Electrocatalytic activity of nanostructured Ni and Pd–Ni on Vulcan XC-72R carbon black for methanol oxidation in alkaline medium

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ABSTRACT

Ni and Pd–Ni nanoparticles were chemically deposited on Vulcan XC-72R carbon black by impregnation method using NaBH₄ as a reducing agent. The prepared electrocatalysts were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDX). The electrocatalytic activity of Ni/C and Pd–Ni/C electrocatalysts towards methanol oxidation in 0.5 M KOH solution was examined using cyclic voltammetry and chronoamperometry. Two methanol oxidation peaks were observed on the Pd–Ni/C at 0 and +0.860 mV. Their current density values are higher than those at Pd/C and Ni/C electrocatalysts by 1.92 and 1.68 times, respectively. The catalytic rate constant of methanol oxidation reaction at Ni/C and Pd–Ni/C electrocatalysts in (0.2 M MeOH + 0.5 M KOH) solution was estimated using double-step chronoamperometry as 5.64 × 10⁻³ and 6.25 × 10⁻³ cm³ mol⁻¹ s⁻¹, respectively. Pd–Ni/C is more stable than Pd/C and Ni/C electrocatalysts. Therefore, Pd–Ni/C is a suitable as a less expensive electrocatalyst for methanol oxidation in alkaline medium.

1. Introduction

An increased interest has been paid to the development of direct methanol fuel cells (DMFCs). They are a promising future technology as alternative power sources to conventional energy-generation devices. They have many advantages such as higher energy conversion efficiency, low-to-zero pollutant emissions and availability of methanol fuel [1]. Pt and Pt-based catalysts such as PtRu [2–4], PtSn [5] and PtNi [6] have been widely investigated for methanol oxidation reaction. However, they could be easily deactivated due to poisoning by the reaction intermediates such as CO in acid medium. Moreover, the high cost of Pt and its rare sources limited the commercial applications of DMFCs [4,7].

Among the Pt metal series, Pd appears as a substitute for Pt, because it has similar properties, lower cost and high availability [8–10]. Pd and Pd/C catalysts can overcome the CO-poisoning effect during alcohol oxidation [11]. However, this electrocatalytic activity of Pd needs to be improved. This
could be achieved by combining Pd with other metals or metal oxides. Wang et al. [9] have prepared Pd–Ag/C electrocatalysts containing different Ag loadings by chemical reduction using NaBH₄. Pd–Ag (1:1)/C catalyst showed the best electrocatalytic activity towards methanol oxidation in alkaline medium. The on-set potential of ethanol oxidation at 10 wt.% Pd–10 wt.% Ag/C electrocatalyst is negatively shifted by approximately 200 mV from that at 10 wt.% Pd/C. In addition, its peak current density is about 3.5 times higher than that at 10 wt.% Pd/C [12]. PdAg/NbₓTi₁₋ₓO₂ electrocatalyst displayed better performance towards ethanol oxidation than PdAg/C and PdAg/TiO₂. PdAg supported on Nb₂O₃–TiO₂ and Nb₀.35Ti₀.7O₂ showed the highest catalytic activity as well as excellent durability in basic solution [13]. Pd₄Ru₁₃ electrocatalyst, prepared by the hydrothermal method, displayed better performance for ethanol oxidation [14]. Enhanced poisoning tolerance was exhibited by Pd–0.5 wt.% C–20 wt.% Ru composite during methanol and ethanol oxidation reactions in 1 M KOH solution [15,16]. CO stripping results revealed that the addition of lead to Pd/C catalyst facilitates the oxidative removal of adsorbed CO. This promoting effect of lead is explained by the bi-functional mechanism and d-band theory [17]. Nguyen et al. [18] have observed that 10 wt.% Pd–2 wt.% Tb/C electrocatalyst gave the lowest activation energy for ethanol oxidation in alkaline media.

