inorganic chemicals were of analytical grade and used as received without further purification.

A standard three-electrode cell for the electrochemical measurements was comprised of a working electrode, a commercial

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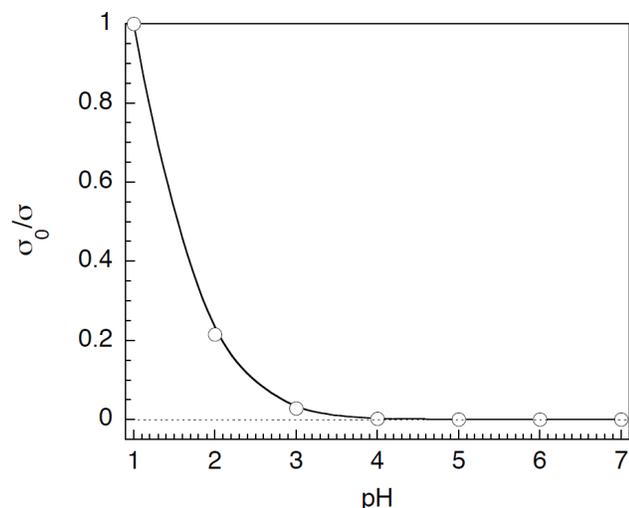


Figure 1. Relationship between the electric conductivity of PANI ( $\sigma$ ) and solution pH of McIlvain's buffer solution with which PANI is equilibrated. The maximum value of  $\sigma$  is 0.11 S/cm and is denoted by  $\sigma_0$ .

Ag/AgCl electrode and a Pt plate counter electrode with an electrode area of ca. 18 cm<sup>2</sup>. Two kinds of working electrodes were employed for each purpose; *i.e.*, a Pt disk electrode with an electrode area of 0.196 cm<sup>2</sup> for cyclic voltammetry and a Pt plate electrode with an electrode area of ca. 8 cm<sup>2</sup> for the preparation of the PANI powder. The electrochemical measurements were performed using a Hokuto Denko HZ-3000 potentiostat connected to a personal computer and a Rikadenki RY-101 *x-y* recorder.

Modification of the PANI, that is the preparation of the PANI-modified electrode, was performed by an electrodeposition method using repeated potential scanning between -0.2 and 1.0 V (100 mV s<sup>-1</sup>) onto the Pt electrodes in a 0.1 M (1 M = mol/dm<sup>3</sup>) H<sub>2</sub>SO<sub>4</sub> solution containing 0.10 M aniline under an N<sub>2</sub> atmosphere. The potential scan was repeated until the potential scan number reached 30, which corresponded to the deposited amount of ca. 190 μg/cm<sup>2</sup> (film thickness of ca. 200 μm). To prepare PANI powder, the potential scan was continued until thicker PANI films were obtained. The thicker films were scratched off the electrode substrates to obtain the PANI powder. In order to examine the effect of the solution pH on the electric conductivity of the PANI, the powder was treated with six types of McIlvain's buffer solutions (citric acid + NaH<sub>2</sub>PO<sub>4</sub> aqueous solutions) with different solution pHs: pH = 2, 3, 4, 5, 6 and 7. The original powder and the six types of powder were washed with excess water and dried in vacuo at 50 °C for 12 h. They were placed in a steel pellet holder and hydraulically pressed at 9.8 MPa. Using the PANI pellet, the electric conductivity was determined by the four-probe method reported by van der Pauw [5]. All the experiments were carried out under an N<sub>2</sub> atmosphere.

### 3. RESULTS AND DISCUSSION

The polaron species as charge carriers can continuously exist on the polymeric backbone of the PANI only when the amine and imine nitrogen atoms are positively charged [2]. The positively

