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Research Article

Synthesis and Characterization of Electrodeposited C-PANI-Pd-Ni Composite Electrocatalyst for Methanol Oxidation

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Electropolymerization of aniline at the graphite electrodes was achieved by potentiodynamic method. Electrodeposition of Pd (C-PANI-Pd) and Ni (C-PANI-Ni) and codeposition of Pd-Ni (C-PANI-Pd-Ni) microparticles into the polyaniline (PANI) film coated graphite (C-PANI) were carried out under galvanostatic control. The morphology and composition of the composite electrodes were obtained using scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX) techniques. The electrochemical behavior and electrocatalytic activity of the electrode were characterized using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and chronoamperometric (CA) methods in acidic medium. The C-PANI-Pd-Ni electrode showed an improved catalytic performance towards methanol oxidation in terms of lower onset potential, higher anodic oxidation current, greater stability, lower activation energy, and lower charge transfer resistance. The enhanced electrocatalytic activity might be due to the greater permeability of C-PANI films for methanol molecules, better dispersion of Pd-Ni microparticles into the polymer matrixes, and the synergistic effects between the dispersed metal particles and their matrixes.

1. Introduction

Direct methanol fuel cell (DMFC) is regarded as a potential candidate as portable power sources [1]. Platinum modified polyaniline (PANI) electrocatalysts for methanol electrooxidation have been widely studied in recent years [2]. But, slow methanol oxidation kinetics, high cost, and limited resource do not allow use of Pt at commercial level. In addition, Pt-based electrocatalysts, generally, undergo deactivation/poisoning by the reaction intermediates, particularly by CO molecule in acid medium. The use of non-platinum metal like palladium in fuel cell catalysts is interesting, because it is more widespread in the Earth crust than platinum (abundance of 1.5×10^{-2} versus 5×10^{-3} parts per million by mass, resp.), and it is less expensive than Pt [3]. In addition, it is very stable in the acidic fuel cell environment and also exhibits interesting electrocatalytic properties for CO electrooxidation. These properties have led to considering Pd as a possible catalyst for those reactions in which CO appears as a poisoning intermediate, such as in the methanol [4]. The catalytic activity of Pd can be modified by alloying with other metals such as Ni; the combination of Pd with Ni is expected to further enhance the tolerance of Pd to poisoning as Ni is an oxophilic element [5]. The study of alloy electrodes is motivated primarily from the anticipation of a synergistic electrocatalytic benefit from the combined properties of the component metals of alloys [6]. The use of Ni enables a reduction in cost of the catalyst [7, 8]. The electrocatalytic activity of Pd-Ni alloy electrode can be further improved by dispersion of catalyst particle on suitable catalyst support [9]. Carbons of different forms are generally used to load the metal catalysts but metal particles are physically isolated in the carbon matrix and the catalyst system does not provide a conductive environment for the migration of protons [10]. In contrast, conducting polymers (CPs) function as redox mediators for electron and proton between the electrodes and the electroactive reactants shows permselectivity towards some species; they permit the diffusion of redox active species (e.g., methanol) to the active sites of electrode and enhance the electrooxidation current [11, 12]. The film of a conducting polymer on the electrode surface improves the interfacial properties between the electrode and electrolyte and the mediation of charge transfer between the substrate and the dispersed metal particles is facile in the matrix of a conducting polymer [13]. CPs deposited on carbon substrates are favorable and attractive hybrid supports for catalyst particles. The hybrid materials, possessing the properties of each component, or even with a synergistic effect, would present improved characteristics and electrocatalytic activity with respect to the individual components. Among conducting polymers, polyaniline (PANI) is one of the most frequently utilized matrixes for dispersing the metal particles because they can easily be prepared on the electrode substrate as a homogeneous and strong adherent film with a desirable thickness, high accessible surface area, low resistance, and good mechanical and chemical stability in acidic media. Introduction of PANI into the electrode catalyst layer increases the catalyst utilization and helps water absorption on the catalyst and formation of an active oxycompound which will promote CO oxidation to CO_2. It also accelerates the Langmuir absorption behavior of methanol [14]. Hence, DMFCs using PANI-containing electrodes are expected to give superior performance. In the present work, the film of PANI was deposited on graphite substrate by cyclic voltammetric method. The metal particles were homogeneously dispersed into a porous PANI film by a constant current electrodeposition technique and C-PANI-Pd, C-PANI-Ni, and C-PANI-Pd-Ni electrocatalysts were prepared. The electrocatalytic activity of the prepared catalysts towards methanol oxidation reaction was investigated by different electrochemical method such as cyclic voltammetry (CV), chronoamperometry, and electrochemical impedance spectroscopy (EIS). Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) was also employed to morphological and elemental studies of the modified catalyst layer.

