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

K. L. Nagashree · M. F. Ahmed

Abstract Electrolytically deposited Cu on polyaniline film covered Pt substrate (Cu/PANI/Pt) is used as anode for the electrooxidation of methanol in alkaline medium. The electrochemical behavior and electrocatalytic activity of the electrode were characterized using cyclic voltammetry, impedance spectroscopy, chronomethods, rotating disc voltammetry and polarization studies. The morphology and composition of the modified film were obtained using SEM and EDAX techniques. The electrooxidation of methanol in NaOH is found to be more efficient on Cu/PANI/Pt than on bare Cu (Cu), electrodeposited Cu on Cu (Cu/Cu) and electrodeposited Cu on Pt (Cu/Pt) substrates. Partial chemical displacement of dispersed Cu on PANI with Pt or Pd further improved its performance towards methanol oxidation.

Keywords Methanol oxidation · Alkaline medium · Polyaniline · Polymer modified electrodes · Cu modification

1 Introduction

The use of metallized polymers is gaining ascendance in recent years due to their varied applications in the field of electrodics, sensors and electrocatalysis [1]. Earlier work in the field of electrocatalysis mainly focused on the use of polymers metallized with Pt group metals and their alloys. For electrocatalysis specifically of methanol oxidation, in view of its relevance to direct methanol fuel cell the use of these metallized polymers was limited to acidic medium [2–5]. The acid medium, however, poses certain limitations on the kinetics of methanol oxidation owing to the strong binding of poisoning species to catalytic centers leading to polarization losses. It was after Parsons and VanderNoot's [6] 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 but also open up the possibilities 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 polycrystalline) like Pt, Au, Ni [7–12], metal alloys like Ni–Cu [13] and other Ni based electrode systems [14–17] as anodes. Studies involving use of polymer modified electrodes as electrocatalysts for methanol oxidation in alkaline medium are rare with few exceptions [18–20]. Here again the studies deal with the use of Pt as the electrocatalyst and there are very few reports of use of dispersed non-noble metals in the polymer matrix for methanol oxidation reaction although such systems have been used for oxidation of other polyhydroxy compounds [21]. In view of this the electrocatalytic oxidation of methanol on polyaniline matrix with dispersed copper particles in alkaline media was undertaken and the results are reported herein. Although PANI is non-conducting in alkaline medium but because of its porous nature it is a very good matrix for the dispersion of catalytic particles which are essentially responsible for the electrocatalytic oxidation of methanol in alkaline medium. Hence we presume that the conductivity of polyaniline will have not much affect on the results pertaining to methanol oxidation.

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2 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 Pt flag of area 0.09 cm^2. Stainless steel (SS) flag and Pt wire of much larger area were used as counter electrodes for polymerization/methanol oxidation and copper deposition respectively. Saturated calomel electrode acted as the reference electrode in all the experiments. Prior to use the working electrode was first mechanically polished on a 4/0 grade emery paper, then with 0.3 μm alumina powder, washed with water and subjected to electrochemical cleaning in 1 M KOH and HCl solutions successively. 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 (EDAX) data from X-ray diffractometer (Oxford ISIS link software). The electrochemical experimental details have been described at appropriate places in the text.

