



Graphite Electrodes Modified with Platinum-Nickel Nano-Particles for Methanol Oxidation

M. A. Abdel Rahim^{1*}, H. B. Hassan¹, and R. M. Abdel Hameed¹

¹ Department of Chemistry, Faculty of Science, Cairo University, 02 Giza, Egypt

Received November 10, 2006; accepted January 17, 2007

Abstract

Methanol electro-oxidation is investigated at graphite electrodes modified with various platinum and nickel nano-particle deposits using cyclic voltammetry. The modified electrodes are prepared by the simultaneous electrodeposition of metals from their salt solutions using potentiostatic and galvanostatic techniques. They show enhanced catalytic activity towards methanol oxidation in KOH solution. The catalytic activity of platinum nano-particles is found to be significantly affected by the presence of relatively small amounts of nickel deposits. A comparison is made between the electrocatalytic activity of Pt/C and (Pt-Ni)/C electrodes. The results show that the methanol electro-oxidation current increases with an increase in the nickel content. In particular, the highest catalytic activity is achieved for platinum

to nickel deposits of 95%:5% (wt-%), in other cases the catalytic activity decreases. It is found that Ni enhances the catalytic activity of Pt by increasing the number of active sites, as well as through an electron donation process from Ni to Pt. This process takes place once the nickel hydroxide (Ni(OH)₂)/nickel oxy-hydroxide (NiOOH) transformation begins. The effect of the methanol concentration on the methanol oxidation reaction is investigated. The order of reaction, with respect to methanol, at the modified (Pt-Ni)/C electrode is found to be 0.5.

Keywords: Alkaline Media, Electrocatalyst, Methanol Fuel Cells, Nano-Particles, Platinum-Nickel

1 Introduction

The electro-oxidation of methanol is a research topic of great importance to the development of high performance methanol fuel cells. The direct alcohol fuel cell appears to be a promising system because the methanol or ethanol used is not reformed into hydrogen gas, but is oxidized directly in the cell. Obviously, in direct methanol fuel cells, the appropriate choice of catalyst is of the utmost importance for the oxidation process. Fundamental worldwide research efforts are currently directed towards the development of anode electrocatalysts with high catalytic activity [1, 2]. Pt metal [3] is considered to be the most active catalyst for the electro-oxidation of methanol, but the reaction on Pt is retarded by strongly adsorbed intermediates such as CO [4]. The oxidation of these intermediates can be enhanced at certain platinum based binary/ternary systems [5] and in some cases quaternary systems [6]. It is known that the incorporation of a second metal can significantly affect the catalyst behaviour, due to the formation of alloys. They exert a promoting effect on the reactant, blocking metal migration as well as creating mixed

active sites [7, 8]. In addition, this reduces the cost of the electrocatalyst [9]. As examples: Ru [6, 10], Mo [11], and Cu [12] have been used as catalysts together with Pt.

The process of modifying Pt electrodes using various metals has been carried out in different ways, including alloying [6], dispersing metal particles on electronically conducting polymer supports [13, 14] or on carbon supports [15, 16], using a zeolite support [10, 17], etc. Recently, Okada et al. [18] developed a new class of low cost electrocatalysts based on platinum and organic metal complexes supported on graphite powder. Of late, numerous attempts have been made to prepare other catalysts, not based on Pt. These were found to have a good promoting effect for methanol oxidation, e.g., iron-ruthenium modified activated carbon [15] and nickel-modified manganese oxide [19].

It is well established that nickel, as well as nickel-platinum, can be used as a catalyst for the electro-oxidation of alcohols. In alkaline solutions, a nickel anode polarized ano-

[*] Corresponding author, mamdouha@tedata.net.eg

dically is covered with a high valency nickel oxy-hydroxide species (NiOOH), which is commonly believed to act as a redox mediator between the substrate and electrode. A platinized Ni electrode is more active than simple nickel or platinized platinum electrodes for methanol oxidation in NaOH solution [20]. It was recently reported [21] that Ni, dispersed on graphite, showed catalytic activity towards methanol oxidation in KOH solution. In the present paper, the aim is to investigate the catalytic properties of platinum-nickel dispersed on a graphite electrode towards this reaction. Special attention is paid to the effect of the relative amount of Pt-Ni simultaneously electrodeposited potentiostatically and galvanostatically.

2 Experimental

In a previous study [22] it was revealed that the catalytic activity of a bimetallic catalyst towards methanol oxidation is strongly dependent on the method of catalyst preparation. Also, the use of the simultaneous electrodeposition method for preparing the bimetallic catalyst was recommended. In the present investigation, electrochemical measurements were performed on spectroscopically pure crystalline graphite disc electrodes, with an apparent surface area of 0.37 cm^2 , modified with platinum and simultaneously electrodeposited with platinum and nickel. Before the electrodeposition of the platinum and nickel, the graphite electrode was mechanically polished using metallurgical papers of various grades and, subsequently, it was degreased with acetone, rinsed with distilled water, and dried with soft tissue paper. The electrode surface was then activated using potentiostatic polarization at $1,400 \text{ mV}$ for 5 minutes. This was followed by cyclic polarization from the potential of hydrogen evolution (-800 mV) to a potential beyond oxygen evolution ($1,400 \text{ mV}$) in $1.0 \text{ M H}_2\text{SO}_4$, at a scan rate of 50 mV s^{-1} for 50 cycles.