2. Experimental

2.1. Materials and Equipment. The graphite block (saw cut finish grade) purchased from Graphite India Limited was used as substrate for the electrode matrix. $PdCl_2$, H_2SO_4, aniline, methanol, and other chemicals were of analytical grades from Merck. All the aqueous solutions were prepared with distilled water. All electrochemical experiments were performed using a CHI680B electrochemical analyzer (CH Instruments, Inc. Austin, USA) controlled by CH instrument electrochemical software by using a double-compartment glass cell with conventional three-electrode configuration. The substrate working electrode was polished graphite (geometric area: $1.0\,\mathrm{cm}^2$). The counter electrode was a large area Pt-wire and the reference electrode was Ag/AgCl electrode.

2.2. Electrode Preparation. Electropolymerization of aniline at the graphite electrodes was achieved by potentiodynamic method. The electrode potential was swept between −0.5 and 0.5 V versus Ag/AgCl at a scan rate of $50\,\mathrm{mV\,s^{-1}}$ using an aqueous solution of 0.1 M H_2SO_4 containing 0.3 M aniline for 40 cycles. The thickness of the deposited films (PANI film thickness: $1.2\,\mu$m) was calculated from the charge consumed during the electrodeposition of PANI considering two electron mechanism [15]:

$$d = \frac{QM}{2F\rho}, \tag{1}$$

where Q is the area specific overall charge ($\mathrm{C\,m^{-2}}$), M is molecular weight of aniline, F is Faraday constant ($\approx 96{,}500\,\mathrm{C\,mol^{-1}}$), and ρ is the density of PANI. The Pd and Ni microparticles were incorporated in the PANI film coated graphite (C-PANI) by electrochemical deposition from an aqueous 0.1 M sulphuric acid solution of 0.05 M $PdCl_2$ and 0.05 M $NiCl_2$, respectively. For electrochemical codeposition of Pd and Ni microparticles, an equimolar mixture of 0.05 M $PdCl_2$ and 0.05 M $NiCl_2$ was used. For each case, electrodeposition was performed at room temperature under galvanostatic control by applying $3\,\mathrm{mA\,cm^{-2}}$ current density. The duration of electrochemical deposition for different metals was varied between 5–10 minutes to keep the metal loading fixed ($2\,\mathrm{mg\,cm^{-2}}$) at the electrode surface. Assuming 100% efficiency for the reduction of M^{n+} to M the amount of metal deposited was evaluated from the quantity of charge, Q_{dep}, that passed during the electrodeposition. In this process, the metal loading (W in $\mathrm{mg\,cm^{-2}}$) is

$$W = \frac{Q_{\mathrm{dep}}M}{nF}, \tag{2}$$

where M is the atomic weight of metal, n is the number of exchanged electrons, and F is the Faraday constant.

2.3. Characterization of the Working Electrodes. The composite electrodes were characterized by scanning electron microscopy (SEM) and their chemical composition was analyzed by energy dispersive X-ray analysis (EDX). The SEM and EDX analysis were performed using electron microscope JSM-6390LV (JEOL Co., Japan) equipped with energy-dispersive full range X-ray microanalysis system. The methanol electrooxidation reaction at surface of the electrode was investigated in electrolyte solution containing 1.0 M methanol and 0.5 M H_2SO_4 by CV, Chronoamperometric, and EIS measurements. In CV measurements, the potential was scanned between −0.8 and 1.0 V at a scan rate of $50\,\mathrm{mV\ s^{-1}}$. In EIS measurements, the A.C. frequency range extended from 100 kHz to 1 Hz with an excitation signal of 5 mV. The impedance spectra were fitted to an equivalent circuit model using a nonlinear fitting program. A constant temperature water bath was used to keep the experiments running at a preset temperature. All current densities were calculated according to geometric areas of electrodes and were normalized to weight of the catalyst.

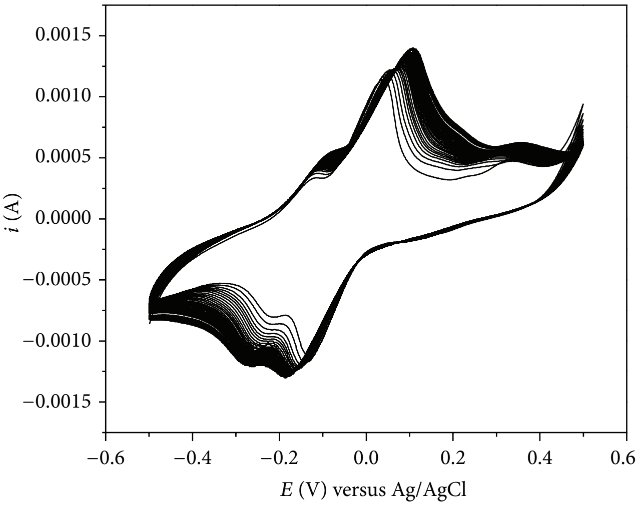


Figure 1: Cyclic voltammograms (40 cycles) during electropolymerization of aniline on graphite in 0.5 M H_2SO_4 solution containing 0.1 M aniline at a scan rate of 50 mV s^{-1} at room temperature.