3 Results and discussion

3.1 Preparation of Cu modified electrodes

Initially, the electropolymerization of aniline was carried out onto the cleaned Pt substrate from a solution of 0.1 M aniline in 0.5 M H$_2$SO$_4$ in the potential range −0.2 to +1.2 V at a scan rate of 50 mV s^{-1}. A sufficiently thick green colored film was obtained which turned dark on exposure to air. The film had a fibrilar branched and porous structure (Fig. 1a) characteristic of electrochemically deposited PANI and hence is highly suitable for dispersion of the catalyst (Cu). In order to select the potential for copper deposition on PANI, the cyclic voltammogram (CV) of PANI covered Pt electrode was recorded in 0.1 M H$_2$SO$_4$ with and without 0.25 M CuSO$_4$. The behavior is typical to that reported earlier involving electrodeposition of metals on polymer films [22–24]. The CV (figure not shown) consists of a prominent cathodic peak at a potential of −0.177 V vs. SCE only in the presence of CuSO$_4$ and is therefore attributed to the reduction of Cu. A potential of −0.2 V vs. SCE was, therefore chosen from these studies for deposition of Cu on all the substrates, either bare or PANI film covered in the present study. Assuming 100%
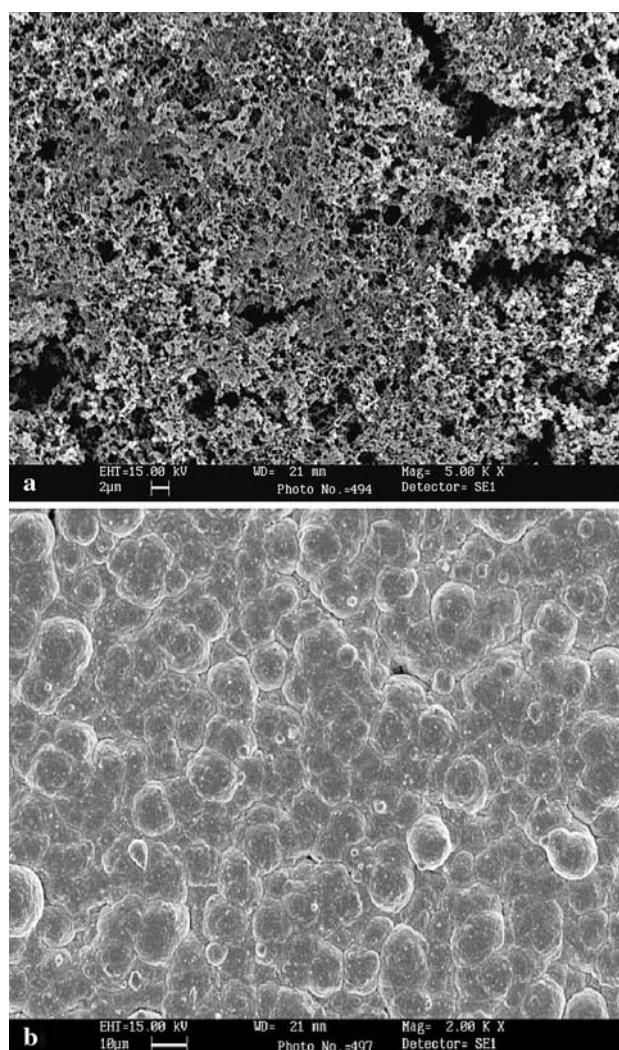

Fig. 1 a SEM of PANI film on Pt. **b** SEM of 2 mg Cu deposit on PANI film covering the Pt substrate

efficiency for the reduction of Cu^{2+} to Cu the amount of Cu deposited was monitored from the charge passed during the reduction process using the relation $N_{Cu} = Q/nF$ where N_{Cu} is the number of moles of copper deposited, n the number of electrons (2), Q and F being the charge and the Faraday values [25]. The amount of Cu deposited was kept constant at 2 mg for all the studies unless otherwise mentioned. The SEM of Cu/PANI/Pt is shown in Fig. 1b which shows coarse grained closely packed clusters on the surface.

3.2 Electrochemical behavior of Cu/PANI/Pt in absence and presence of methanol in NaOH

The inset in Fig. 2 shows the electrochemical behavior of Cu/PANI/Pt in 0.1 M NaOH in the potential range −1.0 to +1.0 V at a scan rate of 25 mV s^{-1}. The behavior is similar to the one reported in the literature [26, 27] on bare
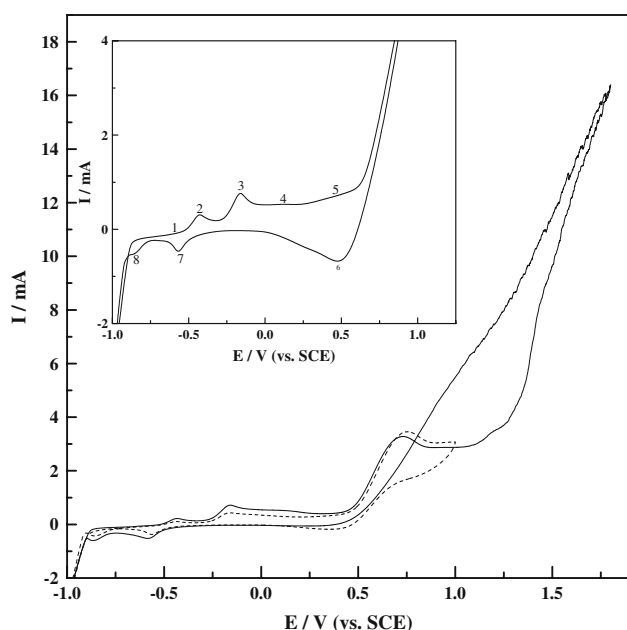
Fig. 2 CV response of Cu/PANI/Pt at 25 mV s^{-1} in a solution of 0.1 M methanol +0.1 M NaOH (dashed line) and the CV with potential extended up to +1.8 V (solid line). Inset shows the CV response of Cu/PANI/Pt at 25 mV s^{-1} in 0.1 M solution of NaOH

