

Electrocatalytic oxidation of methanol on Ni modified polyaniline electrode in alkaline medium

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Abstract Electrolytically deposited Ni on polyaniline film covered carbon paste electrode (Ni/PANI/CPE) was used as anode for the electrooxidation of methanol in alkaline medium. The electrochemical behavior and electrocatalytic activity of the electrode were studied using cyclic voltammetry, impedance spectroscopy, chronomethods, and polarization studies. The morphology and composition of the modified film were obtained using scanning electron microscope and energy dispersive X-ray analysis techniques. The electrooxidation of methanol in NaOH was found to be more efficient on Ni/PANI/CPE than on bare Ni, electrodeposited Ni on Pt, Ni on glassy carbon, and Ni on CPE substrates. Partial chemical displacement of dispersed Ni on PANI with Pt or Pd further improved its performance towards methanol oxidation.

Keywords Methanol oxidation · Alkaline medium · Polyaniline · Polymer-modified electrodes · Ni modification

Introduction

Studies involving the use of non-noble metals either in their pure state or in alloyed form for the oxidation of methanol in relevance to DMFCs are rare [1–3]. However, there have been recent studies [4–7] on the use of non-noble metals and their alloys electrodeposited in their metallic or oxide/hydroxide forms from suitable baths on suitable substrates for the oxidation of methanol. Studies involving the use of polymer electrodes modified by dispersal of non-noble

metals for the methanol oxidation reaction are however rare although such systems have been used for the oxidation of other polyhydroxy compounds [8, 9]. In view of this, the preparation and use of Cu-modified polyaniline electrodes for the oxidation of methanol in alkaline medium was undertaken, the results of which have been published [10]. In a continuation of this work, we report here the preparation and use of Ni-modified PANI electrodes for the oxidation of methanol in alkaline medium.

The use of Ni electrode for the oxidation of methanol is not new. In 1971, Fleischmann et al. [11] reported the efficient conversion of alcohols to carboxylic acids using a Ni anode and suggested that catalysis occurred through the formation of NiOOH. Taraszewska et al. [12, 13] carried out the oxidation of methanol on glassy carbon (GC) electrodes, first modified electrochemically by Ni tetraaza-macrocyclic complexes and secondly by nickel hydroxide through ex-situ chemical precipitation. They reported that the former modification resulted in better catalytic activity in terms of both potential and current. El Shafei [6] modified GC electrode with nickel hydroxide by ex-situ chemical precipitation and studied the kinetics and mechanism of methanol oxidation reaction in alkaline medium on this electrode. Abdel Rahim et al. [4] dispersed Ni on graphite electrodes and obtained high current densities for methanol oxidation reaction on these electrodes. Huang et al. [7] cathodically deposited nickel hydroxide film on nickel substrate and carried out oscillatory electrocatalytic oxidation of methanol. Modification of a substrate like GC with various Ni complexes appears to be a promising methodology for obtaining Ni-based electrode systems as anodes for methanol oxidation reaction [14–18]. A few of such systems have also been used for the oxidation of amino acids and anti-inflammatory drugs [19, 20]. Ni is also widely used for alloying noble metals to enhance their

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Table 1 Optimum bath composition and operating conditions to electrodeposit Ni on PANI films

Composition	Concentration	Operating conditions
NiSO ₄ ·6H ₂ O	2.605 g/50 mL	Temperature 298 K
H ₃ BO ₃	0.31 g/50 mL	pH=3.64
Sodium lauryl sulfate	0.01 g/mL	Deposition potential -1.2 V vs. SCE Q=-1.64 C for a loading of 0.5 mg Ni

performance towards methanol oxidation in both acid and alkaline media [21–25].

Nickel-modified electrodes have also been developed by dipping a conducting polymer in a Ni solution which results in the formation of a complex between Ni ions and amine sites in the polymer backbone [26, 27]. Vilchez et al. [28, 29] have used a co-polymer of aniline and sulfonated polyaniline as matrices for dispersion of Ni-cyclam to obtain catalytic systems to oxidize methanol in alkaline medium. It, therefore, appears that there is scope for studies concerning the use of conducting polymers as a matrix for the dispersion of Ni particles and its subsequent use for the oxidation of methanol, though such systems have been used for hydrogen evolution reaction [30–33] and as corrosion resistant coatings [34]. In view of this, the electrocatalytic oxidation of methanol in alkaline media on polyaniline matrix with dispersed nickel particles was undertaken and the results are reported herein.

Experimental

All solutions were prepared using analytical grade reagents and double distilled water. The electrochemical experiments were performed at room temperature using an Autolab PGSTAT30 potentiostat/galvanostat model with pilot integration controlled by GPES 4.9 software in a three-compartment cell with a Luggin capillary connecting the working and reference electrode chambers. The working electrode was a carbon paste electrode (CPE) with an area of 0.1256 cm². CPE was prepared by blending a mixture of graphite powder and paraffin through hand mixing and the paste was then inserted in a glass tube with electrical contact. A layer of the CPE was removed with a spatula and smoothed on an emery paper to get a smooth and fresh surface. Pt wire and saturated calomel electrode (SCE) acted as counter and reference electrodes, respectively. The morphology of the as such and modified polymer films obtained on the cleaned substrates were examined using a scanning electron microscope (Leica Cambridge Ltd., Leica S 440i). The elemental analyses and the surface composition of the deposits on the polymer matrix were obtained by energy dispersive X-ray analysis (EDX) data from X-ray diffractometer (Oxford ISIS link software). The electrochemical experimental details have been described at appropriate places in the text.

Results and discussion

Preparation of Ni modified electrodes

Initially, the electropolymerization of aniline was carried out onto a clean CPE from a solution of 0.1 M aniline in 0.5 M H₂SO₄ potentiostatically at +1.2 V vs. SCE until a desired amount of charge was passed. The thickness of the polymer film was measured in terms of charge passed during polymerization. In this study, the thickness of the polymer film was kept constant by maintaining the charge passed at a constant value of 100 mC for various studies except for the effect of thickness of the polymer on methanol oxidation after modification. The PANI film obtained on CPE was modified by dispersing Ni particles in the PANI matrix from a bath containing Ni ions. The optimized bath conditions for electrolytic deposition of Ni are as shown in Table 1.

A problem associated with electrodeposition of Ni is that, as Ni gets deposited on a substrate, hydrogen evolution begins on the deposited Ni since the potential used for depositing Ni is highly negative and favorable for hydrogen evolution. Hence, it is difficult to ascertain the efficiency of deposition as the charge associated will be due to both reduction of Ni and hydrogen evolution. Abdel Rahim et al. [4] have calculated an average efficiency of 62.1% for potentiostatic deposition of Ni on a GC electrode

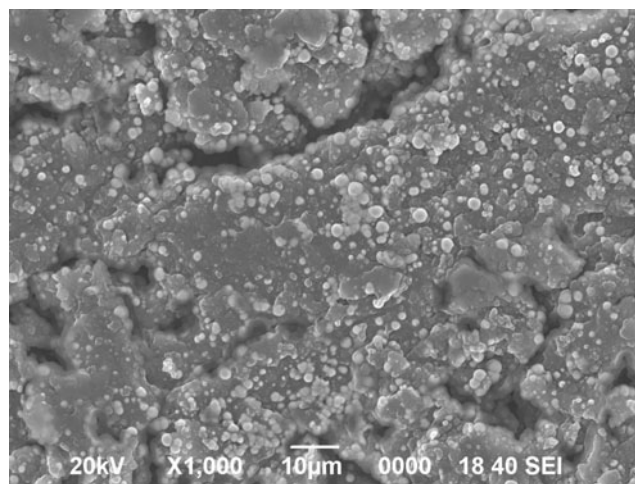


Fig. 1 SEM of Ni deposit on PANI film

by complexation method. However, Maria Hepel et al. [35] in their attempts to deposit Ni on polypyrrole-modified electrodes at a constant potential have observed that the evolution of hydrogen is inhibited to a greater extent on a conductive polymer film than on a metallic electrode resulting in a higher current efficiency for the nickel deposition. The same observation was reported by Lee et al. [36] wherein Ni was deposited using CV onto a polypyrrole film. To compare the behavior during Ni

deposition on CPEs and on PANI-covered CPEs, we carried out the deposition of Ni from the bath given in Table 1 onto PANI-covered CPE and onto bare CPE. It was observed that in the presence of PANI film, the extent of hydrogen evolution during Ni deposition was comparatively lower than on just CPE. Therefore, we expect a higher efficiency for Ni deposition on PANI film; however, we have not attempted to calculate it exactly. For the sake of convenience, we have assumed 100% efficiency for the reduction