Among a series of metal oxides (CeO₂, NiO, Co₃O₄ and Mn₃O₄) promoted Pd catalysts, prepared by intermittent microwave heating method, NiO promoted Pd catalyst gave the highest current density of ethanol oxidation reaction [19,20]. This may be attributed to the adsorption of OH ions on the metal oxide surface that function in the same way as Ru in PtRu catalysts to improve the anti-poisoning ability. Shen et al. [21] have concluded that adding NiO to Pd/C in a weight ratio of 1:4 greatly improves its electrocatalytic activity for methanol oxidation. Miao et al. [22] showed that a superior electrooxidation performance was observed with increasing the operating temperature at silicon microchannel plates modified with nickel–palladium nanoparticles by electroless plating. The anodic peak current density of methanol oxidation at porous nanostructured Pd/Ni/Ni electrocatalyst, prepared by electrodeposition followed by galvanic replacement, was 4.33 and 8.34 times higher than those at flat Pd and smooth Ni electrodes, respectively [23]. X-ray photoelectron spectroscopy of carbon supported Pd–Ni–Ni nanoparticle, formed by simultaneous reduction using NaBH₄, revealed the chemical states of nickel, including metallic Ni, NiO, Ni(OH)₂ and NiOOH. PdₓNiₓ/C catalyst exhibits higher activity and stability for ethanol oxidation than does Pd/C catalyst [24]. The onset potential of methanol oxidation at nanocrystalline PdₓNiₓNiₐ alloy catalyst is negatively shifted by ~300 mV as compared to that at nanoporous palladium [25]. Ni@Pd nanoparticles with core/shell structure on MWCNTs were prepared via a two-step strategy: impregnation-reduction method and replacement method. Their electrocatalytic activity for ethanol oxidation is 2.3 times higher than that of Pd/MWCNTs electrocatalyst containing the same Pd loading. These enhanced electrocatalytic properties could be attributed to the electric synergistic effect between Pd and Ni and the highly used Pd ratio in the shell structure [26].

In this study, carbon supported Ni and Pd–Ni nanoparticles are prepared by impregnation technique using NaBH₄ as a reducing agent. They are characterized by X-ray diffraction, transmission electron microscopy and energy dispersive X-ray analysis. The electrocatalytic activity of the prepared catalysts is studied in 0.5 M KOH solution using cyclic voltammetry and chronoamperometry techniques. Pd/C electrocatalyst is also prepared under the same conditions for comparison.

2. Experimental

2.1. Chemicals

Palladium chloride (PdCl₂), nickel chloride hexahydrate (NiCl₂·6H₂O) and sodium borohydride (NaBH₄) were purchased from Aldrich. Vulcan XC-72R carbon black was obtained from Cabot Corp., USA with a specific surface area (BET) of 240 m² g⁻¹ and an average particle size of 40 nm. Nafion (perfluorosulphonic acid-PTFE copolymer, 5 wt.% mixture of aliphatic alcohol and water) was from Sigma–Aldrich, Germany. Sulfuric acid (H₂SO₄) and methanol (CH₃OH) were from Merck. Double distilled water was used for preparation of solutions and washing.

2.2. Synthesis of electrocatalysts

All prepared electrocatalysts contain total metal loading of 30 wt.%. An appropriate amount of Vulcan XC-72R carbon black was ultrasonically mixed with double distilled water for 30 min until a homogeneous suspension was formed. The metal precursors (PdCl₂ and NiCl₂·6H₂O) were then added in an atomic ratio of 1:1 with mechanical stirring for 30 min, followed by sonication for another 30 min. A freshly prepared NaBH₄ solution, in which the molar ratio of the metal to NaBH₄ was 1:70, was added dropwisely to the mixture with vigorous stirring for 3 h. The resulting powder was finally collected by filtration and washed for several times with double distilled water and dried at 80 °C in an air oven for 6 h. For comparison, Pd and Ni nanoparticles supported on Vulcan XC-72R carbon black were also prepared in the same procedure.

2.3. Physical characterization of electrocatalysts

The phase structure of the prepared electrocatalysts was determined by X-ray diffraction study that was carried out with the help of Rigaku-D/MAX-PC 2500 X-ray diffractometer equipped with Ni filtered Cu Kα as the radiation source. The tube current was 40 mA with a voltage of 40 kV. In order to investigate the size, morphology and dispersion of the electrocatalyst particles, transmission electron microscopy was performed. JEOL-JEM 2010 transmission electron microscope was operated at an accelerating voltage of 160 kV. The catalyst was ultrasonically dispersed in double distilled water to obtain a uniform ink. It was then mounted onto copper grids covered with a carbon film and left to dry in air. Energy dispersive X-ray spectroscopy was applied to investigate the chemical composition. A scanning electron microscope (JEOL...)
JAX-840 and a POEMS ICP-OES instrument (Thermo Jarrell-Ash Corporation, Franklin, MA, USA) were used.

