

Short communication

Electrooxidation of methanol on polyaniline without dispersed catalyst particles

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Abstract

Electrooxidation of methanol in H_2SO_4 is studied on platinum and polyaniline (PANI) deposited platinum electrodes by cyclic voltammetry. In contrast to reports in the literature, which suggest the need of fine particles of a catalyst dispersed in PANI matrix for occurrence of electrooxidation of CH_3OH , in the present study, the reaction is shown to take place on PANI without additional catalyst particles at CH_3OH concentrations higher than 1 M. At lower concentrations, adsorption of CH_3OH occurs on PANI resulting in a reduction in intrinsic voltammetric peak currents of PANI in H_2SO_4 . The kinetics of adsorption follows Langmuir isotherm. By a comparison of cyclic voltammetric peak currents of methanol on platinum and PANI deposited platinum electrodes, the catalytic efficiency of PANI towards oxidation of CH_3OH is evaluated. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Electronically conducting polymers with conjugate structures have been investigated extensively and reviewed in view of their varied applications [1]. The electronic conductivity of the polymers, which is as high as the metallic conductivity, attracts great interest from an electrochemical viewpoint. Some conducting polymers have been studied [2] for their catalytic behavior towards electrochemical reactions. Among this type of polymers, polyaniline (PANI) has been studied extensively as it is easy to synthesize by chemical and electrochemical routes, and it is stable under normal experimental conditions [3]. The electrooxidation of methanol is important in view of its application in fuel-cell technology, and it has been widely investigated on platinum-based electrodes and reviewed in the literature [4,5]. The reaction is sensitive to the catalytic nature of the electrode surface since dissociative adsorption of methanol is a primary step in the mechanism. Formation of several adsorbed intermediates and their accumulation on the electrode surface cause poisoning of catalyst during long periods of the reaction. An attempt was made [6] to study the electrooxidation of CH_3OH on a PANI-coated gold electrode by cyclic voltammetry, but oxidation did not take place. The PANI coated gold electrode was, therefore, modified by

depositing platinum particles into the polymer film. The platinum deposit was shown to behave as a good electrocatalyst for CH_3OH oxidation. In a similar study [7], platinum microparticles were electrodeposited into a modified PANI film for adsorption of methanol. There do not appear to be any studies of methanol electro-oxidation on PANI alone, i.e. without platinum particles dispersed in it [8,9]. It is concluded that for electrochemical reactions involving small organic molecules, PANI can be employed as a conducting matrix for hosting catalyst particles.

In the present study, electrooxidation of CH_3OH in a concentration range from 0.05 to 10 M in 0.5 M H_2SO_4 is studied on platinum and PANI deposited platinum electrodes by cyclic voltammetry and ac impedance spectroscopy. In the low concentration range, the adsorption of CH_3OH is studied. In the high concentration range, the catalytic efficiency of PANI towards electrooxidation of CH_3OH is evaluated.

2. Experimental

AR grade chemicals and double-distilled water were used in all experiments. The working electrode of platinum foil or PANI deposited platinum of geometric area of 0.6 cm^2 was placed symmetrically between two auxiliary platinum foil electrodes in a glass cell of about 50 cm^3 capacity. A saturated calomel electrode (SCE) was used as the reference

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electrode and electrode potentials are reported against this electrode. The platinum working electrode was treated in concentrated HNO_3 , washed thoroughly, and subjected to repeated potential scanning in 0.5 M H_2SO_4 in the potential range from -0.2 to 1.2 V until the resulting voltammograms were reproducible. PANI was deposited on a platinum electrode in 0.5 M H_2SO_4 with 0.5 M aniline (vacuum distilled) by repeated cycling at 100 mV s^{-1} in the potential range 0 – 1.2 V. The thickness, calculated on the basis of the mass and the density of PANI, was about $100 \mu\text{m}$. The PANI/Pt electrode was washed thoroughly in 0.5 M H_2SO_4 and was then subjected to cyclic voltammetry at 50 mV s^{-1} in 0.5 M H_2SO_4 . Experiments were conducted in the concentration range 0.05 – 10 M of CH_3OH in 0.5 M H_2SO_4 . Cyclic voltammetry and ac impedance measurements were performed by EG&G PARC equipment models Versastat and 6310, respectively. The impedance data were collected in the ac frequency range 100 kHz – 0.1 Hz with an excitation signal of 5 mV . All experiments were carried out at $20 \pm 1^\circ\text{C}$.

