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ORIGINAL PAPER

Electrochemical codeposition of nickel oxide and polyaniline

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Abstract Nickel oxide (NiO_x) and polyaniline (PAni) were electrocodeposited from $NiSO_4$ and aniline through cyclic voltammetric scans to afford PAni–NiO_x composite film at controlled pH environment. The electrochemical activities of the film were investigated by cyclic voltammetry in 0.1 M NaOH and 0.1 M H_2SO_4, respectively. Typical redox couples of PAni in 0.1 M H_2SO_4 appeared at approximately 0.2 and 0.4 V vs. saturated calomel electrode (SCE); Ni(II)/Ni(III) redox couple was observed at approximately 0.4 V vs. SCE in 0.1 M NaOH. The morphologies and elemental components of the films were inspected by scanning electron microscopy and energy dispersive X-ray diffraction. The stability of nickel oxide in the films was found to be enhanced against acidic environments. Electrochemical catalytic behavior of NiO_x within the composite film was conserved and demonstrated by catalytic oxidation of methanol and ethanol.

Keywords Nickel oxide · Polyaniline · Composite film · Electrocatalysis

Introduction

Organic–inorganic composites have attracted considerable attention as they can combine the advantages of both components and may offer special properties through reinforcing or modifying each other [1]. Polyaniline (PAni) has been the subject of many studies due to its oxygen and moisture stability and potential applications in many fields [2]. PAni can also provide good network for inorganic components and modify properties and stability of the latter one [3]. Nickel oxide has received considerable attention due to potential applications in many fields such as electrochromics, electrocatalysis, supercapacitor, etc [4–7]. Chemically synthesized PAni and NiO composite by Song and coworkers produced PAni/NiO nanoparticle, nanobelt, and nanotube in the presence of sodium dodecylbenzenesulfonate. The composite materials showed improved conductivity and thermostability [8–10].

Electrocodeposition is an effective way to make composite films with a large variety of tunable parameters and so has the advantage of convenient film control. Generally, PAni is synthesized by anodic polymerization of aniline in acidic aqueous solution [2]. Thus, the electrochemical synthesis of organic–inorganic composites based on PAni and metal oxides are mostly conducted by selecting oxides which can be electrodeposited in low pH media [3, 11–13]. However, most oxides can only be electrodeposited from high pH media, which limits the formation of such PAni composites. Recently, we have demonstrated that it is feasible to form electroactive PAni in aqueous solutions of pH 2 to 12 [14]. PAni–SiO_2 and PAni–MnO_x composites were hence obtained [15, 16]. Nickel oxide was reported to be electrodeposited either at a fixed potential between 0.7 and 1.2 V or by dynamic potential cycling in the potential range of 0–1.2 V vs. saturated calomel electrode (SCE) from Ni^{2+} in neutral to weak basic solutions [17–22]. It is therefore likely that PAni and nickel oxide can be codeposited to form an organic–inorganic composite film. In this paper, we report the electrocodeposition of NiO_x and PAni and the electrochemical activities of the obtained composite film

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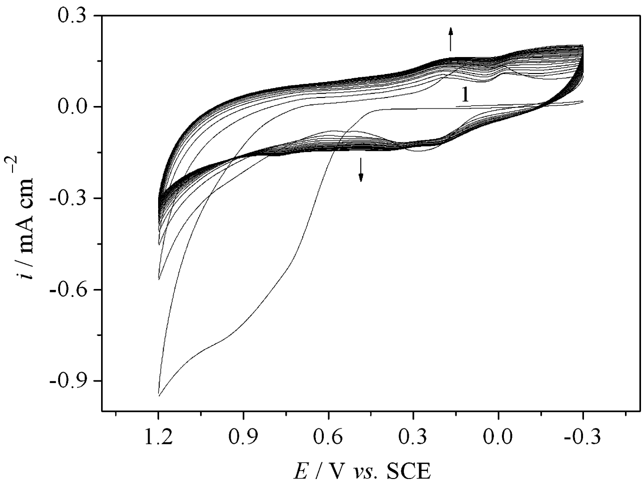


Fig. 1 Cyclic voltammograms obtained for the electrocodeposition of composite film on carbon cloth from a solution containing 0.2 M Ni^{2+} and 0.005 M aniline (pH=7.3). Scan rate is 50 mV s^{-1}

through cyclic voltammetry. The morphologies and elemental components of the film were inspected by scanning electron microscopy (SEM) and energy dispersive X-ray diffraction (EDX), respectively. Film stability in acidic condition was investigated and the electrocatalytic property of the composite film was demonstrated.