3. Results and Discussion

3.1. Electrodeposition of PANI Thin Film. Electropolymerization of PANI offers the possibility of controlling the thickness and homogeneity of the conducting polymer film on the electrode surface. Figure 1 shows the cyclic voltammograms during electropolymerization of aniline on the graphite electrode in 0.1 M H_2SO_4 solution containing 0.3 M aniline. As can be seen, the oxidative polymerization of aniline starts at 0.1 V in the first cycle rendering the first layer of PANI. Subsequent cycles indicate the subsequent growth of the polymer films as evidenced by an increase in the redox current suggested that the film was conductive, electroactive, and also uniform.

The redox peaks at around 0.1 V are attributed to the transformation of PANI from the reduced leucoemaraldine (LE) state to the partly oxidized emeraldine (EM) state, and the redox peaks at around 0.4 V correspond to transition of the PANI, from LE to pernigraniline (PE) state [15, 16]. The film thickness was controlled by controlling the number of potentials cycles and calculated by the height of the first peak. After electropolymerization, a green film was formed on the working electrode.

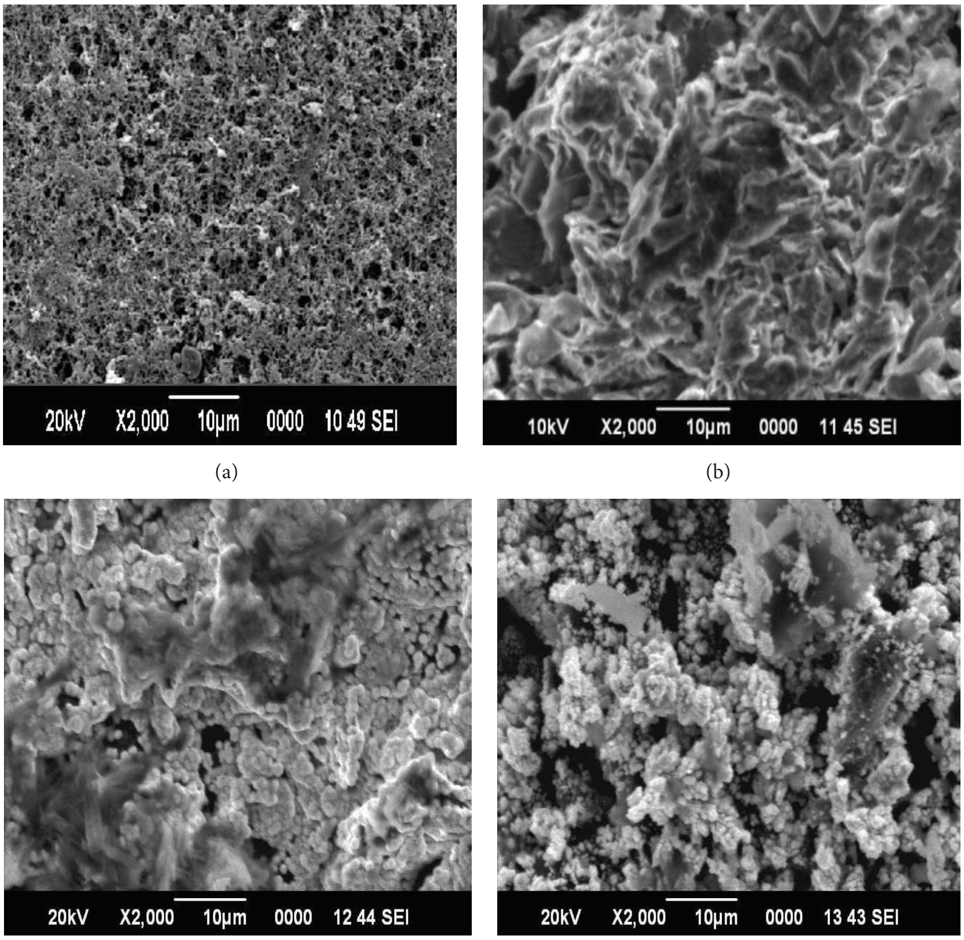
3.2. Physical Characterization of the Electrodes. The surface morphology of the catalyst was revealed through scanning electron microscopy. The SEM of C-PANI film in Figure 2(a) shows a polymeric three-dimensional matrix with randomly grown fibrilar branched and porous structure characteristic of electrochemically deposited PANI and highly suitable for dispersion of the metal particles. The SEM image of C-PANI-Ni electrode in Figure 2(b) shows compact layer structure.

