

Electrocatalytic oxidation of methanol on Pt modified polyaniline in alkaline medium

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ABSTRACT

A comparative study of the electrocatalytic oxidation of methanol is made in NaOH, Na₂CO₃ and NaHCO₃ on bare Pt (Pt), polyaniline covered Pt (PANI) and Pt modified polyaniline film on Pt (Pt/PANI) using cyclic voltammetry, polarization, ac impedance spectroscopy and chronoamperometric techniques at 25 °C. The cyclic voltammetry and polarization studies show that the potentials at which methanol oxidation commences on different electrodes in each of the alkaline medium examined follow the trend Pt/PANI < Pt < PANI whereas the potentials for initiation of oxidation on each electrode in different alkaline media follow the order NaHCO₃ > Na₂CO₃ > NaOH. The oxidation current is highest and charge transfer resistance lowest for Pt/PANI films compared to Pt in all the media studied. However, for the same Pt loading Pt/PANI films exhibit larger oxidation currents in NaOH followed by Na₂CO₃ and NaHCO₃. The Tafel slope for methanol oxidation on Pt/PANI in NaOH, Na₂CO₃ and NaHCO₃ has a value of about 115 mV decade⁻¹. The chronoamperometric response of the Pt/PANI film at the peak potential for methanol oxidation shows lesser sensitivity to poisoning by CO compared to bare Pt and platinumised Pt (Pt/Pt).

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1. Introduction

Electrocatalytic oxidation of methanol is a reaction subject to intense investigation due to its possible application in direct methanol fuel cells [1]. Among the numerous materials, Pt has been established as a powerful electrocatalyst for the oxidation of methanol [2]. But the use of Pt as such in the form of smooth foils for the direct electrooxidation of methanol is found to be inefficient on account of (i) high cost and (ii) formation of strongly adsorbed intermediates like CO as a result of dissociative adsorption of methanol [3]. Many attempts have, therefore, been made to overcome these problems and to develop less expensive anode materials, which have significantly better catalytic activity and are less prone to CO poisoning. These include the use of bimetallic catalysts such as Pt-Ru [4], Pt-WO₃ [5] and alloys of Ru-Pd [6] which reduce the overpotential for methanol oxidation considerably but are however not cost effective. Among the attempts to develop cost effective electrodes it has been shown that the dispersion of Pt in very minute quantities in the form of microparticles inside a polymer matrix, a process generally referred to as polymer electrode modification leads to a remarkable enhancement in the electrocatalytic activity for the oxidation of methanol [7–9], attributed essentially to (i) an increase in active surface area by dispersion of the catalyst and

(ii) a better utilization of Pt crystallites in decreasing the poisoning effect of CO [10–12]. Such systems have not only been used for methanol oxidation but also for oxidation of other small organic molecules such as HCHO, HCOOH, ethylene glycol, D-glucose, etc. [13,14]. Among the polymers that have found favor for use as host matrices for the development of such systems are mainly polyaniline, polypyrrole and polythiophene by virtue of their excellent conducting properties and very good adhesion to the substrate electrode. There have been continuing efforts, however, at finding other conducting polymers as suitable host matrices for developing polymer modified electrodes. Some of the other polymers that have been found to be conducive for such an application are poly (2-hydroxy-3-aminophenazine) [15], poly (o-aminophenol) [16] and poly (o-phenylenediamine) [17].

The use of most of these systems have, however, been restricted to oxidation of methanol in acid medium [7–12,15–17] wherein the poisoning species strongly bind to the catalytic centers imposing limitation in the kinetics of the methanol oxidation leading to polarization losses. It was after Parsons and Van der Noot [2] suggestion of the possibility of using alkaline media for the organic fuel cell reactions that many studies have been oriented in this direction.

The use of alkali electrolytes not only lead to better polarization characteristics of methanol oxidation on unsupported platinum black but also open up the possibility of using non-noble, less expensive metal catalysts for the process. It is, however, found that majority of the studies concerned with the use of alkaline media for the oxidation of methanol employ pure metals (single and polycrys-

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talline Pt, Au, Ni) [18–26], metal alloys like Ni–Cu [27] and other Ni based electrode systems [28–31] as anodes. Studies involving use of Pt modified polymer (or supported) electrodes as electrocatalysts for methanol oxidation in alkaline medium are sparse [32–34]. These studies are confined to either KOH or NaOH as the alkaline media for methanol oxidation. In view of the favorable features of alkaline medium for methanol oxidation with regard to facile polarization, reduction of electrode poisoning and the high corrosion resistance property of polymers we have undertaken the study of electrooxidation of methanol on Pt modified polyaniline electrodes in three different alkaline media namely NaOH, Na_2CO_3 and NaHCO_3 and the results are reported herein.

