

Nickel as a catalyst for the electro-oxidation of methanol in alkaline medium

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Received 24 January 2004; accepted 26 February 2004

Available online 18 May 2004

Abstract

The use of Ni as a catalyst for the electro-oxidation of methanol in alkaline medium was studied by cyclic voltammetry. It was found that only Ni dispersed on graphite shows a catalytic activity towards methanol oxidation but massive Ni does not. Ni was dispersed on graphite by the electro-deposition from acidic NiSO_4 solution using potentiostatic and galvanostatic techniques. The catalytic activity of the C/Ni electrodes towards methanol oxidation was found to vary with the amount of electro-deposited Ni. The dependence of the oxidation current on methanol concentration and scan rate was discussed. It was concluded from the electro-chemical measurements and SEM analysis that methanol oxidation starts as Ni-oxide is formed on the electrode surface.

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Keywords: Nickel catalyst; Electro-catalysis; Methanol fuel cell

1. Introduction

Considerable efforts have been directed towards the study of methanol electro-oxidation in solutions of a high pH. The use of alkaline solutions in a fuel cell has many advantages such as increasing its efficiency [1,2], a wider selection of possible electrode materials, a better efficiency of oxygen cathode and the oxidation reactions of organic fuels exhibit almost no sensitivity to the surface structure [3]. It was found that, the graphite-supported platinum electrodes exhibited almost the same specific activity as a smooth Pt electrode for methanol oxidation in NaOH solution [4]. Smaller or negligible poisoning effects in alkaline solutions were observed [5].

In the electro-chemical oxidation of methanol, the electrode material is clearly an important parameter where a high efficient electro-catalyst is needed. As described previously [6–11], a considerable increase in power density and fuel utilization was obtained by optimizing the different components of fuel cells. Different electrode materials based on Pt and Pt-binary electrodes were commonly used as a catalyst for the electro-chemical oxidation of methanol. Because catalysis is a surface effect, the

catalyst needs to have the highest possible surface area. For this reason, carbon-supported electrodes are generally used as catalyst [12]. Among these electrodes, Pt–Ru and Pt–Ru–P/carbon nano-composites [13], Pt/Ni and Pt/Ru/Ni alloy nano-particles [14]. It is well established that nickel can be used as a catalyst due to its surface oxidation properties. Many electrodes involving nickel as a component in their manufacture can be used as catalysts in fuel cells. It is commonly used as an electro-catalyst for both anodic and cathodic reactions in organic synthesis and water electrolysis [15–18]. One of the very important uses of nickel as a catalyst is for the oxidation of alcohols. Several studies of the electro-oxidation of alcohols on Ni have been reported [19,20]. On the other hand, Taraszewska and Roslonek [21] found that glassy carbon/ $\text{Ni}(\text{OH})_2$ modified electrode acts as an effective catalyst for the oxidation of methanol. Most oxidizable organic compounds were found to oxidize at the same potential and this potential coincided exactly with that at which the surface of the nickel anode becomes oxidized [20,21–24]. Van Effen and Evans [25] found that the oxidation of ethanol in KOH solution involved the formation of a higher valence nickel oxide, which acts as a chemical oxidizing agent. This fact was confirmed by two studies [26]; by cyclic voltammetry, which proved the presence of a mediation process involving the higher oxides and the organic molecules, and by alternating current impedance measurements, which were carried out at various potential values.

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The purpose of the present work is to establish the electro-catalytic oxidation of methanol on graphite electrodes modified with nickel in a solution of 1.0 M KOH. Nickel is obtained on graphite from electro-deposition using the potentiostatic and the galvanostatic methods.

2. Experimental techniques

Electro-chemical measurements were performed on spectroscopically pure crystalline graphite disc electrodes of apparent surface area of 0.37 cm^2 modified by electro-deposited nickel. Before electro-deposition of nickel, the graphite electrode was mechanically polished using metallurgical papers of various grades, and then it was subsequently degreased with acetone, rinsed with distilled water and dried with a soft tissue paper. Before each experiment, the electrode surface was activated via the potentiostatic polarization at anodic potential of 1400 mV (versus Hg/HgSO₄/1.0 M H₂SO₄) for 5 min in order to remove any adsorbed materials. This was followed by polarization in a cyclic mode from the H₂ evolution potential (−800 mV) to a potential beyond O₂ evolution (1400 mV) in 1 M H₂SO₄ at a scan rate of 50 mV s^{-1} for 50 cycles. The apparent surface area was calculated from geometrical area and the current density was referred to it. The electrolytic cell was described elsewhere [27]. The reference electrode to which all potentials are referred is the Hg/HgO/1.0 M NaOH (MMO) (E^0 value equals 140 mV versus NHE) and a Pt sheet was used as the counter electrode. Measurements were carried out in aerated 1.0 M KOH at room temperature of 30 ± 0.2 . Methanol was used as received without further purification. Triply distilled water was used throughout for the preparation of solutions.