The catalyst particles were deposited on the graphite substrate by electrochemical deposition from an aqueous solution. The platinum was deposited potentiostatically at $-1,000 \text{ mV vs. Hg/HgSO}_4/1.0 \text{ M H}_2\text{SO}_4$ (MMS) in $1.0 \text{ M H}_2\text{SO}_4$ solution containing $8 \text{ mM H}_2\text{PtCl}_6$. Similarly, platinum and nickel were electrodeposited simultaneously in H_2SO_4 solution containing $8 \text{ mM H}_2\text{PtCl}_6$ and different concentrations of NiSO_4 . Three electrodes were prepared with different Pt to Ni ratios. This was achieved by changing the molar ratios of the platinum and nickel salts in the deposition bath. The first electrode was prepared potentiostatically at a Pt to Ni molar ratio of 1:1 by the simultaneous deposition of Pt and Ni from a solution of $8 \text{ mM H}_2\text{PtCl}_6$ and 8 mM NiSO_4 . The second electrode was prepared at a Pt to Ni molar ratio of 1:8 from a solution of $8 \text{ mM H}_2\text{PtCl}_6$ and 64 mM NiSO_4 . Finally, the third was prepared at a Pt to Ni molar ratio of 1:16 from a solution of $8 \text{ mM H}_2\text{PtCl}_6$ and 128 mM NiSO_4 . Some deposition experiments were carried out galvanostatically at 1.0 mA cm^{-2} . After the electrodeposition of the Pt and Ni particles, the electrode was removed from the deposition bath,

washed with distilled water, and dried in a jet of air. No further electrode pretreatment was necessary to avoid changes to the substrate surface. The electrode was then transferred to the electrochemical cell containing the test solution, ready for the electro-oxidation of methanol.

The electrochemical measurements were performed using cyclic voltammetry. Details of the electrochemical equipment, as well as the electrolytic cell, are described elsewhere [23]. EDX and SEM analyses were also carried out for the compositional and morphological characterization of the modified electrode, respectively. The reference electrode, to which all potentials are referred, was the $\text{Hg/HgO}/1.0 \text{ M NaOH}$ (MMO) and a Pt sheet was used as the counter electrode. The electrochemical measurements were carried out in aerated 1.0 M KOH at room temperature ($30 \pm 0.2 \text{ }^\circ\text{C}$). Methanol was used as received without further purification. Triply distilled water was used throughout for the preparation of solutions.

3 Results and Discussion

The electrochemical oxidation of methanol was carried out at the modified Pt/C and (Pt-Ni)/C electrodes in an aqueous solution of 1.0 M KOH using cyclic voltammetry. The (Pt-Ni)/C modified electrode used in this study was prepared by the simultaneous electrodeposition of Pt and Ni from a deposition bath containing $8 \text{ mM K}_2\text{PtCl}_6 + 64 \text{ mM NiSO}_4$ in $1.0 \text{ M H}_2\text{SO}_4$. After preparation, a scanning electron micrograph was recorded to examine the electrode surface. The micrograph, shown in Figure 1, shows a homogeneous distribution of both the platinum and nickel particles. Platinum particles were deposited as small particles in the range from 100 to 300 nanometres, while the Ni was in the form of clusters. Under the experimental conditions of the present paper, it was found that the electrodeposited Pt particles were smaller in size than the Ni

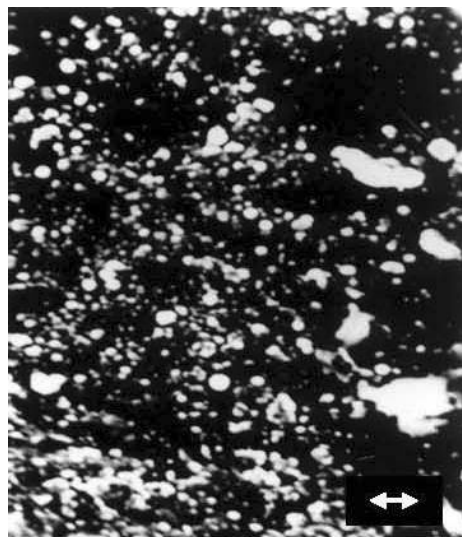


Fig. 1 Scanning electron micrograph for the (Pt-Ni)/C electrode after preparation. (The dimension bar \leftrightarrow is equivalent to $1 \mu\text{m}$.)

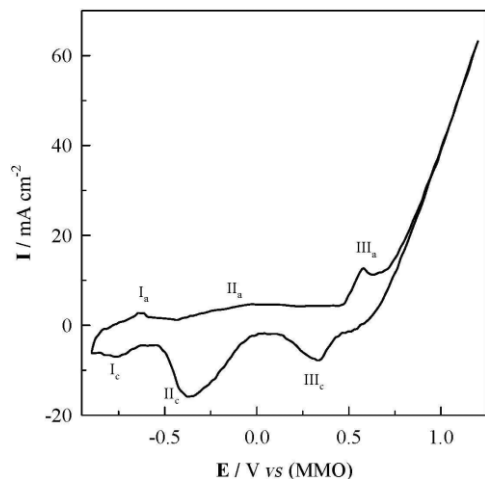


Fig. 2 Cyclic voltammogram of the (Pt-Ni)/C electrode in 1.0 M KOH solution. (The electrode was prepared in a solution of metal ions with a Pt-Ni molar ratio of 1:8)