2. Experimental

All solutions were prepared using analytical grade reagents and double distilled water. The electrochemical experiments were performed at room temperature using an Auto lab PGSTAT 30 potentiostat/galvanostat model with pilot integration controlled by GPES 4.9 software in a three-compartment cell (all interconnected) with a luggin capillary connecting the working and reference electrode chamber. Pt (rotating disc with geometric area 0.0314 cm^2),

Pt gauze and saturated calomel electrode (SCE) were used as working, counter and reference electrodes respectively. Prior to use the working electrode was first mechanically polished on a 4/0 (fine) grade emery paper, then with $0.3\text{ }\mu\text{m}$ alumina powder, washed with water and subjected to ultrasonic agitation for about 30 s. The electrode was then cycled in $0.5\text{ M H}_2\text{SO}_4$ in the potential range of -0.2 V to 1.2 V at 50 mV s^{-1} until a cyclic voltammogram of stable shape was obtained.

The electropolymerisation of aniline was carried out from a solution of 0.1 M aniline in $0.5\text{ M H}_2\text{SO}_4$ in the potential range -0.2 to $+1.2\text{ V}$ at a scan rate of 50 mV s^{-1} for 13 cycles. Reduction of Pt either on to Pt disc or polyaniline film covered Pt disc was carried out from a solution of $10\text{ mM H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in $0.5\text{ M H}_2\text{SO}_4$ at -0.25 V . Assuming 100% efficiency for the reduction of Pt^{4+} to Pt the amount of Pt reduced was monitored from the charge passed during reduction process. The amount of Pt deposited in all the cases studied was 0.1 mg cm^{-2} . Further, oxidation of methanol was carried out from a solution containing 1 M methanol in 1 M solutions of NaOH, Na_2CO_3 and NaHCO_3 .

The cyclic voltammetric studies were carried out in suitable potential ranges and scan rates both in presence and absence of methanol in the three alkali media on the different electrode sys-