The electro-deposition of nickel was performed in a solution composed of 1.0 M NiSO₄ + 1.0 M H₂SO₄ by the po-

tentiostatic technique at −1000 mV versus Hg/HgSO₄/1.0 M H₂SO₄ (MMS) and the galvanostatic technique at current density values of 0.1, 0.2 and 1.0 mA cm^{-2} . After the preparation of the Ni deposits on the graphite electrodes, no further pretreatment of the electrode was necessary to avoid any changes in the substrate surface. Instead, the modified electrodes were activated before each experiment via potentiostatic polarization at −1200 mV (MMO) in 1.0 M KOH for 20 min.

The electro-chemical measurements were performed by the cyclic voltammetric technique using system AMEL 5000 (supplied by Amel Instrument, Italy) driven by an IBM PC for data processing. The PC was interfaced with the instrument through a serial RS-232 card. Amel Easyscan software was used in connection with PC to control the Amel 5000 system. All the reported potentials were corrected by the positive feedback technique. Deposits and electrode surfaces were examined with a scanning electron microscope.

3. Results and discussion

The cyclic voltammetric behaviour of massive nickel electrode in 1.0 M KOH solution is shown in Fig. 1. Polarization was started by potential scanning at a scan rate of 50 mV s^{-1} from −1200 to 700 mV in the anodic direction and then the scan was reversed in the cathodic direction back to −1200 mV. In the voltammogram of Fig. 1a, hydrogen evolution takes place at the starting potential characterized by a high cathodic current. Two regions can be observed in this figure; the first region is observed in the negative potential side comprising a small anodic peak at a potential value of about −550 mV that corresponds to the oxidation of nickel according to the reaction [28,29]:

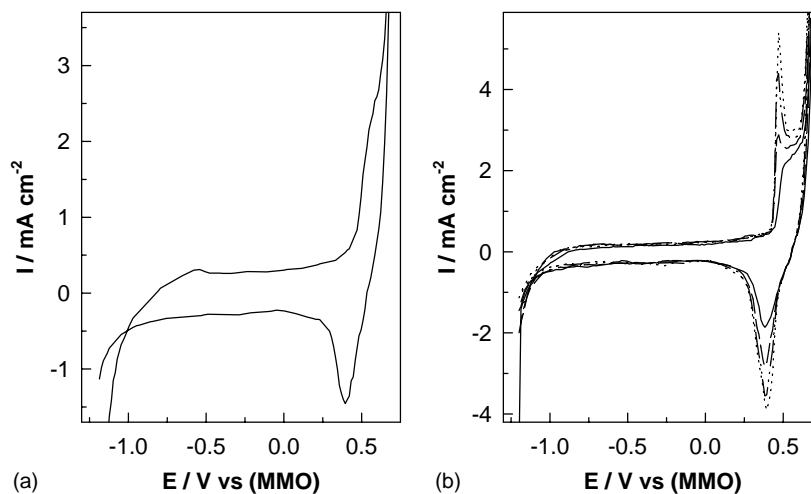
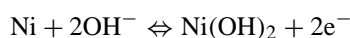


Fig. 1. Cyclic voltammograms of Ni electrode in 1.0 M KOH at a scan rate of 50 mV s^{-1} : (a) 1st cycle; (b) (—) 2nd cycle; (---) 10th cycle; (-·-·-) 30th cycle; (...) 50th cycle.

This peak almost disappeared in the subsequent cycles, as also observed by other authors [30] (see Fig. 1b). Along the potential range from -500 to 400 mV, the transformation of α -Ni(OH)₂ to β -Ni(OH)₂ takes place [30]. The second region is observed in the positive potential side comprising a peak at 470 mV and another one at 400 mV in the anodic and the cathodic directions, respectively. This couple of peaks corresponds to the oxidation of Ni(OH)₂ to NiOOH in accordance with the reaction [20,30,31]:



Increasing the number of potential sweeps results in a progressive increase of the current density values of the anodic and cathodic peaks because of the entry of OH⁻ into the Ni(OH)₂ surface layer, which leads to the progressive formation of a thicker NiO(OH) layer corresponding to the Ni(OH)₂/NiOOH transition. Fig. 1b shows some selected cycles up to 50th cycle. During the reverse sweep and after the reduction peak at 400 mV, the current remains almost constant except in the cathodic region where hydrogen evolution occurs again.