The SEM images of C-PANI-Pd and C-PANI-Pd-Ni electrodes in Figures 2(c) and 2(d) show a wide spread of coarse grained closely packed clusters of Pd and Pd-Ni metal particles distributed over the whole polymeric film. The Pd-Ni particles show better dispersion on the C-PANI. As Pd and Ni were coelectrodeposited on the C-PANI surface both the metals were grown together on the same sphere making an assembly of ad-atoms in the form of agglomerated particles. The elemental compositions of electrocatalysts were investigated using EDX spectroscopy as shown in Figures 3(a)–3(c).

The depositions of metal particles are evident from EDX spectra. The atomic percent ratio of Pd/Ni in the C-PANI-Pd-Ni catalyst is 27 : 0.1. The relative low content of Ni element in the C-PANI-Pd-Ni catalyst is ascribed to the higher reduction potential of Pd^{2+}/Pd compared to Ni^{2+}/Ni.

3.3. Electrochemical Characterization of the Synthesized Electrode. Electrocatalytic properties of the synthesized electrodes toward methanol oxidation were investigated by cyclic voltammetry in a solution of 0.5 M H_2SO_4 and 1.0 M CH_3OH at a scan rate of 50 mV s^{-1} at room temperature as shown in Figure 4.

The current density was normalized by the geometric area of the working electrode to indicate the catalyst mass activity. The C-PANI electrode shows small methanol oxidation peak at −0.05 V which is in agreement with the reported results [17], whereas C-PANI-Ni electrode shows small methanol oxidation peak at higher potential. For C-PANI-Pd and C-PANI-Pd-Ni electrodes, two well-defined current peaks in the forward scans were observed. The first peak corresponds to the oxidation of freshly chemisorbed methanolic species and the second peak corresponds to oxide formation at higher potential. The oxide reduction peak was observed for Pd containing electrodes only. Increasing current was not observed in the reverse scan; therefore, methanol was not oxidized in reverse. Values of CV parameters such as onset potential (E_{op}), peak current density (i_p), and peak potential (E_p) for MOR on different electrodes are shown in Table 1. The onset potential of C-PANI-Pd-Ni for methanol oxidation occurs at −0.32 V, which is more negative than that of the other three



(a) (b)

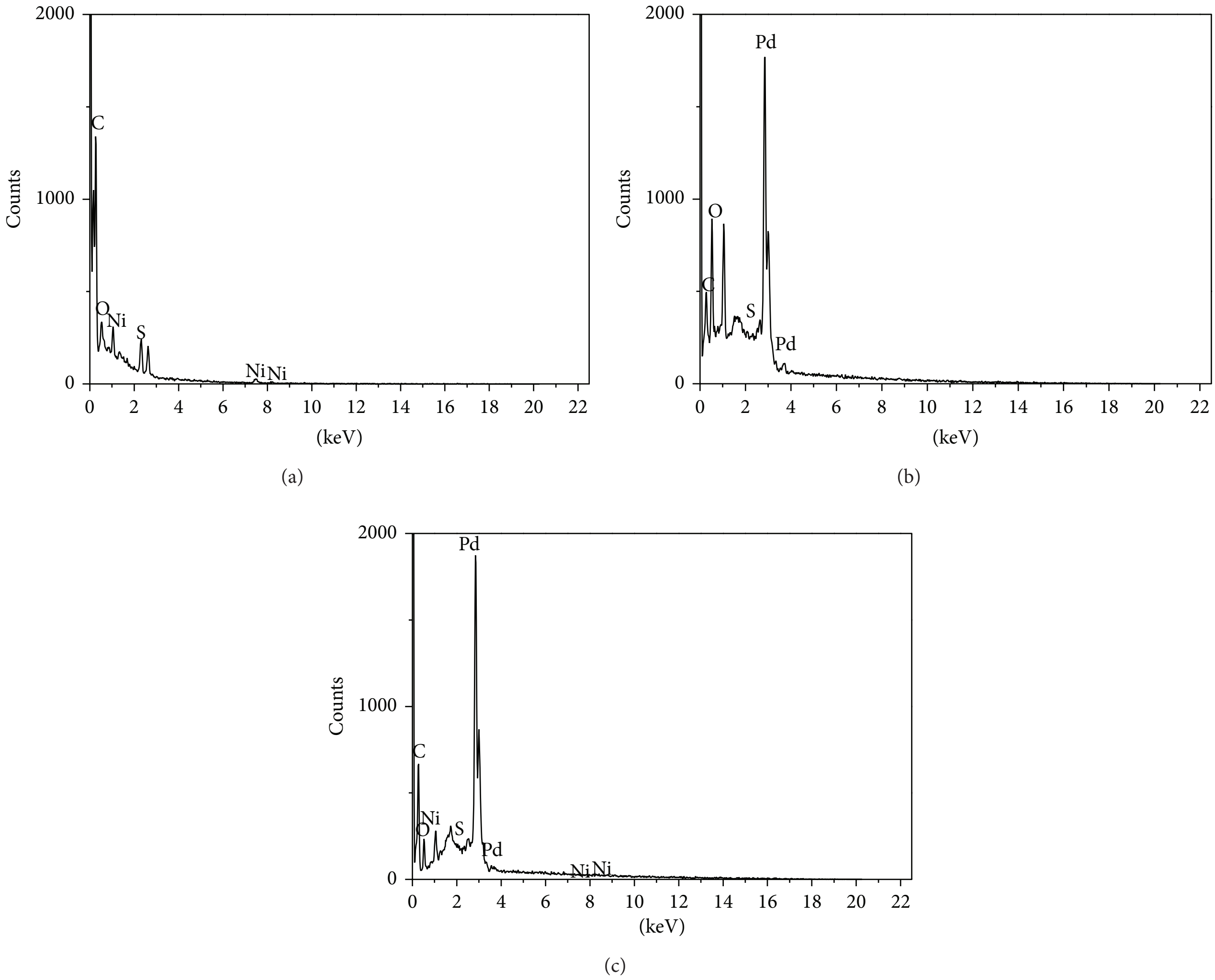
(c) (d)