Experimental

Materials

Aniline was distilled under vacuum before use. Other chemicals were of analytical grade and used as received. Electrochemical depositions were performed on electrochemical analyzer system, CHI 660B, on carbon cloth, using platinum plate and SCE as counter and reference electrode, respectively.

Synthesis of PAni–NiO_x composite film

Prior to electrodeposition, the carbon cloth was cleaned by acetone followed by distilled water. Electrochemical codeposition of NiO_x and PAni was carried out in a solution containing 0.2 M $NiSO_4$ and 0.005 M aniline adjusted to pH 7.3 by H_2SO_4 or NaOH. Cyclic voltammetry (CV) with fixed scans (25 consecutive cyclic scans) between −0.3 and 1.2 V vs. SCE at 50 mV s^{-1} were performed. Pure nickel oxide and PAni films were electrodeposited similarly.

PAni–NiO_x film characterization

Electrochemical activities of the films were studied by cyclic voltammetry at 50 mV s^{-1} in 0.1 M NaOH and 0.1 M H_2SO_4, respectively. The morphologies of the film and the elemental components were inspected by SEM and EDX on SHIMADZU SSX-550 scanning electron microscope.

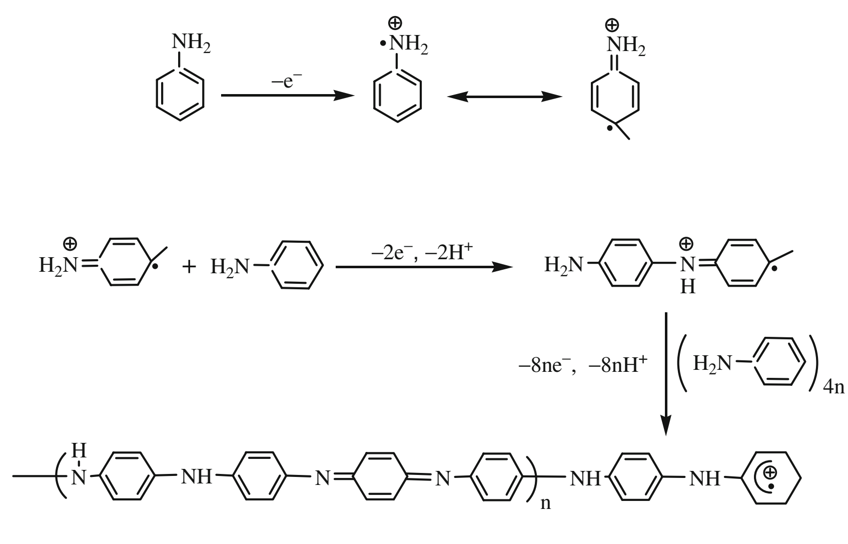
Stability of nickel oxide within the composite film in acidic solutions was investigated through cyclic voltammetry in 0.1 M NaOH at 50 mV s^{-1} after immersion for 3 h in H_2SO_4 solutions of different pH (1.0, 2.0, 2.5, 3.0, 3.5, 4.0). Electrochemical catalytic properties of the films were investigated by cyclic voltammetry at 5 mV s^{-1} in solution containing 1.0 M NaOH with different concentrations of MeOH and EtOH.

Results and discussion

Synthesis of PAni–NiO_x composite film

Our previous work has shown that electroactive PAni film can be fabricated through electro-oxidative polymerization

Scheme 1 Electropolymerization of aniline showing protons being generated during the anodic oxidation process



of aniline in aqueous solution at pH 2.0 to 12.0 [14]. Nickel oxide film can generally be obtained from neutral to weak basic solutions of Ni^{2+} through similar electro-oxidation technique [17–21]. Thus, it is probable that PAni–nickel oxide composite film can be formed by electrochemical codeposition from a single solution. Hence, by using a solution containing 0.2 M Ni^{2+} and 0.005 M aniline adjusted to pH 7.3, a composite film was successfully deposited onto the carbon cloth electrode.