Experiments carried out to study the electro-chemical oxidation of methanol on massive nickel electrode in 1.0 M KOH solution show that such electrode is not efficient catalyst for this reaction. Maximovitch and Bronoel [32] reported that it is difficult to measure the oxidation current of methanol on smooth nickel, because it is difficult to obtain a surface free from adsorbed oxygen. Smooth nickel is very sensitive to molecular oxygen dissolved in the solution that adsorbs on the electrode and inhibits the reaction. However, good catalytic activity was observed for nickel electrochemically deposited on graphite substrate. For this purpose, nickel was deposited on graphite by the potentiostatic and the galvanostatic methods from a solution of 1.0 M NiSO₄ (see Section 2). Before the electro-deposition of nickel, the cyclic voltammetric behaviour of the graphite electrode was examined. The cyclic voltammetric behaviour of this electrode, at a scan rate of 50 mV s^{-1} traced in the supporting electrolyte (1.0 M KOH) in presence of 0.5 M MeOH in the potential region from -900 to 1600 mV versus (MMO), showed no evidence for methanol oxidation indicating that methanol is electro-inactive on the graphite electrode.

Fig. 2 shows the cyclic voltammograms recorded in 1.0 M KOH solution after the electro-deposition of nickel on the graphite electrode by the potentiostatic method at -1000 mV for 30 min. Beside the peaks corresponding to the oxidative corrosion of graphite and the reduction of dissolved oxygen, the figure shows the existence of an anodic peak (a₁) at about $+100$ mV and a pair of peaks (a₂ and c₂) corresponding to Ni(OH)₂/NiOOH transformation at about 800 mV for the anodic peak (a₂) and at about 100 mV for the cathodic peak (c₂). The anodic peak at $+100$ mV corresponds to the oxidation of nickel to nickel hydroxide, Ni(OH)₂, then the transformation of α -Ni(OH)₂/ β -Ni(OH)₂ takes place [30]. Comparing the potential and current values of the pair of peaks (a₂ and c₂) on dispersed nickel (Fig. 2) and the cor-

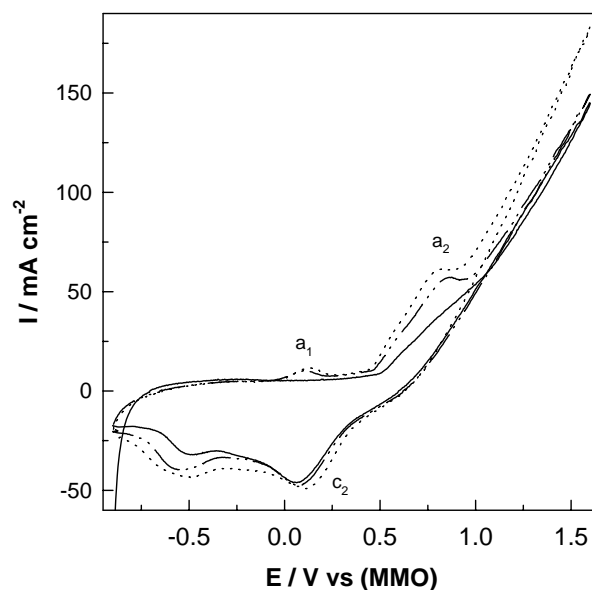


Fig. 2. Cyclic voltammograms of C/Ni electrode in 1.0 M KOH at a scan rate of 50 mV s^{-1} : (—) 1st cycle; (---) 5th cycle; (...) 50th cycle (Ni was deposited by the potentiostatic method at 1.0 V for 15 min).

responding peaks on massive nickel (Fig. 1), it is noted that the Ni(OH)₂/NiOOH transformation occurred on massive nickel reversibly as noted from the potential peak separation. On the other hand, on dispersed nickel this transformation occurred quasi-reversibly or irreversibly. This could possibly be due to the IR drop across the graphite substrate. On the other hand, it was found that the shape of the Ni^{II}/Ni^{III} transition (i.e. peak separation, peak current ratios and peak potentials), is influenced by the thickness of the nickel film [33] and for thicker deposited nickel oxide films, the voltammogram begins to show the typical features of an electrode with higher resistance: the potential difference between the anodic and the cathodic peak drastically increases [34]. The high surface area accompanied by the dispersed Ni on graphite is the reason for the relatively high current density values of the redox reaction than in case of massive Ni. Repeating the potential sweep several cycles causes an increase in the current density values of these peaks indicating an increase in the nickel oxides thickness.