particles (this is according to our previous study [21]). Figure 2 shows the cyclic voltammetric behaviour of the modified (Pt-Ni)/C electrode in 1.0 M KOH, at a scan rate of 10 mV s^{-1} . As seen in Figure 2, anodic and cathodic peaks are detected, reflecting the features of both nickel and platinum. The peaks appearing at -625 mV (I_a) and -750 mV (I_c) in the anodic and the cathodic directions, respectively, are associated with the adsorption and desorption of bound hydrogen atoms on the platinum surface [24]. A very broad anodic peak (II_a) was observed in the range between -400 and 450 mV . The formation of monolayer platinum hydroxide was previously reported in the same potential range [25, 26]. The cathodic peak at -380 mV (II_c) is related to platinum hydroxide reduction in the negative sweep [27]. Oxygen evolution starts at about 700 mV (MMO). In addition to the characteristic features of platinum, a redox couple, (III_a) and (III_c), appears in Figure 2 at 590 and 350 mV in the anodic and cathodic directions, respectively. These peaks correspond to the oxidation of $\text{Ni}(\text{OH})_2$ to NiOOH , in accordance with the reaction [28, 29]:



The voltammetric response of the (Pt-Ni)/C electrode (Pt to Ni molar ratio of 1:8) in KOH solution containing 0.5 M methanol at a scan rate of 10 mV s^{-1} is represented in Figure 3, in addition to that of the Pt/C electrode, for comparison. The voltammogram for the Pt/C electrode shows an increase in the anodic current, starting at about -0.52 V , leading to an anodic peak at about 0.98 V , which corresponds with methanol oxidation. The modification of the Pt/C electrode by the co-deposition of platinum with nickel (to form (Pt-Ni)/C) enhances the anodic peak current density for methanol oxidation by about 2.6 times. In addition, the anodic peak potential was slightly shifted towards a less positive value. At both electrodes, the methanol oxidation reaction starts at -0.52 V , after hydrogen adsorption, and is linked

with OH_{ads} layer formation, where the onset of the reaction coincides with the beginning of OH_{ads} layer formation and takes place in the potential region associated with OH^- electrosorption [30]. The reaction reaches a maximum rate at the peak potential $+0.965 \text{ V}$, which is located close to the end of OH adsorption. The oxidation rate decreases beyond this potential value, which is probably due to oxide layer formation [31] and the decrease in the surface coverage of methanol. In addition, methanol oxidation recommences in the reverse scan at about -0.175 V , reaching its maximum rate at -0.225 V . T.-C. Wen et al. [32] conclude that methanol oxidizes again in the reverse scan after the partial reduction of monolayer-like $\text{Pt}(\text{OH})_2$, which commences at about 0.00 V (MMO).

In the present results, the cyclic voltammograms for methanol oxidation, obtained on both modified electrodes (Pt/C and (Pt-Ni)/C), are the same shape. This led to the conclusion that Pt atoms represent the main active sites for the oxidation reaction. Therefore, the enhanced electrocatalytic activity of the (Pt-Ni)/C electrode may result from one or both of the following:

- (i) The increase in electroactive platinum species, due to the increase in the defects in the Pt deposit, caused by the introduction of nickel [32]. In other words, Ni, like Sn [33, 34], facilitates the adsorption of oxygen containing species, such as OH_{ads} , so, the adsorbed Pt-OH reacts with the organic poison.
- (ii) It has been reported that enhanced methanol oxidation on Pt-based nano-particles that have been alloyed with a transition metal such as nickel, which has a lower electronegativity than platinum, can be attributed to a change in the electronic properties of platinum [35, 36].

Experiments were carried out to estimate the true surface area of both modified electrodes. The Hydrogen adsorption measurements can be used to estimate the true surface area. The charge due to hydrogen adsorption on both electrodes was evaluated. This charge was then used to estimate the surface area, as in the method cited in reference [37 (and 33 herein)]. Values of 124.9 cm^2 and 104.6 cm^2 were estimated for the true surface area of the Pt/C and (Pt-Ni)/C electrodes, respectively. According to these values, the higher currents for methanol oxidation observed at the modified (Pt-Ni)/C electrode, compared to that obtained at the Pt/C electrode, Figure 3, could possibly be due to the first reason stated above. It is proposed that further enhancement could arise through electron donation from nickel to platinum, modifying its electronic properties, improving the electrocatalytic activity, and preventing the adsorption of the poisoning intermediates on the Pt surface. The electron donation process takes place once the nickel hydroxide ($\text{Ni}(\text{OH})_2$)/nickel oxy-hydroxide (NiOOH) transformation has taken place. It is noted that this transformation commences at 0.5 V , Figure 2. Figure 4 represents a relation derived from the voltammograms in Figure 3. It relates changes in the methanol oxidation current with potential (dI/dE) and the corresponding polarization potential (E). It is clear from this figure that

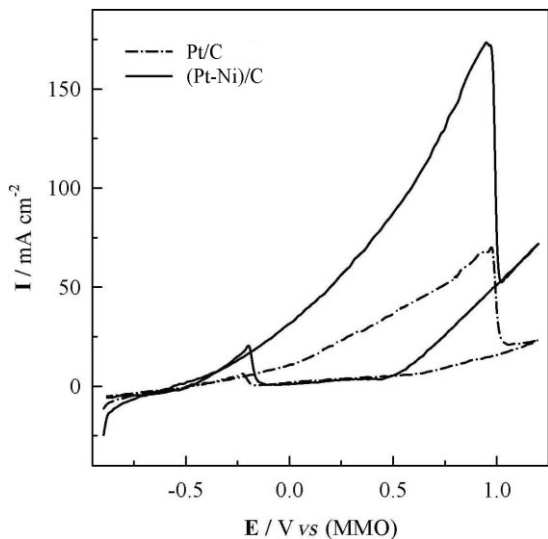


Fig. 3 Voltammetric behaviour of Pt/C and (Pt-Ni)/C electrodes (Pt-Ni molar ratio of 1:8) in 1.0 M KOH solution in the presence of 0.5 M methanol.