Figure 2: SEM images of (a) C-PANI, (b) C-PANI-Ni, (c) C-PANI-Pd, and (d) C-PANI-Pd-Ni electrodes.

Table 1: Comparison of different electrochemical parameters for methanol oxidation on different electrodes.

Electrochemical parameters	Electrodes			
	C-PANI	C-PANI-Pd	C-PANI-Ni	C-PANI-Pd-Ni
E_{op} (V)	−0.297	−0.303	−0.203	−0.320
E_p (V)	−0.054	0.190	0.473	0.350
i_p ($\mathrm{A\,cm^{-2}\,mg^{-1}}$)	0.0058	0.031	0.0045	0.186
δ (% per s) $\times 10^{-5}$	13.62	8.24	13.30	3.70
E_{app} ($\mathrm{kJ\,mol^{-1}}$)	108.4	45.2	75.3	30.6
R_{ct} (ohm)	—	40	250	20

catalysts. The peak current density of the methanol oxidation on C-PANI-Pd-Ni is $0.186\,\mathrm{A\,cm^{-2}\,mg^{-1}}$, which is much higher than C-PANI ($0.0058\,\mathrm{A\,cm^{-2}\,mg^{-1}}$), C-PANI-Ni ($0.0045\,\mathrm{A\,cm^{-2}\,mg^{-1}}$), and C-PANI-Pd ($0.031\,\mathrm{A\,cm^{-2}\,mg^{-1}}$). It is clear that the current densities are higher at corresponding potentials on C-PANI-Pd-Ni electrode than that on other electrodes. The current density of methanol oxidation on C-PANI-Pd-Ni electrode begins to rise more sharply at much more negative potential compared to the other electrodes. Thus, the C-PANI-Pd-Ni catalyst is capable of oxidizing methanol at lower potential than that of other electrode. The enhancement in catalytic activity with codeposited catalyst may be attributed to the increase in surface area, synergic effect by the interaction between Ni and Pd, and the fact that the occluded hydrogen can accelerate dehydrogenation and at the same time prevent adsorption of intermediate species on the electrode surface so that more active sites are available for adsorption of methanol. The increase in surface area is due to the better dispersion of metal particles in polymer matrix. The enhancement in activity on Ni or Pd based alloy catalysts is correlated to the geometric and electronic change of the metal [18]. From Table 1 it is evident that C-PANI-Pd-Ni is the most



(a)

(b)

(c)

Figure 3: EDX spectra of (a) C-PANI-Ni, (b) C-PANI-Pd, and (c) C-PANI-Pd-Ni catalysts.

