

# Electrooxidation of Ascorbic Acid on a Polyaniline-Deposited Nickel Electrode: Surface Modification of a Non-Platinum Metal for an Electrooxidative Analysis

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**The electrooxidation of ascorbic acid ( $H_2A$ ), which does not occur on a bare Ni electrode, has been shown to take place on a polyaniline (PANI)-coated Ni electrode in aqueous electrolytes of a wide pH range. The characteristic voltammetric peak of PANI in 0.1 M  $H_2SO_4$  at 0.2 V vs SCE corresponding to the transformation of leucoemeraldine to emeraldine gradually diminishes with an increase in concentration of  $H_2A$  as a result of adsorption. This peak disappears before the appearance of another peak corresponding to the oxidation of  $H_2A$  at a concentration of 1 mM. The irreversible oxidation current of  $H_2A$  exhibits a linear dependence on the concentration. The effect of adsorption of  $H_2A$  on PANI has been shown to increase the voltammetric peak current. A study on the variation of the PANI thickness and its influence on the voltammetric oxidation of  $H_2A$  has led to an optimum thickness of 1.6  $\mu m$ . The oxidation currents on the porous PANI/Ni electrode have been found to be several times higher at lower potentials in comparison with the data of a Pt electrode. The reaction has also been studied by ac impedance spectroscopy. In alkaline electrolytes, the Nyquist impedance plot is characterized by two semicircles instead of a single semicircle in acidic electrolytes. Thus, Ni, which is a non-platinum metal, has been found to be useful, by surface modification with PANI, for electrooxidation of  $H_2A$ . The data are reproducible in the electrolytes of a wide pH range, thus suggesting a good stability, reusability and a long life for the PANI/Ni electrodes.**

The electronically conducting polymers, such as polythiophene, polypyrrole, polyaniline (PANI), etc., possess interesting chemical as well as electrochemical properties as a result of their conjugate bond structure.<sup>1–3</sup> These polymers are studied for their electro-

catalytic activity and reviewed in the literature.<sup>4–8</sup> For these studies, a conducting polymer is generally coated on an inert support, such as Pt or Au. The bare Pt itself is a suitable catalyst material for several electrochemical reactions and the enhancement in catalytic activity because the conducting polymer present on the metal appears to be insignificant.<sup>7</sup> We recently reported<sup>9</sup> that some non-platinum metals, which do not support electrochemical redox reactions on bare surfaces, allow the reactions to take place when covered with PANI.

The electrooxidation of ascorbic acid ( $H_2A$ ) has been a subject of several studies on various kinds of electrodes.<sup>10–20</sup> The electrode materials include Pt,<sup>10</sup> Au,<sup>11</sup> graphite,<sup>12</sup> chemically modified Pt metals,<sup>13</sup> Pt metal dispersed carbon paste electrodes,<sup>14</sup> polyaniline–polyvinylsulfonate-coated Pt,<sup>15</sup> polyaniline-coated glassy carbon,<sup>16</sup> 1,5,8,12-tetraaza-2,4,9,11-tetramethyl-cyclo-tetradecanonic nickel (II) modified glassy carbon,<sup>17</sup> polypyrrole-coated Pt,<sup>18</sup> modified Au microdisk,<sup>19</sup> etc. Azar et al.<sup>20</sup> deposited Ni on Al by electroless plating and modified the surface with a nickel pentacyanonitrosylferrate film. The surface-modified Al electrode has been shown to catalyze the oxidation of  $H_2A$  via a surface-layer-mediated charge-transfer process. In all these studies, except in ref 20, the reaction has been studied on the bare or the surface-modified noble metals or glassy carbon. The noble metals and

- (4) Malinauskas, A. *Synth. Met.* **1995**, *107*, 75–83.
- (5) Noufi, R.; Nozik, A. J.; White, J.; Warren, L. F. *J. Electrochem. Soc.* **1982**, *129*, 2261–2267.
- (6) Yano, J.; Ogura, K.; Kitani, A.; Sasaki, K. *Synth. Met.* **1992**, *52*, 21–31.
- (7) Mandic, Z.; Duic, L. *J. Electroanal. Chem.* **1996**, *403*, 133–141.
- (8) Lamy, C.; Leger, J. M.; Garnier, F. In *Handbook of Organic Conductive Molecules and Polymers*; Nalwa, H. S., Ed.; John Wiley & Sons: Chichester, 1997; Vol. 2; p 470.
- (9) Rajendra Prasad, K.; Munichandraiah, N. *Synth. Met.* **2001**, *253*, 459–468.
- (10) Dong, S.; Che, G. *J. Electroanal. Chem.* **1991**, *315*, 191–199.
- (11) Rueda, M.; Aldaz, A.; Burgos, F. S. *Electrochim. Acta* **1978**, *23*, 419–426.
- (12) Chen, Z.; Yu, J. C. *Talanta* **1999**, *49*, 661–665.
- (13) Petersson, M. *Anal. Chim. Acta* **1986**, *187*, 333–338.
- (14) Wnag, J.; Naser, N.; Angnes, L.; Wu, H.; Chen, L. *Anal. Chem.* **1992**, *64*, 1285–1288.
- (15) Bartlett, P. N.; Wallace, E. N. K. *Phys. Chem. Chem. Phys.* **2001**, *3*, 1491–1496.
- (16) Zhou, D. M.; Xu, J. J.; Chen, H. Y.; Fang, H. Q. *Electroanalysis* **1997**, *9*, 1185–1188.
- (17) Bae, Z. U.; Lee, J. H.; Chang, Y. H.; Lee, S. H. *Anal. Sci.* **1999**, *15*, 795–797.
- (18) Lyons, M. E. G.; Breen, W. *Chem. Soc. Faraday Trans.* **1991**, *87*, 115–123.
- (19) Sun, J. J.; Zhou, D. M.; Fang, H. Q.; Chen, H. Y. *Talanta* **1998**, *45*, 851–856.
- (20) Azar, M. H. P.; Nerbin, H. R. *J. Electroanal. Chem.* **2000**, *488*, 17–24.