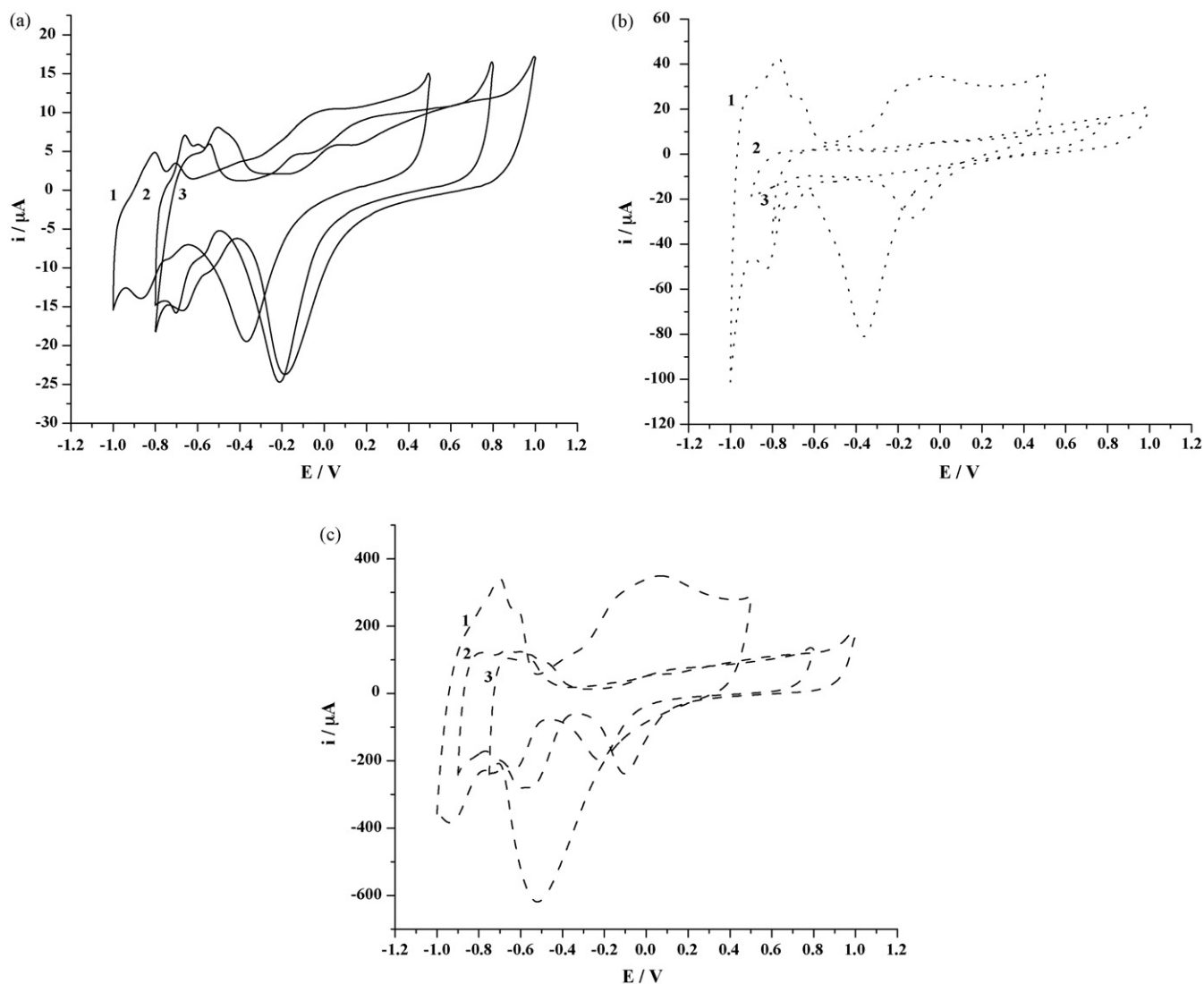


Fig. 1. CV response at 50 mV s^{-1} in 1 M solutions of NaOH (1), Na_2CO_3 (2) and NaHCO_3 (3) on (a) Pt, (b) PANI and (c) Pt/PANI.

tems. The quasi steady state polarization studies were done at a scan rate of 1 mV s^{-1} . The electrochemical impedance spectra were recorded in the frequency range of 100 KHz and 1 mHz with the amplitude of the sine wave being 10 mV. The stability of the electrodes towards CO poisoning was studied using chronoamperometry at the peak potentials for methanol oxidation for 1000 s.

3. Results and discussion

3.1. Electrochemical behavior of Pt, PANI and Pt/PANI in alkaline media

To compare the electrochemical response of Pt (Pt), polyaniline covered Pt (PANI) and Pt modified polyaniline film on Pt (Pt/PANI) in alkaline media, cyclic voltammograms were recorded in the potential range -1.2 to $+1.2$ V with respect to SCE on these electrodes in 1 M NaOH (pH 13.94), 1 M Na_2CO_3 (pH 11.12) and 1 M NaHCO_3 (pH 8.48) respectively at a scan rate of 50 mV s^{-1} . In Fig. 1 are shown the superposed cyclic voltammograms of each electrode in different media. In Fig. 1a the cyclic voltammograms marked as 1, 2 and 3 show the characteristic electrochemical response

of Pt in NaOH, Na_2CO_3 and NaHCO_3 respectively [24,32], this being adsorption/desorption of hydrogen in the early stages of the scans, reversible adsorption of OH^-/OH^- , $\text{CO}_3^{2-}/\text{OH}^-$, HCO_3^- in the respective media in the middle stages of the scans and formation of oxide in the last stages of the scans. The potential ranges over which these processes occur, however, shift towards more noble direction as the medium changes from NaOH to Na_2CO_3 and then to NaHCO_3 . A prominent peak marks the cathodic scans in each case, which may be due to the reduction of the oxide layer.

The electrochemical response of PANI in the three media is reflected by the cyclic voltammograms marked 1, 2 and 3 in Fig. 1b. The behavior of PANI in NaOH (curve 1 of Fig. 1b) is very much similar to that of Pt in the same medium (curve 1 of Fig. 1a) except for the very large enhancement in current observed on PANI. This indicates that PANI film is permeable to hydroxyl ions and hence the response observed on the PANI electrode is actually the response of the Pt surface underneath since PANI has little electrochemical activity at $\text{pH} > 4$ [35]. The observance of large currents on PANI, however, suggests greater facility of the adsorption processes on the polymer matrix than on the bare Pt surface. The activity of PANI electrode in NaHCO_3 (curve 3 of Fig. 1b) is quite similar to that of