3. Results and discussion

PANI exhibits multiple redox behavior during potentiodynamic cycling in acidic media at positive potentials. It is generally accepted that the redox processes are accompanied by structural transformations by the doping and undoping of protons and anions [10]. Each transformation is characterized by a current peak on the cyclic voltammogram. The voltammogram for the PANI/Pt electrode in 0.5 M H_2SO_4 recorded at 50 mV s^{-1} is shown in Fig. 1 (curve 1). The oxidation current peak at 0.15 V is due to the transformation of PANI from the leucoemeraldine state (LM) to the emeraldine state (EM). The oxidation peak at 0.75 V, which is due to the transformation of the EM state to the pernigraniline

state (PE), is less intense. The PANI exhibits high conductivity in the potential region between the LM/EM and the EM/PE transitions.

Cyclic voltammograms for the PANI/Pt electrode in 0.5 M H_2SO_4 in the presence of CH_3OH at low concentrations are shown in Fig. 1. It is seen that intensities of the PANI peaks decrease with an increase in CH_3OH concentration from 0.05 to 1.0 M. In addition, the corresponding peak potentials shift gradually. At all concentrations, oxidation of CH_3OH does not take place, which is evident from the absence of corresponding current peaks. This feature of the cyclic voltammograms may be explained on the basis of adsorption of CH_3OH . In order to establish the coverage (θ) of adsorbed CH_3OH on PANI, the concentration should be in the range 0.05 – 1.0 M, i.e. unlike in the case of platinum, where the oxidation of CH_3OH takes place at lower concentrations. The value of θ is calculated from the peak currents of the LM/EM transition, namely

$$\theta = \frac{I_p^* - I_p}{I_p^*} \quad (1)$$

where I_p^* and I_p are the current value of the LM/EM peak in the absence and presence of CH_3OH , respectively. The values of θ are calculated from the voltammograms at several scan rates in the CH_3OH concentration range 0.05 – 1 M. At all scan rates, θ increases with CH_3OH concentration as shown in Fig. 2a. There is a steep increase in θ at low concentrations of CH_3OH , followed by a gradual increase at high concentrations. The value of θ reaches about 0.7 at 1 M CH_3OH and a scan rate of 5 mV s^{-1} , and it increases to about 0.9 at 100 mV s^{-1} . The adsorption kinetics are examined in terms of the Langmuir adsorption isotherm, i.e.