Figure 1 shows the cyclic voltammograms obtained during the deposition process. Initially, a clear oxidation peak showed up at around 1.1 V vs. SCE. After the first scan, this oxidation current appeared to be much smaller. This is due to a number of factors that include proton generation from aniline oxidation (Scheme 1) which significantly reduced the amount of hydroxyl ions available for the Ni^{2+} oxidation [23, 24]; secondly, the electrode surface was being deactivated (partially blocked) by the presence of PAni film that reduced the mass transport process. However, it was observed that the current density increased gradually with successive scans after the initial drop, indicating that oxidation of Ni^{2+} still occurred readily but at a much slower rate on the electrode surface.

Similar conditions were used to deposit NiO_x film. Figure 2 shows the CV scans obtained during the deposition process. An oxidation peak appeared at approximately 1.1 V initially, which increased in height with progressive scans and gradually shifted to approximately 1.2 V. Simultaneously, there was also a distinct reduction peak started at 0.65 V which increased in current density with successive scans and shifted down to 0.5 V.

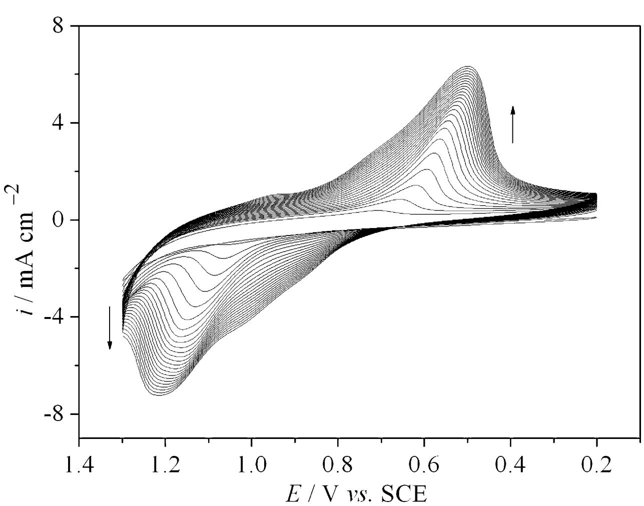


Fig. 2 Cyclic voltammograms obtained for the electrodeposition of nickel oxide on carbon cloth from a solution of 0.2 M Ni^{2+} (pH=7.3). Scan rate is 50 mV s^{-1}

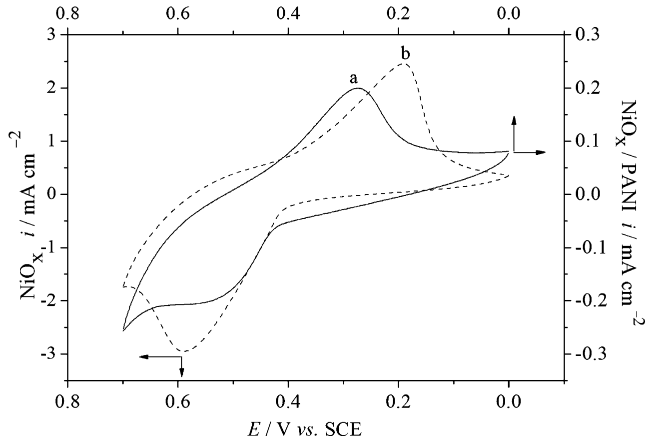


Fig. 3 Cyclic voltammograms of PAni–NiO_x (*a*, *solid line*) and similarly prepared nickel oxide (*b*, *dash line*) films in 0.1 M NaOH. Scan rate is 50 mV s^{-1}

The anodic electrochemical reactions are more complex but can be summarized as follows [20, 25]:

$$Ni^{2+} + 2OH^- \rightarrow Ni(OH)_2 \downarrow \text{(chemical reaction on electrode surface)} \quad (1)$$

$$Ni(OH)_2 + OH^- \rightarrow NiO-OH + H_2O + e^- \quad (2)$$

$$NiO-OH + OH^- \rightarrow NiO_2 + H_2O + e^- \quad (3)$$

whereas the reduction reaction observed can be simplified as:

$$NiO_2 + 2H_2O + 2e^- \rightarrow Ni(OH)_2 + 2OH^- \quad (4)$$

Equations 2, 3 and 4 suggest that the product obtained was a mixture of NiO_2 and NiO-OH. Both pure and composite films displayed characteristic NiO_x electroactivities as previously reported for nickel oxides [5–7, 18] suggesting