2.4. Electrochemical characterization of electrocatalysts

Electrochemical studies were carried out using Voltalab 6 potentiostat. A standard three-electrodes cell was constructed to evaluate the electrochemical reactivity of electrocatalysts by cyclic voltammetry and chronoamperometry techniques. A platinum wire was used as the counter electrode, while mercury/mercury oxide Hg/HgO/1.0 M NaOH (MMO) was the reference electrode. The working electrode was a commercial carbon disk covered with a thin layer of Nafion-impregnated catalyst. The potential values mentioned in this work are referred to (MMO) [its potential = +140 mV (NHE)]. Before applying the catalyst powder on the working electrode, carbon surface was polished with emery papers in different grades and cleaned with ethanol. It was then scanned in 0.5 M H2SO4 solution in the potential range from −800 to +1600 mV versus mercury/mercurous sulphate electrode [Hg/Hg2SO4/1.0 M H2SO4 (MMS)] for 50 cycles at a scan rate of 50 mV s−1 in order to get an active surface. The thin-film electrode was prepared as follows: 1.1 mg of catalyst powder was dispersed in 0.6 ml 5 wt.% Nafion solution and isopropyl alcohol. This ink was then spread over the working electrode surface using a micropipette. It was left to dry overnight. Cyclic voltammetric experiments were performed in the condition range from −700 to +1300 mV (MMO) in 0.5 M KOH solution in absence and in presence of methanol at a scan rate of 10 mV s−1. The current density values were calculated based on the geometrical surface area of different electrocatalysts. All electrochemical measurements were operated in aerated electrolytes at room temperature of 30 °C ± 0.2.

3. Results and discussion

Fig. 1 showed X-ray diffraction patterns of Ni/C, Pd/C and Pd−Ni/C electrocatalysts. The broad peak at 2θ value of 18−30° in all patterns is related to the graphite (002) facet of Vulcan XC-72R carbon black. X-ray diffraction pattern of Ni/C electrocatalyst has two additional reflection planes at 2θ values of 33.68° and 59.93°. They correspond to (100) and (110) facets of Ni(OH)2, respectively [24,27,28]. For Pd/C electrocatalyst, Pd(111), Pd(200) and Pd(220) diffraction planes of face-centered cubic (fcc) crystalline structure of Pd appeared at 2θ values of 39.93°, 46.40° and 67.67°, respectively [26,29−32]. These three diffraction peaks are shifted in the negative direction in Pd−Ni/C electrocatalyst [39.39° (111), 45.75° (200) and 67.46° (220)]. This slight shift strongly indicates the incorporation of Pd and Ni atoms in the same lattice. In another word, a number of Pd atoms was displaced by Ni atoms, leading to a lattice expansion due to the formation of Pd−Ni alloy. Wang et al. [17] have observed an appreciable shift to lower 2θ values for different Pd diffraction peaks when Pb is added by co-reduction method in Pd:Pt atomic ratio of 2:1 in Pd−P/C electrocatalyst. A similar trend was also shown by Pd−Ag(1:1.5)/C [9] and Pd6Pt4 alloy nanoparticles highly loaded on different carbon supports by a modified polyl reduction route [33,34] when compared to Pd/C. No diffraction peaks of nickel or nickel oxides/hydroxides were detected in Pd−Ni/C electrocatalyst. It suggests that Ni atoms either form an alloy with Pd or exist as oxides in amorphous phase [35]. The average crystallite size of Pd/C and Pd−Ni/C electrocatalysts was calculated based on the broadening of Pd(220) diffraction peak using Debye−Scherrer’s equation [36]. It was found as 5.9 and 4.4 nm for Pd/C and Pd−Ni/C electrocatalysts, respectively. Shen et al. [24] have simultaneously reduced PdNi catalysts in different atomic ratios on carbon surface using NaBH4 as a reductant. They had average Pd particle size of 3−3.2 nm. Pd3Ni1/C catalyst with a Pd loading of ~20 wt.% showed Pd particle size of 3.9 nm [37]. The chemical reduction of PdNi nanoparticles on Vulcan XC-72 carbon black support using formic acid and thiourea resulted in larger Pd crystal sized particles of 4.66 nm. Core/shell Ni@Pd nanoparticles supported on MWCNTs with 20 wt.% total metal content and Pd:Ni atomic ratio of 1:1 had particle size of 6.8 nm using NaBH4 as a reducing agent [30].

TEM images of Pd/C, Ni/C and Pd−Ni/C electrocatalysts were shown in Fig. 2. Spherical carbon particles were clearly observed in TEM image of Pd/C powder [see Fig. 2(a)]. Palladium either spreads as separate nanoparticles outside carbon matrix or agglomerated in large supported groups. For Ni/C powder, nickel nanoparticles are completely covering carbon surface as dense aggregates [see Fig. 2(b)]. Less extent of agglomeration was obtained after combining nickel and palladium in Pd−Ni/C powder [see Fig. 2(c)]. The simultaneous reduction of Co [39] or Tb [18] together with Pd on carbon support using NaBH4 was found to improve the metallic nanoparticles dispersion when compared to Pd/C powder. The particle size of metallic deposits in Pd/C and Ni/C powders is ranged as 7.1−7.5 and 10−15 nm, respectively. This particle size is greatly reduced to 3−4 nm in Pd−Ni/C powder. The chemical composition of Pd/C, Ni/C and Pd−Ni/C electrocatalysts was determined using energy dispersive X-ray analysis in Fig. 3. Palladium, nickel and carbon are obviously detected. For Pd−Ni/C powder, the total weight percentage of palladium and nickel was 27.33%, which is close to the actually added weights of metallic precursors during the preperation steps.