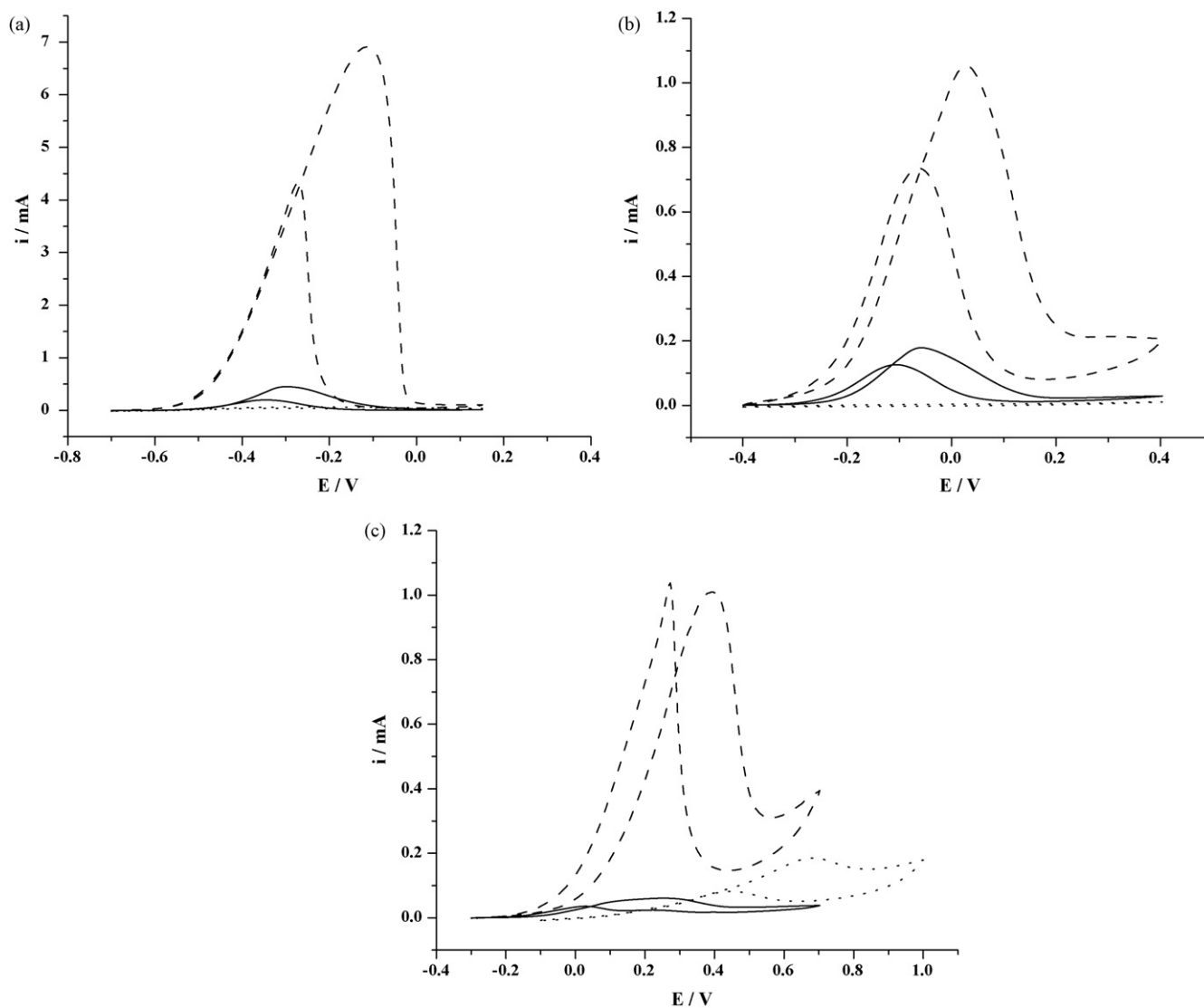


Fig. 2. CVs for the oxidation of methanol (1 M) at 20 mV s^{-1} on Pt (solid line), PANI (dotted line) and Pt/PANI (dashed line) in 1 M solutions of (a) NaOH (b) Na_2CO_3 and (c) NaHCO_3 .

Table 1

The anodic peak currents (I_a) and anodic peak potentials ($E_{p,a}$) obtained from CVs for the oxidation of methanol (1 M) in 1 M solutions of NaOH, Na₂CO₃ and NaHCO₃ on different electrodes

Medium	NaOH			Na ₂ CO ₃			NaHCO ₃		
	Pt	PANI	Pt/PANI	Pt	PANI	Pt/PANI	Pt	PANI	Pt/PANI
I_a (μ A)	442	063	6917	178	–	1050	059	185	1010
$E_{p,a}$ (mV)	–296	–277	–112	–055	–	+029	+245	+688	+390

Pt in NaHCO₃ (curve 3 of Fig. 1a) and the currents are also comparable but the behavior of PANI in Na₂CO₃ (curve 2 of Fig. 1b) is however different from that of bare Pt. PANI shows little or no electrochemical activity due probably to the restriction of adsorption and permeation of hydroxyl ions in the presence of CO₃^{2–} onto the Pt surface. The observation that the same electrode when subsequently used in NaOH solution regains its activity corroborates the above contention. The permeability of the PANI film supports its porous nature and hence its use as a matrix for catalyst dispersion.

The cyclic voltammetric response of Pt/PANI in the three media is marked by curves 1, 2 and 3 in Fig. 1c. It is evident from curve 1 that Pt/PANI behaves exactly in the same manner as Pt (curve 1 of Fig. 1a) or PANI (curve 1 of Fig. 1b) in NaOH. The currents exhibited by Pt/PANI are, however nearly 25 times more than that observed on Pt and approximately 10 times more than that observed on PANI. This can be easily attributed to the large surface area provided by the dispersed catalytic particles for the various processes to occur. The cyclic voltammetric features characterizing the various processes are more prominent on Pt/PANI in Na₂CO₃ and NaHCO₃ (curves 2 and 3 of Fig. 1c) when compared to PANI in these media (curves 2 and 3 of Fig. 1b) and resemble those of Pt (curves 2 and 3 of Fig. 1a) in the same media. Although the currents observed on Pt/PANI in Na₂CO₃ and NaHCO₃ are greater than those observed either on Pt or PANI, they are much less than the currents obtained on the same film in NaOH.