$$\frac{\theta}{1 - \theta} = KC_{\text{CH}_3\text{OH}} \quad (2)$$

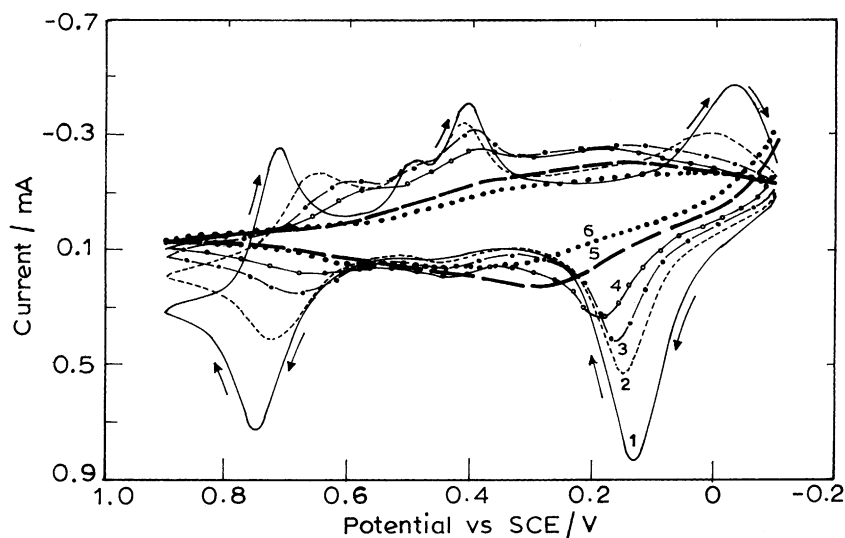


Fig. 1. Cyclic voltammograms of PANI/Pt electrode at 5 mV s^{-1} scan rate in 0.5 M H_2SO_4 with CH_3OH at (1) 0 M, (2) 0.05 M, (3) 0.1 M, (4) 0.2 M, (5) 0.5 M and (6) 1.0 M. Electrode area = 0.6 cm^2 .

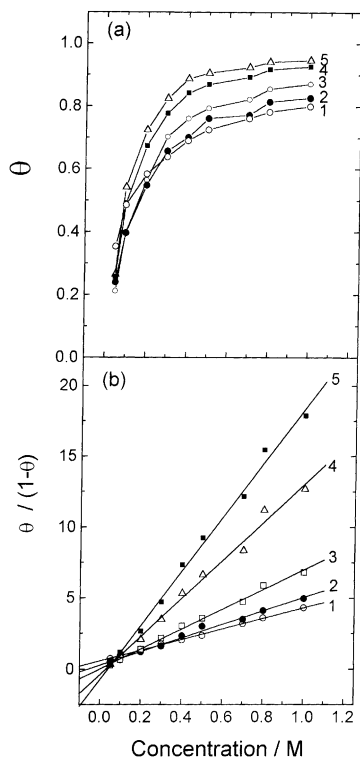


Fig. 2. (a) Surface coverage (θ) of CH_3OH on PANI/Pt electrode; (b) $\theta/(1-\theta)$ calculated at a scan rate of (1) 5 mV s^{-1} , (2) 10 mV s^{-1} , (3) 20 mV s^{-1} , (4) 50 mV s^{-1} and (5) 100 mV s^{-1} against concentration of CH_3OH .

where K is a constant. The plot of $\theta/(1-\theta)$ versus methanol concentration ($C_{\text{CH}_3\text{OH}}$) is linear for all scan rates (Fig. 2b), which confirms a Langmuir type of adsorption of CH_3OH on the PANI surface.

Adsorption of CH_3OH on the PANI electrode was also studied by ac impedance measurements. The impedance spectra of the PANI/Pt electrode in $0.5 \text{ M H}_2\text{SO}_4$ with several concentrations of CH_3OH are shown in Fig. 3. The data take the shape of a semi-circle at all concentrations. The potential of the PANI/Pt electrode in $0.5 \text{ M H}_2\text{SO}_4$ in the absence of CH_3OH is 0.25 V , which corresponds to the LM/EM transition. The impedance semi-circle is therefore attributed to a parallel combination of the charge-transfer resistance (R_{ct}) of the LM/EM transition and the double-layer capacitance (C_{dl}) of the PANI/Pt electrode. The value of R_{ct} is obtained from the diameter of the semi-circle, and the value of C_{dl} is calculated by

$$C_{\text{dl}} = \frac{1}{2\pi f^* R_{\text{ct}}} \quad (3)$$

where f^* is the frequency corresponding to maximum of the semi-circle. The values of R_{ct} and C_{dl} obtained for the PANI/Pt electrode in $0.5 \text{ M H}_2\text{SO}_4$ are $0.9 \Omega \text{ cm}^2$ and $52.5 \mu\text{F cm}^{-2}$, respectively. In the presence of CH_3OH in $0.5 \text{ M H}_2\text{SO}_4$, the electrode potential shifts to about 0.4 V . This shift is virtually invariant with CH_3OH concentration. The size of the impedance spectrum increased with increase