Cu electrode. While features marked 1–5 characterize the anodic region of the CV, 6–8 mark the cathodic region in excellent agreement with earlier observations although the exact potential values characterizing each feature may differ due to differences in experimental conditions. Ignoring the actual products formed and confining only to the changes in oxidation states the various features on the CVs can be unambiguously attributed to the following transitions in the light of the earlier observations [28, 29]. While peak 1 at less than −0.5 V vs. SCE may be attributed to the electrosorption of oxygen, peak 2 to the transition Cu/Cu^{I}, peak 3 to the transition Cu/Cu^{II} as well as Cu^{I}/Cu^{II}, peak 4 to Cu/Cu^{II} (soluble species) and peak 5 to Cu^{II}/Cu^{III} beyond which evolution of oxygen occurs. The peaks 6–8 in the reverse direction can accordingly be attributed to the transitions Cu^{III}/Cu^{II}, Cu^{II}/Cu^{I} and Cu^{I}/Cu respectively. The effect of scan rate and pH on the CVs of Cu/PANI/Pt in NaOH was found to be similar to that of bare Cu electrode in NaOH [30].

In Fig. 2 the dashed line represents the CV observed on a Cu/PANI/Pt electrode in 0.1 M NaOH with 0.1 M methanol in the potential range −1.0 to +1.0 V at a scan rate of 25 mV s^{-1}. In the presence of methanol (dashed line) there is diminution of currents at potentials corresponding to redox reactions involving low oxidation states of Cu (peaks 1–4 on the CV in inset) and a new anodic peak accompanied by an additional anodic peak in the reverse scan characteristic of methanol oxidation appears at potentials corresponding to Cu^{II}/Cu^{III} redox reaction (peaks

5 and 6 on the CV in inset).The additional anodic peak in the reverse scan characteristic of methanol oxidation is not so pronounced at this scan rate probably due to the rate of desorption of oxidized product exposing fresh surface for methanol oxidation is not matching with the scan rate. However this anodic peak was very much pronounced at lower scan rates, figures pertaining to which are not presented here.

It is evident, therefore, that while the low valence state oxides of copper do not support oxidation of methanol and serve merely to adsorb it, it is the Cu^{III} species that is generated at more positive potentials that acts as a redox mediator in the oxidation of methanol in accordance with earlier observations on the oxidation of carbohydrates at copper electrodes [31–34]. Thus while mechanistically the behavior of Cu/PANI/Pt electrode towards methanol oxidation appears to be very similar to that of bare Cu, the magnitude of oxidation currents are however several times higher on the former than on the later as will be shown from the results to be presented later. To rule out the possibility that oxygen evolution also contributes to this peak since oxygen evolution occurs at lower potentials in the absence of methanol (CV in inset), the CV was extended up to a potential of +1.8 V on Cu/PANI/Pt in 0.1 M NaOH containing methanol (solid line). It is clear that the onset of oxygen evolution is delayed in the presence of methanol and occurs at a potential >1.0 V while the characteristic peak at ∼0.75 V is essentially due to the oxidation of methanol.

3.3 Optimization of electrode variables for efficient performance of Cu/PANI/Pt towards methanol oxidation

3.3.1 Effect of copper loading

Figure 3 shows the affect of the amount of copper dispersed in PANI on the maximum oxidation currents of 0.1 M methanol in 0.1 M NaOH recorded in the potential range 0 to 1 V at a scan rate of 10 mV s^{-1}. It was observed that at copper loadings of >0.5 mg, the currents were not steady and decreased continuously with successive cycling owing probably to the non-uniform and non-adherent deposits formed at these loadings. The currents however attained steady values and did not show much variation for loadings between 0.5 and 1.5 mg. At 2.0 mg loadings when the deposit uniformly covers the surface as evidenced by the SEM (Fig. 1b) the oxidation current attained the maximum value and remained steady for several successive cycles. For loadings exceeding 2.0 mg the currents once again decreased gradually owing probably to the coalescence of microparticles favoring island growth leading to a decrease in surface area and hence the activity.
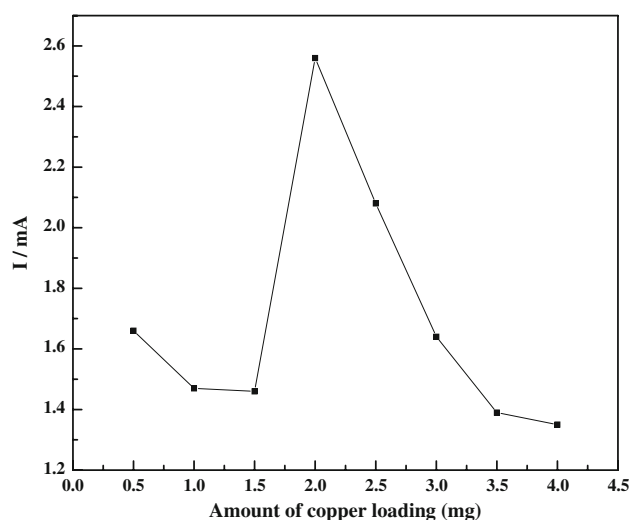
Fig. 3 Variation of currents for oxidation of 0.1 M methanol in 0.1 M NaOH at 10 mV s^{-1} at various copper loadings on PANI film