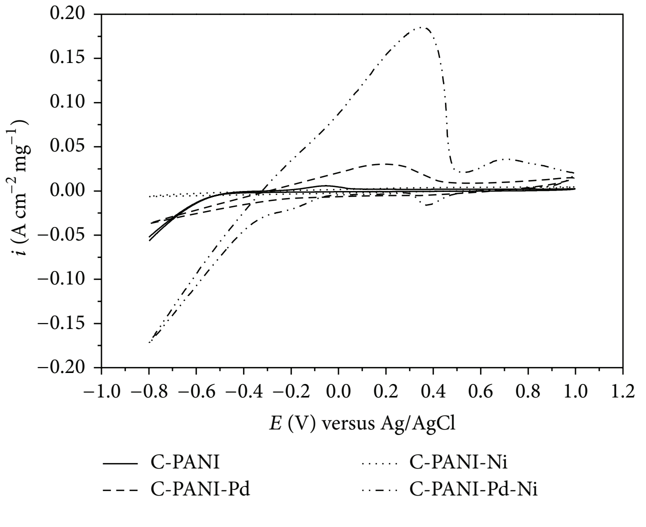


Figure 4: Cyclic voltammograms for methanol oxidation on different electrodes in 0.5 M H_2SO_4 solution containing 1.0 M methanol at a scan rate of 50 mV s^{-1} at room temperature.

effective electrode in terms of onset potential and anodic peak current density.

The stability and electrocatalytic activity of different catalysts were evaluated by chronoamperometry. Figure 5 shows the chronoamperograms of the C-PANI, C-PANI-Pd, C-PANI-Ni, and C-PANI-Pd-Ni electrodes in a solution of 0.5 M H_2SO_4 containing 1.0 M CH_3OH at a fixed potential of 0.2 V. It can be is observed from Figure 5 that the C-PANI-Pd-Ni catalyst exhibits higher current density and slower rate of decay in comparison to other catalysts during the time of experiment.

The current density decreases as a function of time, at a given potential for all electrodes. This current decrease can be attributed to adsorption of poisonous intermediates, anion adsorption in the case of the H_2SO_4 system, and the decrease in production of CO_2 as the surface oxide was consumed, leading to the formation of other soluble intermediates [19]. The final current densities at 1000 s are 0.24×10^{-3}, 0.64×10^{-3}, 0.56×10^{-3}, and 1.77×10^{-3} A cm^{-2} mg^{-1} for C-PANI, C-PANI-Pd, C-PANI-Ni, and C-PANI-Pd-Ni catalysts,

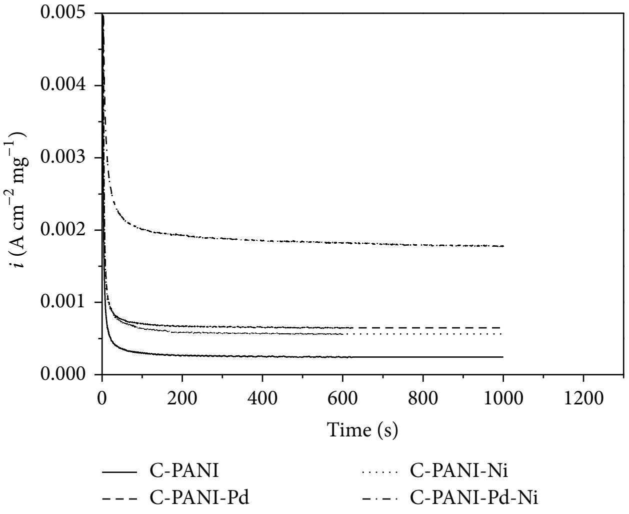


Figure 5: Chronoamperograms for methanol oxidation on different electrodes in 0.5 M H_2SO_4 solution containing 1.0 M methanol at 0.2 V.

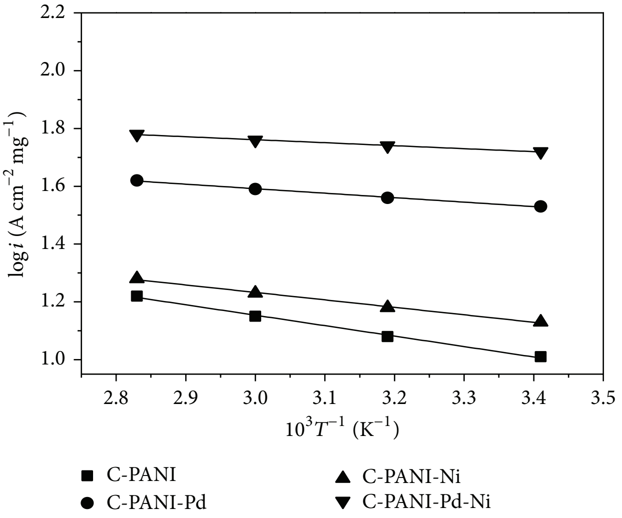


Figure 6: Arrhenius plots for methanol oxidation on different electrodes in 0.5 M H_2SO_4 solution containing 1.0 M methanol at 0.2 V.