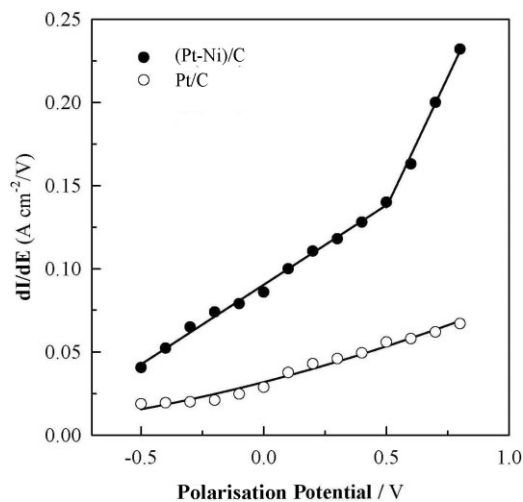


Fig. 4 Variation of (dI/dE) for methanol oxidation at the (Pt-Ni)/C electrode (Pt-Ni molar ratio of 1:8) with the polarisation potential.

the presence of nickel in the modified electrode enhances the catalytic activity of platinum and that a more enhancing effect is achieved starting from 0.5 V (the inflection point of the (Pt-Ni)/C curve in Figure 4), the potential at which the $\text{Ni}(\text{OH})_2/\text{NiOOH}$ transformation commences. This assumption is in agreement with the work of Toda et al. [36], who also attributed the enhanced electrocatalytic activity of a Pt/C electrode, after the introduction of nickel, to the action of the redox couple $\text{Ni}(\text{II})/\text{Ni}(\text{III})$, which promotes the formation of an electroactive hydroxyl Pt(I) species. This hydroxyl platinum species is an intermediate between Pt(0) and Pt(II).

The effect of the amount of platinum and nickel, deposited on graphite, on the methanol oxidation reaction was investigated. Three modified (Pt-Ni)/C electrodes, differing in the Pt:Ni ratios, were prepared. Different ratios were achieved by

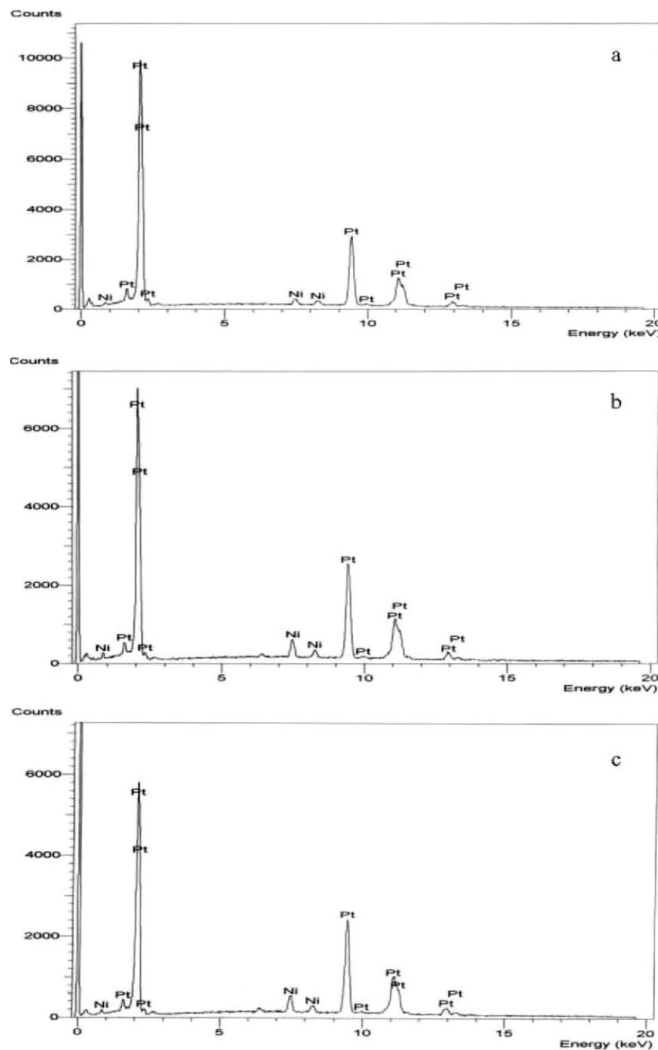


Fig. 5 EDX spectra of the modified (Pt-Ni)/C electrodes. The molar concentrations of platinum and nickel ions in the deposition baths were (a) 1:1, (b) 1:8, and (c) 1:16, respectively.

changing the relative concentration of the Pt and Ni salt solutions in the deposition bath. As mentioned in the experimental, the electrodeposition of platinum and nickel was conducted in 1.0 M H_2SO_4 solution, containing 8 mM K_2PtCl_6 and 8, 64, or 128 mM NiSO_4 , i.e., the molar ratios of platinum:nickel ions were 1:1, 1:8, and 1:16, respectively. Figure 5 shows the EDX spectra recorded for the three electrodes prepared potentiostatically at $-1,000$ mV (MMO) for 30 minutes. The compositions (Pt:Ni ratio, by weight) of the three electrodes were found to be 98.09%:1.91%, 94.98%:5.02%, and 94.45%:5.55%, respectively. The ratios obtained from the EDX analyses are not an exact match for the molar concentrations of metal ions in the deposition solution. However, there is an indication that the Ni content in the modified electrodes increases as the concentration of Ni ions in solution increases. The variation of the oxidation peak current density values, as well as peak potentials, for methanol oxidation with deposition time for the various modified electrodes prepared in the