Fig. 1 — XRD patterns of Ni/C, Pd/C and Pd−Ni/C electrocatalysts.
The electrocatalytic activity of an electrocatalyst depends upon its geometrical as well as electronic properties. Fig. 4 shows the cyclic voltammograms of Pd/C and Pd–Ni/C electrocatalysts in 0.5 M KOH solution in the potential range from -800 to +600 mV (MMO) at a scan rate of 50 mV s^{-1}. It can be observed that the adsorption/desorption region of hydrogen is located between -800 and -350 mV (MMO) at Pd/C. However, this potential window at Pd–Ni/C electrocatalyst is extended to more positive value at -284 mV (MMO). Moreover, the peak associated with the reduction of palladium oxide at Pd–Ni/C electrocatalyst is shifted in the negative direction by 33 mV when compared to that at Pd/C. The redox couple at potential values of +563 and +178 mV (MMO) in the forward and backward directions, respectively at Pd–Ni/C electrocatalyst was assigned to Ni^{2+}/Ni^{3+} transformation [40,41]. The
Electrochemical active surface area (EAS) of Pd/C and Pd–Ni/C electrocatalysts has been measured by calculating the coulombic charge (Q) for the reduction of palladium oxide according to the following equation:

\[ \text{EAS} = \frac{Q}{SI} \]  

where: Q is the coulombic charge for the reduction of palladium oxide, S is the proportionality constant used to relate charge with area and I is the catalyst loading in g m\(^{-2}\). A charge value of 405 \(\mu\)C cm\(^{-2}\) is assumed for the reduction of PdO monolayer \([42,43]\). EAS values were found to be 13.66 and 34.75 m\(^2\) g\(^{-1}\) for Pd/C and Pd–Ni/C electrocatalysts, respectively. This higher EAS of Pd–Ni/C electrocatalyst is probably due to the better dispersion and smaller size of catalyst particles.

The electrochemical behavior of Ni/C and Pd–Ni/C electrocatalysts in 0.5 M KOH solution was investigated at different scan rates in Figs. 5 and 6, respectively. In general, an
increase in the current density of Ni(OH)$_2$/NiOOH redox couple was shown with increasing the scan rate. Moreover, the anodic peak potential is shifted in the positive direction, while the cathodic one is shifted towards more negative potential values. Laviron [44] presented a theory for manifesting the slow electron transfer of attached electroactive species. The electron transfer rate constant ($k_s$) can be calculated based on Laviron’s theory:

$$E_{pa} = E_o + \frac{RT}{(1 - \sigma)nF} \ln \left(\frac{(1 - \sigma)nF}{RTk_s}\right)$$  \hspace{1cm} (2)$$

$$E_{pc} = E_o + RT/(anF) \ln \left(a nF / RTk_s\right)$$ \hspace{1cm} (3)$$

$$\ln k_s = a \ln (1 - \sigma) + (1 - \sigma) \ln \sigma - \ln (RT/nF) - a(1 - \sigma)nFE/RT$$ \hspace{1cm} (4)$$

where: $E_{pa}$ and $E_{pc}$ are the anodic and cathodic peak potentials in V, respectively, $E_o$ is the standard electrode potential, $R$ is the universal gas constant (8.314 J mol$^{-1}$ K$^{-1}$), $T$ is the absolute temperature in K, $F$ is Faraday’s constant (96485.3 C mol$^{-1}$), $n$ is the electron transfer number, $v$ is the scan rate in V s$^{-1}$ and $k_s$ is the electron transfer rate constant in s$^{-1}$. The anodic and cathodic peak potentials are plotted versus the natural logarithm of scan rate at Ni/C and Pd–Ni/C electrocatalysts in Figs. 5(B) and 6(B), respectively. From the slope of the linear portions at higher scan rates [200–500 mV s$^{-1}$] and using the above equations, the electron transfer rate constant ($k_s$) is estimated as 0.1582 and 0.2098 at Ni/C and Pd–Ni/C electrocatalysts, respectively.