Addition of 0.5 M methanol to the electrolyte changes the voltammetric response of the modified electrode (C/Ni electrode). Fig. 3 shows the cyclic voltammograms of C/Ni electrode in 1.0 M KOH in presence of 0.5 M MeOH in the potential range from -900 to $+1600$ mV (MMO) (Fig. 3a) at a scan rate of 50 mV s^{-1} for 50 cycles. The electro-oxidation of methanol on the modified C/Ni electrode is represented, in figure, by an anodic peak at 1250 mV (MMO) whose potential is shifted towards lower values by repeated potential cycling. Another relatively small peak was observed in the cathodic direction at a potential value of about 325 mV. According to the result of Fig. 2, oxygen evolution started at about 1000 mV (MMO) at the modified C/Ni electrode which indicates that the anodic peak in Fig. 3a represents a

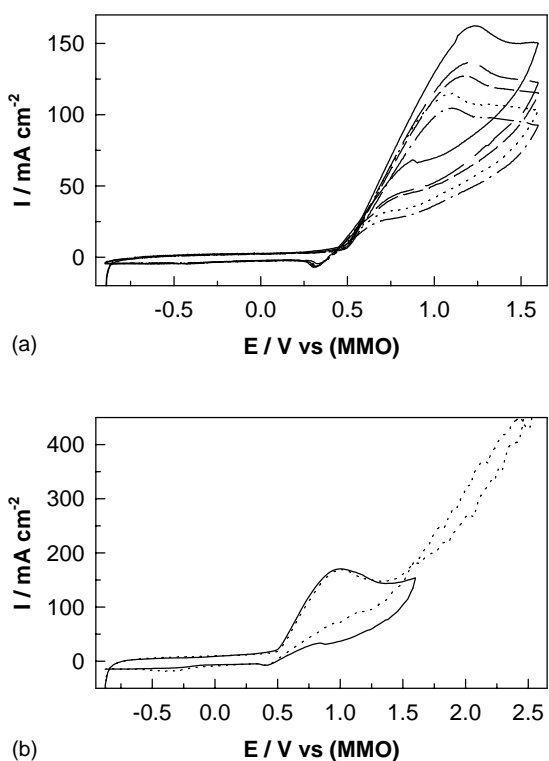


Fig. 3. (a) Repeated cyclic voltammograms of methanol oxidation on C/Ni electrode at 50 mV s^{-1} . (b) Effect of the upper potential limit on the cyclic voltammogram of methanol oxidation (0.5 M) at C/Ni electrode. Scan rate = 50 mV s^{-1} : (—) up to 1.6 V; (...) up to 2.6 V (MMO).

parallel reaction of O_2 evolution with methanol oxidation. But when extending the upper potential limit of methanol oxidation to a higher value (see Fig. 3b), the result shows that the presence of methanol in the electrolyte only delays the O_2 evolution reaction. It is assumed in this case that, methanol oxidation reaction is more favorable than O_2 evolution one under the given experimental conditions. Accordingly, the anodic peak of Fig. 3a is considered to represent the oxidation of methanol at the C/Ni electrode.

At the potential value of methanol oxidation (1250 mV) the composition of the surface layer of nickel is NiOOH. It was suggested that methanol is oxidized on the nickel electrode through the reaction with NiO(OH) to form Ni(OH)₂ [20,35]. Accordingly, the oxidation of methanol reduces the amount of NiO(OH) on the electrode surface. This could explain the large decrease in the magnitude of the cathodic peak current at 325 mV which corresponds to the NiO(OH)/Ni(OH)₂ transformation. This transformation was found to take place at a more cathodic potential in absence of methanol (see Fig. 2) and could be explained by the formation of nickel oxides of different morphologies in the presence of methanol. In the oxidation of alcohols at the nickel electrode covered by nickel hydroxide in alkaline solution, different hypotheses are given in the literature. In the oxidation of alcohols on the nickel electrode covered by nickel hydroxide in 1.0 M KOH, Fleischmann et al. [20,36] proposed a mechanism of alcohol oxidation and suggested