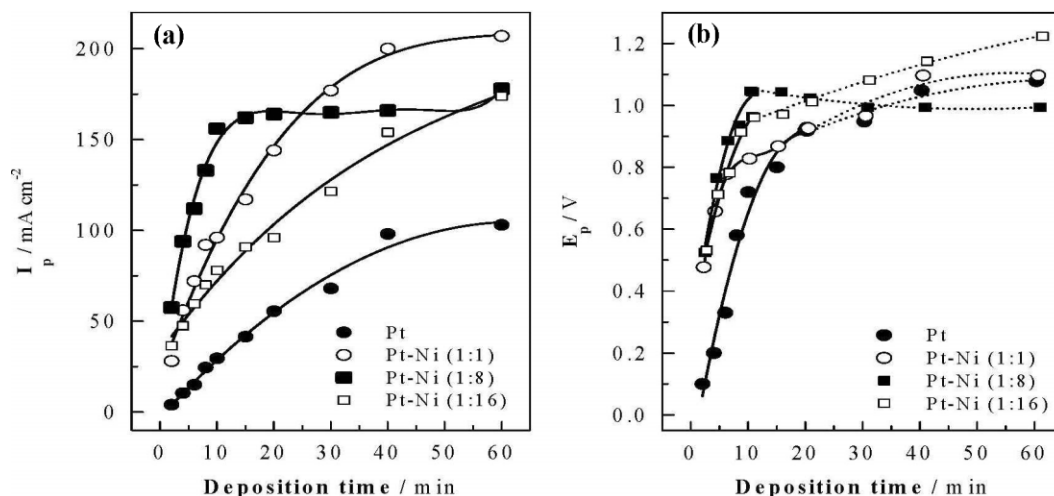


Fig. 6 Variation of peak current densities (a) and peak potentials (b) for methanol oxidation at various modified electrodes with deposition time. (Metals are simultaneously deposited potentiostatically and the Pt-Ni ratios indicated are molar ratios).

deposition baths of different Pt-Ni molar ratios are shown in Figure 6. It is observed that, for all modified electrodes, the oxidation peak current densities increase with increasing deposition time (Figure 6). On the other hand, a potential shift towards more positive values was observed for deposition times up to about 10 minutes, after which a slight increase in peak potential was observed in all cases except for the (Pt-Ni)/C electrode prepared in the bath of molar ratio 1 Pt:8 Ni, where a slight decrease in peak potential was observed with increasing deposition time (Figure 6b). The introduction of small amounts of nickel, up to about 5% (see EDX analyses in Figure 5), enhances the methanol oxidation reaction. This may be attributed to the increase in the number of electroactive platinum species with the increase in the defects in the Pt deposit, due to the presence of nickel [32]. When the nickel content is greater than 5%, i.e., in the case of an electrode prepared in a deposition bath with a Pt to Ni molar ratio of 1:16, a decrease in the current density for methanol oxidation is observed (see Figure 6a). Increasing the Ni content beyond 5% may facilitate the formation of a passive and irreducible β -Ni(OH)₂ film, which inhibits the methanol oxidation process.

The simultaneous electrodeposition of nickel and platinum metals on a graphite electrode was carried out using the galvanostatic method, at a constant current density of 1.0 mA cm⁻². For comparison, a Pt/C electrode was prepared by the electrodeposition of platinum on a graphite electrode at the same current density. The same behaviour was observed compared to electrodes prepared *via* the potentiostatic technique. However, lower oxidation current density values are observed. This could be attributed to the effect of the deposition technique on the metal particle growth rate. The galvanostatic deposition technique produces relatively large particles [21], of lower actual surface area, which approach the behaviour of the bulk metal and with their tendency to inhibit methanol adsorption.

A set of experiments was carried out at different methanol concentrations. The methanol concentrations used ranged from 0.10 to 0.75 M in 1.0 M KOH. A modified (Pt-Ni)/C electrode, of ratio 1:8, prepared *via* the potentiostatic technique at -1,000 mV (MMS) for 1 hour was used for these experiments. Figure 7 shows the dependence of the peak current density (Figure 7a) and peak potential (Figure 7b) for methanol oxidation at the (Pt-Ni)/C electrode on the bulk methanol concentration. It can be seen from this figure that both the methanol oxidation peak heights and peak potentials

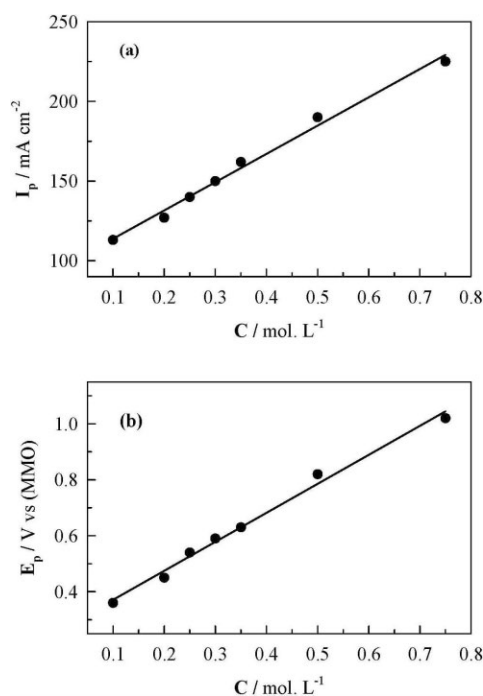


Fig. 7: Variation of peak current densities (a) and peak potentials (b) for methanol oxidation with its concentration at the (Pt-Ni)/C electrode.