The current density values of anodic and cathodic peaks of Ni(OH)$_2$/NiOOH redox couple at Ni/C and Pd–Ni/C electrocatalysts are linearly dependent on the scan rate at lower values from 10 to 100 mV s$^{-1}$ in Figs. 5(C) and 6(C), respectively. This may be due to the electrochemical activity of immobilized redox species at the surface of modified electrodes. From the
slope of this relation and using the following equation, the electrode surface coverage ($G^*$) can be calculated [45]:

$$I_p = \left( \frac{n^2F^2}{4RT} \right) aA^*$$

where: $I_p$ is the peak current in Ampere, $A$ is the electrode surface area in cm$^2$ and $A^*$ is the surface coverage of redox species in mol cm$^{-2}$. By taking the average of both anodic and cathodic sides, $I^*$ is calculated as $3.366 \times 10^{-8}$ and $5.683 \times 10^{-8}$ mol cm$^{-2}$ at Ni/C and Pd–Ni/C electrocatalysts, respectively. At scan rates higher than 100 mV s$^{-1}$, the current density values of Ni(OH)$_2$/NiOOH redox couple are proportional to the square root of the scan rate as evident in Figs. 5(D) and 6(D) at Ni/C and Pd–Ni/C electrocatalysts, respectively. It signifies the dominance of a diffusion-controlled process as the rate-limiting step in the redox transition of the modified electrode. This was reported for many nickel modified electrodes [41,46–49].

Fig. 7 shows the cyclic voltammograms of prepared electrocatalysts in (0.6 M MeOH + 0.5 M KOH) solution at 10 mV s$^{-1}$. An oxidation peak was observed at Ni/C electrocatalyst at a potential value of $+770$ mV with a current density of 20.78 mA cm$^{-2}$. Methanol oxidation reaction starts when NiOOH is formed [50–52]. The addition of Pd in Pd–Ni/C electrocatalyst shifts the potential of this oxidation peak in the positive direction by 90 mV [$+860$ mV] with the appearance of another oxidation peak at 0 mV. This new peak was observed at Pd/C in Fig. 7(b) as a result of the oxidation of freshly chemisorbed methanol species at Pd surface [38,42,53,54]. The current density of this oxidation peak at Pd–Ni/C electrocatalyst is 1.92 times higher than that at Pd/C. This could indicate the contribution of nickel in enhancing methanol oxidation reaction at this potential region. Many workers have observed that the activity of Pd is improved by adding Ni in Pd–Ni/C electrocatalysts [30,38,42,55]. The current density of the second methanol oxidation peak [at $+860$ mV] at Pd–Ni/C electrocatalyst is 1.68 times higher than that at Ni/C. Kumar et al. [56] have reported the current density increase of Pd–Ni alloy at 700 mV (MMO) when methanol is added to KOH solution. It shows two folds increment when compared to that at plain nickel electrode. Methanol oxidation reaction starts with OH$^-$ adsorption. NiOOH species that did not be consumed during methanol oxidation at Pd–Ni/C electrocatalyst is reduced at a potential value of $+350$ mV in the backward direction. Its current density is much reduced than that in 0.5 M KOH solution. This reduction peak is not shown at Ni/C. A reoxidation peak was also observed at Pd–Ni/C electrocatalyst at $-276$ mV in the reverse direction [57,58]. It precedes the corresponding one at Pd/C by 7 mV. It reflects that the presence of nickel facilitates the removal of incompletely oxidized carbonaceous species formed in the

\[\text{Fig. 6 - (A) Cyclic voltammograms of Pd–Ni/C electrocatalyst in 0.5 M KOH solution at scan rates of (a) 10, (b) 20, (c) 30, (d) 40, (e) 50, (f) 75, (g) 100, (h) 200, (i) 300, (j) 400 and (k) 500 mV s}^{-1}. (B) \text{The dependence of the anodic and cathodic peak potential values on the natural logarithm of the scan rate. The linear dependence of the anodic and cathodic peak current density on the scan rate at lower values (10–100 mV s}^{-1}) \text{(C) and on the square root of the scan rate at higher values (100–500 mV s}^{-1}) \text{(D).} \]
forward scan at a lower potential value. Cyclic voltammograms of Ni/C, Pd–Ni/C and Pd/C electrocatalysts in 0.5 M KOH solution containing various concentrations of methanol were represented in Fig. 8(a), (b) and (c), respectively. It was observed that as methanol concentration increases, the current density values of oxidation peaks at these electrocatalysts would increase with a slight potential shift in the positive direction. However, the second oxidation peak at Pd–Ni/C showed a stabilized current density at methanol concentration ≥0.2 M. The variation of methanol oxidation peak current density with methanol concentration at studied electrocatalysts is shown in Fig. 8(d). It indicates that the first oxidation peak at Pd–Ni/C electrocatalyst had higher current density values than that at Pd/C at most methanol concentrations.

According to the above results of our prepared Pd–Ni/C electrocatalyst, an improved performance was achieved when compared with other Pd–Ni based electrocatalysts in the literature [30,37,38,42,55,59] as shown in Table 1 as follows:

1. The potential value of the first oxidation peak at Pd–Ni/C electrocatalyst precedes that at both Ni–Pd/Si and Ni–Pd/Si-microchannel plates, prepared by electroless plating followed by annealing at 300 °C [59] by 42 and 32 mV, respectively and that at Pd–1 wt.% MWCNTs–5 wt.% Ni electrocatalyst by 37 mV [42].