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- (1) Curran, S.; Stark-Hauser, A.; Roth, S. In *Handbook of Organic Conductive Molecules and Polymers*; Nalwa, H. S., Ed.; John Wiley & Sons: Chichester, 1997; Vol. 2; p 1.
- (2) Doblhofer, K.; Rajeshwar, K. In *Handbook of Conducting Polymers*; Skotheim, T. A.; Elsenbaumer, R. L.; Reynolds, J. R., Eds.; Marcel Dekker: New York, 1998; p 531.
- (3) Kim, Y.; Teshima, K.; Kobayashi, N. *Electrochim. Acta* **2000**, *45*, 1549–1553.

glassy carbon are good catalysts on their own for oxidation reactions. Surface modification of such electrodes yields insignificant improvement in kinetics of the reactions. For example, a bare glassy carbon electrode allows the electrooxidation of  $\text{H}_2\text{A}$ , and the increase in current due to the surface modification is only about 25%.<sup>16</sup> It would be more interesting to study the reactions by modification of nonnoble metals, which are not suitable to study the reactions in their native states. Additionally, a low cost and an ease of electrode assembly are favorable factors in using nonnoble metals. Because ascorbate sensors are anticipated to have potential application, it would be beneficial to employ a common metal for electrooxidation of  $\text{H}_2\text{A}$ . To the best of these authors' knowledge, the electrooxidation of  $\text{H}_2\text{A}$  on a PANI-coated non-platinum metal is not reported in the literature.

In the present study, PANI is potentiodynamically deposited on a Ni surface, and the irreversible electrooxidation of  $\text{H}_2\text{A}$  is investigated in a wide pH range, for example, to demonstrate the use of the electrodes. The reaction is shown to occur on PANI-coated Ni, whereas the bare Ni does not allow the reaction to take place. The reaction is also studied on Pt for the purpose of comparison. Because of the adsorption of  $\text{H}_2\text{A}$  on a porous PANI with a large specific surface, the catalytic activity of PANI-coated Ni electrodes is several times higher than that of Pt. The results obtained from cyclic voltammetry, amperometry, and ac impedance spectroscopy are reported.

## EXPERIMENTAL SECTION

Anal grade chemicals, vacuum-distilled aniline, and double-distilled water were used in all experiments. The working electrode (area =  $0.6 \text{ cm}^2$ ) of Pt foil or Ni foil was placed symmetrically between two auxiliary Pt foil electrodes in a glass cell of  $\sim 50 \text{ cm}^3$  capacity. A saturated calomel electrode (SCE) was used as the reference electrode, and the potential values are reported against the SCE. The Pt electrodes were dipped in concentrated  $\text{HNO}_3$  for about 30 min., washed thoroughly, and subjected to repeated potential sweeps at a rate of  $100 \text{ mV s}^{-1}$  in  $0.5 \text{ M H}_2\text{SO}_4$  in the potential range between  $-0.2$  and  $1.2 \text{ V}$  until reproducible voltammograms were obtained. The nickel electrode was polished to a smooth finish using successive grades of emery, washed thoroughly, and rinsed with double distilled water. The PANI was deposited potentiodynamically on the Ni electrode in  $0.5 \text{ M H}_2\text{SO}_4$  containing  $0.1 \text{ M}$  aniline at a sweep rate of  $100 \text{ mV s}^{-1}$  in the potential range between  $-0.2$  and  $1.2 \text{ V}$ . The electrodes were washed copiously in  $0.1 \text{ M H}_2\text{SO}_4$  before using for further experiments. For studying the electrooxidation of  $\text{H}_2\text{A}$ , a majority of the experiments were carried out in  $0.1 \text{ M H}_2\text{SO}_4$  as the supporting electrolyte. The required mass of  $\text{H}_2\text{A}$  was dissolved in it. For the purpose of pH-dependent experiments,  $0.1 \text{ M Na}_2\text{SO}_4$  supporting electrolyte was used, and the required pH was obtained by the addition of  $\text{H}_2\text{SO}_4$  or KOH. Cyclic voltammetry and electrochemical impedance spectroscopy were performed by EG&G PARC equipment models Versastat and 6310, respectively. All experiments were carried out at  $20 \pm 1^\circ \text{C}$ .

## RESULTS AND DISCUSSION

The electrochemical deposition and growth of PANI on an inert electrode has been studied widely by the potentiodynamic method.<sup>21</sup> The PANI exhibits a multiple redox behavior in acidic media during a potentiodynamic cycling between  $0.0$  and  $1.0 \text{ V}$ .

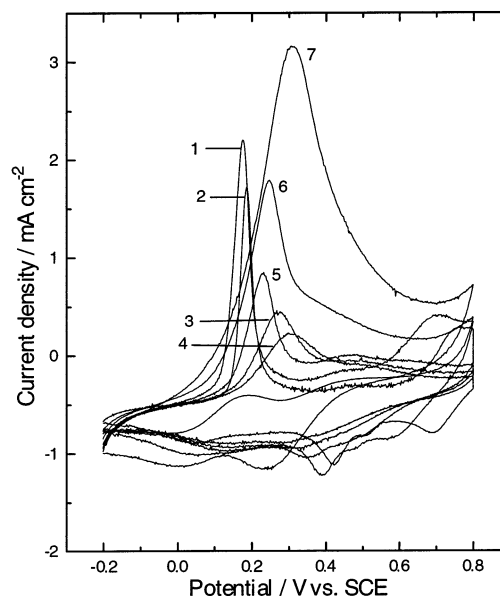


Figure 1. Cyclic voltammograms of PANI/Ni electrode in  $0.1 \text{ M H}_2\text{SO}_4$  containing  $\text{H}_2\text{A}$  at a concentration of  $0$  (1),  $10^{-6}$  (2),  $10^{-5}$  (3),  $10^{-4}$  (4),  $10^{-3}$  (5),  $5 \times 10^{-3}$  (6), and  $10^{-2} \text{ M}$  (7) at  $5 \text{ mV s}^{-1}$  sweep rate.