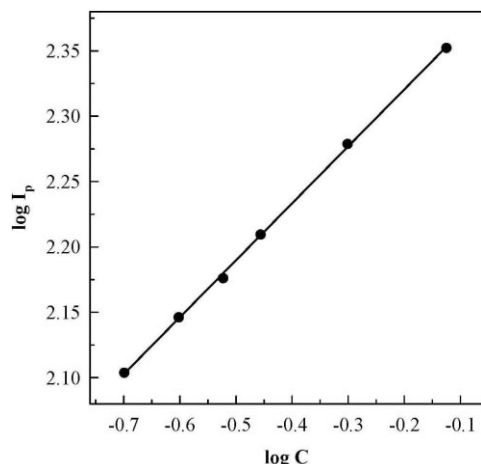


Fig. 8 Relation between the logarithm of methanol concentration and the logarithm of its oxidation peak current density at the (Pt-Ni)/C electrode.

increase linearly with increasing methanol concentration over the full concentration range studied. Increasing the methanol concentration tends to increase the electrode surface coverage of methanol adsorption intermediates, thus increasing the oxidation current density and in turn the adsorbed hydroxyl species coverage will decrease. As a result, the assumed magnitude of the hydroxyl species current densities may only be reached by increasing the oxidation potentials. This may explain the shift in the oxidation peak potentials towards more positive values with increasing methanol concentration (see Figure 7b). The logarithmic plot of the peak current density *vs.* the bulk methanol concentration, in Figure 8, shows a straight-line relation for the slope close to 0.5, which represents the order of reaction with respect to methanol at the modified (Pt-Ni)/C electrode.

With repeated potential sweeps, up to 50 cycles at 50 mV s^{-1} , the height of the methanol oxidation peak decreases to 85% with respect to its value in the first cycle

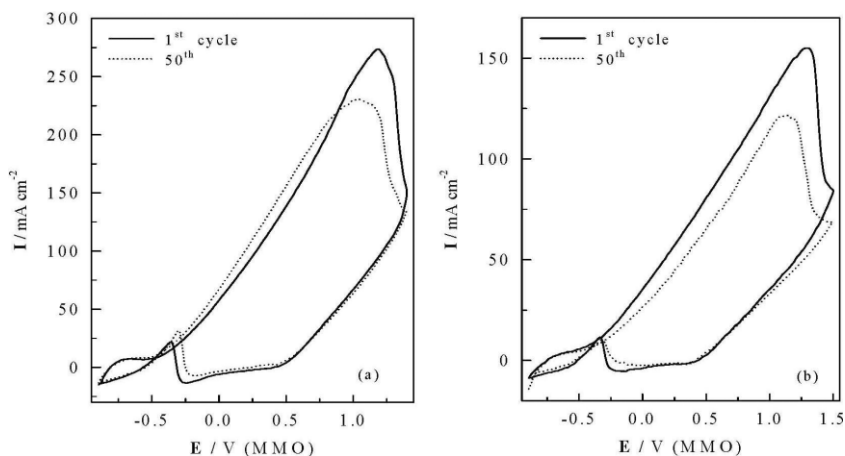


Fig. 9 Repeated cyclic voltammograms of methanol oxidation at the (Pt-Ni)/C electrode (a) and at the Pt/C electrode (b) at a scan rate of 50 mV s^{-1} . ((Pt-Ni)/C electrode is of Pt to Ni molar ratio of 1:8, respectively).

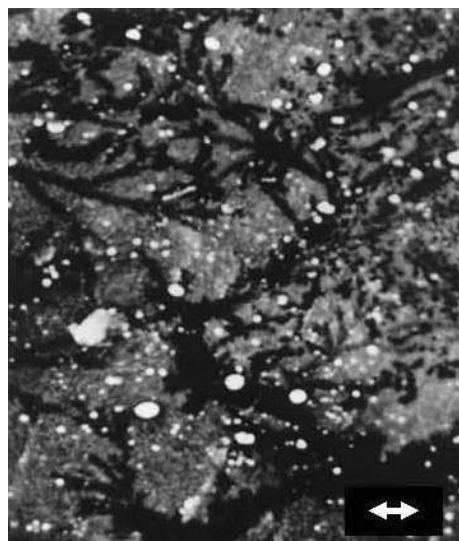
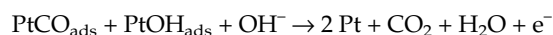
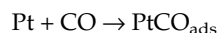


Fig. 10 Scanning electron micrograph for the (Pt-Ni)/C electrode after potentiostatic polarisation at 1,000 mV (MMO) for 2 hours in KOH solution containing 0.5 M MeOH. (Pt:Ni molar ratio of 1:8) (The dimension bar \leftrightarrow is equivalent to $1 \mu\text{m}$.)