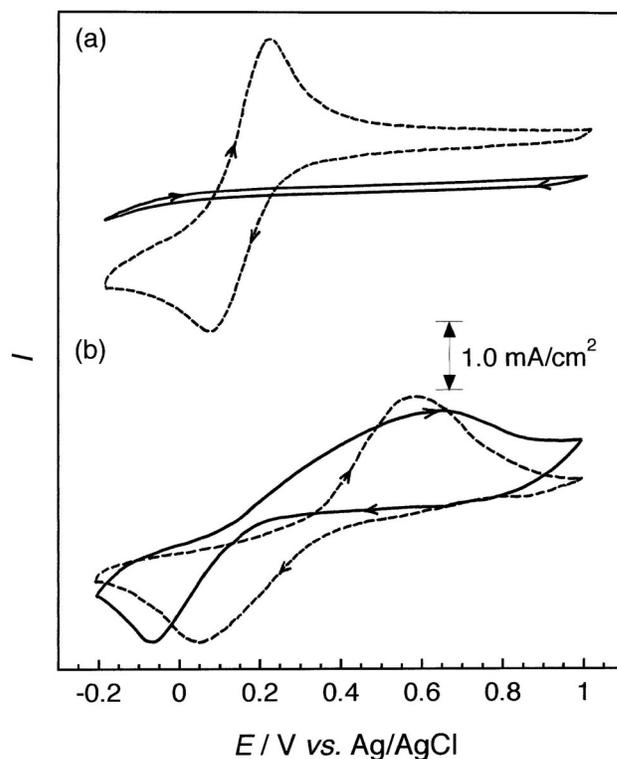


Figure 2. (a) Cyclic voltammograms of 10 mM K<sub>3</sub>[Fe(CN)<sub>6</sub>] in pH 5 McIlvain's buffer solution at 100 mV/s on a bare Pt electrode (-----) and on the PANI-modified Pt electrode (—————). (b) Cyclic voltammograms of 5 mM hydroquinone in pH 5 McIlvain's buffer solution at 100 mV/s on a bare Pt electrode (-----) and on the PANI-modified Pt electrode (—————).

charged amine and imine nitrogen atoms decrease with the solution pH and the PANI becomes an electric insulator in a less acidic solution whose pH exceeds 3.5, which is the pK<sub>a</sub> value of PANI [3]. Figure 1 shows the relationship between the electric conductivity ( $\sigma$ ) and solution pH. As expected,  $\sigma$  drastically decreases with the solution pH and the PANI becomes an electric insulator when solution pH exceeds 3.0.

Figure 2 (a) shows the cyclic voltammograms (CVs) of the dissolved [Fe(CN)<sub>6</sub>]<sup>3-</sup> in a less acidic solution (pH = 5) measured using a bare Pt electrode and the PANI-modified Pt electrode. As can readily be seen in this figure, no redox current of [Fe(CN)<sub>6</sub>]<sup>3-</sup> is evident for the PANI-modified Pt electrode. In addition, no redox currents of Fe<sup>3+</sup>, Mn<sup>2+</sup>, TI<sup>+</sup> and [Fe(edta)]<sup>-</sup> were observed although their CVs are not shown in Fig. 2 (a). On the other hand, the redox current of hydroquinone is evident even in the less acidic solution, in which PANI is an insulator. This means that hydroquinone selectively permeates through the PANI film to reach the electrode substrate.

It is interesting to find that the PANI-modified electrode is comparable to the bare Pt electrode regarding the anodic peak current of hydroquinone. This suggests that hydroquinone not only permeates through the PANI film, but also is concentrated inside the PANI film. To confirm this hypothesis, the polarization curve (steady-