An oxidation current peak at  $\sim 0.2 \text{ V}$  appears to be due to the transformation of the PANI from leucoemeraldine (LM) to emeraldine (EM) state. Another oxidation peak around  $0.7 \text{ V}$  corresponds to the transformation from EM to the pernigraniline (PE) state. The PANI possesses a high conductivity in the potential region between LM/EM and EM/PE transformations.<sup>21</sup>

During the potentiodynamic deposition of PANI on a Ni substrate, there was an oxidation of the Ni surface in the initial cycle at  $\sim 0.15 \text{ V}$  before the oxidation of aniline to PANI occurred at  $1.1 \text{ V}$ .<sup>9</sup> After the formation of an initial layer of PANI, the voltammetric peak corresponding to the oxidation of Ni did not appear during subsequent potentiodynamic sweeps. The electrode was subjected to several continuous cycles at  $100 \text{ mV s}^{-1}$  to grow the PANI layer. The voltammogram of the PANI-coated Ni (hereafter referred to as PANI/Ni electrode) in  $0.1 \text{ M H}_2\text{SO}_4$  differs marginally from that of PANI deposited on Pt with respect to the symmetry of the anodic and cathodic parts as well as the peak intensities.<sup>9</sup> Nevertheless, the anodic current peak at about  $0.2 \text{ V}$  corresponding to the transition of PANI from LM to EM is prominent, as shown in Figure 1 (curve 1). The oxidation of LM to EM is accompanied by doping of anions from the electrolyte. In the presence of  $\text{H}_2\text{A}$  in  $0.1 \text{ M H}_2\text{SO}_4$  electrolyte containing  $\text{H}_2\text{A}$  at low concentrations, the intensity of the LM/EM peak decreases gradually with an increase in the concentration of  $\text{H}_2\text{A}$ , as shown in Figure 1 (curves 1–4). Furthermore, there is an increase in peak potential ( $E_p$ ). These features of the voltammograms suggest that there is an adsorption of  $\text{H}_2\text{A}$  on the PANI, and the degree of adsorption increases with the concentration. The PANI peak disappears on further increasing the concentration of  $\text{H}_2\text{A}$ , and a new anodic peak at  $\sim 0.22 \text{ V}$  (Figure 1 curve 5) appears at a concentration of  $1 \text{ mM}$ . This peak increases in intensity with an increase in concentration of  $\text{H}_2\text{A}$  (Figure 1 curves 6 and 7) and,

(21) Trivedi, D. C. In *Handbook of Organic Conductive Molecules and Polymers*; Nalwa, H. S., Ed.; John Wiley & Sons: New York, 1997; Vol. 2, p 505.

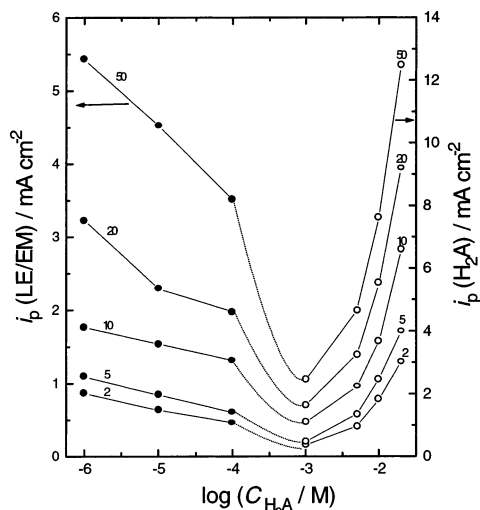
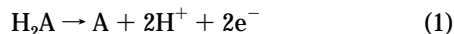


Figure 2. Voltammetric peak current density ( $i_p$ ) on PANI/Ni electrode as a function of concentration of  $H_2A$  ( $C_{H_2A}$ ). The sweep rate in  $mV s^{-1}$  is indicated at each curve. Closed symbols represent the  $i_p$  of LE/EM transformation of PANI ( $i_p(LE/EM)$ ) and open symbols represent the  $i_p$  of oxidation of  $H_2A$  ( $i_p(H_2A)$ ).

therefore, is attributed to the oxidation of  $H_2A$ . The decrease in intensity of the LM/EM peak and the increase in the  $H_2A$  oxidation peak with an increase in concentration of  $H_2A$  is shown in Figure 2 for several scan rates. It is found that the effect of  $H_2A$  is noticeable prominently at high scan rates.

Rueda et al.<sup>11</sup> studied the oxidation of  $H_2A$  on a gold electrode in a wide pH range. The products of the reaction have been identified by chromatography. From chronoamperometry experiments, the total number of electrons taking part in the oxidation has been estimated to be 1.9. On the basis of their results, these authors have proposed the following mechanism:



where A stands for the dehydro ascorbic acid (DHAA) and P, the hydrated dehydro ascorbic acid ( $DHAA \cdot H_2O$ ). The formation of DHAA takes place via a radical anion intermediate, monodehydroascorbic acid from  $H_2A$ . The DHAA undergoes a hydration reaction characteristic of the carbonyl groups to form the final product  $DHAA \cdot H_2O$ , which is electroinactive. Accordingly, the electrooxidation of  $H_2A$  is irreversible, and this is supported by the absence of a cathodic current peak in Figure 1.