2. An increased current density value by 4.6 times was shown at the first oxidation peak of our Pd–Ni/C electrocatalyst, in relation to that of ethanol oxidation reaction at Pd2Ni3/C, prepared by solution phase-based nanocapsule method [37]. It is comparable to that obtained at Pd3Ni5/C electrocatalyst, prepared by impregnation method using NaBH4 as a reducing agent, during allyl alcohol oxidation [55].

Linear sweep voltammograms of methanol oxidation at Ni/C, Pd–Ni/C and Pd/C electrocatalysts in (0.6 M MeOH + 0.5 M KOH) solution at different scan rates are represented in Fig. 9(a), (b) and (c), respectively. It can be seen that the oxidation peak current density at these electrocatalysts increases with increasing the scan rate. The first oxidation peak at Pd–Ni/C electrocatalyst showed a slight current density increase when compared to the corresponding one at Pd/C. On the other hand, two folds increment was recorded in the
current density of Pd–Ni/C electrocatalyst at the second oxidation position at a scan rate of 100 mV s\(^{-1}\) in relation to that at Ni/C. A plot of methanol oxidation peak current density at Ni/C, Pd/C and Pd–Ni/C electrocatalysts versus the square root of the scan rate showed a linear relationship [see Fig. 9(d)]. It suggests that the electrocatalytic oxidation of methanol at these electrocatalysts may be controlled by a diffusion process [60,61]. Moreover, as the scan rate increases, the oxidation peak potential is shifted towards more positive values. This potential shift is possibly due to the IR drop generated at high current density values [62]. The potential values of the first oxidation peak at Pd–Ni/C electrocatalyst were almost unchanged when compared to those at Pd/C at various scan rates. However, at higher scan rates, the second oxidation peak at Pd–Ni/C electrocatalyst was observed at more positive potential values relative to that at Ni/C. A linear plot was obtained between the natural logarithm of scan rate and oxidation peak potential at the three studied
Comparison of the preparation method, potential and current values of various organic substrates oxidation at different prepared Pd–Ni based electrocatalysts with our present work.

<table>
<thead>
<tr>
<th>Electro catalyst</th>
<th>Preparation method</th>
<th>Organic substrate</th>
<th>Oxidation solution</th>
<th>First oxidation peak from cyclic voltammetry at a scan rate of 50 mV s⁻¹</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-Pd/Si</td>
<td>Electroless plating followed by annealing at 300 °C</td>
<td>Methanol</td>
<td>(2 M KOH + 1 M methanol)</td>
<td>+50 3.28 mA</td>
<td>[59]</td>
</tr>
<tr>
<td>Ni-Pd/Si- microchannel plates</td>
<td>Electroless plating followed by annealing at 300 °C</td>
<td>Methanol</td>
<td>(2 M KOH + 1 M methanol)</td>
<td>+40 33.93 mA</td>
<td>[59]</td>
</tr>
<tr>
<td>Pd₂Ni₃/C</td>
<td>Solution phase-based nanocapsule method</td>
<td>Ethanol</td>
<td>(1 M NaOH + 1 M ethanol)</td>
<td>−150 1.66 mA cm⁻²</td>
<td>[37]</td>
</tr>
<tr>
<td>Pd₁Ni₃/C</td>
<td>Impregnation method using NaBH₄</td>
<td>Allyl alcohol</td>
<td>(0.5 M NaOH + 0.1 M allyl alcohol)</td>
<td>−1 9 mA cm⁻²</td>
<td>[55]</td>
</tr>
<tr>
<td>Pd–1 wt.% MWCNTs–5 wt.% Ni</td>
<td>Impregnation method using NaBH₄</td>
<td>Methanol</td>
<td>(1 M KOH + 1 M methanol)</td>
<td>+45 341.68 mA cm⁻²</td>
<td>[42]</td>
</tr>
<tr>
<td>Pd–Ni/MWCNTs</td>
<td>Impregnation method using NaBH₄</td>
<td>Methanol</td>
<td>(0.5 M NaOH + 1 M methanol)</td>
<td>−80 482.2 mA mg⁻¹ (Pd)</td>
<td>[30]</td>
</tr>
<tr>
<td>Ni-Pd/MWCNTs</td>
<td>Core and shell method</td>
<td>Methanol</td>
<td>(0.5 M NaOH + 1 M methanol)</td>
<td>−66 770.7 mA mg⁻¹ (Pd)</td>
<td>[30]</td>
</tr>
<tr>
<td>Pd–Ni/C</td>
<td>Impregnation method using formic acid</td>
<td>Methanol</td>
<td>(1 M NaOH + 1 M methanol)</td>
<td>−41 530 mA mg⁻¹ (Pd)</td>
<td>[38]</td>
</tr>
<tr>
<td>Pd–Ni/C</td>
<td>Impregnation method using NaBH₄</td>
<td>Methanol</td>
<td>(0.5 M KOH + 0.6 M methanol)</td>
<td>+8 7.64 mA cm⁻²</td>
<td>Our work</td>
</tr>
</tbody>
</table>