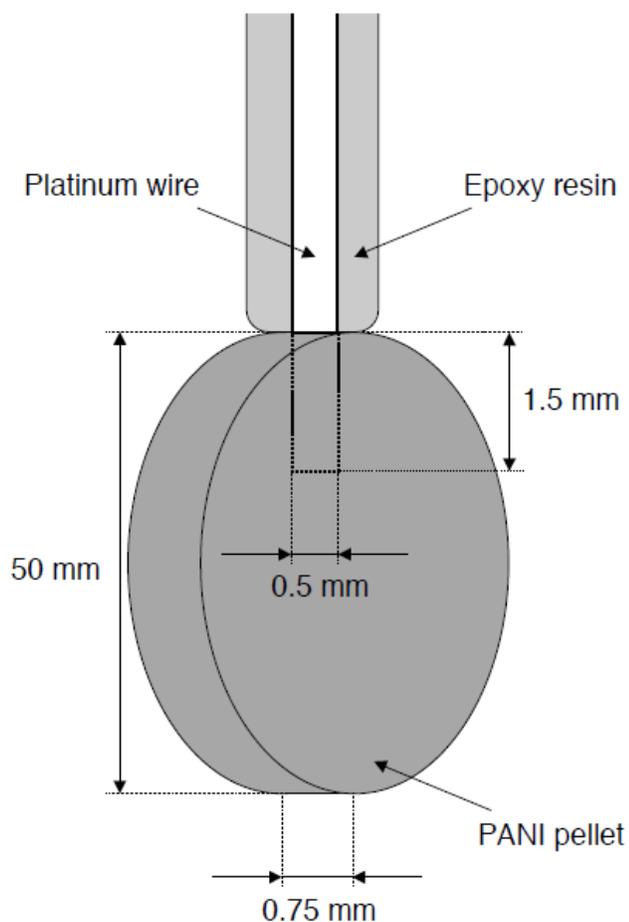


Figure 3. Dimensions of the PANI pellet electrode.

state current-potential curve) for the oxidation of hydroquinone was measured using the PANI pellet electrode shown in Figure 3. The geometric area of the PANI pellet was  $0.314 \text{ cm}^2$  and that of the platinum wire inside the pellet was  $0.026 \text{ cm}^2$ . Figure 4 shows the steady-state current-potential curve for the oxidation of hydroquinone in McIlvain's buffer solution ( $\text{pH} = 5$ ) using both the PANI pellet electrode and a platinum wire electrode with an electrode area of  $0.026 \text{ cm}^2$ . The oxidative current of hydroquinone is evident and the current for the PANI pellet electrode is about 10 times greater than that for the platinum wire electrode. This result clearly implies that hydroquinone is concentrated in the PANI pellet because the PANI pellet behaves as an electric insulator in less acidic solutions.

The concentration of hydroquinone in the PANI enhanced its electric conductivity. The conductivity of the PANI pellet was  $6.50 \times 10^{-7} \text{ S/cm}$ , whereas it increased to  $2.73 \times 10^{-3} \text{ S/cm}$  after the electro-oxidation of the hydroquinone in Figure 4. This increase is probably caused by the electronic interaction between the PANI and hydroquinone. The interaction is probably the formation of a charge transfer complex, and hydroquinone perhaps acts as an appropriate acceptor.

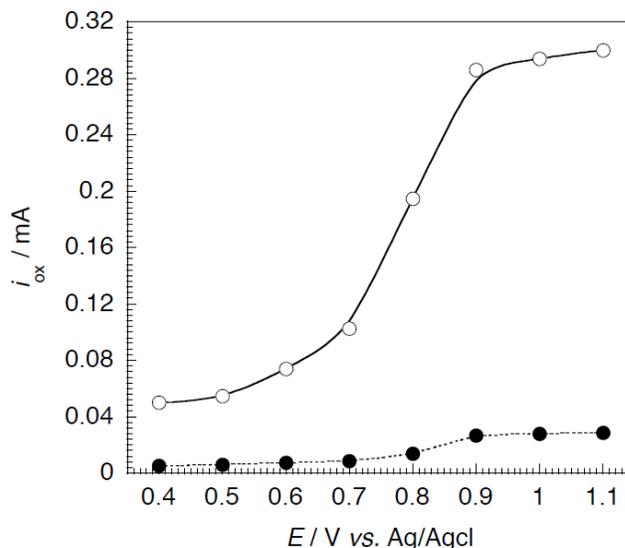


Figure 4. Steady-state current-potential ( $i_{\text{ox}}-E$ ) curves for the oxidation of 10 mM hydroquinone in pH 5 McIlvain's buffer solution obtained using the PANI pellet electrode (—○—) and a Pt wire electrode having the electrode area of  $0.026 \text{ cm}^2$  (---●---).

#### 4. CONCLUSIONS

In a less acidic solution ( $\text{pH} > 4$ ), the electric conductivity of PANI is lost and no redox reactions of the dissolved species take place on the PANI-modified electrode. Even in the less acidic solution, however, the redox current of the dissolved hydroquinone is obviously observed using the PANI-modified electrode, implying that the PANI film has a permselectivity toward dissolved hydroquinone, that is, hydroquinone selectively permeates through the PANI film to reach the electrode substrate. The results of the steady-state current-potential curves for the oxidation of hydroquinone using the PANI pellet electrode shows that hydroquinone is concentrated in the PANI during the electro-oxidation. The concentration of hydroquinone increases the electric conductivity of the PANI and the increase is probably due to the formation of a charge transfer complex between the PANI and hydroquinone.

#### 5. ACKNOWLEDGEMENTS

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