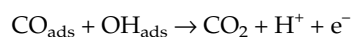
compared to 78% in the case of the Pt/C electrode (see Figures 9a and 9b). The (Pt-Ni)/C electrode shows good stability with multi-potential cycling in the presence of Ni, which proves the role of Ni in enhancing the electrocatalytic activity of Pt. The deviation from 100% efficiency, upon repeated potential cycling, could be due to the partial flaking of both Pt and Ni from the electrode surface during the process, as confirmed by a scanning electron micrograph (Figure 10). The micrograph was recorded for the (Pt-Ni)/C electrode after methanol oxidation in KOH solution containing 0.5 M MeOH at the peak potential for 2 hours. It was observed that, after methanol oxidation, the electrode exhibited deposits that differed in morphology from those recorded in Figure 1, due to the formation of $\text{Ni}(\text{OH})_2$.

For the Pt/C electrode, the loss in activity for the methanol oxidation reaction, after potential cycling, may be attributed to the coverage of the active sites by poisoning species, such as CO. It forms quite slowly and irreversibly replaces the reactive intermediates, which are less strongly adsorbed [36]. Therefore, it is CO_{ads} that actually plays the role of catalyst poison. The carbon monoxide formed in alkaline media is bound to the platinum surface in both linear and bridged forms [38], where the formation of linearly bound CO is favoured at high surface coverage and high positive potentials. Conversely, at low levels of surface coverage and low potentials, bridge-bonded CO is observed [39]. With platinum in the presence of nickel, the poisoning species can be further oxidized at higher potentials by the action of the

nickel as oxygen containing species (OH_{ads}), according to the following mechanism [40]:



Or in a more simple form [41]:



The instability can also be explained as the change of the surface structure after repeated cycling [42]. In general, the electro-oxidation of methanol at platinum proceeds much more favourably in alkaline rather than in acidic media, due to the absence of poisoning intermediates other than CO [43], where the intermediate products are not adsorbed on the electrode surface. Therefore, the surface concentration of adsorbed hydroxyl radicals would increase, thus increasing the oxidation rate [44]. Many authors have stated that the deactivation of the oxidation reaction at graphite based platinum electrodes modified with metal oxides is not due to the formation of CO itself but other CO like poisoning species [45]. Platinum-nickel catalysts show the best tolerance for carbon monoxide, where their performance was unquestionably superior to that of Pt-Ru catalysts. Platinum-nickel catalysts showed good stability, high corrosion resistance, and low polarizations in the presence of CO. This effect may be related to the strength of chemisorbed carbon monoxide bonding to the catalyst surface [46]. The bonding of hydroxyl ions is faster on a nickel surface than on platinum because of the greater bonding energy of this oxygen containing species on the nickel metal due to its ability to form lower valency hydroxides at cathodic potentials [47]. Therefore, the presence of nickel enhances the electro-oxidation of carbon monoxide, thus enhancing the oxidation rate of methanol and other organic compounds.

4 Conclusion

Graphite electrodes modified with dispersed Ni and Pt nano-particles showed good catalytic activity towards methanol oxidation in 1.0 M KOH solution. The modification of the Pt/C electrode by the co-deposition of about 5% nickel with platinum enhanced the methanol oxidation peak current density by about 2.6 times. The results showed that the performance of the (Pt-Ni)/C electrode and its stability with potential cycling were much better than that of the Pt/C electrode. The catalytic activity was found to depend on the relative Pt:Ni ratio. If the nickel content in the modified electrode was above or below 5% with platinum a relatively lower catalytic activity was observed. The electrochemical deposition of Ni and Pt, either potentiostatically or galvanostatically, showed almost the same catalytic behaviour, but relatively low oxida-

tion current densities were obtained in the case of electrodes prepared using the galvanostatic method. It was concluded that nickel enhanced the catalytic activity of platinum through an electron donation process that takes place once the nickel hydroxide ($\text{Ni}(\text{OH})_2$)/nickel oxy-hydroxide (NiOOH) transformation begins. The reaction order for methanol oxidation at the (Pt-Ni)/C electrode was estimated to be 0.5 with respect to methanol concentration.

References

- [1] F. Vigier, C. Coutanceau, A. Perrard, E. M. Belgsir, C. Lamy, *J. Appl. Electrochem.* **2004**, *34*, 439.
- [2] W. J. Zhou, S. Q. Song, W. Z. Li, Z. H. Zhou, G. Q. Sun, Q. Xin, S. Douvartzides, P. Tsiakaras, *J. Power Sources* **2005**, *140*, 50.
- [3] F. Seland, D. A. Harrington, R. Tunold, *Electrochimica Acta* **2006**, *52*, 773.
- [4] H. F. Oetjen, V. M. Schmidt, U. Stimming, F. Trila, *J. Electrochem. Soc.* **1996**, *143*, 3838.
- [5] S. Wasmus, W. Vielstich, *J. Appl. Electrochem.* **1993**, *23*, 120.
- [6] K.-W. Park, J.-H. Choi, S.-A. Lee, C. Pak, H. Chang, Y.-E. Sung, *Journal of Catalysis* **2004**, *224*, 236.
- [7] B. Coq, F. Figueras, *J. Mol. Catal. A: Chem.* **2001**, *173*, 117.
- [8] L. Gucci, I. Kiricsi, *Appl. Catal. A: Gen.* **1999**, *186*, 375.
- [9] A. S. Acario, V. Antonucci, N. Giordano, A. K. Shukla, M. K. Ravikumar, A. Roy, S. R. Burman, D. D. Sharma, *J. Power Sources* **1994**, *50*, 295.
- [10] P. V. Samant, J. B. Fernandes, *J. Power Sources* **2004**, *125*, 172.
- [11] G. Samjeske, H. Wang, T. Löffler, H. Baltruschat, *Electrochim. Acta* **2002**, *47*, 3681.
- [12] T. P. Minyukova, I. I. Simentsova, A. V. Khasin, N. V. Shtertser, N. A. Baronskaya, A. A. Khasn, T. M. Yurieva, *Appl. Catal. A* **2002**, *237*, 171.
- [13] B. Rajesh, K. R. Thampia, J.-M. Bonard, A. J. McEvoy, N. Xanthopoulos, H. J. Mathieu, B. Viswanathan, *J. Power Sources* **2004**, *133*, 155.
- [14] H. H. Zhou, S. Q. Jiao, J. H. Chen, W. Z. Wei, Y. F. Kuang, *J. Appl. Electrochem.* **2004**, *34*, 455.
- [15] D. Paneva, T. Tsoncheva, E. Manova, I. Mitov, T. Ruskov, *Appl. Catal. A: General* **2004**, *267*, 67.
- [16] T. Kawaguchi, W. Sugimoto, Y. Murakami, Y. Takasu, *J. Catal.* **2005**, *229*, 176.
- [17] M. W. Khalil, M. A. Abdel Rahim, A. Zimmer, H. B. Hassan, R. M. Abdel Hameed, *J. Power Sources* **2005**, *144*, 35.
- [18] T. Okadaa, Y. Suzuki, T. Hirose, T. Ozawa, *Electrochim. Acta* **2004**, *49*, 385.
- [19] P. V. Samant, J. B. Fernandes, *J. Power Sources* **1999**, *79*, 114.
- [20] B. Beden, F. Hahn, S. Juanto, C. Lamy, J.-M. Leger, *J. Electroanal. Chem.* **1987**, *225*, 215.