that the NiOOH acts as an electro-catalyst. This suggestion was mainly based on the experimental observation that alcohols and other organic compounds are oxidized at a potential which coincided exactly with that where NiOOH was produced, and on the disappearance of the NiOOH reduction peak in the negative sweep. However, the role of NiOOH as an electro-catalyst has been questioned by other authors [37]. Others also reported that methanol oxidation takes place after the complete oxidation of Ni(OH)₂ to NiOOH [21–23]. El-Shafei [38] studied the oxidation of methanol on the nickel hydroxide/glassy carbon modified electrode in alkaline medium and found that methanol oxidation occurred via Ni³⁺ species (mainly NiOOH). On the other hand, another conception was proposed by Taraszewska and Roslonek [21] that methanol molecules penetrate the nickel hydroxide film and were oxidized by the OH⁻ ions trapped in the film. Based on the above hypotheses, it is considered that during methanol oxidation the electrodic system of the catalyst changes. In the present study, the scanning electron micrographs of a C/Ni sample after methanol oxidation (see Fig. 4a) and for another C/Ni sample polarized in the supporting electrolyte without methanol (i.e. covered with NiOOH layer) (see Fig. 4b) have different morphological structures. This arises from the fact that some changes within the electrodic system take place. Scanning electron micrographs show that the oxide deposits are in the form of islands having a circular shape and that a large part of the electrode surface remains uncovered with the deposits. The morphological structure of the electrode surface seen in Fig. 4b changes after reducing the film by the potential holding at +100 mV for 2 h, i.e. the formation of Ni(OH)₂ layer (see Fig. 4c).

On repeated cyclization up to 50 cycles at 50 mV s^{-1} the peak height of methanol oxidation decreases to 65% with respect to its value in the first cycle. On the other hand, the peak potential is slightly shifted towards less positive potential values. The assumption that methanol oxidation takes place by the reduction of NiO(OH), to Ni(OH)₂, makes this result surprising. From the results of Figs. 1 and 2, continuous potential sweep of the Ni electrode in KOH solution results in increasing the peak current densities of NiO(OH)/Ni(OH)₂ transformation. So, it is expected to have thicker nickel oxide layers by potential cyclization, i.e. higher thickness of NiO(OH) and accordingly higher rate of methanol oxidation. But the decrease of the peak current density of methanol oxidation in Fig. 3 by cyclization could possibly be attributed to the activity loss of the nickel oxide [39–42]. This passive oxide film blocks the electrode surface due to its compactness and poor conducting behaviour that isolate the active material electrically from the reaction zone [43,44]. In another opinion, the activity loss is attributed to the flaking off the nickel oxide from the electrode surface [43]. Another possible explanation for the decrease of the peak current density of methanol oxidation is cited, where, the high NiO(OH) thickness, formed after several cycles, acts as a barrier inhibiting the charge transfer process for methanol

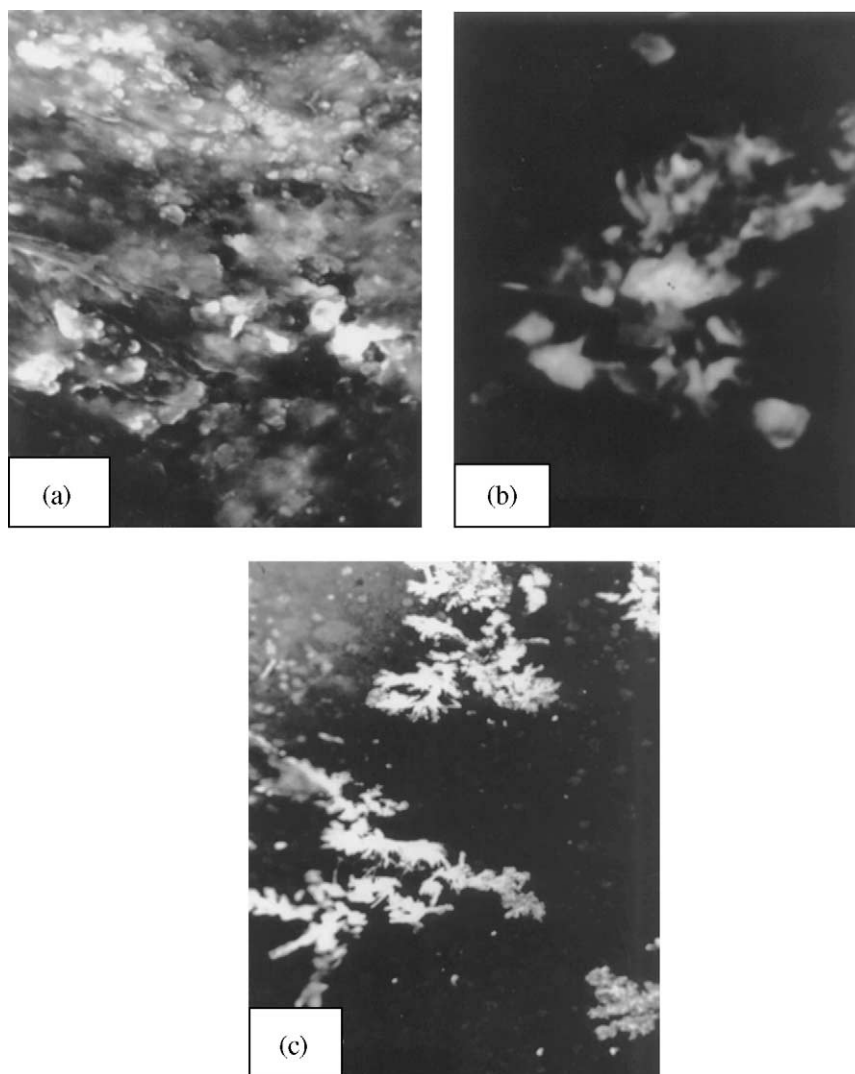
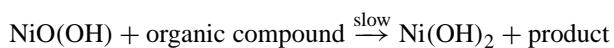
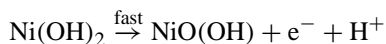