3.2. Methanol oxidation on Pt, PANI and Pt/PANI in 1 mol L^{–1} solutions of NaOH, Na₂CO₃ and NaHCO₃

3.2.1. Cyclic voltammetric (CV) studies

A comparison of the CVs for the oxidation of methanol (1 M) on Pt, PANI and Pt/PANI in 1 M solution each of NaOH, Na₂CO₃ and NaHCO₃ are presented in Fig. 2(a–c) respectively. The CVs on Pt (solid lines) and Pt/PANI (dashed lines) in the three media have characteristic peaks of methanol oxidation in the anodic and cathodic scans similar to those observed in acid medium [7–12] but at much more favorable potentials. Leaving the specifics which have been discussed in detail in [7–12], the overall process of oxidation on Pt has been explained to proceed via the adsorption of methanol molecules on the Pt sites covered by OH[–]/OH[–], CO₃^{2–}/OH[–], HCO₃[–] in the respective media in the anodic direction and produces maximum current at the peak potentials after which the currents decrease due to the passivation of the catalytic sites. The appearance of a pronounced anodic peak current in the cathodic potential scan is attributed to the high activity of the Pt particles which are now divested of the passive film formed in the anodic cycle [36].

It is observed that while PANI supports oxidation of methanol in NaOH and NaHCO₃ (at a potential of ~1 V more anodic to that in NaOH), it does not support oxidation of methanol in Na₂CO₃.

The anodic peak currents (I_a) and anodic peak potentials ($E_{p,a}$) for methanol oxidation on different electrodes in the three media are listed in Table 1.

It is evident from the CV data that Pt/PANI offers the maximum electrocatalytic activity towards the oxidation of methanol when compared to Pt and PANI in all the three media. The catalytic

activity of Pt/PANI however declines as reflected by the decrease in anodic peak currents and shift in anodic peak potentials in the more noble direction (Fig. 3) as we move from NaOH to Na₂CO₃ and then to NaHCO₃. The maximum electrocatalytic activity of Pt/PANI as compared to Pt and PANI can be attributed to the large surface area amenable to reaction on the electrode due to the cumulative effect of the dispersed Pt microparticles and the polymer matrix. The decline of the activity in Na₂CO₃ and NaHCO₃ can be attributed to inefficient adsorption of methanol, which is a vital step in the oxidation due to the competition, by both OH[–] and CO₃^{2–} in Na₂CO₃ and OH[–] and HCO₃[–] in NaHCO₃ media.

In order to compare the electrocatalytic activity of Pt/PANI with platinumised Pt (Pt/Pt), methanol oxidation was carried out on Pt/Pt containing the same amount of dispersed Pt as in the PANI matrix in all the three media. In Fig. 4 only the anodic scans of the CVs recorded on Pt/PANI (dashed line) and on Pt/Pt (bold solid line) in 1 M solutions of the three alkalis are compared. It is evident that Pt/PANI is approximately twice more active than Pt/Pt towards methanol oxidation in both NaOH and Na₂CO₃ but the activity in NaHCO₃ remain approximately the same on the two electrodes.

3.2.2. Polarization studies

The quasi steady state anodic polarization of Pt, PANI and Pt/PANI in 1 M solutions of NaOH, Na₂CO₃ and NaHCO₃ each containing 1 M methanol was carried out from the open circuit potential (OCP) values in each case, at a scan rate of 1 mV s^{–1}. It is observed that in each medium, oxidation currents appear at more favorable potentials on Pt/PANI followed by Pt and then PANI (figures not shown). It is also evident that the Tafel region characteristic of methanol oxidation is least on PANI in Na₂CO₃ as compared to that in NaOH and NaHCO₃ in agreement with the CV data reported earlier that PANI does not favor oxidation of methanol in 1 M Na₂CO₃. It is also observed that the electrodes especially, Pt