Fig. 2 **a** Electrochemical behavior of Ni/PANI/CPE in 0.1 M NaOH at different scan rates, **b** electrochemical behavior of Ni/PANI/CPE in different concentrations of NaOH. Scan rate 25 mV s^{-1} , **c** CVs for the oxidation of 0.1 M Methanol in 0.1 M NaOH on different electrode systems. *Inset* CVs for methanol oxidation on Ni/PANI/CPE for different cycles. Scan rate 25 mV s^{-1}

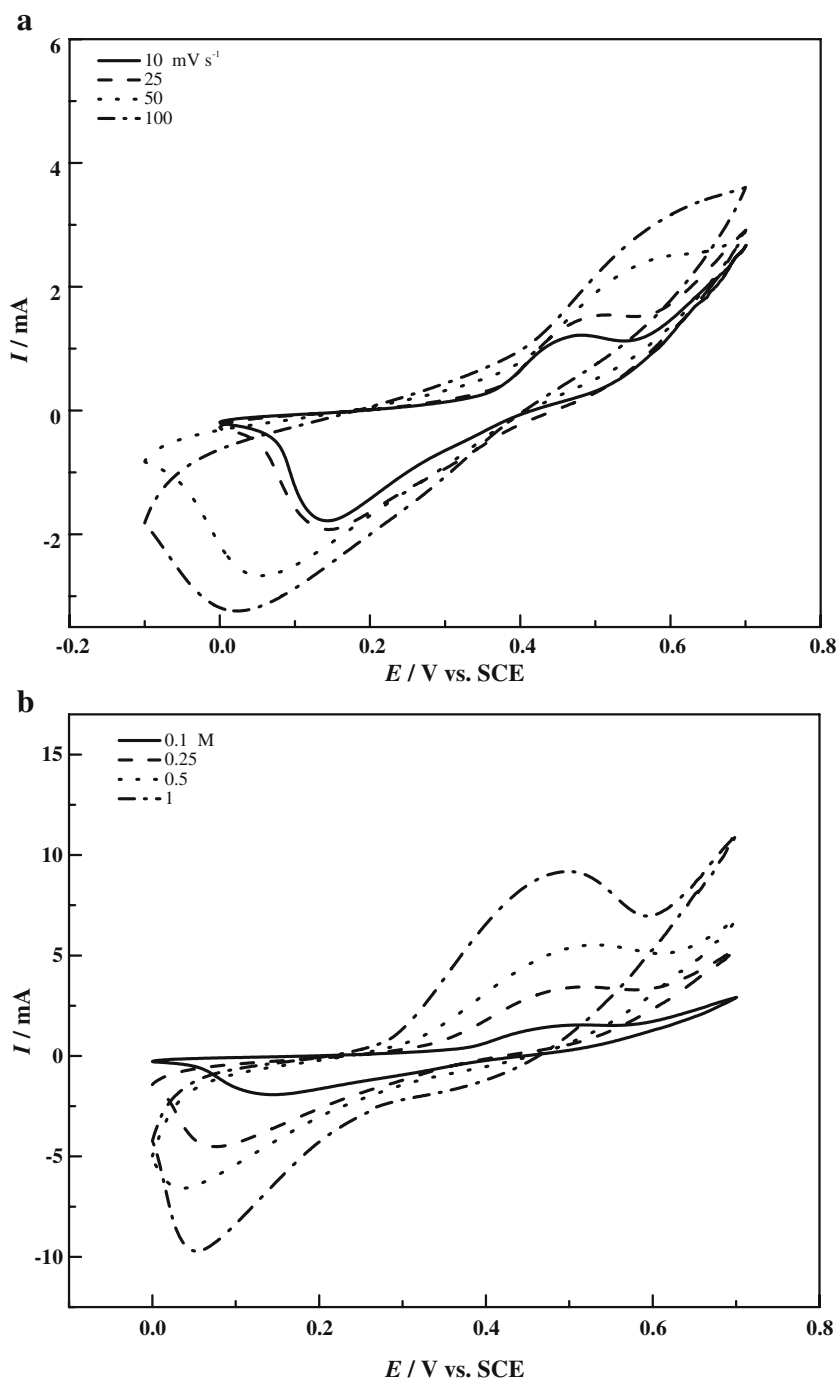
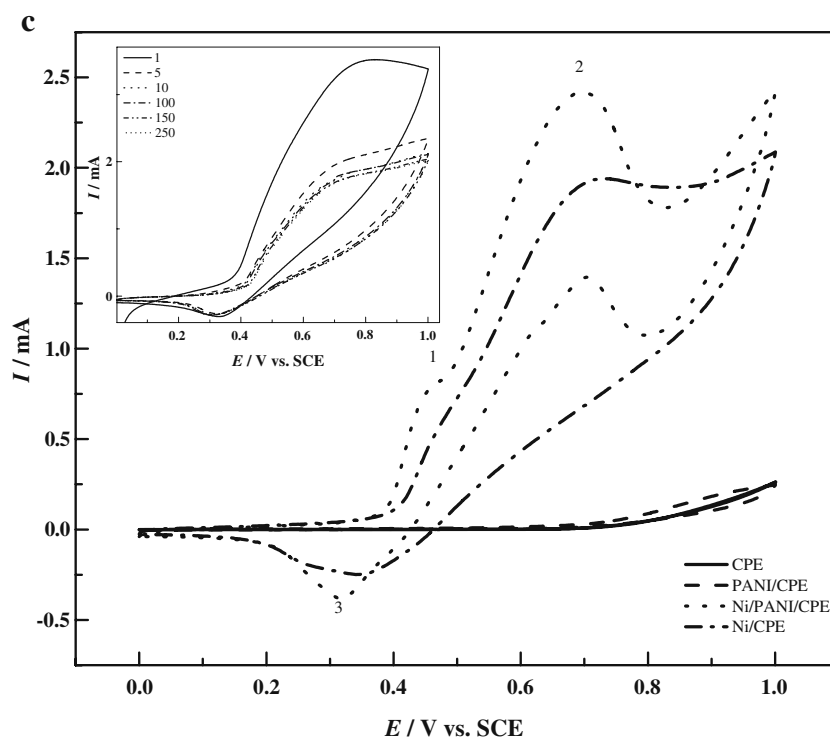


Fig. 2 (continued)



of Ni^{2+} to Ni and the amount of Ni deposited was monitored from the charge passed during the reduction process using the relation $N_{\text{Ni}} = Q/nF$ where N_{Ni} is the number of moles of nickel deposited, n the number of electrons (2), Q and F being the charge and the Faraday values, respectively. The amount of Ni deposited was kept constant at 0.5 mg (on the basis of theoretical calculation) for all the studies unless otherwise mentioned. The scanning electron micrograph (SEM) of PANI modified with 0.1 mg of Ni on a CPE is shown in Fig. 1. It shows uniform and three-dimensional distribution of Ni in the form of spherical clusters on the PANI matrix. There is complete absence of a continuous PANI phase and the deposit is highly porous in accordance with the earlier observations [36].

The Ni-modified PANI film on CPE (Ni/PANI/CPE) obtained from the above procedure was used for the oxidation of methanol followed cyclic voltammetrically in NaOH solution.