3.3.2 Effect of method of copper incorporation into PANI

The oxidation of methanol was studied with Cu/PANI/Pt loaded with 2 mg of Cu by controlling the charge passed potentiostatically at −0.2 V and cyclically in the potential range 0.1 to −0.4 V. It is observed that potentiostatic incorporation of Cu in PANI favors better performance than the cyclic incorporation because of incomplete deposition of Cu due to its partial dissolution probably in the latter mode.

3.3.3 Effect of polymer deposition potential, deposition method and polymer thickness

The study of the effect of polymer deposition method (cyclically from −0.2 to +1.2 V and potentiostatically at 0.9, 1.0, or 1.1 V) and polymer film thickness (thickness corresponding to passage of charge for 5, 8, 13 and 20 cycles) on the behavior of the modified electrode revealed that the PANI films obtained after 13 cycles in the potential range −0.2 to +1.2 V had the right morphology for efficient dispersion of 2 mg of copper and therefore showed the maximum electrocatalytic activity towards methanol oxidation. The polymer film thickness plays an important role in its electroactivity due to non-uniform film formation or film degradation occurring when the electropolymerization is carried out for lesser and higher amount of charge passed respectively.

3.4 Effect of bath variables on oxidation current

3.4.1 Methanol concentration

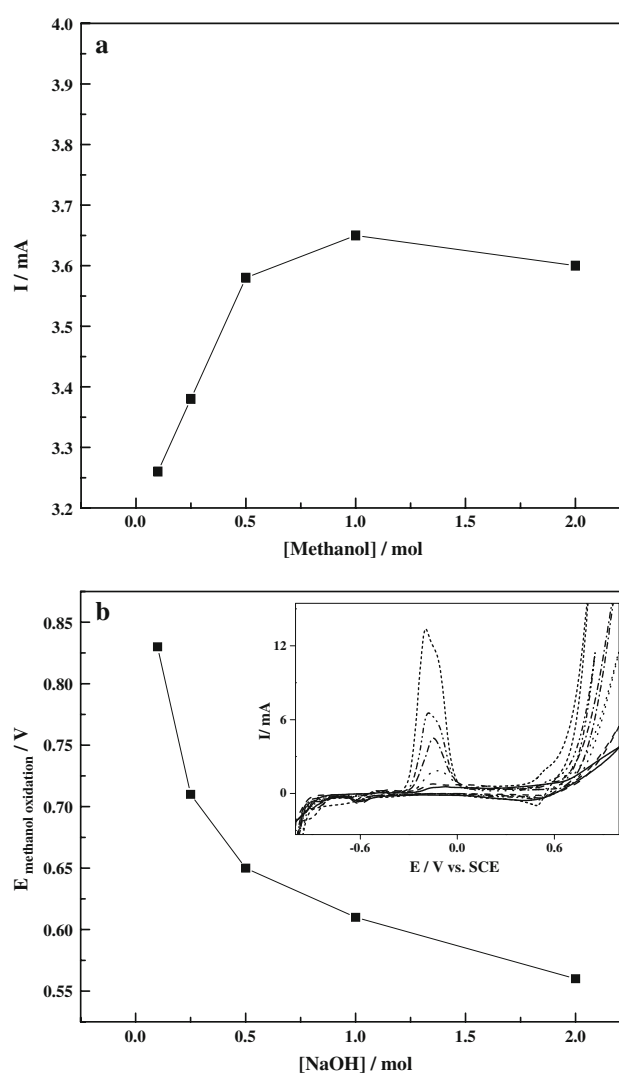Figure 4a is the profile of oxidation current vs. methanol concentration, which shows a steady increase in current up

Fig. 4 a Effect of methanol concentration on its oxidation currents in 0.1 M NaOH on Cu/PANI/Pt (Cu loading 2 mg) at 25 mV s^{-1}. **b** Effect of NaOH concentration on oxidation potential of 0.1 M methanol on Cu/PANI/Pt (Cu loading 2 mg) at 25 mV s^{-1}. Inset shows the effect of NaOH concentration on the CV response of Cu/PANI/Pt (Cu loading 2 mg) at 25 mV s^{-1} in the absence of methanol

to a methanol concentration of 1 M after which it plateaus. It appears that at concentrations exceeding 1 M, methanol adsorption has reached a saturation limit and no fresh Cu sites are available for further adsorption.