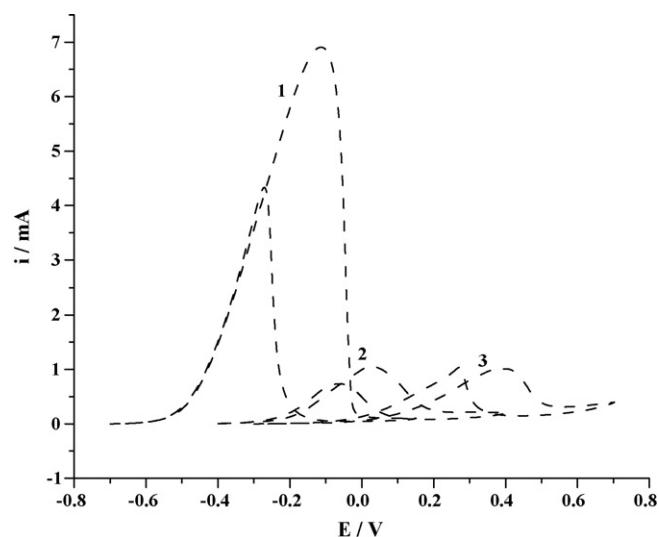


Fig. 3. CVs for the oxidation of methanol (1 M) at 20 mV s^{–1} on Pt/PANI in 1 M solutions of NaOH (1), Na₂CO₃ (2) and NaHCO₃ (3).

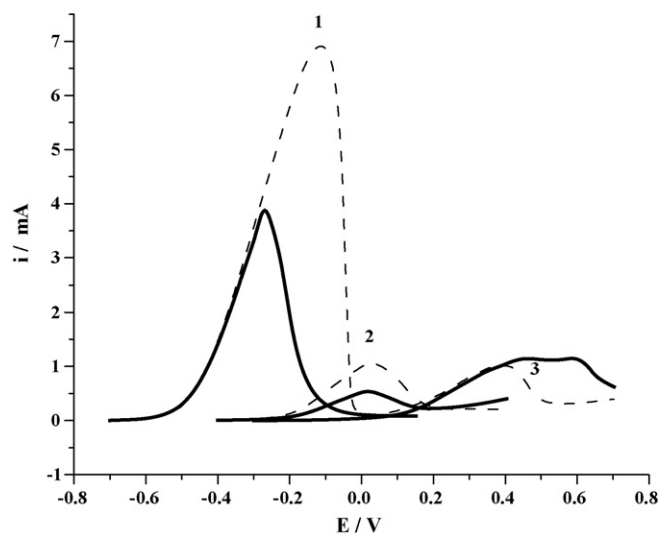


Fig. 4. Forward scans of the CVs for the oxidation of methanol (1 M) at 20 mV s^{-1} on Pt/PANI (dashed line) and platinised Pt (bold solid line) in 1 M solutions of NaOH (1), Na_2CO_3 (2) and NaHCO_3 (3).

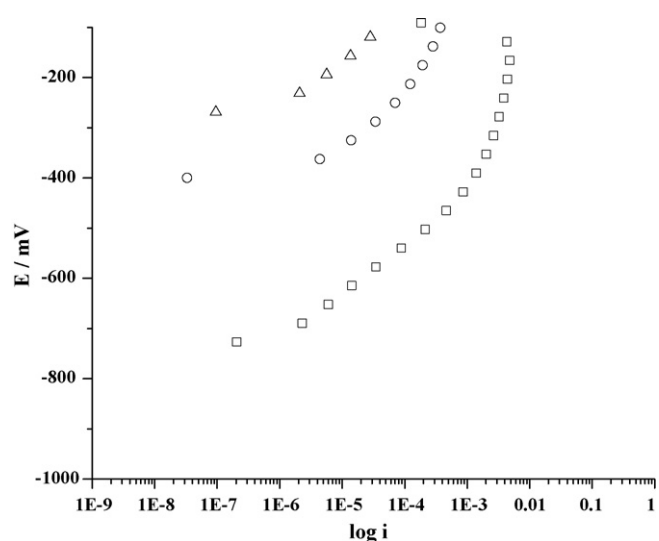


Fig. 5. Tafel plots for the oxidation of methanol (1 M) at 1 mV s^{-1} on Pt/PANI in 1 M solutions of NaOH (□), Na_2CO_3 (○) and NaHCO_3 (△).

and Pt/PANI in each medium undergo extensive passivation at more positive potentials.

In Fig. 5 the Tafel plots for the oxidation of methanol on Pt/PANI in the three media viz., NaOH, Na_2CO_3 and NaHCO_3 are compared and the Tafel parameters for the same are listed in Table 2. It is observed that the methanol oxidation has the lowest potential and highest exchange current density on Pt/PANI in NaOH compared to that in Na_2CO_3 and NaHCO_3 . This suggests that methanol oxidation is most facile on Pt/PANI in NaOH when compared to other alkaline media. The Tafel slope for the oxidation of methanol on Pt/PANI in

Table 2

Tafel parameters for the oxidation of methanol (1 M) in 1 M solutions of NaOH, Na_2CO_3 and NaHCO_3 recorded at 1 mV s^{-1} on Pt/PANI