Fig. 4. Scanning electron micrograph of C/Ni electrode: (a) after methanol oxidation; (b) before methanol oxidation; (c) covered with Ni(OH)₂ layers. All $\times 1000$.

oxidation. Fleischmann et al. [20] suggested that the organic species are oxidized by the mechanism:



and not by a mechanism involving direct electron transfer from the organic compound to the anode. According to this mechanism, in presence of methanol there is an accumulation of Ni(OH)₂ species. This hydroxide necessarily evolves towards more stable species and its oxidation is attained at more positive potentials. For this reason, the quantity of NiO(OH) species necessary for methanol oxidation begins to decrease and accordingly a decrease in the methanol oxidation current density is observed. The results represented in our work do not provide sufficient data to discuss the mechanism of methanol oxidation on dispersed nickel, however

they lead to the conclusion that the oxidation of methanol seems to be mainly governed by charge transfer through the film, and by surface electro-catalysis on thick films in agreement with the results of Taraszewska and Roslonek [21]. On the other hand, it was found that the presence of several layers of Ni(OH)₂ on the electrode surface [32] or increasing amounts of NiO(OH) [37] seem to have an inhibiting effect that causes the inactivity of the electrode.

Some experiments were carried out in order to study the effect of nickel oxide thickness, dispersed on graphite electrode, on the oxidation of methanol. Nickel was electro-deposited on graphite electrode potentiostatically at -1000 mV for 15 min from a 1.0 M solution of NiSO₄ in 1.0 M H₂SO₄ solution. After electro-deposition the modified electrode then was subjected to an anodic potential in 1.0 M KOH solution at 900 mV (MMO) for a certain time to insure the formation of NiO(OH) layer on the electrode surface. The experiment was then repeated several times on

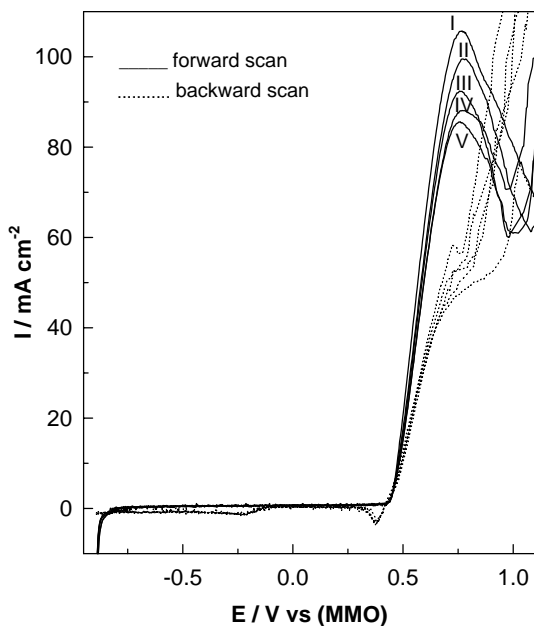


Fig. 5. Cyclic voltammograms of methanol oxidation after nickel oxide formation at different time intervals on C/Ni electrode: (I) 5 min; (II) 10 min; (III) 20 min; (IV) 25 min; (V) 30 min.

a new C/Ni electrode (formed exactly at the same experimental conditions as above) but in every case each modified electrode was subjected to a potential holding in the 1.0 M KOH solution for different time in order to get finally modified electrodes covered by nickel oxides of various thickness. Fig. 5 shows cyclic voltammograms for methanol electro-oxidation over the nickel oxide covered-C/Ni electrodes in (0.5 M MeOH + 1.0 M KOH) at 10 mV s^{-1} . A decrease in the peak current density values for the methanol oxidation is observed as the time (i.e. the amount) of nickel oxide formation increases.