3.4.2 NaOH concentration

The potential for methanol oxidation appears to be strongly dependent on NaOH concentration (Fig. 4b). It is observed that as the concentration of NaOH is increased from 0.05 to 2 M, the methanol oxidation peak is shifted to less positive values. It has been reported [30] that some of the oxidation peaks of Cu shift towards more negative values of potential as the alkali concentration increases and is also shown by

the inset of Fig. 4b. Hence it is probable that the reactive redox species of Cu is generated at less positive potentials as the concentration of NaOH is increased so that the methanol oxidation peak is also shifted towards less positive values. As regards the oxygen evolution reaction, its potential is also observed to decrease with increase in pH of the medium.

3.5 Electrochemical characterization of the process of methanol oxidation in NaOH on Cu/PANI/Pt

3.5.1 RDE studies

The oxidation of 0.1 M methanol in 0.1 M NaOH was carried out on a Pt rotating disc (diameter, 0.2 cm) covered with PANI and modified with Cu at various rotation rates (ω) at 5 mV s^{-1}. In Fig. 5a is shown the Koutecky-Levich plot (I^{-1} vs. $\omega^{-1/2}$) obtained with this electrode for methanol oxidation current at 0.65 V. The plot is linear indicating that adsorption and diffusion of methanol through the PANI film is a controlling factor in its oxidation [35].

3.5.2 Polarization studies

Potentiostatic anodic polarization of the Cu/PANI/Pt electrode was carried out in 0.1 M NaOH solution containing different concentrations of methanol at 0.1 mV s^{-1}. It is observed from Fig. 5b that in 0.1 M NaOH containing 0.1 M methanol (solid line) the oxidation commences around 0.4 V and the current continues to rise up to a potential of 0.7 V after which it plateaus indicating diffusion controlled process. The Tafel Slope is found to be 130 mV dec^{-1} suggesting the involvement of one electron transfer as the rate determining step in the overall mechanism of methanol oxidation reaction on this electrode in agreement with earlier reports on Pt electrodes [18]. With increase in methanol concentration the anodic polarization curves show a proportionate increase in the current up to a concentration of 1 M after which saturation appears to set in.

3.5.3 Impedance studies

The electrochemical impedance spectroscopic studies for the oxidation of 0.1 M methanol in 0.1 M NaOH on Cu/PANI/Pt was carried out at three potential values chosen from the foot and rising portion of the currents in the voltammetric curve (Fig. 2, dashed line) i.e., 0.55, 0.65 and 0.75 V respectively in the frequency range 10 KHz–50 mHz with an amplitude of 5 mV of the ac voltage employed and the impedance response of the system was recorded. The electrochemical parameters were obtained by fitting the circuit parameters to the measured data using the non-linear least squares method based on the program EQUIVCRT available with the Autolab. In Fig. 5c squares, circles and triangles show the Nyquist plot at 0.55, 0.65 and 0.75 V, respectively and the fitted data is shown in the form of solid lines overlying on the geometrical symbols. The plots show characteristic semicircular behavior in the high frequency region associated with charge-transfer process tending towards linear behavior in the low frequency region associated with diffusion controlled process. It is evident from these plots that at higher oxidation potentials the charge transfer resistance decreases due to increased kinetics and at 0.75 V a potential very close to the peak potential the response in the low frequency region is slightly distorted probably due to oxidation of methanol by different mechanisms and may be for the same reason data at 0.65 and 0.75 V are coincident in the high and intermediate frequency ranges. This is further evident from the Bode plot (Fig. 5d) wherein the Bode Phase curve at 0.75 V is highly distorted and seems to have many loops in the low frequency region, which is an indication of the redox process being carried out by different routes.

3.5.4 Stability of the electrode

The stability of the Cu/PANI/Pt electrode towards methanol oxidation was tested in different ways. In one experiment, the electrode was subjected to the whole ranges of currents and potentials used in various electrochemical experiments like CV, CA, polarization and impedance studies. After subjecting to this treatment the electrode showed the same behavior towards methanol oxidation as a fresh electrode. In another experiment, the Cu/PANI/Pt electrode was cycled in the potential range for methanol oxidation namely 0 to 1 V in alkaline methanol solution for 30 cycles intermittently every day for 30 days. The steady currents observed on the electrode over this period are indicative of the stability of the electrode at ambient atmospheric conditions.