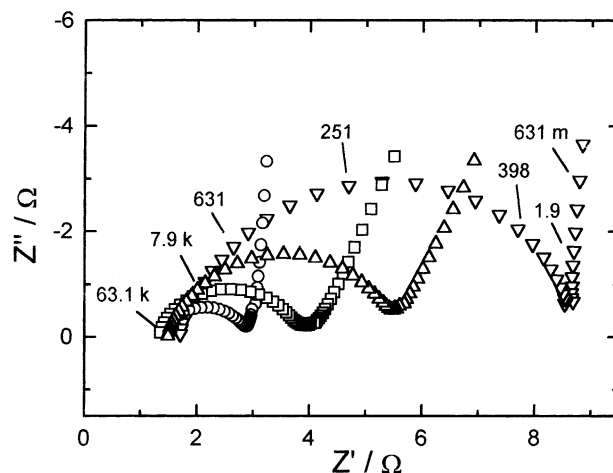


Fig. 3. Complex plane impedance diagrams of PANI/Pt electrode in $0.5 \text{ M H}_2\text{SO}_4$ containing CH_3OH at (○) 0 M , (□) 0.1 M , (△) 0.2 M and (▽) 0.5 M (numbers are values of ac frequency (Hz) corresponding to some of the data points). Electrode area = 0.6 cm^2 .

in CH_3OH concentration, as shown in Fig. 3. Since the electrode potential (0.4 V) does not correspond to CH_3OH oxidation, R_{ct} obtained is considered to be for the LM/EM transition alone. The values of R_{ct} and C_{dl} obtained for several concentrations of CH_3OH are given in Table 1. The value of R_{ct} increases with concentration of CH_3OH . The value of C_{dl} increases from $50 \mu\text{F cm}^{-2}$ at $0.1 \text{ M CH}_3\text{OH}$ to about $90 \mu\text{F cm}^{-2}$ at $1 \text{ M CH}_3\text{OH}$, and then remains nearly invariant with further increase of CH_3OH concentration up to about 8 M . These observations of the impedance spectroscopy of the PANI/Pt electrode further support the adsorption phenomenon indicated by cyclic voltammetric studies.

From the above studies, it is clear that adsorption of CH_3OH is likely to hinder doping of ions into the PANI which results in the disappearance of the LM/EM transformation. Furthermore, adsorption is found to be reversible, i.e. by recording voltammograms in CH_3OH -free supporting electrolyte, PANI peaks are restored. There is no irreversible

Table 1
Charge-transfer resistance (R_{ct}) and double-layer capacitance (C_{dl}) of PANI/Pt electrode at different concentrations of CH_3OH in $0.5 \text{ M H}_2\text{SO}_4$

CH_3OH (M)	R_{ct} ($\Omega \text{ cm}^2$)	C_{dl} ($\mu\text{F cm}^{-2}$)
0.0	0.9	52.5
0.1	1.0	49.6
0.2	1.1	49.5
0.5	1.7	38.0
1.0	2.8	89.1
2.0	4.2	89.1
3.0	7.1	89.2
4.0	7.4	89.2
5.0	8.8	89.6
6.0	8.9	89.9
7.0	18.9	94.0
8.0	34.3	94.9
9.0	41.3	149.5
10.0	60.2	154.3