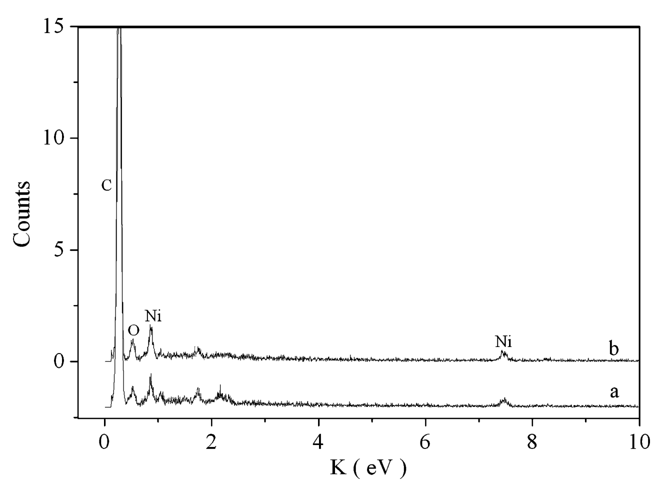


Fig. 4 EDX spectra of *a* PAni–NiO_x and *b* NiO_x

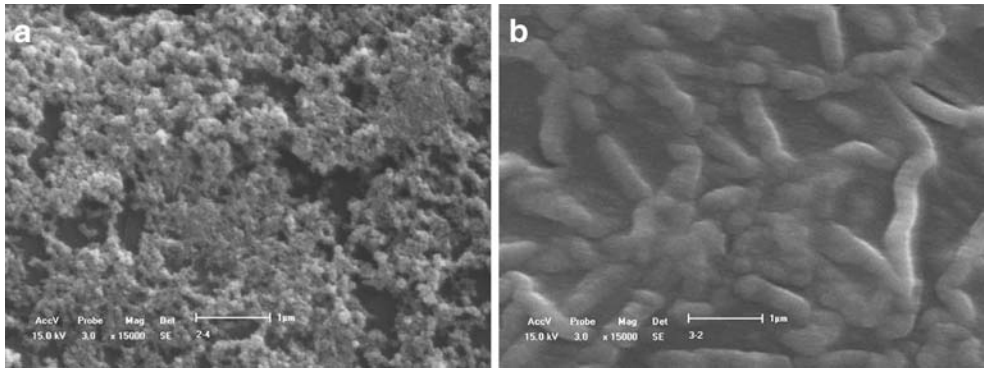


Fig. 5 SEM images of **a** PAni–NiO_x composite and **b** similarly prepared nickel oxide films

successful electrocodeposition of PAni and NiO_x from a single solution. Comparing the oxidation current densities from the two separate deposition processes that produced the composite film and the NiO_x film, it was expected that there were much less NiO_x deposited into the composite film. This is confirmed by the CV scans of the two materials presented in Fig. 3 that shows, according the current density observed, the composite film that is estimated to contain less than a tenth of NiO_x compared to the pure NiO_x membrane. However, this estimation can only be used as a general indication because the electron transfer efficiencies and inherent electrical resistance between the pure and composite films are expected to be quite different.

Characterization of PAni–NiO_x composite film

Elemental analysis of PAni–NiO_x composite and nickel oxide films were carried out by EDX technique. Similar spectra were obtained for the two films which identified the presence of more than one form of nickel oxides (Fig. 4). Therefore, a mixture of NiO_2 and NiO-OH may coexist in the film according to Eqs. 2, 3 and 4. SEM images of the films revealed very different surface morphologies. PAni–NiO_x composite adopted a much smoother morphology consisting of aggregations of submicron particles, whereas the nickel oxide film was made up of much bigger worm-like tubules several microns long (Fig. 5). As shown in Fig. 5a, nickel oxide particles are indistinguishable from that of the PAni, which may suggest that they are well dispersed in polymer network of the composite film. This may explain why the ΔE for Ni(II)/Ni(III) couple (shown in Eq. 3) obtained from the composite film is smaller than that obtained from the pure nickel oxide film as the fine dispersion of nickel oxide particle within the PAni network facilitates the electron exchange. However, the difference in ΔE observed may also be attributable to an uncompensated resistance effect.