In the above results (Figs. 3 and 5), starting the polarization potential at a potential value of -900 mV seems to be a necessary procedure in order to study the electro-oxidation of methanol by the cyclic voltammetric technique. A decrease of the height of the methanol oxidation peak was observed when starting the polarization from potential values more positive than -900 mV . Therefore, to get a reproducible methanol oxidation peak, it is necessary to start the polarization potential from at least -900 mV . At -900 mV hydrogen evolution is observed characterized by a high cathodic current. The partial reduction of the surface oxide takes place at a potential where hydrogen is evolved [44,45] and accordingly reactivates the electrode. It was reported that hydrogen plays an important role in nickel catalysis. The presence of hydrogen on Raney nickel induces the hydroxide reduction which is slow and irreversible reaction on pure smooth nickel [46]. Fig. 6a shows a cyclic voltammogram for methanol electro-oxidation recorded after 50th cycle at C/Ni electrode in 0.5 M MeOH in 1.0 M KOH at 50 mV s^{-1} in the potential range from -900 to 1600 mV (MMO). At

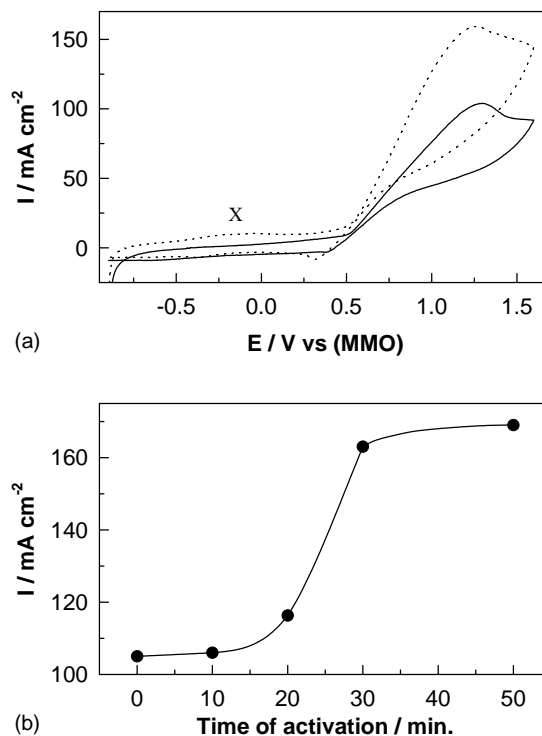


Fig. 6. (a) Effect of activation of C/Ni electrode (in 1.0 M KOH) at the hydrogen evolution potential on the methanol oxidation peak height. Scan rate = 50 mV s^{-1} : (—) before activation; (...) after 30 min activation. (b) Variation of the steady state current density of methanol oxidation with the time of activation of the C/Ni electrode.

the end of the 50th cycle, another cyclic voltammogram was recorded but after maintaining the C/Ni electrode potential in the hydrogen evolution region at -1200 mV in 1.0 M KOH for 30 min. An increase in the peak height of the methanol oxidation was observed after the activation process and a new relatively poor distinguishable anodic peak (X in Fig. 6a) was observed at the potential of the anodic oxidation of Ni to $\text{Ni}(\text{OH})_2$. This could indicate that, at the 30 min activation, most of the oxide layer on the surface of nickel could be reduced in the hydrogen evolution region. The experimental conditions used for the oxide formation (up to $+1600 \text{ mV}$) induce a highly stabilized $\text{NiO}(\text{OH})$ that results in a decrease in the methanol oxidation activity with the polarization time. The reduction of this oxide taking place by holding the electrode potential at -1200 mV could also give another explanation for restoring the catalyst activity. According to the above result, it is expected that the extent of maintaining the height of methanol oxidation after the 50th cycle depends on the time of activation in the hydrogen evolution potential region. Variation of the peak current density of methanol electro-oxidation with the time of activation is shown in Fig. 6b. It is noted in this figure that the best activation time for the given Ni deposit is 30 min, after which no appreciable increase in current density is observed.