Medium	Tafel slope (mV decade^{-1})	I_0 (mA)	E (A cm^{-2})
NaOH	106	$3.51\text{E}-7$	-732
Na_2CO_3	114	$1.09\text{E}-9$	-399
NaHCO_3	101	$7.42\text{E}-12$	-266

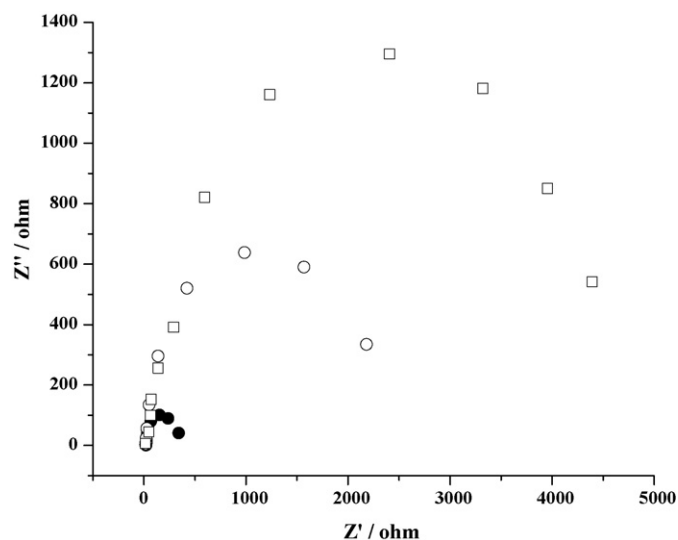


Fig. 6. Nyquist plots for the oxidation of methanol (1 M) on Pt (○), PANI (□) and Pt/PANI (●) in 1 M NaOH.

all the three media is in the range of $110 \pm 5 \text{ mV}$, which is characteristic of a mechanism involving one-electron transfer as the rate determining step for methanol oxidation.

3.2.3. Impedance studies

Fig. 6 represents the impedance response (Nyquist plots) recorded for the oxidation of methanol (1 M) in 1 M NaOH on Pt (open circles), PANI (open squares) and Pt/PANI (filled circles) at potential values where the oxidation of methanol just begins in each case. All the impedance spectra are characterized by a semi-circular region indicative of charge transfer process and that the diameter of the circles increase in the order Pt/PANI < Pt < PANI suggesting that Pt/PANI associated with the least charge transfer resistance offers the most conducive surface for the oxidation of methanol in NaOH. The relative impedance response of the three electrodes is found to be very similar in the other two media (figures not included) except for the difference in magnitudes of charge transfer resistance values.

In Fig. 7 the impedance response of Pt/PANI alone for methanol oxidation (1 M) is compared in 1 M solutions of NaOH (1), Na_2CO_3

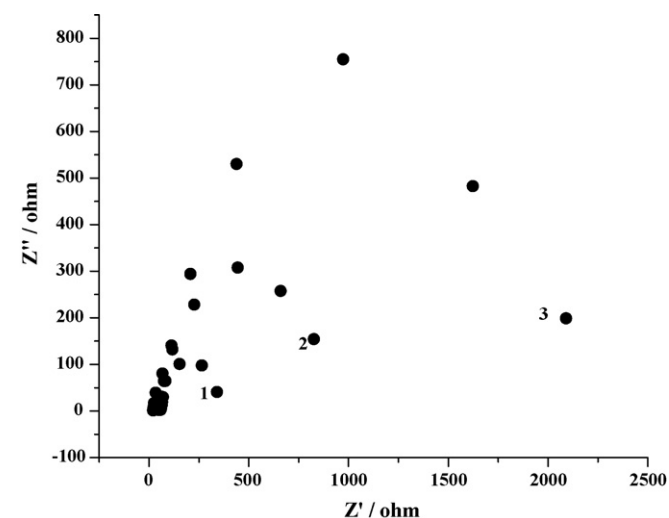


Fig. 7. Nyquist plots for the oxidation of methanol (1 M) on Pt/PANI in 1 M solutions of NaOH (1), Na_2CO_3 (2) and NaHCO_3 (3).

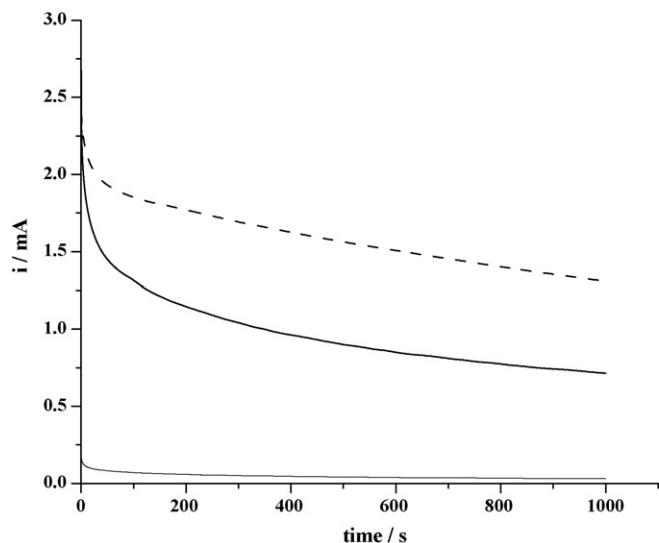


Fig. 8. Chronoamperometric response during oxidation of methanol (1 M) on Pt (solid line), Platinised Pt (bold solid line) and Pt/PANI (dashed line) at peak potentials in 1 M NaOH.