Electrochemical properties

PAni–NiOx composite film displayed two pairs of redox peaks in 0.1 M H_2SO_4 which were similar to a PAni film made under similar conditions (Fig. 6). The first couple at approximately 0.2 V corresponded to the exchange between

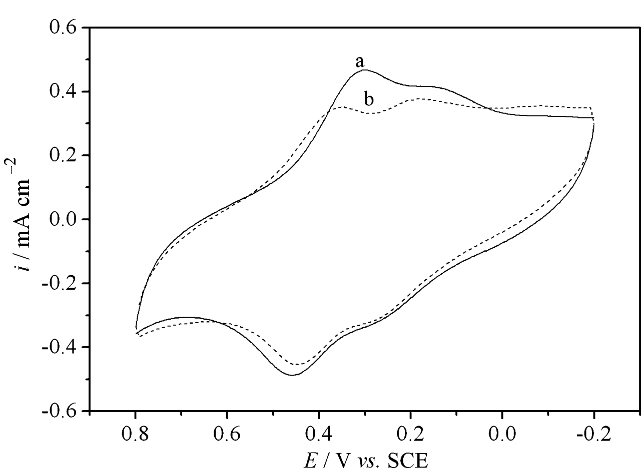


Fig. 6 Cyclic voltammograms of PAni–NiO_x (*solid line*) and similarly prepared PAni (*dash line*) films in 0.1 M H_2SO_4. Scan rate is 50 mV s^{-1}

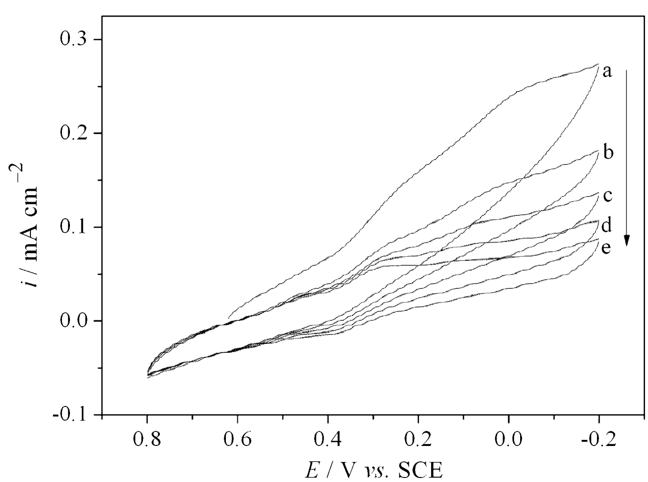


Fig. 7 Cyclic voltammograms of NiO_x film in H_2SO_4 solution at pH 2.1. Scan rate is 50 mV s^{-1}. *a–e* Cycles 1 to 5 showing progressive reduction in current density

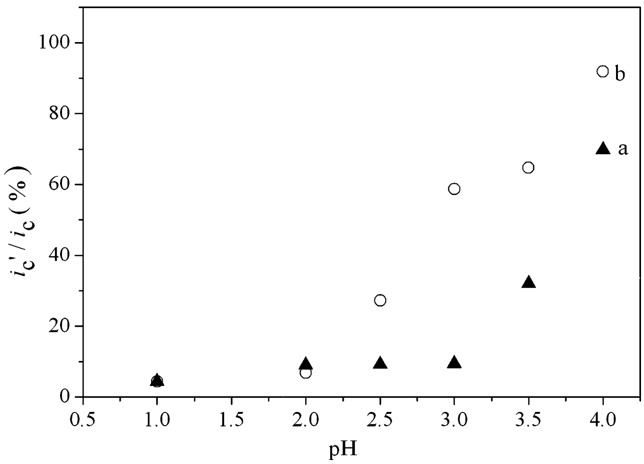


Fig. 8 Normalized percentage cathodic current density obtained after 20 scan cycles in 0.1 M NaOH for *a* nickel oxide (*closed triangle*) and *b* the PAni–NiOx composite (*open circle*) after the electrodes were immersed for 3 h in various H_2SO_4 solutions of pH 1 to 4. i_c and i_c' denotes current obtained before and after acid immersion. Peak currents were obtained at 0.2 and 0.25 V vs. SCE for nickel oxide and PAni–NiO_x composite films, respectively