respectively. Long-term poisoning rates (δ) were evaluated from the record of current decay (Figure 5) at times greater than 500 s using the following equation [20]:

$$\delta = \frac{100}{i_0} \times \left(\frac{di}{dt}\right)_{t>500\,\mathrm{s}} \quad (\%\ \text{per s}), \tag{3}$$

where $(di/dt)_{t>500\,\mathrm{s}}$ is the slope of the linear portion of the current decay and i_0 is the current at the start of polarization back extrapolated from the linear current decay. It is evident from Table 1 that the long-term poisoning effect for methanol oxidation can be significantly controlled on C-PANI-Pd-Ni whereas other electrode suffers from extensive poisoning.

The results are consistent with those of CV measurements. The improved antipoisoning ability of the electrode may be attributed to the reaction between strongly bound CO species and OH_{ads} on neighboring of C-PANI-Pd-Ni sites [21]. The C-PANI-Pd-Ni electrode shows good methanol oxidation kinetics and stability over a longer period of time.

The apparent activation energy (E_{app}) value determined using electrochemical techniques gives information regarding the chemical rate determining step. Figure 6 shows the Arrhenius plots for methanol oxidation on the C-PANI, C-PANI-Pd, C-PANI-Ni, and C-PANI-Pd-Ni electrodes at a fixed potential of 0.2 V and different temperatures.

The activation energies were obtained from the slopes of the $\log i$ versus $1/T$ plots constructed from chronoamperometric experiments by fitting the Arrhenius equation [22]. The activation energies from these plots are summarized in Table 1. The order of activity in terms of activation energy was C-PANI-Pd-Ni > C-PANI-Pd > C-PANI-Ni > C-PANI, in agreement with the order of onset potential and oxidation current at a constant temperature. This drastic decrease in activation energy for C-PANI-Pd-Ni electrode leads to the increase in methanol oxidation current.

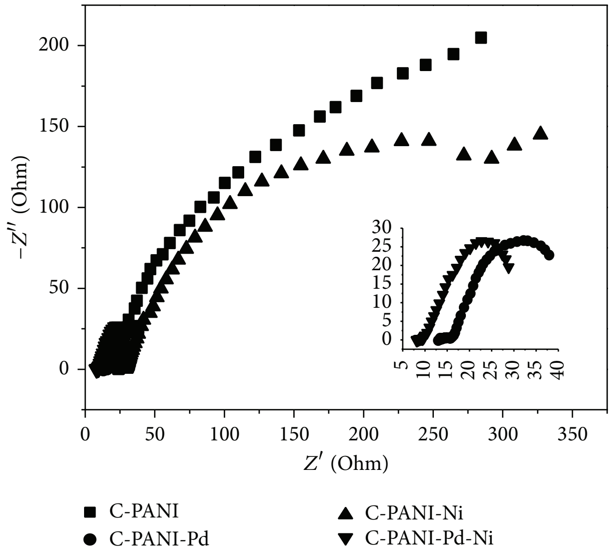


Figure 7: Electrochemical impedance spectra (Nyquist) for methanol oxidation on different electrodes in 0.5 M H_2SO_4 solution containing 1.0 M methanol at 0.2 V.

Electrochemical impedance spectroscopy was used to investigate reaction process and kinetics of methanol oxidation on the different electrodes at a fixed potential of 0.2 V. The Nyquist plots for methanol oxidation in a solution containing 0.5 M H_2SO_4 and 1.0 M methanol are shown in Figure 7. The absence of semicircular behavior for the C-PANI electrode is indicative of very little methanol oxidation and a diffusion controlled process at this electrode whereas semicircular behavior is evident for other three electrodes. The C-PANI-Ni electrode shows 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, whereas C-PANI-Pd and C-PANI-Pd-Ni electrodes show single semicircle indicating charge-transfer process only. Although the shape of the impedance spectroscopy for C-PANI-Pd and C-PANI-Pd-Ni electrode is similar, but differ in the diameters of the two semicircles. The diameter of the semicircle with C-PANI-Pd is larger than that of C-PANI-Pd-Ni. The charge transfer resistance (R_{ct}) was obtained from the Nyquist plot by taking the diameter of the semicircle and summarized in Table 1.

The lower value of R_{ct} for the C-PANI-Pd-Ni electrode indicates faster rate of electrochemical charge transfer. Thus, it is possible to attribute the increased electrocatalytic activity of the PANI-Pd-Ni composites with incorporated conducting polymers can promote the formation of a three-dimensional layer, enhancing methanol oxidation through increases in the surface area and the number of active sites [23].