Electrochemical behavior of Ni/PANI/CPE in absence and presence of methanol in NaOH

Figure 2a shows the electrochemical behavior of Ni/PANI/CPE in 0.1 M NaOH in the potential range 0–0.7 V at different scan rates. The behavior is similar to that reported in the literature on Ni anode [11] and on different Ni systems [4, 14–18]. In the cyclic voltammograms (CVs),

the pair of peaks may be attributed to $\text{Ni}(\text{OH})_2/\text{NiOOH}$ transformation which is in excellent agreement with earlier observations although the exact potential values characterizing each feature may differ due to differences in experimental conditions. At potentials higher than 0.7 V, oxygen evolution is observed. As the scan rate is increased, the currents for the redox process also increase. The effect of pH on the behavior of Ni/PANI/CPE in NaOH was also studied and the corresponding CVs are given Fig. 2b. It is evident that with increase in NaOH concentration the peak currents increase and the potentials shift in the negative direction along with a decrease in potential for oxygen evolution. These changes are due to more facile formation of $\text{Ni}(\text{OH})_2$ and its transformation to oxyhydroxide at higher concentrations of OH^- .

In Fig. 2c are shown the CVs for bare CPE (solid line), polyaniline covered carbon paste electrode (PANI/CPE; dashed line), Ni-dispersed polyaniline film on carbon paste electrode (Ni/PANI/CPE; dotted line) and Ni dispersed on carbon paste electrode (Ni/CPE; dash-dotted line) recorded in 0.1 M NaOH+0.1 M methanol in the potential range 0–1 V at 25 mV s^{-1} . From the CVs of CPE and PANI/CPE, it is clear that the two electrodes exhibit no activity towards oxidation of methanol. However, Ni/PANI/CPE shows a good electrocatalytic activity towards oxidation of methanol. In presence of methanol, the pair of peaks (1 and 3) corresponding to the $\text{Ni}(\text{OH})_2/\text{NiOOH}$ transformation are shifted towards lower potential values with diminished

currents resulting from the adsorption of methanol molecules on the Ni sites and an additional peak 2 which may be attributed to the oxidation of methanol appears around 0.68 V. Apparently, methanol is oxidized on nickel electrode through the formation of NiOOH as has been suggested in earlier studies [11, 27]. The additional anodic peak in the reverse scan characteristic of methanol oxidation is also very much clear. On successive cycling, the currents for methanol oxidation decrease up to 10 cycles and thereafter remain fairly constant even up to 300 cycles (CVs in the inset of Fig. 2c). The Ni/PANI/CPE shows a negative shift in the

potential and a little higher current for methanol oxidation when compared with Ni/CPE.

Optimization of electrode and bath variables for efficient performance of Ni/PANI/CPE towards methanol oxidation

Effect of nickel loading

Assuming 100% efficiency for reduction of Ni, charge corresponding to the deposition of different amounts of Ni on the PANI film was passed and the electrodes so prepared

Fig. 3 a Variation of currents for oxidation of 0.1 M methanol in 0.1 M NaOH at various nickel loadings on PANI film. Scan rate 25 mV s^{-1} . Effect of 0.5 mg Ni-modified PANI prepared **b** potentiodynamically for different cycles **c** potentiostatically for various amounts of charge passed on the oxidation currents of 0.1 M methanol in 0.1 M NaOH. Scan rate 25 mV s^{-1}

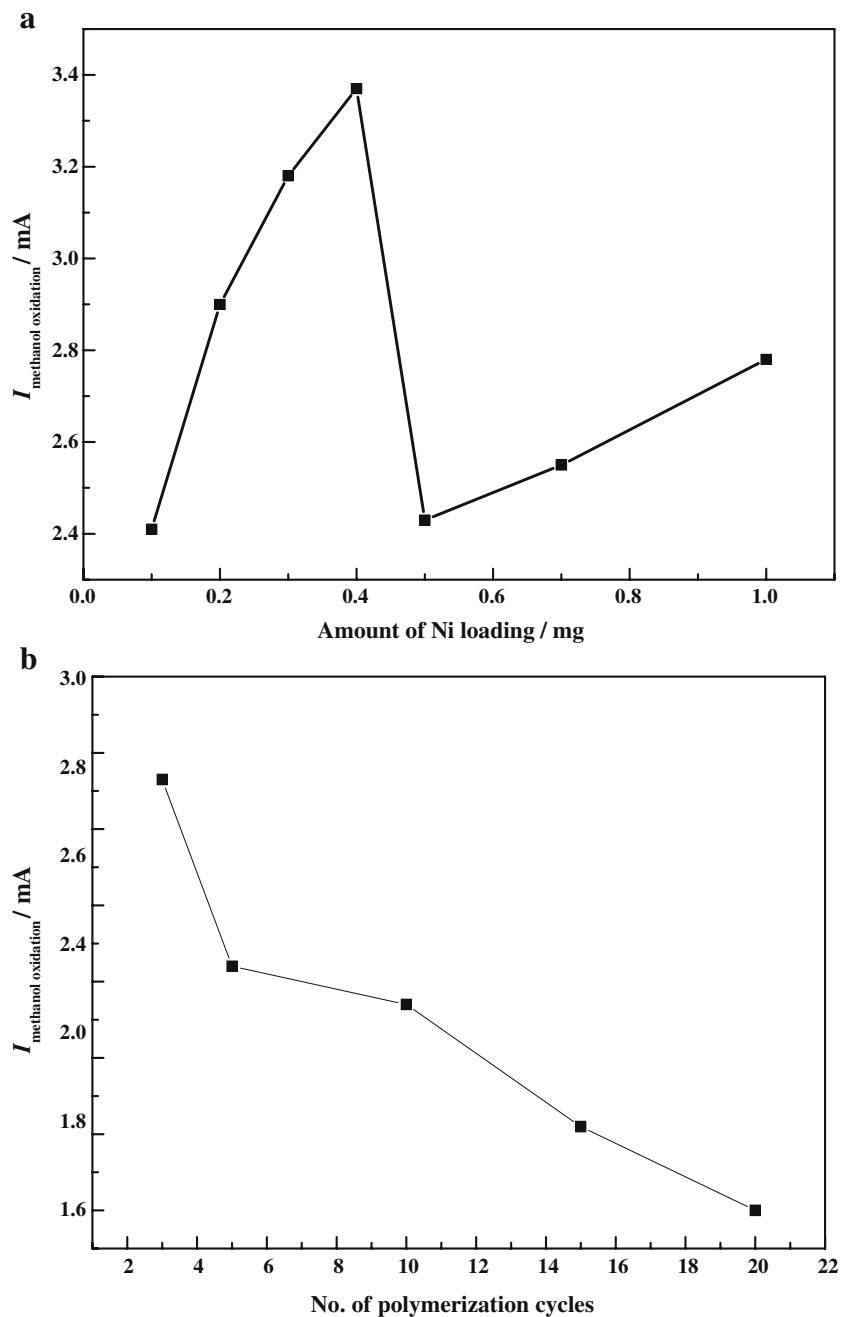
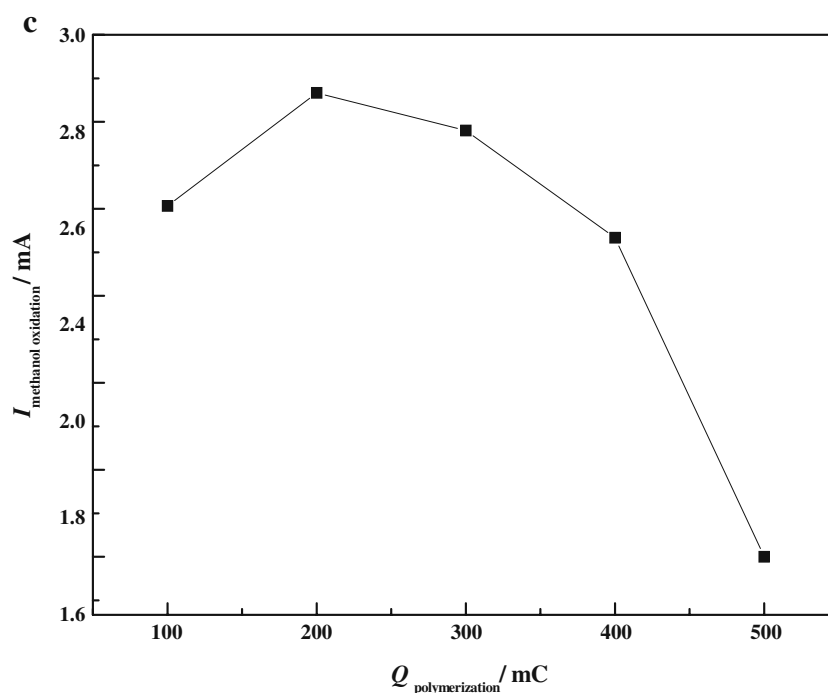


Fig. 3 (continued)



were used for methanol oxidation. It was observed that as the amount of Ni in the film increased, the methanol oxidation currents also increased up to a loading of 0.4 mg; after which, there was no regular variation in the currents with further increase in the time of charge passed during deposition (Fig. 3a). This may be due to the fact that continuous evolution of hydrogen over a longer period of time probably hinders further deposition of Ni and adversely affects the morphology of the deposit.