In amperometric experiments, the current flowing through the PANI/Ni electrode at 0.3 V was measured as a function of concentration of  $H_2A$  in 0.1 M  $H_2SO_4$  (Figure 3). The electrolyte was stirred with the help of a PTFE-covered magnetic paddle during the experiments. The data of a bare Ni electrode are also shown in Figure 3 for comparison. The PANI/Ni electrode shows a rapid current response to  $H_2A$  addition. At each addition, a steady current is obtained due to a fast mass transport, which arises from the stirring of the electrolyte. On the other hand, the Ni electrode does not respond. The initial addition of  $H_2A$  is at a concentration of 5 mM. There is a considerable increase in the current. However, it may be noted that the PANI/Ni is sensitive to a concentration

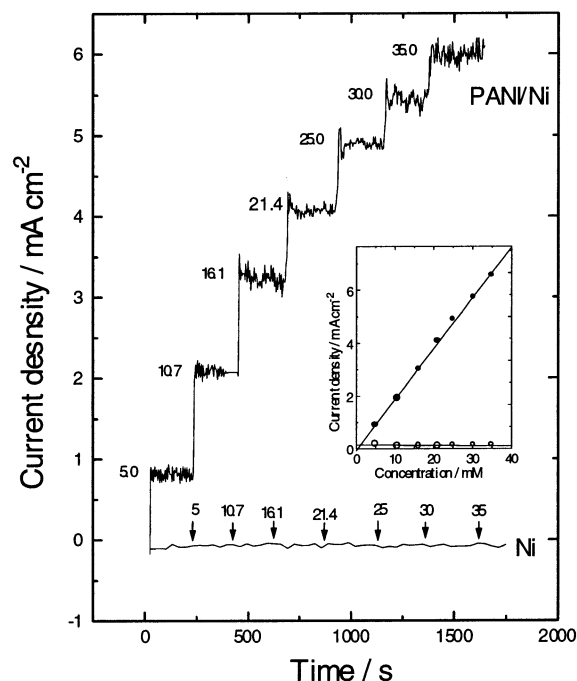


Figure 3. Amperometric response of PANI/Ni and bare Ni electrodes to changes in concentration of  $H_2A$  in 0.1 M  $H_2SO_4$ . The concentration of  $H_2A$  at each step is given as millimolar. Inset shows the average current density at each step plotted against the concentration of  $H_2A$  for the PANI/Ni electrode (●) and the bare Ni electrode (○).

of 1 mM of  $H_2A$  (Figure 1). There is a linear increase in current of the PANI/Ni electrode with an increase in  $H_2A$  concentration (Figure 3 inset). These results further support that the oxidation of  $H_2A$  takes place on the PANI/Ni electrode, and does not occur on the bare Ni. The current ( $I$ ) is related to the concentration ( $c$ ) as

$$I = nFAkc \quad (3)$$

where  $k$  is the rate constant of the reaction;  $A$ , the area of the electrode; and the other symbols have their usual meanings. Since the oxidation of  $H_2A$  is a two-electron-transfer process,  $n$  is taken as 2, and an approximate value of the rate constant calculated from the data of Figure 3 is  $1 \times 10^{-3} cm s^{-1}$  by taking the geometric area of the PANI/Ni electrode. Values of similar magnitude for  $k$  of the electrooxidation of  $H_2A$  are reported in the literature.<sup>22</sup> It may be noted that the value of  $k$  depends on the mass transport at the electrode surface, the electrode potential, and the supporting electrolyte. Hence, the value of  $k$  is expected to alter if the stirring rate, potential, and supporting electrolyte are varied.

**Effect of Thickness of PANI.** From the above studies, it is interesting to note that the bare Ni is not suitable as an anode for the electrooxidation of  $H_2A$ , and it is useful if the surface is modified with PANI. The PANI is known to be electronically conducting as a result of the transport of polarons and bipolarons along the polymer chain. The electron exchange from  $H_2A$  to the PANI (reaction 1) appears to be more energetically favorable than from

(22) Xing, X.; Shao, M.; Hsiao, M. W.; Adzic, R. R.; Liu, C. C. *J. Electroanal. Chem.* **1992**, 339, 211–225.

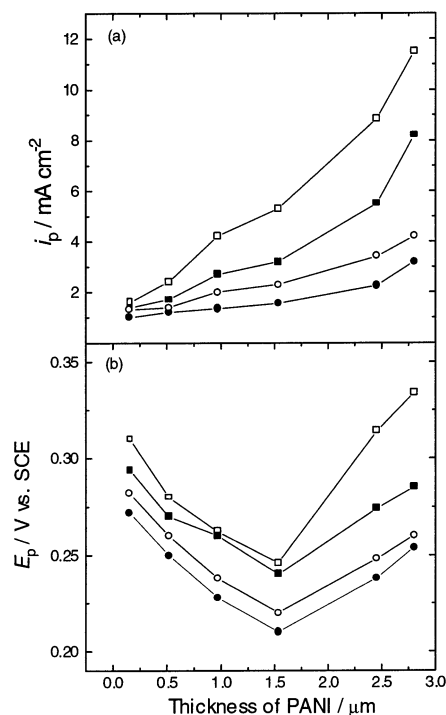


Figure 4. Variation of (a) peak current density ( $i_p$ ) and (b) peak potential ( $E_p$ ) of oxidation of H<sub>2</sub>A (10 mM) in 0.1 M H<sub>2</sub>SO<sub>4</sub> with the thickness of PANI at a sweep rate of 2 (●), 5 (○), 10 (■), and 20 mV s<sup>-1</sup> (□).

H<sub>2</sub>A to bare Ni. Thus, the PANI/electrolyte interface is conducive for electrooxidation of H<sub>2</sub>A.