4. Conclusion

The C-PANI-Pd-Ni electrode exhibited an excellent electrocatalytic activity for methanol oxidation and stability compared to C-PANI, C-PANI-Ni, and C-PANI-Pd catalysts. The metal microparticles were well distributed into the polyaniline matrix. Introduction of PANI as a conductive polymer within catalyst layer (i) improves electron transfer between catalyst particles and PANI matrix and also act as accessible mesoporous network for catalytic particles; (ii) it hinders the formation of strong adsorbed poisons and catalyzes the oxidation of strongly and weakly adsorbed poisons, so it prevents catalyst from more poisoning by intermediate products of methanol oxidation such as CO, and (iii) improves the mechanical properties of the catalyst layer by providing good and flexible connections between metal particles. Moreover, the amount of noble metal platinum at the prepared electrode was remarkably reduced, the cost of the processed catalyst was greatly decreased and the procedure was very simple. In fact, PANI acts also as a binder in catalyst layer without serious restriction in methanol diffusion to the active site. The performance of the electrode is enhanced after partial chemical displacement of dispersed Ni with Pd. Polyaniline matrix with higher electrochemical surface area and lower resistance of charge transfer to electrode manifest themselves to be highly suitable candidate for use in DMFC applications.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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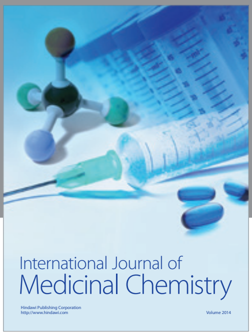
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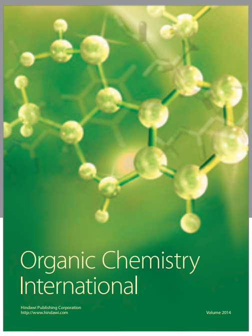
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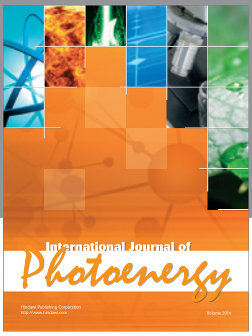
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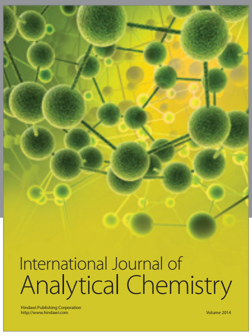
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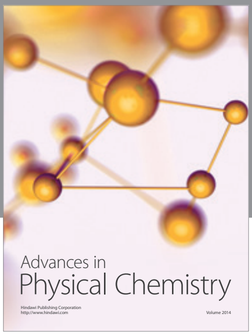
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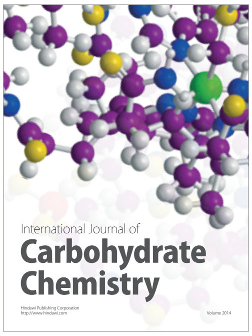
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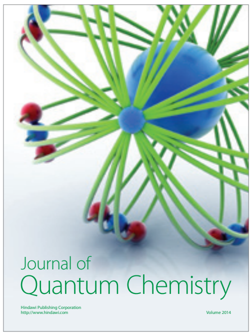
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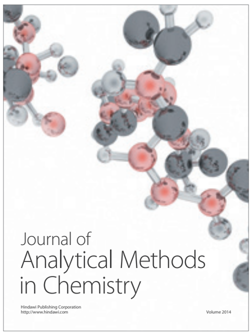
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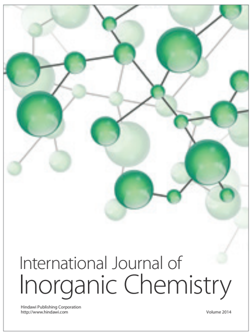
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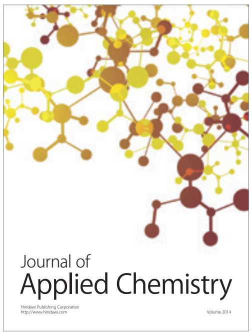
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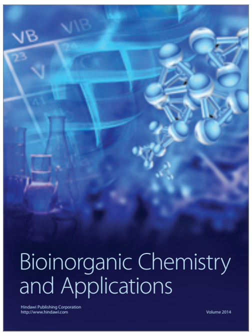
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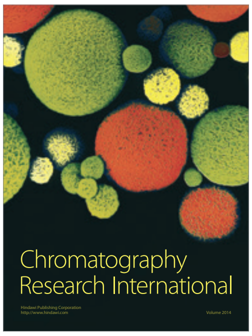
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