Plots the current ratio (Ic/Ii) with respect to the square root of time showed linear relationships at Ni/C and Pd–Ni/C electrocatalysts using different concentrations of methanol in Fig. 10(c) and (d), respectively. Based on the slope of this straight line, the catalytic rate constant of methanol oxidation reaction at Ni/C and Pd–Ni/C electrocatalysts in 0.2 M methanol solution was found to be 5.64 × 10⁻⁴ and 6.25 × 10⁻⁴ cm³ mol⁻¹ s⁻¹, respectively.

When the net current of methanol oxidation reaction at Ni/C and Pd–Ni/C electrocatalysts in various methanol concentrations [0–0.2 M] was plotted against the minus square root of time, straight lines were found in Fig. 10(e) and (f), respectively. Therefore, it confirms that the oxidation reaction is a diffusion-controlled process. Higher transient current density values were generally observed at Pd–Ni/C electrocatalyst. The diffusion coefficient of methanol was calculated according to Cottrell’s equation [63]:

\[
I = nFAD^{0.5}C_{\text{m}}^{-0.5}t^{-0.5}
\]

where: I is the net current in Ampere, D is the diffusion coefficient in cm² s⁻¹ and C is the bulk concentration of methanol in mol cm⁻³. The value of the diffusion coefficient of methanol was calculated in 0.2 M methanol solution as 3.87 × 10⁻⁶ and 2.09 × 10⁻⁵ cm² s⁻¹ at Ni/C and Pd–Ni/C electrocatalysts, respectively.

The long-term stability of Ni/C and Pd–Ni/C electrocatalysts was examined using cyclic voltammetry and chronoamperometry techniques. By potential scanning up to 10 cycles at 10 mV s⁻¹ in (0.6 M MeOH + 0.5 M KOH) solution,
Fig. 9 – Linear sweep voltammograms of (a) Ni/C, (b) Pd–Ni/C and (c) Pd/C electrocatalysts in (0.6 M MeOH + 0.5 M KOH) solution at different scan rates. Their methanol oxidation peak current density values are plotted as a function of the square root of scan rate in (d). A plot of methanol oxidation peak potential values at Ni/C, Pd–Ni/C and Pd/C electrocatalysts versus the natural logarithm of scan rate is shown in (e).
methanol oxidation peak current density at Ni/C electrocatalyst reached 79.27% of its value in the first cycle in Fig. 11(a). Adding Pd in Pd–Ni/C electrocatalyst improves this stability percentage to 88.25% for the second oxidation peak, while almost no change was observed in the first one as a result of repeated cyclization [see Fig. 11(b)]. The catalytic activity loss with repeated potential scanning may generally result from the consumption of methanol during consecutive cyclic voltammograms. The change in the nickel structure due to the perturbation of the potentials in aqueous solution could result in the formation of poisoning species, especially in the presence of organic compound such as methanol. The diffusion process between the electrode surface and the bulk solution could play an additional role. With increasing the scan number, methanol gradually diffuses from the bulk solution to the electrode surface causing a decrease in its concentration. This stability trend was further confirmed from the chronoamperograms of Ni/C, Pd/C and Pd–Ni/C.

Fig. 10 – Double-step chronoamperograms of (a) Ni/C and (b) Pd–Ni/C electrocatalysts in 0.5 M KOH solution containing various methanol concentrations [0, 0.05, 0.10, 0.15, 0.20, 0.25 and 0.30 M]. The potential steps were 750 and 430 mV (MMO), respectively. The dependence of ($I_C/I_L$) on $t^{1/2}$ derived from the data of chronoamperograms in (a) at Ni/C electrocatalyst is shown in (c) and that from the data in (b) at Pd–Ni/C electrocatalyst is shown in (d). The dependence of the transient current density values at Ni/C (e) and Pd–Ni/C (f) electrocatalysts on $t^{1/2}$ in 0.5 M KOH solution containing various methanol concentrations.