Since the PANI deposits are porous, the true surface available for the heterogeneous reaction is expected to vary with the PANI thickness. During the deposition of PANI on Ni by repeating the potential sweeps, the charge of the voltammogram increases with the number of sweeps as a result of an increase in thickness. This feature is similar to the growth of PANI on an inert metal electrode.<sup>21</sup> The charge of the final voltammogram during deposition is a measure of the thickness on the PANI. The thickness of PANI on Ni was estimated using the relationship between the charge and thickness.<sup>23</sup> The PANI/Ni electrodes of different thickness values were used for the oxidation of H<sub>2</sub>A in 0.1 M H<sub>2</sub>SO<sub>4</sub>. The peak current density calculated on the basis of geometric area ( $i_p$ ) of H<sub>2</sub>A oxidation was found to increase with the thickness of PANI (Figure 4a), which is due to the increase in specific surface of the PANI/electrolyte interface, as anticipated. An interesting aspect of the voltammograms was that there was a variation of  $E_p$  with the thickness of PANI, as shown in Figure 4b. The value of  $E_p$  is minimal at all scan rates for a thickness value of 1.6  $\mu\text{m}$ , and there is an increase in  $E_p$  for thickness values greater or less than 1.6  $\mu\text{m}$ . Thus, the thickness of PANI on Ni for an optimum activity for H<sub>2</sub>A oxidation is  $\sim 1.6 \mu\text{m}$ . Electron-transfer processes at modified electrodes have been reported in the literature.<sup>24</sup> Electron hopping has to occur between the reaction site and the metal surface. Perhaps 1.6  $\mu\text{m}$  is the optimum thickness of PANI for facilitation of electron transfer within the polymer in a less energetic pathway. The rest of the experiments were studied with a PANI thickness of 1.6  $\mu\text{m}$ .

(23) Stilwell, D. E.; Park, S. M. *J. Electrochem. Soc.* **1988**, *135*, 2491–2496.

(24) Andrieux, C. P.; Saveant, J. M. *J. Electroanal. Chem.* **1980**, *111*, 377–383.

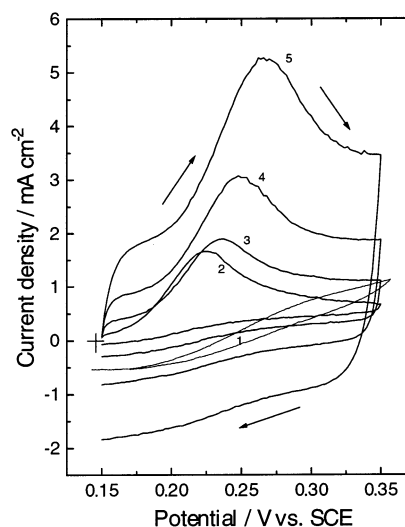


Figure 5. Cyclic voltammograms of PANI/Ni electrode in 0.1 M H<sub>2</sub>SO<sub>4</sub> containing 10 mM H<sub>2</sub>A at a sweep rate of 2 (2), 5 (3), 10 (4), and 20 mV s<sup>-1</sup> (5). The voltammogram of the bare Ni electrode consisting of 50 mM H<sub>2</sub>A in 0.1 M H<sub>2</sub>SO<sub>4</sub> at a sweep rate of 50 mV s<sup>-1</sup> is shown as curve 1.

**Cyclic Voltammetry.** The cyclic voltammograms of the PANI/Ni electrode, with PANI thickness of 1.6  $\mu\text{m}$  for the oxidation of H<sub>2</sub>A in 0.1 M H<sub>2</sub>SO<sub>4</sub> at several sweep rates, are shown in Figure 5. The voltammogram of a bare Ni (Figure 5 curve 1) is also shown for comparison. It is seen that the H<sub>2</sub>A oxidation current peak is absent on the Ni. On the other hand, the reaction takes place on the PANI/Ni electrode, and the peak current increases with the sweep rate. There is an increase in  $i_p$  with the sweep rate. Furthermore, there is a positive shift in the value of  $E_p$ . The relationship between  $E_p$  and sweep rate ( $\nu$ ) for an irreversible reaction is given by eq 4,<sup>25</sup>

$$E_p = K + (2.3RT/2\alpha_a n_a F) \log \nu \quad (4)$$

where  $K$  is a constant;  $\alpha_a$ , the transfer coefficient;  $n_a$ , the number of electrons transferred up to the rate-determining step of the oxidation; and the other symbols have their usual meanings. The product  $(2.3RT/\alpha_a n_a F)$  is equivalent to the Tafel slope. Thus, the value of  $\alpha_a$  of the oxidation of H<sub>2</sub>A can be evaluated using eq 4. A plot of  $E_p$  versus  $\log \nu$  is shown in Figure 6. The value of  $(dE_p/d\log \nu)$  obtained for several concentrations of H<sub>2</sub>A is in the range 0.055–0.070 V. Accordingly, the Tafel slope has a value in the 0.11–0.14 V range, and thus, the value of  $(\alpha_a n_a)$  is 0.54–0.42. Since the value of  $n_a$  has been taken as unity,<sup>15</sup> that is, uni-electron electron-transfer up to the rate-determining step and for the appearance of the cyclic voltammogram, the value of  $\alpha_a$  obtained is in the range of 0.54–0.42.

Cyclic voltammograms of the PANI/Ni and Pt electrodes in 0.1 M H<sub>2</sub>SO<sub>4</sub> containing H<sub>2</sub>A at several concentrations were recorded at different sweep rates for the purpose of comparison. The data of the 5 mV s<sup>-1</sup> sweep rate and 5 mM H<sub>2</sub>A are shown in Figure 7. The value of  $i_p$  is 1.9 mA cm<sup>-2</sup> on PANI/Ni, compared with 0.7 mA cm<sup>-2</sup> on Pt. Furthermore, the value of  $E_p$  is 0.23 V

(25) Greef, R.; Peat, R.; Peter, L. M.; Pletcher, D.; Robinson, J. *Instrumental Methods in Electrochemistry*; John Wiley & Sons: New York, 1985; p 178.



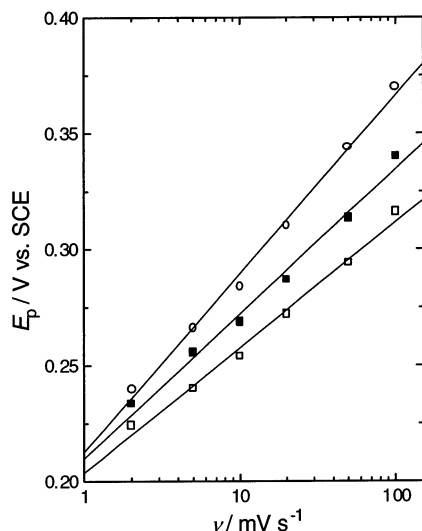


Figure 6. Peak potential ( $E_p$ ) of oxidation of  $H_2A$  on PANI/Ni electrode as a function of logarithmic sweep rate ( $\nu$ ) for a concentration of 10 ( $\square$ ), 20 ( $\blacksquare$ ), and 50 mM  $H_2A$  ( $\circ$ ) in 0.1 M  $H_2SO_4$ .