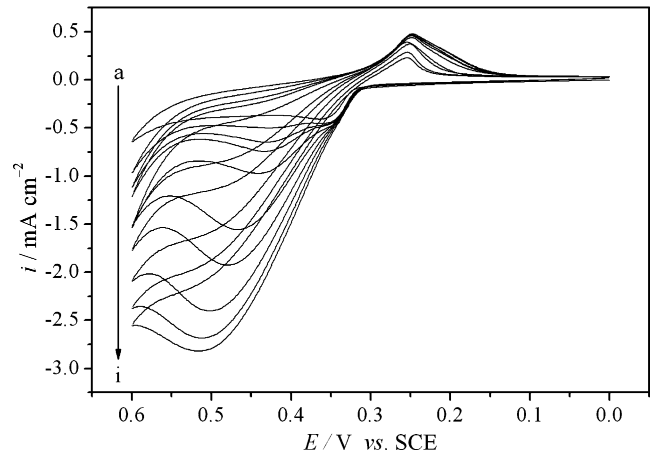


Fig. 10 Cyclic voltammograms of PAni–NiO_x composite film in 1.0 M NaOH and different concentrations of ethanol. Scan rate is 5 mV s^{-1}; concentration of ethanol is 0 (*a*), 0.02 (b), 0.06 (c), 0.08 (d), 0.2 (e), 0.4 (f), 0.6 (g), 0.8 (h), and 1.0 M (*i*)

leucoemeraldine and emeraldine states of PAni. The second couple at approximately 0.4 V was related to the exchange between emeraldine and pernigraniline [26]. However, these redox couples did not exist in alkaline solution as PAni was not electroactive under alkaline media (approximately pH>10.0). Meanwhile, NiO_x was unstable in acidic conditions as the compound dissolved relatively rapidly in acids. Figure 7 is a typical example of CVs obtained from a NiO_x film at pH 2.1. The cathodic current reduced quickly with progressive scans and almost completely lost its activity after just five cycles. These contrasts in property had made the study of PAni–NiO_x composite film more challenging as solutions of two extreme pHs had to be used to investigate the activities of PAni and NiO_x components, i.e., acidic media for PAni and alkaline for NiO_x.

By comparing the cathodic current of the composite film at 0.25 V vs. SCE to that of the pure nickel oxide film at 0.2 V vs. SCE after 20 scan cycles, we have demonstrated that PAni–NiO_x composite film has enhanced stability in acidic media (Fig. 8). The modified electrodes were immersed in acidic solutions ranging from pH 4.0 to 1.0 for 3 h before the cathodic current was measured in 0.1 M NaOH. Results show that significant electroactivity could be detected for PAni–NiO_x composite films at low pHs as detailed in Fig. 8. The data showed that above pH 2.5, the composite film remained electrochemically active and was relatively stable, whereas the pure

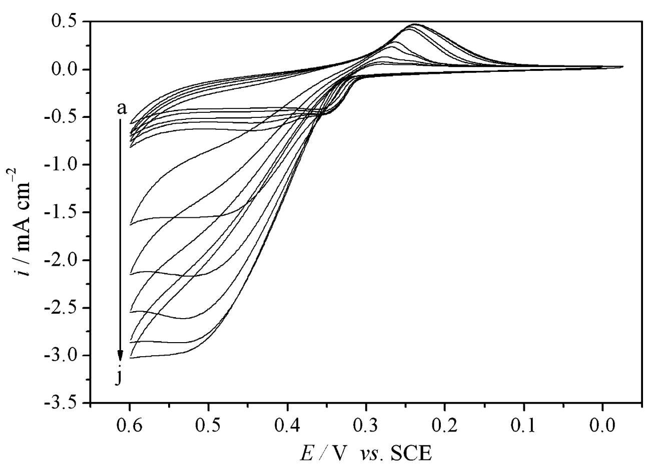


Fig. 9 Cyclic voltammograms of PAni–NiO_x composite film in 1.0 M NaOH and different concentrations of methanol. Scan rate is 5 mV s^{-1}; concentration of methanol is 0 (*a*), 0.006 (b), 0.01 (c), 0.02 (d), 0.04 (e), 0.2 (f), 0.4 (g), 0.6 (h), 0.8 (i), and 1.0 M (*j*)