Effect of nickel incorporation method into PANI

The oxidation of methanol was studied with Ni/PANI/CPE loaded with 0.5 mg of Ni by controlling the charge passed potentiostatically at -1.2 V and potentiodynamically in the potential range -0.3 V to -1.2 V. It was observed that potentiostatic incorporation of Ni in PANI favors better performance than the potentiodynamic incorporation due to incomplete deposition of Ni because of its partial dissolution probably in the latter mode. It was also observed that when -1.0 and -0.9 V were used for Ni deposition, there was no significant affect on its catalytic activity but the hydrogen evolution had significantly reduced at these two lower potentials. At potentials higher than -1.2 V, hydrogen evolution was further enhanced and affected the polymer stability.

Effect of polymer deposition method

In order to check whether the method of deposition of the polymer had any influence on the electrocatalytic

activity of the modified electrode, methanol oxidation was carried out first on an electrode wherein the polymer had been deposited potentiodynamically for different number of cycles (Fig. 3b) followed by the electrode on which the polymer was deposited potentiostatically for different amounts of charge passed (Fig. 3c). It was observed that the maximum methanol oxidation currents obtained were approximately the same (2.7 mA) on the two electrodes when the polymer in the former was obtained by cycling the potential between -0.20 to $+1.2$ V thrice while the polymer in the latter was obtained by the passage of 200 mC of charge at a constant potential of $+1.2$ V. The potentiostatically prepared electrodes appeared to sustain the oxidation currents for longer periods and, therefore, more durable than the potentiodynamically prepared electrodes.

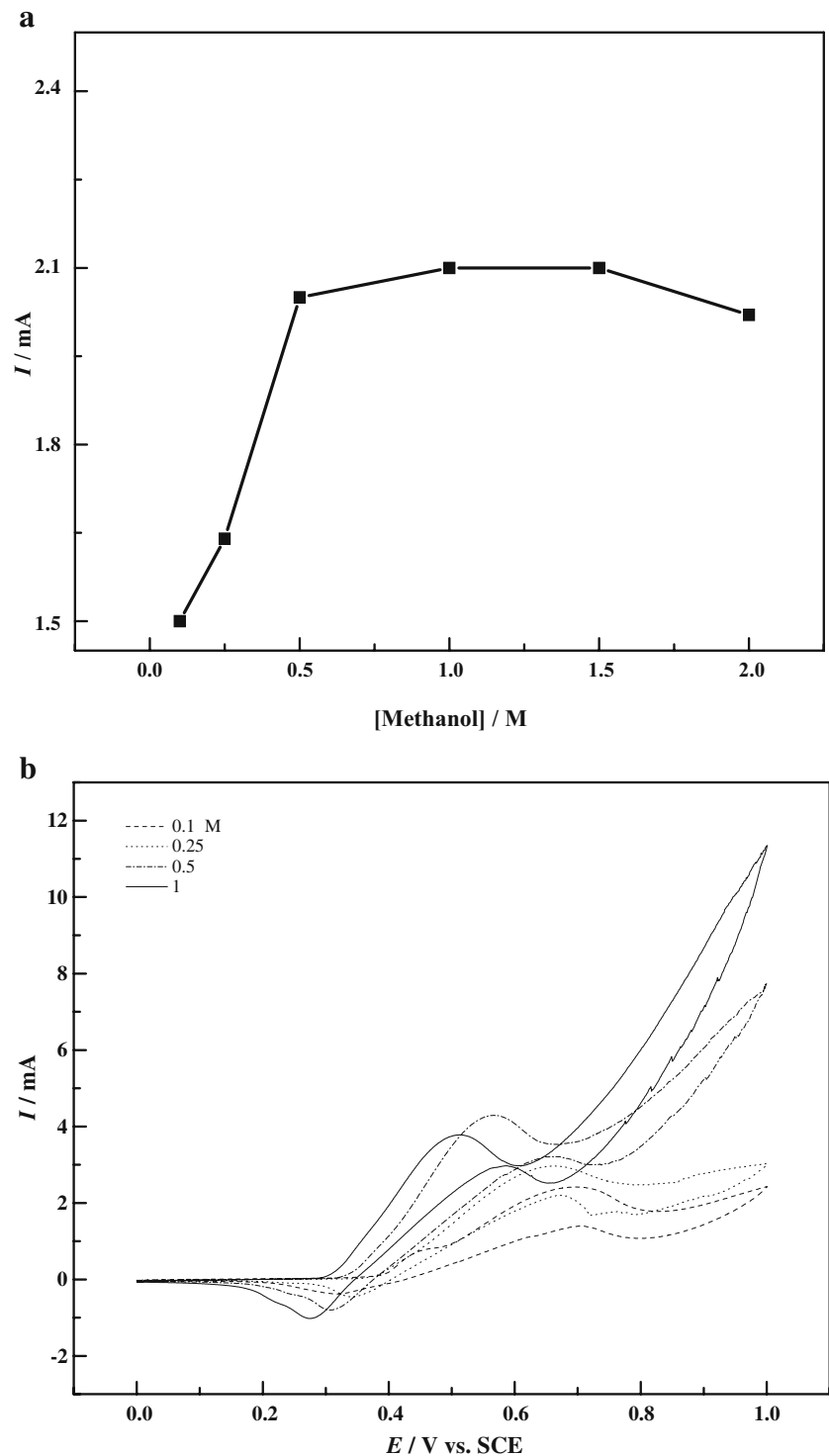
Methanol concentration

The methanol oxidation current increased steadily up to a concentration of 1 M of methanol after which it remained almost constant (Fig. 4a). It appears that the reaction sites get saturated at this concentration and hence the constancy of current beyond 1 M.

NaOH concentration

In Fig. 4b are shown the CVs recorded on a Ni/PANI/CPE at various concentrations of NaOH containing 0.1 M methanol. It is observed that as the concentration of NaOH

Fig. 4 Effect of **a** methanol concentration on its oxidation currents in 0.1 M NaOH, **b** NaOH concentration on oxidation currents of 0.1 M methanol, on Ni/PANI/CPE (Ni loading 0.5 mg). Scan rate 25 mV s^{-1}