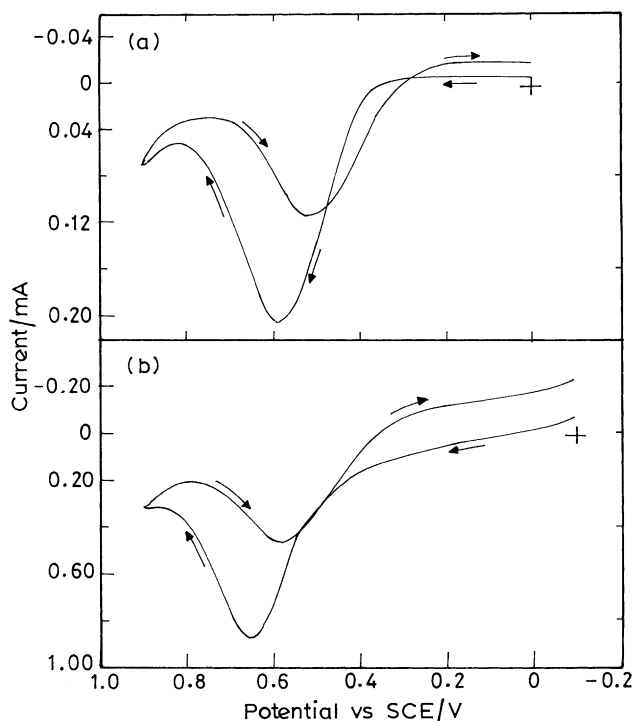


Fig. 4. Cyclic voltammograms for CH_3OH oxidation on (a) Pt and (b) PANI/Pt electrodes at 10 mV s^{-1} scan rate in $0.5 \text{ M H}_2\text{SO}_4$ containing $2 \text{ M CH}_3\text{OH}$. Electrode area = 0.6 cm^2 .

destruction of the PANI layer by CH_3OH . The oxidation occurs when the CH_3OH concentration is $\geq 2 \text{ M}$ in $0.5 \text{ M H}_2\text{SO}_4$, as demonstrated by the voltammograms shown in Fig. 4 for Pt and PANI/Pt electrodes. It is evident from Figs. 1 and 4 that the peaks of PANI corresponding to LM/EM and EM/PE transitions gradually decrease with CH_3OH concentration, and finally disappear at $2 \text{ M CH}_3\text{OH}$ before the peaks corresponding to CH_3OH oxidation start appearing.

The cyclic voltammogram for the platinum electrode in $0.5 \text{ M H}_2\text{SO}_4$ containing $2 \text{ M CH}_3\text{OH}$ (Fig. 4) consists of current peaks in the forward and reverse scans which correspond to the oxidation process [4]



The currents (I_p) of both peaks increase with the square root of scan rate, as well as with the concentration of CH_3OH (Fig. 5). This suggests that the oxidation reaction is controlled by a diffusion step. The PANI/Pt electrode also shows a dependence of peak current on the square root of scan rate and the CH_3OH concentration (Fig. 5), and thus obeys the following relationship [11]:

$$I_p = (2.99 \times 10^5) A n \alpha n_\alpha^{1/2} C D^{1/2} \nu^{1/2} \quad (5)$$

where A is area of the electrode, n_α the number of electrons transferred up to the rate-determining step, α the transfer coefficient, C the concentration, D the diffusion coefficient and ν the scan rate.