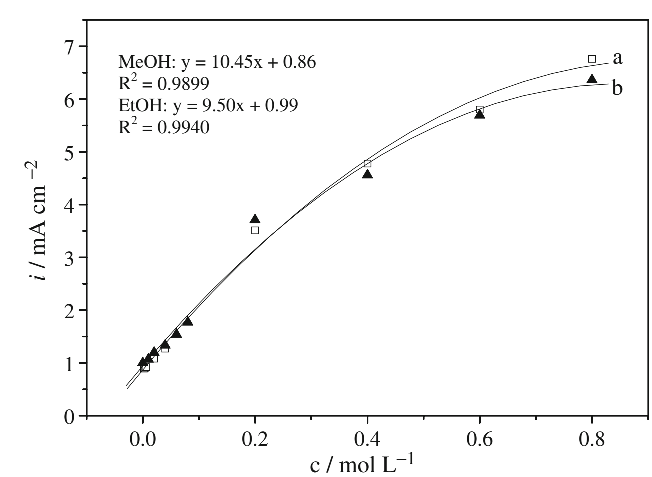


Fig. 11 Calibration plot for the electrocatalytic oxidation of methanol (*a*, *open square*) and ethanol (*b*, *closed triangle*) on the PAni–NiOx composite film

NiO_x film was only stabilized above pH 3.5. It was demonstrated that this simple technique for immobilization of nickel oxide into PAni matrix has resulted in a more stable material.

Catalytic properties

It is known that nickel oxide is an electrocatalyst for hydroxylated organic compounds [5, 6, 27, 28]. It is envisaged that this composite material may retain and enhance the catalytic properties of the nickel oxide through fine dispersion of the catalyst particles into the conductive PAni matrix to result in a drastic increase in surface area. Additionally, the conductive PAni matrix, being closely associated to the nickel oxide catalyst as a result of codeposited film, is expected to facilitate electron transfer during the electrocatalytic reaction. These effects were demonstrated in the catalytic oxidation of alcohols in alkaline media.

Figures 9 and 10 were data obtained during the electro-oxidation of methanol and ethanol, respectively, monitored by cyclic voltammetry. On addition of the substrates, large anodic current increases appeared above 0.3 V (vs. SCE) which was corresponding to the Ni(II) to Ni(III) transition, indicating that electrocatalytic oxidation of the alcohols had occurred. The catalytic anodic reactions are summarized as follows:

$$\begin{array}{ll} R-OH+Ni^{III}O-OH \rightarrow Ni^{II}(OH)_2+RO^{\bullet} & R = Me, Et \\ Ni(OH)_2+OH^- \rightarrow NiO-OH+H_2O+e^- & \text{At anode} \end{array}$$

Figure 11 presents two very similar calibration plots using the data shown in Figs. 9 and 10 which show that the composite film exhibited very high catalytic efficiency for methanol and ethanol oxidation. Given that only small amount of nickel oxide catalyst was present in the composite film, very fast mass transport and efficient electron transfer must have achieved to produce the observed catalytic behavior.

These data also indicate that the composite film may offer an electrochemical way of detecting alcohols in aqueous media across a broad concentration range of approximately 2 to 400 mM. Detail sensing investigation is beyond the scope of this work and will be discussed elsewhere.

We have reported the synthesis and characterization of PAni–NO_x composite film. This composite material is stable in pH>2.5 and in basic environments and remains electrochemical active. The distinct physical configuration of the composite has led to enhanced catalytic properties which may have good potential in application areas such as electrocatalysis, sensing, and fuel cell, etc.

Conclusions

PAni–NiOx composite film was obtained through cyclic voltammetric technique in the solution containing 0.2 M $NiSO_4$ and 0.005 M aniline at pH 7.3. The cyclic voltammogram of the composite film displayed well-defined anodic and cathodic peaks associated with Ni(II)/Ni(III) redox couple in 0.1 M NaOH, which was similar to that of nickel oxide film. Nickel oxide particles were well dispersed in polymer network of the composite film and were witnessed by the facilitated Ni(II)/Ni(III) redox transition, enhanced catalytic activities, and increased NiO_x stability within the composite material.

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