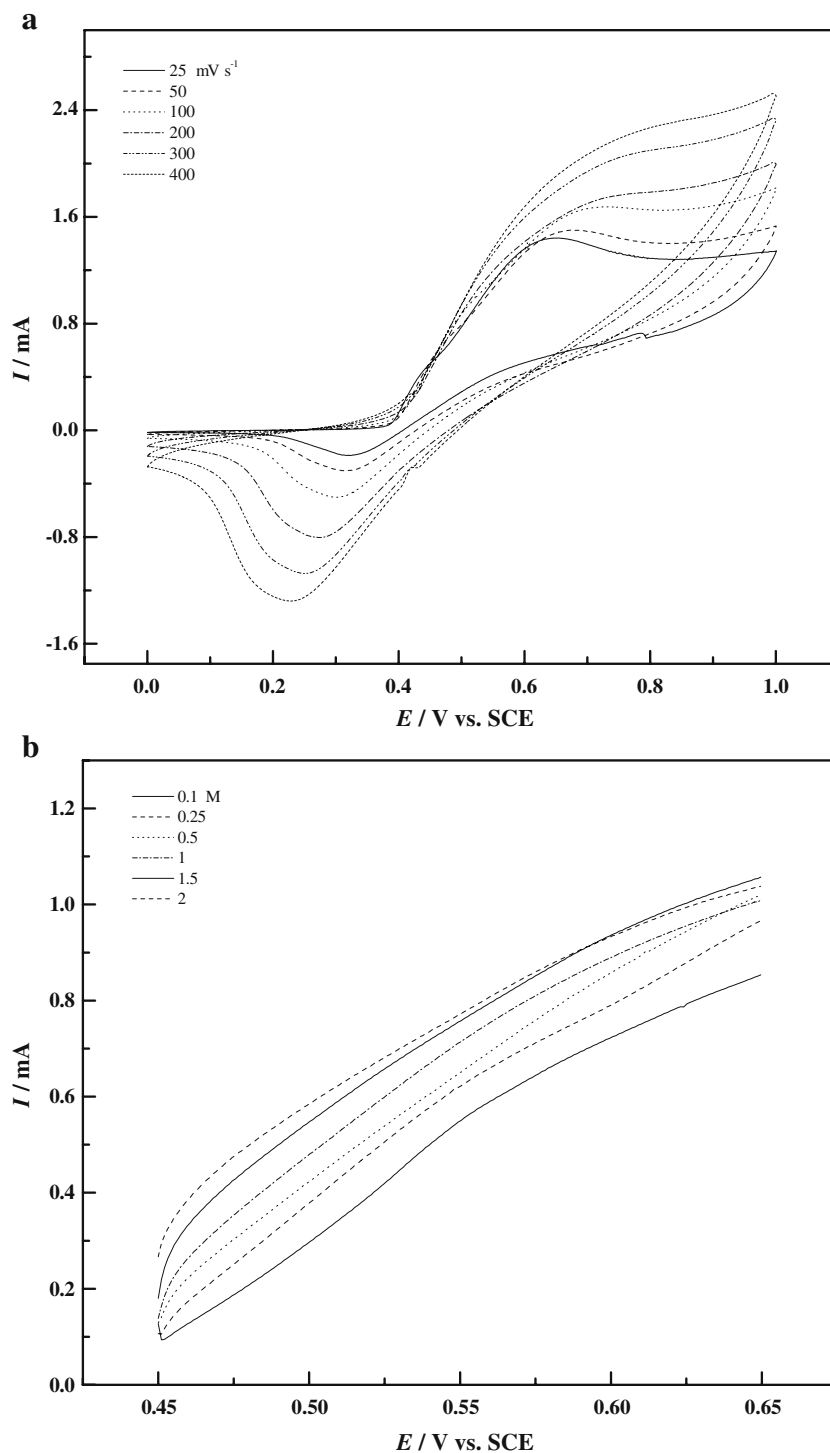
is increased from 0.1 to 1 M, the methanol oxidation currents increase and the peak potentials get shifted to less noble values in the very same manner observed for the transformation of $\text{Ni}(\text{OH})_2/\text{NiOOH}$ as a function of $[\text{OH}^-]$ (Fig. 2b). This is because the electroactive species that is assumed to be detrimental for methanol oxidation is the NiOOH.

Electrochemical characterization of the process of methanol oxidation in NaOH on Ni/PANI/CPE

Effect of scan rate

Figure 5a represents cyclic voltammograms for methanol oxidation at different scan rates in a solution of

Fig. 5 a Effect of scan rate on the CVs for oxidation of 0.1 M methanol in 0.1 M NaOH on Ni/PANI/CPE, **b** potentiostatic anodic polarization of Ni/PANI/CPE in 0.1 M NaOH solution containing different concentrations of methanol. Scan rate 5 mV s^{-1} . **c** Nyquist, **d** Bode plots for the oxidation of 0.1 M methanol in 0.1 M NaOH at 0.5 V on Ni/PANI/CPE. *Solid lines* represent fitted curves. **e** Chronoamperograms, **f** chronopotentiograms for the oxidation of 0.1 M methanol in 0.1 M NaOH at various potentials and currents respectively on Ni/PANI/CPE

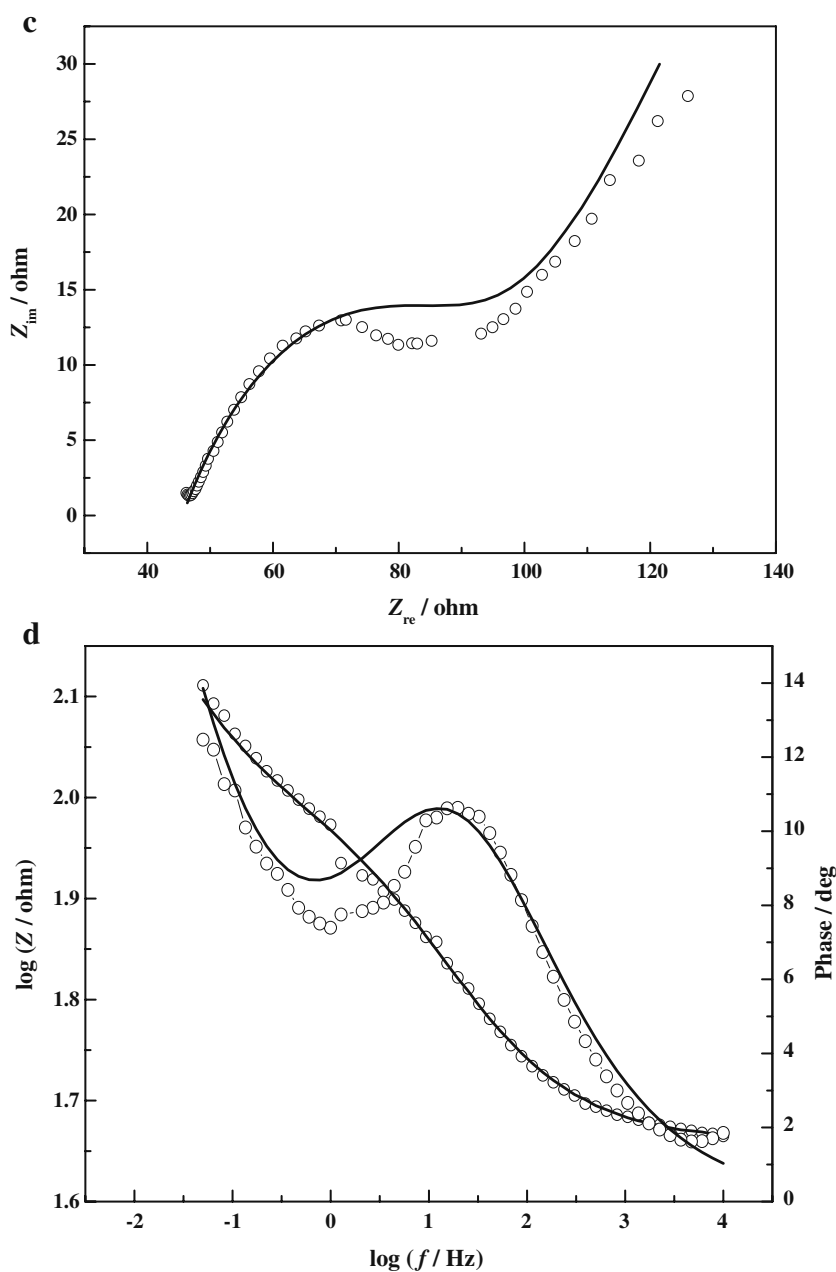


0.1 M methanol+0.1 M NaOH. The height of the oxidation peak of methanol increases with increase in the scan rate and a potential shift towards more positive values is observed. The positive shift in the peak potential may be due to the IR drop generated at high current density values. The increase in currents with scan rate indicates a diffusion-controlled process for methanol oxidation at these electrodes.