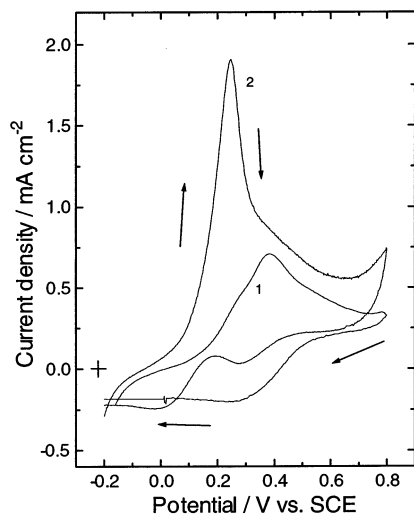


Figure 7. Cyclic voltammogram of Pt (1) and PANI/Ni (2) electrodes in 0.1 M  $H_2SO_4$  containing 5 mM of  $H_2A$  at a sweep rate of 5  $mV s^{-1}$ .

on PANI/Ni compared with 0.40 V on Pt. Although the higher values of  $i_p$  could be attributed to a large specific surface of PANI, the lower  $E_p$  values suggest that the oxidation of  $H_2A$  is catalyzed at the PANI/Ni electrode in relation to Pt. As discussed later, the adsorption of  $H_2A$  on PANI is a responsible factor for the catalysis of the reaction. The catalytic effect of the PANI/Ni electrode was observed for all concentrations of  $H_2A$  and all sweep rates studied. The apparent catalytic efficiency ( $\gamma$ ) of the PANI/Ni electrode is defined as

$$\gamma = 100[i_p(\text{PANI}) - i_p(\text{Pt})]/i_p(\text{Pt}) \quad (5)$$

The variation of  $\gamma$  with  $c$  at several scan rates is shown in Figure 8. Thus, the oxidation of  $H_2A$  is catalyzed by 100–2000%, depending on the scan rate and concentration, on the PANI/Ni electrode in comparison with the Pt. The catalytic efficiency is more at higher concentrations and fast sweep rates.

**Effect of Holding Time at Starting Potential.** Because the organic molecules tend to undergo adsorption at the electrode/

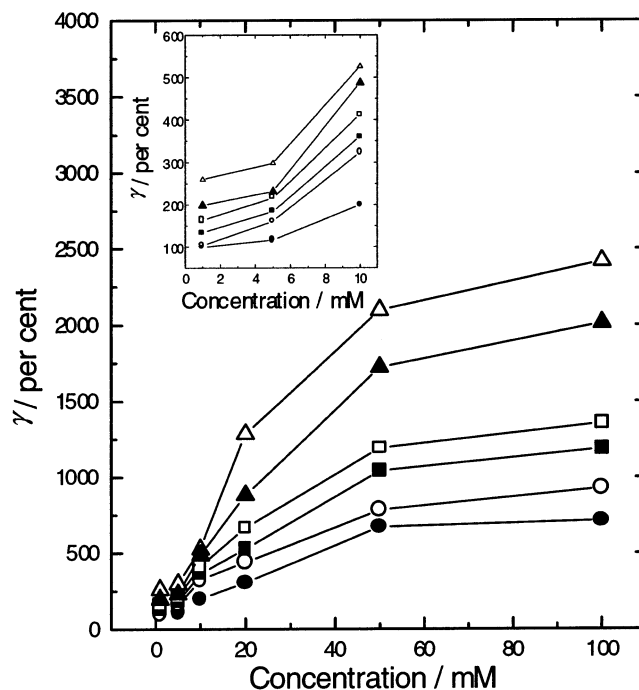


Figure 8. Catalytic efficiency ( $\gamma$ ) of PANI/Ni electrode against the concentration of  $H_2A$  at a sweep rate of 2 ( $\bullet$ ), 5 ( $\circ$ ), 10 ( $\blacksquare$ ), 20 ( $\square$ ), 50 ( $\blacktriangle$ ), and 100  $mV s^{-1}$  ( $\triangle$ ).

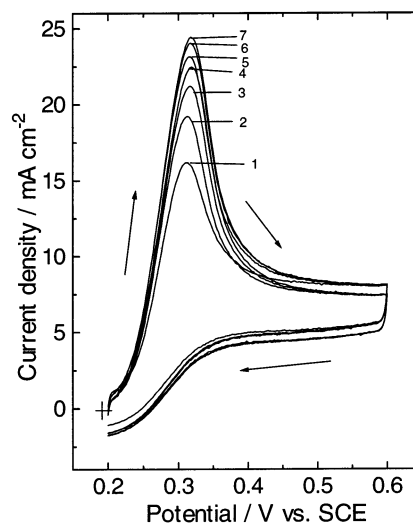


Figure 9. Cyclic voltammograms of PANI/Ni electrode consisting of 50 mM of  $H_2A$  at a sweep rate of 10  $mV s^{-1}$  in 0.1 M  $H_2SO_4$  recorded after holding the electrode at 0.2 V for 0 (1), 30 (2), 60 (3), 120 (4), 180 (5), 240 (6) and 300 s (7).

electrolyte interface, a high specific surface of the PANI is likely to facilitate diffusion into the porous PANI layer, followed by adsorption of a large quantity of  $H_2A$ . To illustrate this, cyclic voltammograms of the PANI/Ni electrode were recorded by holding the electrode at 0.2 V for different times before starting the potential scan. The effect of the holding time is noted as shown in Figure 9. There is an increase in  $i_p$  with an increase in the holding time. The  $i_p$  increased from  $\sim 16 \text{ mA cm}^{-2}$ , when the voltammogram was recorded without holding the electrode potential, to  $\sim 24 \text{ mA cm}^{-2}$ , when the holding time was 420 s (Figure 9). Thus, there is an  $\sim 50\%$  increase in  $i_p$  for 50 mM  $H_2A$ . It is also found that  $i_p$  increases by  $\sim 70\%$  for 5 mM  $H_2A$ . It is, thus, inferred that greater catalytic activity of a PANI/Ni electrode