3.6 Comparison of performance of Cu/PANI/Pt with other electrode systems

To assess the performance of Cu/PANI/Pt in relation to other electrode systems, methanol oxidation was carried out on bare Cu, Cu/Cu, Cu/Pt, Cu/GC (glassy carbon) and Cu/PANI/GC in the latter four of which the same amount of Cu (2 mg) had been loaded as in Cu/PANI/Pt. The relative oxidation currents on these electrodes along with that of Cu/PANI/Pt are shown in the form of a bar graph in Fig. 6. It is clearly evident that the performance of Cu/PANI/Pt towards methanol oxidation is far superior to that of bare Cu, Cu/Cu, Cu/Pt and Cu/GC. This of course is attributed to the role of PANI, which favors efficient dispersal of Cu microparticles thereby enhancing its activity.
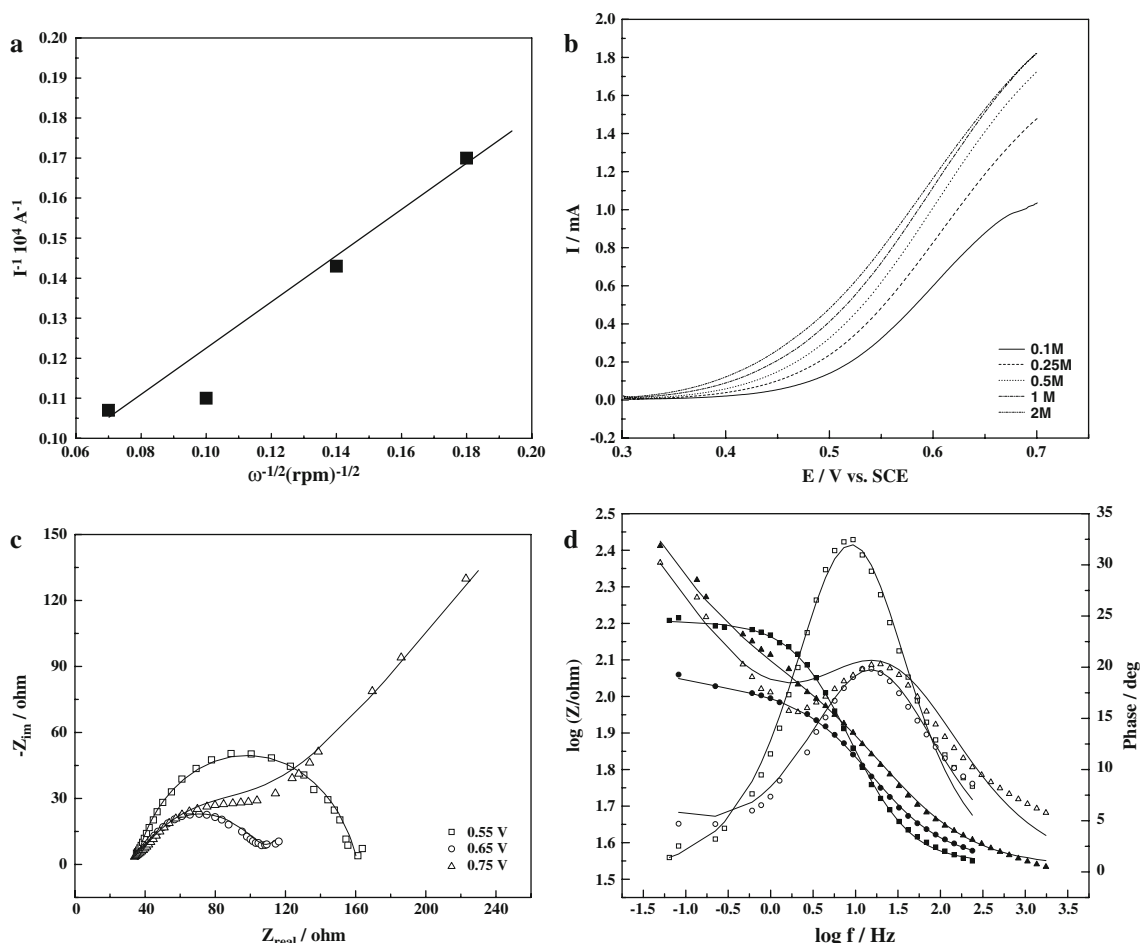
Fig. 5 a Koutecky-Levich (I^{-1} vs. $\omega^{-1/2}$) plot for the oxidation of 0.1 M methanol in 0.1 M NaOH on Cu/PANI/Pt at 0.65 V vs. SCE. **b** Potentiostatic anodic polarization of Cu/PANI/Pt in 0.1 M NaOH solution containing different concentrations of methanol at 0.1 mV s^{-1}. **c** Nyquist plot for the oxidation of 0.1 M methanol in