methanol oxidation peak current density at Ni/C electrocatalyst reached 79.27% of its value in the first cycle in Fig. 11(a). Adding Pd in Pd–Ni/C electrocatalyst improves this stability percentage to 88.25% for the second oxidation peak, while almost no change was observed in the first one as a result of repeated cyclization [see Fig. 11(b)]. The catalytic activity loss with repeated potential scanning may generally result from the consumption of methanol during consecutive cyclic voltammograms. The change in the nickel structure due
electrocatalysts in Fig. 11(c). They were recorded for 80 min in (0.6 M MeOH + 0.5 M KOH) solution at potential values of 0 mV for Pd/C and Pd–Ni/C [1st oxidation peak] and 750 mV for Ni/C and Pd–Ni/C [2nd oxidation peak]. It was found that the methanol oxidation current density on all electrocatalysts rapidly decreases at first until the steady state value was attained. The first oxidation peak at Pd–Ni/C electrocatalyst showed higher current density than that at Pd/C for the first 1200 s; afterwards, no appreciable improvement was noticed. On the other hand, the steady state current density value of the second oxidation peak at Pd–Ni/C electrocatalyst increased by 1.69 times when compared to that at Pd/C for the first 80 min [6.75 and 11.43 mA cm$^{-2}$ at Ni/C and Pd–Ni/C electrocatalysts, respectively]. Miao et al. [59] have observed an enhanced limiting current density value of methanol oxidation reaction at Pd–Ni nanoparticles produced by electroless plating onto three-dimensional silicon microchannel plates. Accordingly, the good electrocatalytic properties and stability of Pd–Ni/C electrocatalyst elect it as a less expensive material for methanol oxidation reaction in alkaline medium.

The promoting effect of adding a metal like Ni to a noble metal like Pd could be explained by the bi-functional mechanism and electronic ligand effects [64–66]. According to bi-functional mechanism, nickel is an oxophilic element like Ru. It has the capacity to generate OH$_{ads}$ at a lower potential value and facilitates the oxidative desorption of intermediate products, thus enhancing the stability of Pd–Ni electrocatalysts [24]. The addition of nickel can also promote methanol oxidation reaction by changing the electronic properties of Pd [67]. According to XRD study, the formed alloy between nickel and palladium tends to shift the d-band center of Pd down, while that of Ni is shifted up. It means that the adsorption ability of methanol would be weaker on Pd sites and stronger on Ni sites. This may help to improve methanol...
oxidation reaction on bimetallic surfaces. In addition, the presence of nickel hydroxide species plays an important role in facilitating the oxidation of Hads on a Pd surface via the hydrogen spillover effect \[35\]. The uniform distribution of Ni species around Pd, prepared by the simultaneous reduction method, can also contribute to the catalytic activity of Pd–Ni/C electrocatalyst compared with that formed by applying two-step preparation method. The reduced particle size of Pd–Ni/C electrocatalyst relative to that of Ni/C and Pd/C could also increase the catalytic surface area subjected to the reaction zone, thus enhancing its electrocatalytic performance.

4. Conclusion

Ni and Pd–Ni nanoparticles were deposited on Vulcan XC-72R carbon black by impregnation method using NaBH₄ as a reducing agent. XRD pattern of Pd–Ni/C electrocatalyst indicated the incorporation of Pd and Ni atoms in the same lattice to form Pd–Ni alloy. The particle size of Pd–Ni/C powder is reduced to 3–4 nm as shown by TEM. The electron transfer rate constant was calculated as 0.1582 and 0.2098 s⁻¹ at Ni/C and Pd–Ni/C electrocatalysts, respectively. The presence of nickel in Pd–Ni/C was found to enhance methanol oxidation at 0 mV. Moreover, methanol oxidation peak at Pd–Ni/C at 860 mV has an increased current density by 1.68 times when compared to that at Ni/C. Incompletely oxidized carbonaceous species can be easily removed at a lower potential value at Pd–Ni/C when compared to that at Pd/C. The diffusion coefficient of methanol was estimated as 3.87 × 10⁻⁶ and 2.09 × 10⁻⁵ cm² s⁻¹ at Ni/C and Pd–Ni/C electrocatalysts, respectively. The long-term stability test at Pd–Ni/C electrocatalyst showed a better performance in relation to that at Ni/C.

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REFERENCES


Zhang M, Yan Z, Xie J. Core/shell Ni@Pd nanoparticles supported on MWCNTs at improved electrocatalytic performance for alcohol oxidation in alkaline media. Electrochim Acta 2012;77:237–42.


Yang S, Zhang X, Mi H, Ye X. Pd nanoparticles supported on functionalized multi-walled carbon nanotubes (MWCNTs) and electrooxidation for formic acid. J Power Sources 2008;175(1):26–32.


Sun Z-P, Zhang X-G, Liang Y-Y, Li H-L. Highly dispersed Pd nanoparticles on covalent functional MWCNT surfaces for...