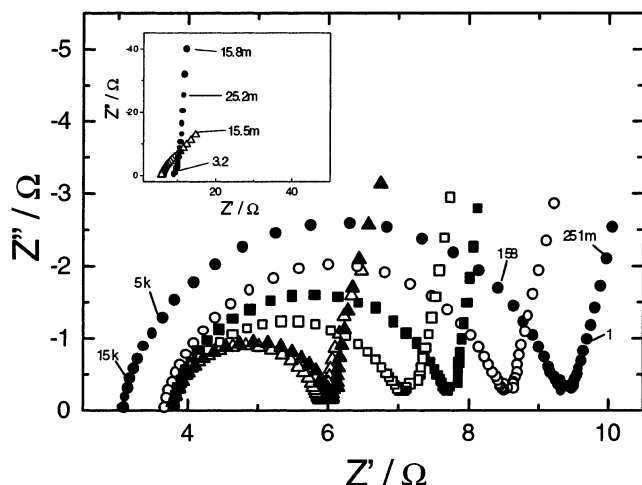


Figure 10. Electrochemical impedance spectra of a PANI/Ni electrode in 0.1 M  $\text{H}_2\text{SO}_4$  containing  $\text{H}_2\text{A}$  at a concentration of 1 (●), 5 (○), 10 (■), 20 (□), 50 (▲) and 100 mM (Δ). Ac frequency (Hz) values corresponding to some of the data points are given.  $Z'$  and  $Z''$ , respectively, refer to the real and imaginary components of impedance. Area of the electrode,  $0.6 \text{ cm}^2$ . The low-frequency parts of impedance spectra at  $\text{H}_2\text{A}$  concentration of 1 (●) and 100 mM (Δ) are shown in the inset.

for electrooxidation of  $\text{H}_2\text{A}$  is achieved by holding the electrode at 0.2 V before commencing the potential sweep and that the effect is higher at low concentrations of  $\text{H}_2\text{A}$ . This experiment clearly demonstrates an increase in concentration of  $\text{H}_2\text{A}$  at the PANI/electrolyte interface due to adsorption.

**Electrochemical Impedance Spectroscopy.** The electrochemical impedance spectra of a PANI/Ni electrode at several concentrations of  $\text{H}_2\text{A}$  in 0.1 M  $\text{H}_2\text{SO}_4$  are shown in Figure 10. The spectrum is characterized by a semicircle in the high-frequency range and a linear part in the low-frequency range.<sup>26</sup> In the presence of 1 mM  $\text{H}_2\text{A}$  in 0.1 M  $\text{H}_2\text{SO}_4$ , the angle of the linear spike is  $\sim 90^\circ$ , suggesting the capacitive behavior of PANI in the low-frequency range (Figure 10 inset). The diameter of the semicircle decreases with an increase in concentration of  $\text{H}_2\text{A}$ . The low-frequency linear part remains capacitive with an angle close to  $90^\circ$  in the concentration range up to about 20 mM. However, it shifts to Warburg nature with an angle close to  $45^\circ$  at higher concentrations (Figure 10 inset). These features of impedance spectra further support the occurrence of electrooxidation of  $\text{H}_2\text{A}$  on the PANI/Ni electrode.

**Effect of pH.** The cyclic voltammograms of a PANI/Ni electrode for 10 mM  $\text{H}_2\text{A}$  in supporting electrolytes of different pH values are shown in Figure 11. It is seen that there is a decrease in  $i_p$  with an increase of pH from 1 to 13. Furthermore, there is a positive shift in  $E_p$ . It is thus inferred that the electrocatalytic effect of PANI/Ni electrode toward the oxidation of  $\text{H}_2\text{A}$  decreases with an increase in pH. This is in contrast to the studies,<sup>27</sup> wherein an increase in oxidation current with pH has been reported on glassy carbon electrodes modified by some macrocyclic compounds. The decrease in  $i_p$  in the present study is due to a decrease in the electrochemical activity of PANI. The polymer possesses higher electronic conductivity in acidic elec-

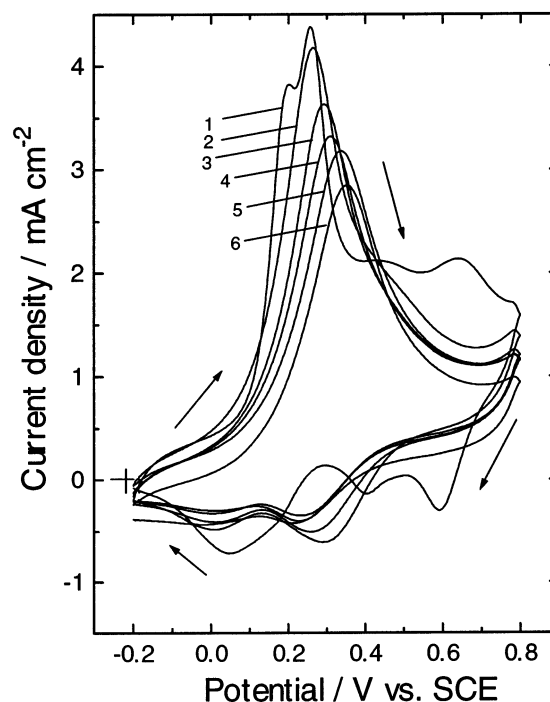
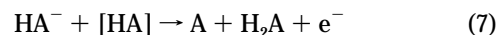
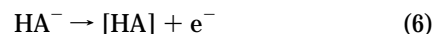


Figure 11. Cyclic voltammograms of PANI/Ni electrode at  $5 \text{ mV s}^{-1}$  in supporting electrolytes consisting of 10 mM  $\text{H}_2\text{A}$  at pH values of 1 (1), 3 (2), 5 (3), 7 (4), 9 (5), and 13 (6).

trolytes, and the conductivity decreases with an increase in pH.<sup>21</sup> Accordingly, the electrooxidation of  $\text{H}_2\text{A}$  on the PANI/Ni electrode is catalyzed more in acidic electrolytes than in neutral and alkaline electrolytes. It is reported<sup>22</sup> that a second oxidation peak of the cyclic voltammogram appears at potential values  $> 1 \text{ V}$  in alkaline electrolytes. However, in the case of the PANI/Ni electrodes, because the oxidation of PANI starts around 1.2 V, the second anodic peak is not noticed.