0.1 M NaOH at different potentials on Cu/PANI/Pt. Solid lines represent fitted curves. **d** Bode plot for the oxidation of 0.1 M methanol in 0.1 M NaOH at potentials of 0.55 V ($\square$, $\blacksquare$), 0.65 V ($\bigcirc$, $\bullet$) and 0.75 V ($\triangle$, $\blacktriangle$) on Cu/PANI/Pt. Solid lines represent fitted curves

Though bare GC, which hardly supports methanol oxidation either in acid or alkaline medium becomes active after copper is deposited on it. However the activity of Cu/GC is no better than that of bare Cu or Cu/Pt. The efficiency of Cu/PANI/GC is also similar to that of Cu/PANI/Pt, which suggests that the morphology of PANI film on GC is more or less similar to that on Pt. This is also suggestive of the fact that instead of an expensive substrate such as Pt, other substrates such as glassy carbon can also be made use of for the purpose of dispersion of less expensive metal catalysts on a polymer matrix.

However in all our studies we have employed Pt as a substrate only for the sake of convenience.

It is difficult to compare the results of methanol oxidation in 0.1 M NaOH on copper modified PANI with Pt modified PANI because of difficulties in maintaining identical conditions such as extent of loading, nature and
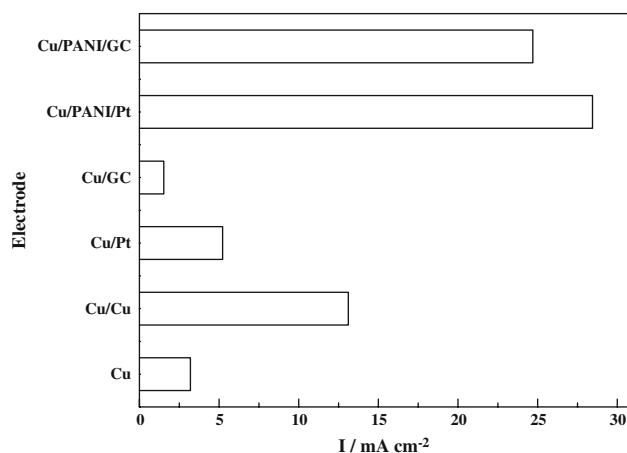