(2) and NaHCO₃ (3). It is seen that the charge transfer resistance on Pt/PANI is least in NaOH medium followed by Na₂CO₃ and NaHCO₃ which favors NaOH as a better medium for the oxidation of methanol compared to Na₂CO₃ and NaHCO₃.

3.2.4. Chronoamperometric studies

Fig. 8 shows chronoamperograms (current–time transients) recorded for the oxidation of methanol (1 M) on Pt (solid line), platinised Pt (bold solid line) and Pt/PANI (dashed line) at peak potential values. Taking the currents at the beginning of each transient as 100% (initial value), the currents at the end of the transient (end value) on each electrode was calculated. It was found that the end value of the current on the current–time transient for methanol oxidation (1 M) in 1 M NaOH recorded with Pt/PANI (dashed line) was 61% of its initial value, on Pt/Pt (bold solid line) it was 44% of its initial value and on Pt (solid line) it was 27% of its initial value. This suggests that the poisoning effect of the intermediate species

of methanol oxidation generated copiously at the peak potentials is least on Pt/PANI when compared to that on Pt/Pt and Pt. In Fig. 9 are shown the chronoamperograms recorded on Pt/PANI alone in 1 M solutions of NaOH (1), Na₂CO₃ (2) and NaHCO₃ (3) at the respective peak potential values. It is observed that while the current at the end of the transient on Pt/PANI is 61% of its initial value in NaOH, it is 44% in 1 M Na₂CO₃ and only 33% in 1 M NaHCO₃. This again suggests that the poisoning effect of the intermediate species on methanol oxidation is least on Pt/PANI in 1 M NaOH when compared to the other two media.

4. Conclusions

The following conclusions may be drawn from cyclic voltammetric, polarization, impedance and chronoamperometric studies on the electro oxidation of methanol in 1 M solutions of NaOH, Na₂CO₃ and NaHCO₃ on Pt, Pt/Pt, PANI and Pt/PANI electrodes at 25 °C.

- PANI supports the oxidation of methanol in NaOH and NaHCO₃ but not in Na₂CO₃.
- The maximum electrocatalytic activity towards methanol oxidation is exhibited by Pt/PANI when compared to Pt/Pt, PANI and Pt electrodes in all the alkaline media studied.
- The electrocatalytic activity of Pt/PANI towards methanol oxidation in the various media follows the order NaOH > Na₂CO₃ > NaHCO₃.
- Pt/PANI is least susceptible to intermediate poisoning when compared to other electrodes in all the media studied and that the poisoning effect on Pt/PANI is least in NaOH compared to the other two media.

It can, therefore, be concluded that polymer modified electrodes can be good alternatives as anodes for methanol oxidation when compared to pure metal electrodes in alkaline media.

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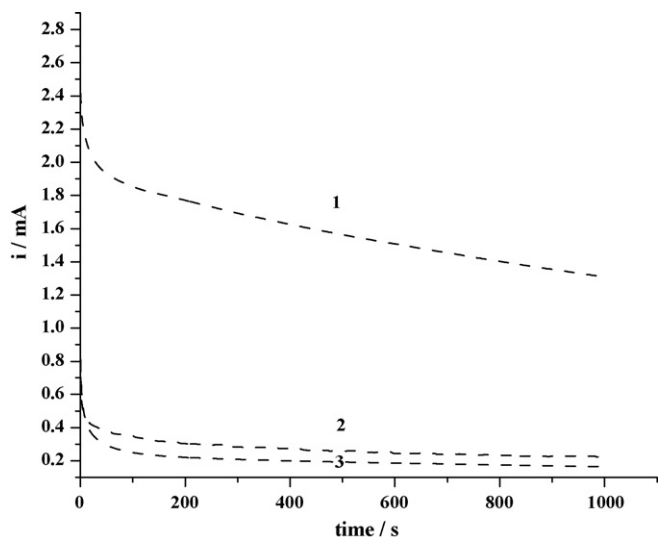


Fig. 9. Chronoamperometric response during oxidation of methanol (1 M) on Pt/PANI at the respective peak potentials in 1 M solutions of NaOH (1), Na₂CO₃ (2) and NaHCO₃ (3).

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