It is known<sup>28</sup> that  $\text{H}_2\text{A}$  undergoes a 2-step dissociation with  $\text{p}K_a$  values of 4.1 and 11.8, respectively. Hence, in neutral and alkaline electrolytes, the oxidizable species is  $\text{HA}^-$ , and the reaction occurs as<sup>28</sup>



The free radical  $[\text{HA}]$  formed in step 6 undergoes further oxidation (step 7). As a result of the dissociation and the above reaction, the pH of the analyte is expected to be lower than the pH of the unbuffered supporting electrolyte. Consequently, the  $\text{H}_2\text{A}$  is generated at the anode/electrolyte interface (step 7). The results suggest that the PANI/Ni electrodes are useful for electrooxidation of  $\text{H}_2\text{A}$  in the electrolytes of a wide pH range.

The pH dependence of  $\text{H}_2\text{A}$  oxidation was also studied by the ac impedance spectroscopy. The impedance spectra of a PANI/Ni electrode for 10 mM  $\text{H}_2\text{A}$  in the supporting electrolytes of several pH values are shown in Figure 12. The diameter of the semicircle in the high frequency region increases with an increase

(26) Johnson, B. J.; Park, S. M. *J. Electrochem. Soc.* **1996**, *143*, 1269–1276.

(27) Ren, J.; Zhang, H.; Ren, Q.; Xia, C.; Wan, J.; Qin, Z. *J. Electroanal. Chem.* **2001**, *504*, 59–63.

(28) Sawyer, D. T.; Sobkowiak, A.; Roberts, J. L. *Electrochemistry for Chemists*; Wiley & Sons: New York, 1995; p 442.

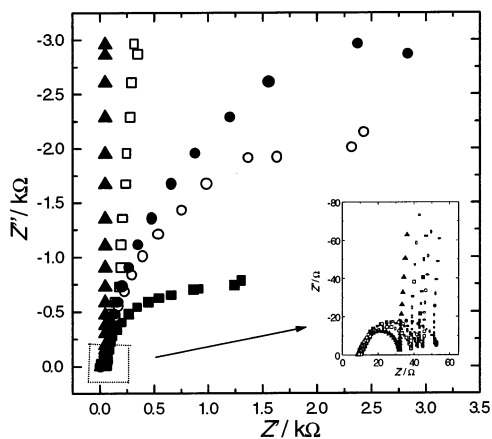


Figure 12. Electrochemical impedance spectra of PANI/Ni electrode in supporting electrolytes consisting of 10 mM  $\text{H}_2\text{A}$  at a pH values of 3 ( $\blacktriangle$ ), 5 ( $\square$ ), 7 ( $\blacksquare$ ), 9 ( $\circ$ ), and 13 ( $\bullet$ ). Area of the electrode,  $0.6 \text{ cm}^2$ .

in pH. This is in accordance with the decrease in the peak current values in the cyclic voltammograms. The data in the low frequency region also tend to take the shape of a semicircle at pH values  $> 5$ . The appearance of two semicircles is probably due to oxidation of  $\text{HA}^-$  in two consecutive steps, each a single electron transfer in neutral and alkaline electrolytes.

**Durability of the Electrodes.** The results reported in this paper were found to be reproducible by repeating the experiments with several electrodes that were similarly prepared. Furthermore, they were used repeatedly back and forth in acidic and alkaline electrolytes, and the electrodes were found to possess electrochemical activity the same as that of fresh electrodes. These reproducibility studies conducted using cyclic voltammetry and ac impedance experiments reveal that the PANI/Ni electrodes

are durable for a large number of experiments in acidic as well as alkaline electrolytes. However, it is advisable to store the electrodes in a mild acidic aqueous electrolyte (e.g.,  $0.1 \text{ M H}_2\text{SO}_4$  solution) in order to retain the electrochemical activity of PANI during idle periods.

## CONCLUSIONS

The bare Ni surface is not useful for studying the oxidation of  $\text{H}_2\text{A}$ . However, the PANI/Ni is shown to possess catalytic activity toward the oxidation reaction. Studies based on cyclic voltammetry, chronoamperometry, and ac impedance methods support the use of the PANI/Ni electrodes in a wide pH range for the electrooxidation of  $\text{H}_2\text{A}$  at concentrations above  $1 \text{ mM}$ . For analysis of  $\text{H}_2\text{A}$  below the  $1 \text{ mM}$  concentration level, the transition of PANI from leucoemeraldine to emeraldine appears to be interfering in the present experimental conditions. However, it may be noted that the electrochemical behavior of PANI depends on the conditions of its deposition. Thus, it may be possible by suitable modification of the deposition conditions to reduce or eliminate the interference from PANI transformations. It was found that PANI/Ni electrodes are durable for a large number of experiments in a wide pH range. The lower cost of Ni (or other non-platinum metals) in comparison with Pt favors a potential application of PANI/Ni electrodes for electrooxidation of  $\text{H}_2\text{A}$ . Since the potentiodynamic technique is a convenient method of polymerization of PANI, it can allow the use of micro- or microarray Ni substrates, and such PANI/Ni microelectrodes are expected to be useful for a variety of applications.

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