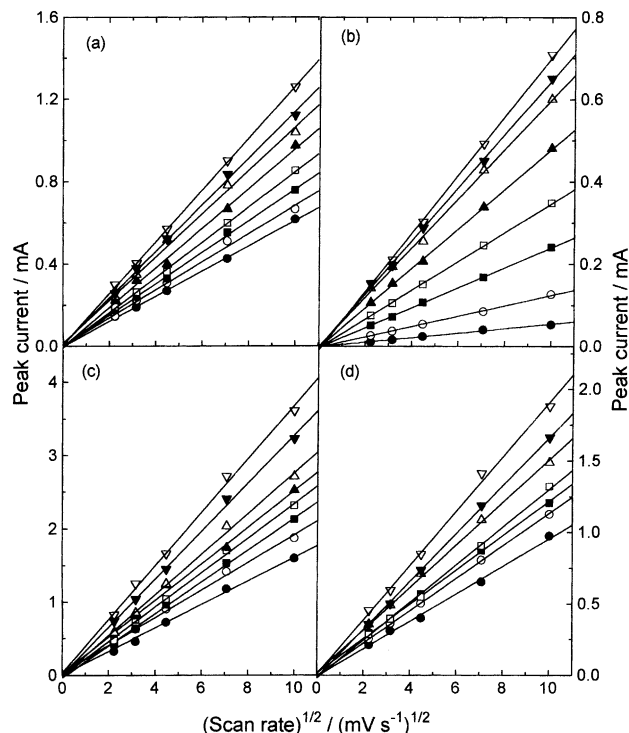


Fig. 5. Voltammetric peak current of CH_3OH oxidation for (a) forward and (b) reverse scan of Pt electrode, and for (c) forward and (d) reverse scan of PANI/Pt electrode as function of square root of scan rate. Data are for CH_3OH concentrations of (●) 3 M , (○) 4 M , (■) 5 M , (□) 6 M , (▲) 7 M , (△) 8 M , (▼) 9 M and (▽) 10 M in $0.5 \text{ M H}_2\text{SO}_4$. Electrode area = 0.6 cm^2 .

A comparison of voltammograms for Pt and PANI/Pt electrodes of equal geometric area recorded for Eq. (4) suggests that the voltammetric peak potentials are nearly the same for both the electrodes. Moreover, the magnitude of I_p is always higher with the PANI/Pt electrode than with the Pt electrode, which suggests a catalytic effect of PANI towards Eq. (4).

Although platinum is considered to be an inert metal, it is known that the surface is covered with a thin oxide or hydroxide film. On the other hand, the PANI is free from such a surface film and the electron exchange for Eq. (4) occurs without hindrance. Additionally, the high porosity and, therefore, the high surface area of the PANI, which could be due to the long polymer chain, promotes the catalysis of Eq. (4) on the PANI/Pt surface.

The catalytic efficiency (γ) of PANI towards oxidation of CH_3OH is defined as

$$\gamma = \frac{100 \times [I_p(\text{PANI}) - I_p(\text{Pt})]}{I_p(\text{Pt})} \quad (6)$$

where $I_p(\text{PANI})$ and $I_p(\text{Pt})$ are the peak current values of CH_3OH oxidation on PANI/Pt and Pt electrodes at a given scan rate, respectively. The value of γ calculated using the cyclic voltammetric forward peak currents at several scan rates are shown as a function of concentration in Fig. 6. The

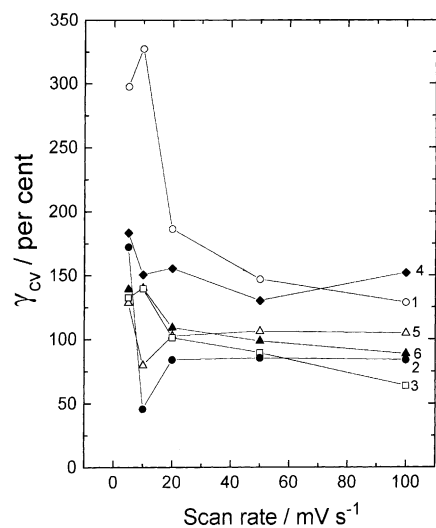


Fig. 6. Catalytic efficiency (γ_{cv}) of PANI/Pt electrode for CH_3OH oxidation as function of scan rate for concentration of (1) 2 M, (2) 3 M, (3) 4 M, (4) 5 M, (5) 7 M and (6) 10 M of CH_3OH in 0.5 M H_2SO_4 .

value of γ is higher than 50% in all concentrations. These studies suggest that the electrooxidation of CH_3OH proceeds on the PANI/Pt electrode with good catalytic efficiency, but

only at concentrations higher than 1 M in 0.5 M H_2SO_4 electrolyte.

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