- [21] M. A. Abdel Rahim., R. M. Abdel Hameed, M. W. Khalil, *J. Power Sources* **2004**, *134*, 160.
- [22] M. A. Abdel Rahim., R. M. Abdel Hameed, M. W. Khalil, *J. Power Sources* **2004**, *135*, 42.
- [23] M. A. Abdel Rahim, H. B. Hanaa, M. W. Khalil, *J. Appl. Electrochem.* **2000**, *30*, 1151.
- [24] C.-C. Hu, K.-Y. Liu, *J. Electrochim. Acta* **1999**, *44*, 2727.
- [25] G. Tremiliosi-Filho, G. Jerkiewicz, B. E. Conway, *J. Langmuir* **1992**, *8*, 658.
- [26] L. D. Burke, M. M. Murphy, *J. Electroanal. Chem.* **1991**, *305*, 301.
- [27] C.-C. Hu, C.-Y. Lin, T.-C. Wen, *J. Mat. Phys. Chem.* **1996**, *44*, 233.
- [28] M. Vukovic, *J. Appl. Electrochem.* **1994**, *24*, 878.
- [29] G. R. Mundy, R. J. Potter, P. A. Christensen, A. Hamnett, *J. Electroanal. Chem. Interfacial Electrochem.* **1990**, *279*, 257.
- [30] A. V. Tripkovic, K. D. Popovic, J. D. Momcilovic, D. M. Drazic, *Electrochim. Acta* **1998**, *44*, 1135.
- [31] H. Kita, S. Ye, A. Aramata, N. Furuya, *J. Electroanal. Chem.* **1990**, *295*, 317.
- [32] T.-C. Wen, C.-H. Hu, C.-C. Hu, *J. Chin. Inst. Chem. Eng.* **1999**, *30*, 515.
- [33] Y. B. Vassiliev, V. S. Bagotzky, N. V. Osetrova, A. A. Mikhailova, *J. Electroanal. Chem.* **1979**, *97*, 63.
- [34] M. Shibata, S. Motoo, *J. Electroanal. Chem.* **1986**, *209*, 151.
- [35] K.-W. Park, J.-H. Choi, Y.-E. Sung, *J. Phys. Chem. B* **2003**, *107*, 5851.
- [36] T. Toda, H. Igarashi, H. Uchida, M. Watanabe, *J. Electrochem. Soc.* **1999**, *146*, 3750.
- [37] M. H. Pournaghi-Azar, B. Habibi-A, *J. Electroanal. Chem.* **2005**, *580*, 23.
- [38] E. Morallon, A. Rodes, J. L. Vazquez, J. M. Perez, *J. Electroanal. Chem.* **1995**, *391*, 149.
- [39] B. Beden, C. Lamy, N. R. de Tacconi, A. J. Arvia, *Electrochim. Acta* **1990**, *35*, 691.
- [40] S.-G. Sun, A.-C. Chen, *J. Electroanal. Chem.* **1992**, *323*, 319.
- [41] A. B. Anderson, E. Grantscharova, S. Seong, *J. Electrochem. Soc.* **1996**, *143*, 2075.
- [42] E. Morallon, J. F. Cases, J. L. Vazquez, A. Aldaz, *Electrochim. Acta* **1992**, *37*, 1883.
- [43] R. Parsons, T. Vander Noot, *J. Electroanal. Chem.* **1988**, *257*, 9.
- [44] C. Lamy, *Electrochim. Acta* **1984**, *29*, 1581.
- [45] P. C. Biswas, Y. Nodasaka, M. Enyo, M. Haruta, *J. Electroanal. Chem.* **1995**, *381*, 167.
- [46] D. W. McKee, M. S. Pak, *J. Electrochem. Soc.* **1969**, *116*, 516.
- [47] R. F. Scarr, *J. Electrochem. Soc.* **1969**, *116*, 1526.