Fig. 6 Comparison of maximum currents for the oxidation of methanol observed on Cu, Cu/Cu, Cu/Pt, Cu/GC, Cu/PANI/Pt and Cu/PANI/GC
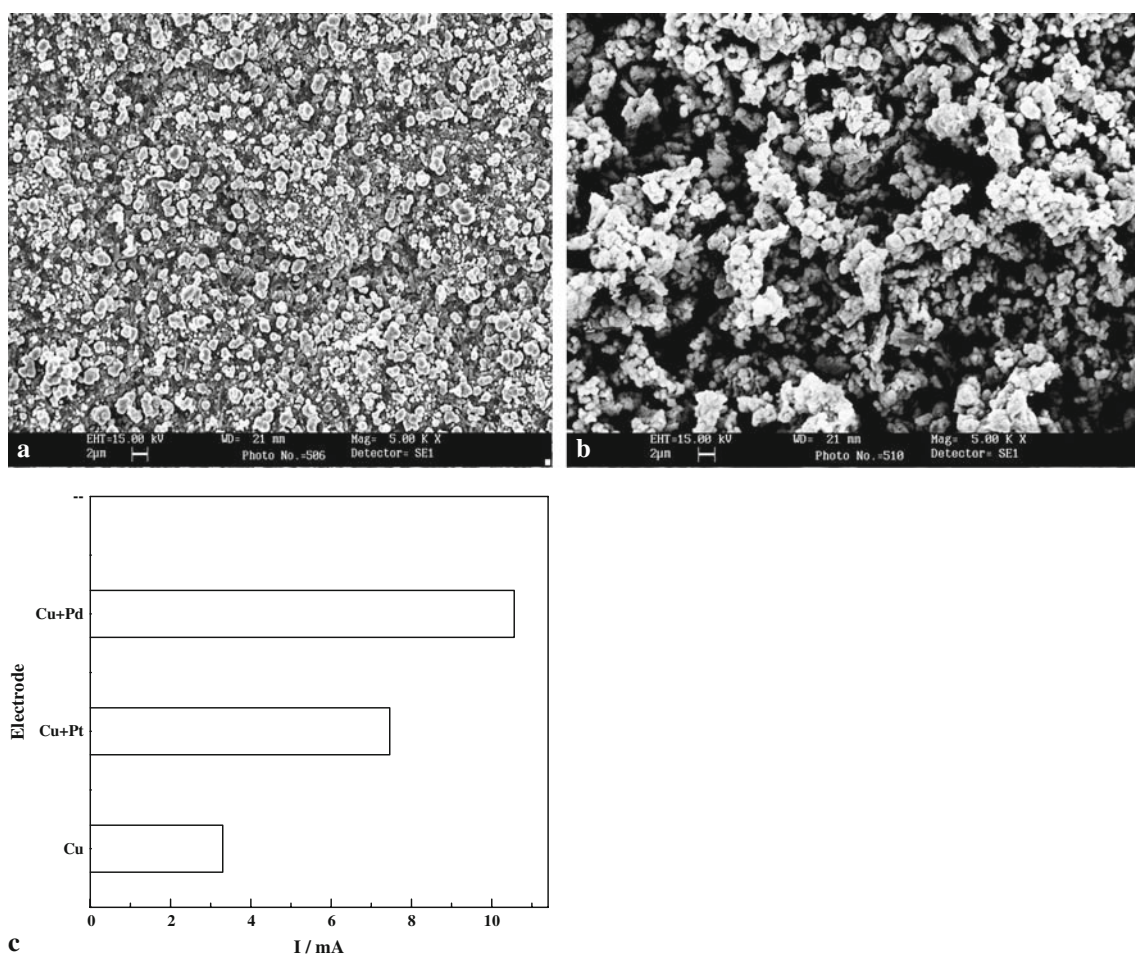
Fig. 7 **a** SEM of partially displaced Cu deposit on PANI film with Pt. **b** SEM of partially displaced Cu deposit on PANI film with Pd. **c** Maximum methanol oxidation currents observed on Cu/PANI/Pt and Cu/PANI/Pt with partially replaced Cu by Pt and Pd

extent of dispersion on the two electrodes to get a realistic estimate of their relative performance.

However, a comparison of methanol oxidation on bare Pt and bare Cu in 0.1 M NaOH reveals that Pt certainly outweighs Cu in terms of its performance with respect to both potential and current features. The justification for employing Cu is purely on ground of its cost effectiveness.

Attempts were also made to obtain Cu/PANI/Cu i.e., to use copper as a substrate for development of Cu modified polymer electrodes. Stable and adherent films of PANI were obtained on Cu foil from a sodium tartrate bath. However on dispersion of copper particles into the PANI film, the film swelled and got detached itself from the substrate after removing it from the copper sulphate solution and hence Cu/PANI/Cu system could not be developed in the present study.

3.7 Enhancement of the performance of Cu/PANI/Pt

In recent years there have been many attempts [36–38] to obtain active electrocatalysts with considerably reduced noble metal loading through chemical displacement of a less noble deposited metal by a monolayer of more noble metal. Following this procedure the less noble Cu surface of the Cu/PANI/Pt has been partially chemically replaced by the noble Pt and Pd by dipping the electrode in 1% chloroplatinic and palladium chloride solution respectively for two minutes. The SEM of the displaced surfaces is shown in Fig. 7a and b for Pt and Pd, respectively. They now show a fine grained structure probably resulting from the competition between the oxidation of copper and reduction of platinum or palladium which now cover the underlying copper [38]. The EDAX data showed an incorporation of 4.28% Pt and 11.19% Pd in the displaced films respectively. When methanol oxidation was studied with these electrodes, it was found that the oxidation currents showed a considerable increase when compared to that on Cu/PANI/Pt as could be seen from Fig. 7c. Further the durability of the electrodes in terms of the reproducibility and constancy of currents with cycling was found to be far better than that on Cu/PANI/Pt probably because of the synergistic effects of the two metals.

4 Conclusions

(i) Cu modified PANI films on both Pt and GC substrates were found to be effective catalysts for methanol oxidation in alkaline medium in terms of reproducibility as well as durability.

(ii) Electrode parameters such as its preparation method (both PANI and Cu/PANI/Pt) and amount of copper loading, bath variables such as methanol and NaOH concentration influence the activity of the electrode towards methanol oxidation.

(iii) The mechanism of oxidation of methanol on dispersed Cu in PANI in NaOH appears to be very similar to that on bare Cu in NaOH.

(iv) The performance of the electrode towards methanol oxidation is enhanced after partial chemical displacement of dispersed Cu with Pt and Pd.

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