Polarization studies

Potentiostatic anodic polarization curves recorded with a Ni/PANI/CPE electrode in 0.1 M NaOH solutions containing different concentrations of methanol at 5 mV s^{-1} are shown in Fig. 5b. It is observed that the oxidation commences around 0.45 V and the current continues to rise up to a potential of 0.65 V after which it plateaus

Fig. 5 (continued)



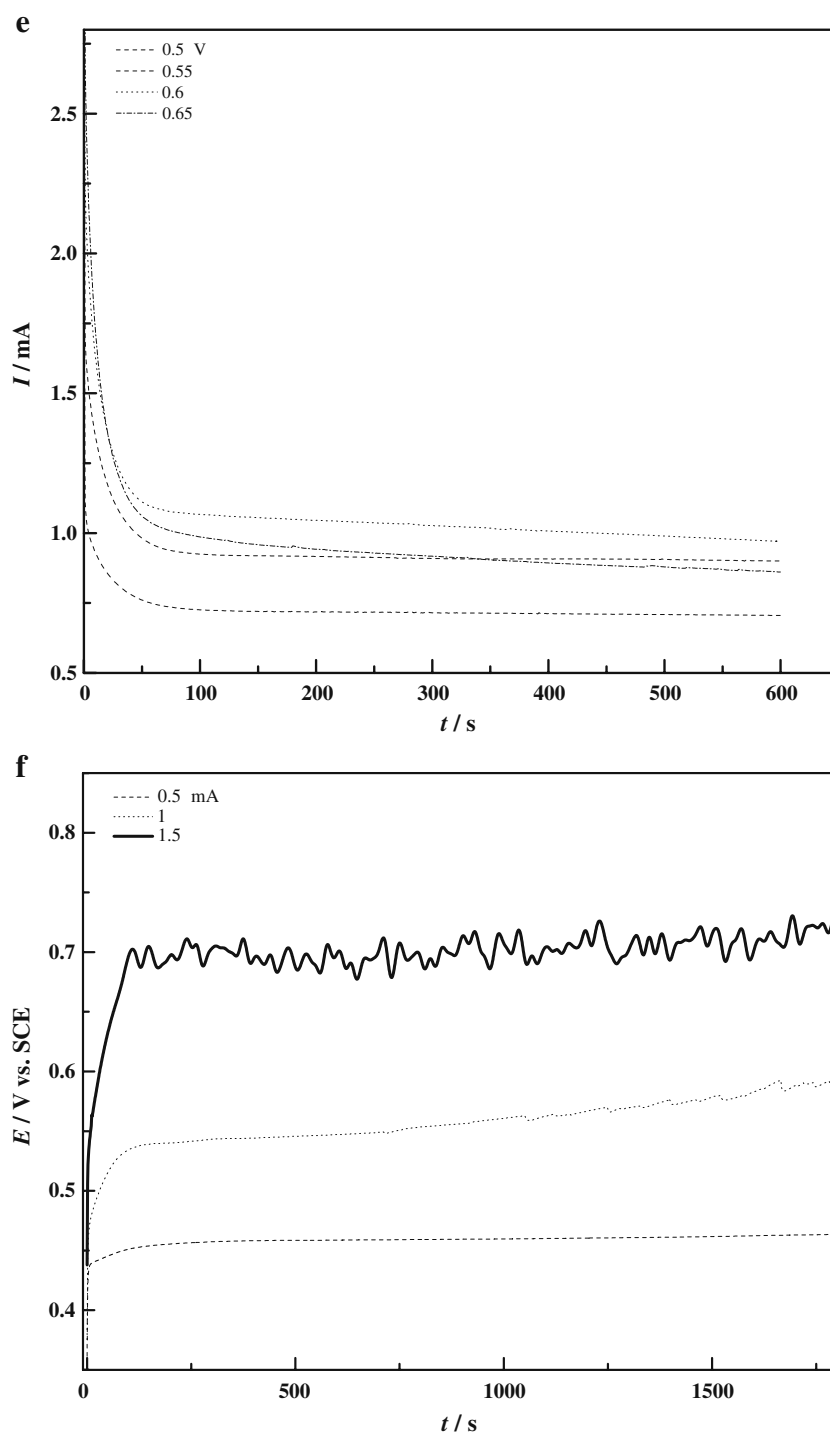
indicating diffusion controlled process. The Tafel slope was found to be 100 mV dec^{-1} suggesting the involvement of an electron transfer in the rate determining step.

Impedance studies

The electrochemical impedance spectroscopic studies for the oxidation of 0.1 M methanol in 0.1 M NaOH on Ni/PANI/CPE was carried out at different potential values chosen from the foot and rising portion of the currents in the voltammetric curve in the frequency range 100 KHz–50 mHz with an amplitude of 5 mV of the ac voltage employed and the impedance response of the system was

recorded. The Nyquist plots at lower potentials, i.e., 0.4, 0.45, and 0.5 V were associated with two semicircles which may be due to redox reaction associated with Ni and for methanol oxidation. However, the plots at higher potentials, i.e., 0.55, 0.6, and 0.65 V showed only one semicircle in the high-frequency region associated with charge-transfer process involved in methanol oxidation tending towards linear behavior in the low frequency region corresponding to diffusion-controlled process. A circuit involving the Warburg impedance fitted well with the experimental data. At 0.7 V, a potential very close to the peak potential, the response in the low frequency region was slightly distorted probably due to the oxidation of methanol by different

Fig. 5 (continued)



mechanisms. The Nyquist and Bode plots at 0.55 V are shown in Fig. 5c and d with the solid lines representing the fitted curves.

Chrono studies

From the chronoamperometric (Fig. 5e) and chronopotentiometric (Fig. 5f) studies, it is found that the reaction is

catalyzed over a range of applied potentials and currents and gives an idea about the stability of the electrode during prolonged electrolysis. The chronopotentiograms recorded at low current values of 0.5 and 1 mA (Fig. 5f) initially show a small rise in potential and later the potential seems to attain higher values indicating the methanol oxidation reaction being catalyzed by the formation of higher valent nickel. The initial rise in the

Fig. 6 Comparison of maximum currents for the oxidation of methanol observed on different electrode systems

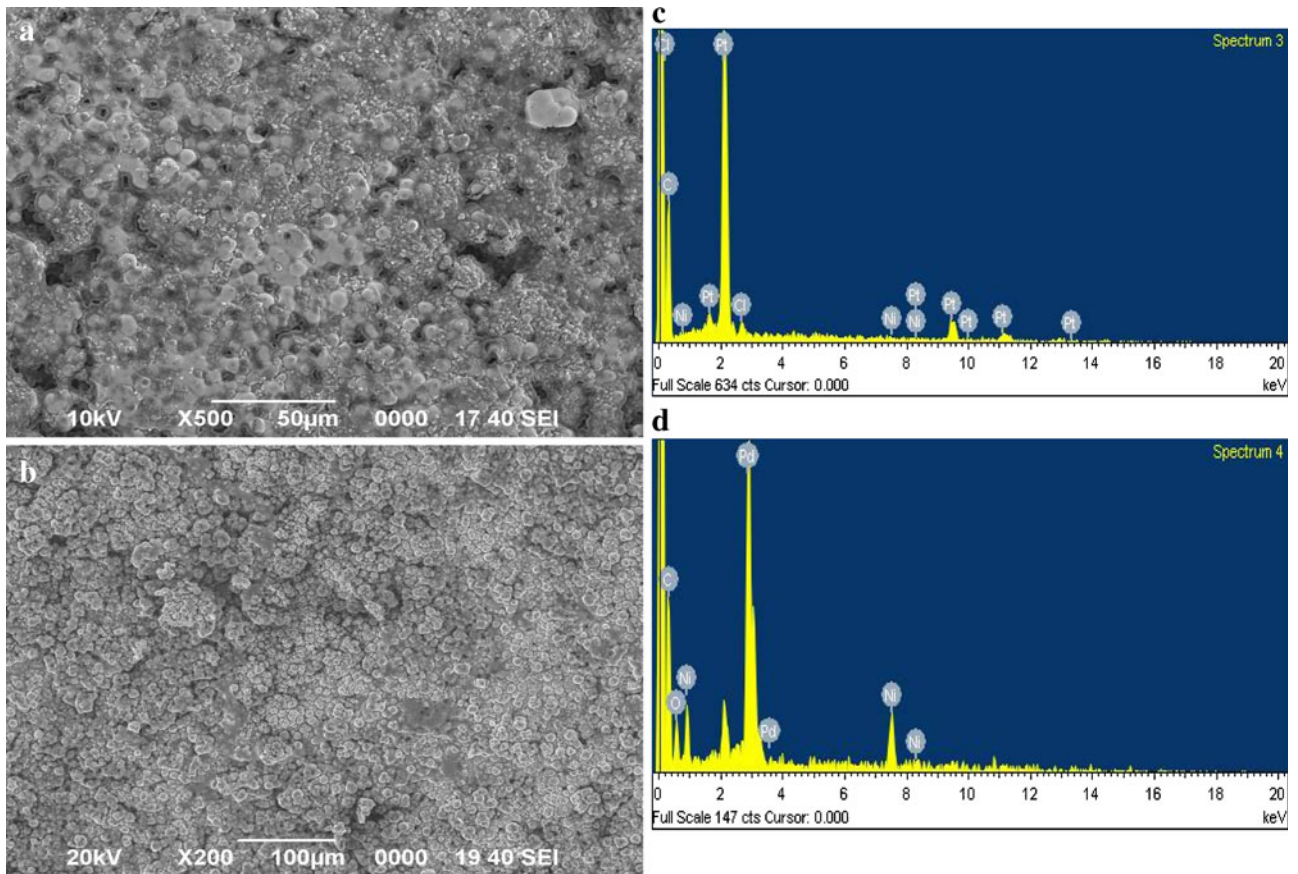
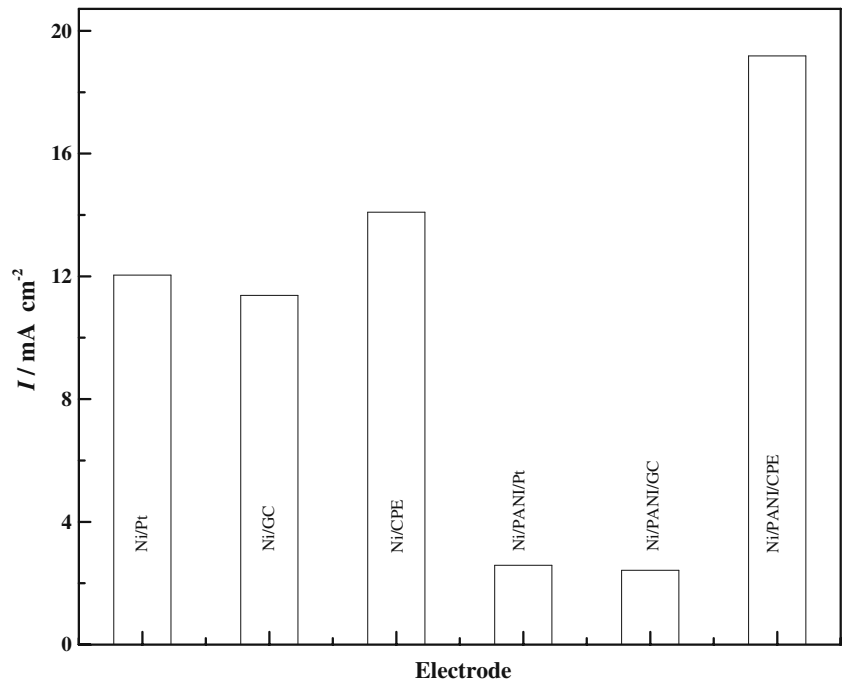
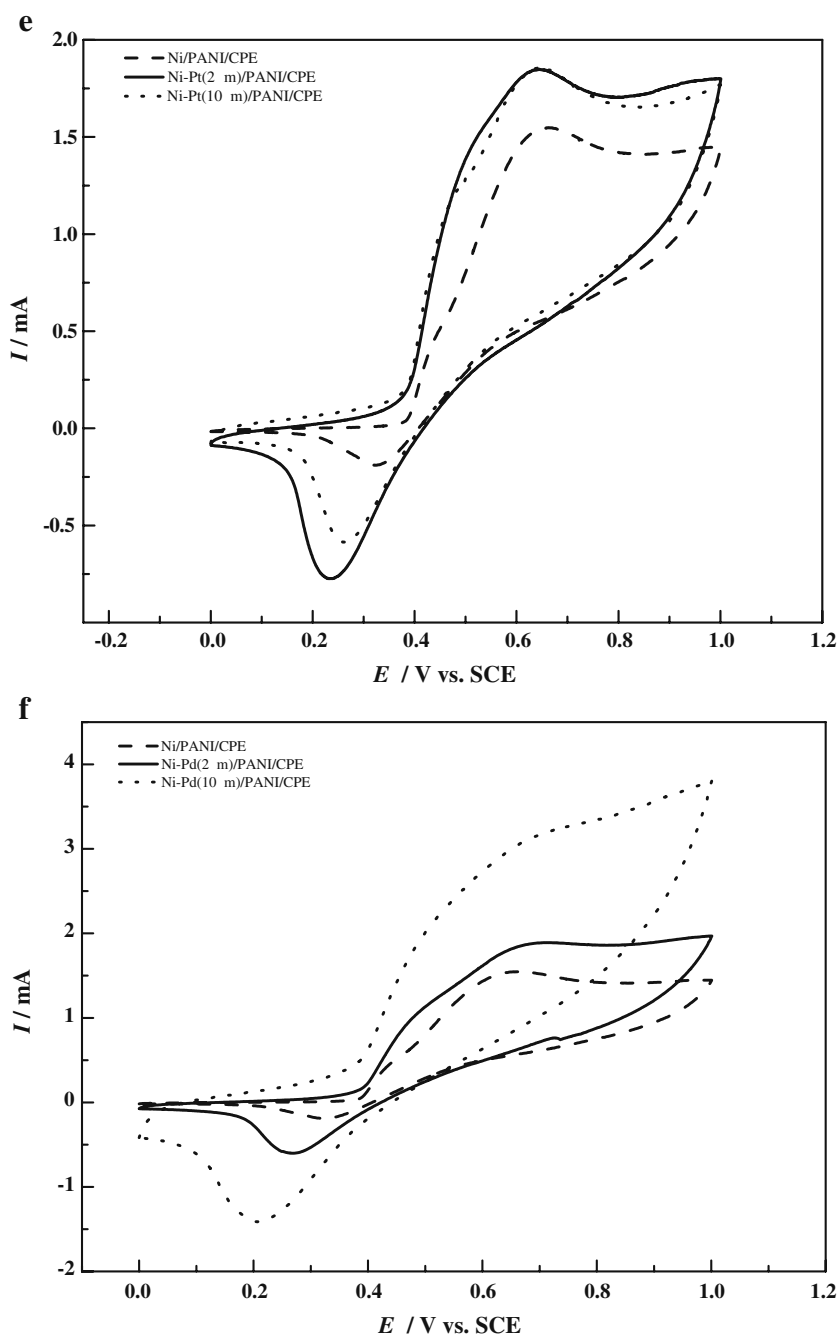


Fig. 7 SEM of partially displaced Ni deposit on PANI film with **a** Pt, **b** Pd. EDX of partially displaced Ni deposit on PANI film with **c** Pt, **d** Pd. CVs for the oxidation of 0.1 M methanol in 0.1 M NaOH on partially displaced Ni deposit on PANI film with **e** Pt **f** Pd. Scan rate 25 mV s^{-1}

Fig. 7 (continued)



potential may correspond to the oxidation of lower valent nickel species.

Comparison of performance of Ni/PANI/CPE with other electrode systems

To assess the performance of Ni/PANI/CPE in relation to other electrode systems, methanol oxidation was carried out on bare Ni, Ni on Pt (Ni/Pt), Ni on glassy carbon (Ni/GC), Ni/PANI/GC, and Ni/PANI/Pt in the latter four of which the

same amount of Ni (0.1 mg) had been loaded as in Ni/PANI/CPE. It was found that bare Ni did not support methanol oxidation in agreement with previous reports [4]. Though GC hardly supports methanol oxidation either in acid or alkaline medium, it became active after Ni was deposited on it. The relative oxidation currents on different electrodes along with that of Ni/PANI/CPE and Ni/CPE are shown in the form of a bar graph in Fig. 6. It is evident that the performance of Ni/PANI/CPE towards methanol oxidation is relatively better among the different electrode

systems. This can be attributed to both CPE and the PANI matrix which favor efficient dispersal of Ni microparticles thereby enhancing its activity.

Enhancement of the performance of Ni/PANI/CPE

In principle, Ni can be partially replaced by Pd, Pt, Cu, Ag, and Au due to the displacement reactions on its surface leading to bimetallic systems that can be used for catalyzing electrochemical reactions. Wang et al. [37] prepared a series of bimetallic systems involving dispersed monolayers of Pd, Pt, and Cu on Ni by displacement reactions and have characterized them by XRD and XPS. Papadimitriou et al. [38] prepared platinum- and gold-coated copper, iron, cobalt, and nickel on glassy carbon substrates by displacement reactions and demonstrated the utility of these electrodes towards hydrogen evolution reaction. Monolayer-dispersed Pt/Ni bimetallic catalyst was prepared through replacement reaction by Wang et al. [39] and its catalytic activity for the hydrogenation of cyclohexene, styrene, acetone, and butyl aldehyde was demonstrated. These attempts show that active electrocatalysts with considerably reduced noble metal loading through chemical displacement of a less noble deposited metal by a monolayer of more noble metal can be very conveniently obtained. Based on this procedure, the less noble Ni surface of the Ni/PANI/CPE has been partially chemically replaced by more noble Pt and Pd by dipping the electrode in 1% chloroplatinic and palladium chloride solutions, respectively, for 2 min initially. The displaced surfaces showed a rough-grained structure (Fig. 7a, b) probably resulting from the competition between the oxidation of nickel and reduction of platinum or palladium which cover the underlying nickel. The EDX data (Fig. 7c, d) showed an incorporation of 6.26% Pt and 16.8% Pd (atomic %) in the displaced films, respectively.

When methanol oxidation was studied on these electrodes, it was found that the oxidation currents increased considerably along with a small decrease in onset potential when compared to that observed on Ni/PANI/CPE (Fig. 7e, f.) It was also observed that increasing the dipping time of the electrode in Pt and Pd solutions increased the activity for methanol oxidation only in case of Pd and remained constant in case of Pt. Further, the durability of these electrodes in terms of reproducibility and constancy of currents with cycling was found to be far better than that on Ni/PANI/CPE. Shobha et al. [22] have attributed the higher activity of Ni-Pd alloys prepared electrochemically to an increase in surface area due to alloying of Ni by Pd. Liu et al. [40] have shown that PdNi/C catalyst has higher electrocatalytic activity for methanol oxidation in alkaline media than a comparative Pd/C catalyst. Singh et al. [41] have reported that Pd-1% MWCNT-1% Ni composite electrode had the greatest electrocatalytic activity towards oxidation of methanol which is ascribed to their improved geometrical as well as electronic properties.

Therefore, it may be surmised that partial chemical displacement of dispersed Ni on PANI with Pt or Pd further improved its performance towards methanol oxidation probably due to synergistic effects of the two metals and an increase in surface area.

Conclusions

1. Ni-modified PANI films on Pt, GC, and CPE substrates were found to be effective catalysts for methanol oxidation in alkaline medium in terms of reproducibility as well as durability.
2. Electrode parameters such as its preparation method (both PANI and Ni/PANI/CPE), amount of nickel loading, and bath variables such as methanol and NaOH concentration influence the activity of the electrode towards methanol oxidation.
3. The mechanism of oxidation of methanol on dispersed Ni in PANI in NaOH appears to be very similar to that on different Ni electrodes.
4. The performance of the electrode towards methanol oxidation is enhanced after partial chemical displacement of dispersed Ni with Pt and Pd.

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References

1. Jafarian M, Moghaddam RB, Mahjani MG, Gopal F (2006) *J Appl Electrochem* 36:913
2. Heli H, Jafarian M, Mahjani MG, Gopal F (2004) *Electrochim Acta* 49:4999
3. Vijayarathi T, Muzhumathi S, Noel M (2007) *J Appl Electrochem* 37:297
4. Abdel Rahim MA, Abdel Hameed RM, Khalil MW (2004) *J Power Sources* 134:160
5. Shafia Hoor F, Tharamani CN, Ahmed MF, Mayanna SM (2007) *J Power Sources* 167:18
6. El Shafei AA (1999) *J Electroanal Chem* 471:89
7. Huang W, Li ZL, Peng YD, Chen S, Zheng JF, Niu ZJ (2005) *J Solid State Electrochem* 9:284
8. Guascito MR, Boffi P, Malitesta C, Sabbatini L, Zamboni PG (1996) *Mat Chem Phys* 44:17
9. Fabiana DE, Marioli JM, Alejandro HA, Leonides ES (2003) *Talanta* 61:341
10. Nagashree KL, Ahmed MF (2009) *J Appl Electrochem* 39:403
11. Fleischmann M, Korinek K, Pletcher D (1971) *J Electroanal Chem* 31:39
12. Roslonek G, Taraszewska J (1992) *J Electroanal Chem* 325:285
13. Taraszewska J, Roslonek G (1994) *J Electroanal Chem* 364:209
14. Golikand AN, Maragheh MG, Irannejad L, Asgari M (2006) *Russ J Electrochem* 42:167

15. Golabi SM, Nozad A (2004) *Electroanalysis* 16:199
16. Ciszewski A, Milczarek G (1997) *J Electroanal Chem* 426:125
17. Gonzalez Fuentes MA, Manriquez J, Granados SG, Ordaz AA, Godinez LA (2005) *Chem Commun* 7:898
18. Golikand AN, Raof J, Baghayeri M, Asgari M, Irannejad L (2009) *Russ J Electrochem* 45:192
19. Hajjizadeh M, Jabbari A, Heli H, Moosavi Movahedi AA, Haghgoo S (2007) *Electrochim Acta* 53:1766
20. Majdi S, Jabbari A, Heli H, Moosavi Movahedi AA (2007) *Electrochim Acta* 52:4622
21. Suresh Kumar K, Prathap Haridoss, Seshadri SK (2008) *Surf Coat Tech* 202:1764
22. Shobha T, Aravinda CL, Parthasarathi Bera, Gomathi Devi LG, Mayanna SM (2003) *Mater Chem Phys* 80:656
23. Mathiyarasu J, Remona AM, Mani A, Phani KLN, Yegnaraman V (2004) *J Solid State Electrochem* 8:968
24. Wen TC, Hu CH, Hu CC (1999) *J Chin Inst Chem Eng* 30:515
25. Choi JH, Park KW, Kwon BK, Sung YE (2003) *J Electrochem Soc* 150:A973
26. Ojani R, Raof JB, Sayed Reza Hosseini Zavvaramahalleh (2008) *Electrochim Acta* 53:2402
27. Ojani R, Raof JB, Fathi S (2009) *J Solid State Electrochem* 13:927
28. Vilchez F, Granados SG, Ordaz AA, Galicia L, Herrasti P (2008) *J Electroanal Chem* 614:8
29. Vilchez F, Ordaz AA, Galicia L, Herrasti P, Granados SG (2009) *J Solid State Electrochem* 13:861
30. Flores EN, Omanovic S (2005) *J Mol Catal A Chem* 242:182
31. Damian A, Omanovic S (2006) *J Power Sources* 158:464
32. Abrantes LM, Correia JP (1998) *Surf Coat Tech* 107:142
33. Saleh ZB, Omanovic S (2009) *J Nanosci Nanotechnol* 9:2469
34. Kumar SA, Meenakshi KS, Sankaranarayanan TSN, Srikanth S (2008) *Prog Org Coat* 62:285
35. Maria Hepel, Min Chen Y, Stephenson R (1996) *J Electrochem Soc* 143:498
36. Lee JY, Tan TC (1990) *J Electrochem Soc* 137:1402
37. Wang S, He J, Xie J, Zhu Y, Xie Y, Chen JG (2008) *App Surf Sci* 254:2102
38. Papadimitriou S, Tegou A, Pavlidou E, Armyanov S, Valova E, Kokkinidis G, Sotiropoulos S (2008) *Electrochim Acta* 53:6559
39. Wang S, Lin W, Zhu Y, Xie Y, Chen JG (2006) *Chin J Catalysis* 27:301
40. Liu Z, Zhang X, Hong L (2009) *Electrochem Commun* 11:925
41. Singh RN, Singh A, Anindita (2009) *Int J Hydrogen Energy* 34:2052