A set of experiments was made to study the effect of methanol concentration. For this purpose C/Ni electrode

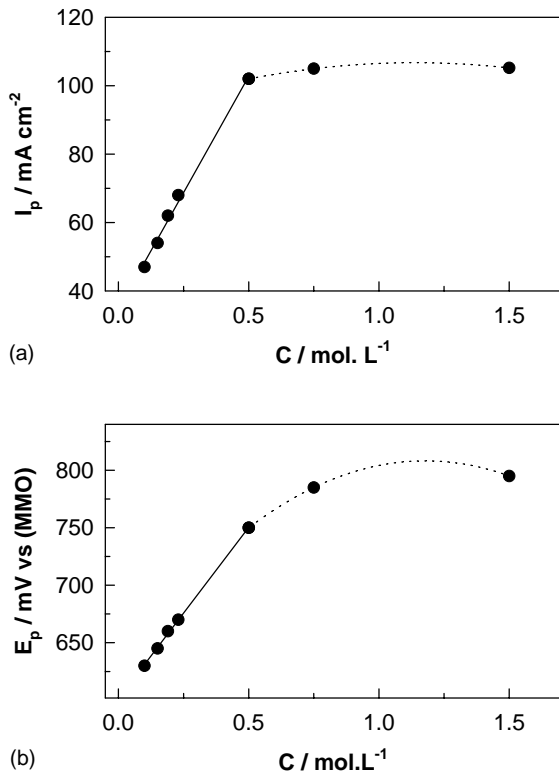


Fig. 7. Variation of the peak current density (a) and peak potential (b) of methanol oxidation on C/Ni electrode with its concentration.

was prepared by the potentiostatic deposition of nickel on graphite electrode at -1000 mV for 15 min from the acidic nickel sulphate solution. Cyclic voltammetric curves of the modified electrode were then recorded in KOH solution in presence of various concentrations of methanol in the potential range from -900 to 1600 mV (MMO) at a scan rate of 10 mV s⁻¹. Various methanol concentrations ranging from 0.10 to 1.5 M in 1.0 M KOH were used. Fig. 7 represents the dependence of the peak current density (Fig. 7a) and peak potential (Fig. 7b) of methanol oxidation on the bulk concentration of methanol. It was found from this figure that both the methanol oxidation peak current density and peak potential linearly increase with increasing methanol concentration up to 0.5 M, after which they reach almost constant values independent of the concentration. Thus, a concentration value of 0.5 M represents a critical concentration after which the adsorption of the oxidation products at the electrode surface causes the hindrance of further oxidation. On the other hand, the same deviation in the relation between methanol concentration and the oxidation peak potential may be attributed to the IR drop due to high oxidation current at high concentrations. The logarithmic plot (Fig. 8) of the peak current density of methanol oxidation with its concentration up to a value of 0.5 M produces a straight line of a slope equal to the order of the reaction with respect to methanol concentration according to the relation:

$$\text{rate} \equiv I = k C^n$$

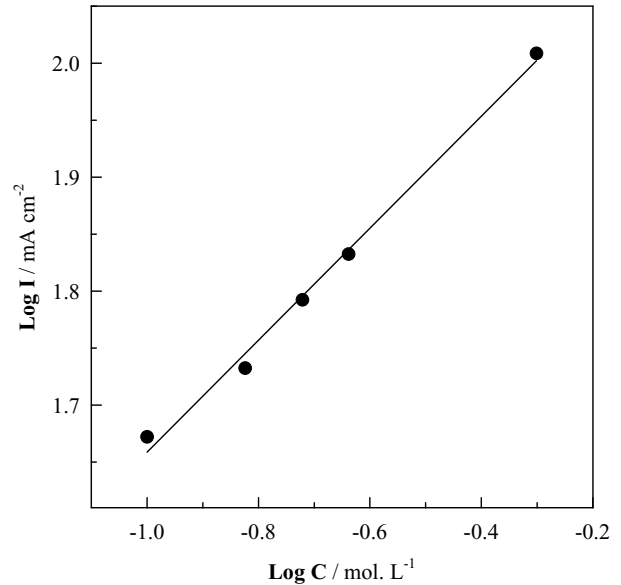


Fig. 8. Variation of the logarithm of methanol oxidation peak current density at C/Ni electrode with the logarithm of methanol bulk concentration.

$$\log I = \log k + n \log C$$

where I is the peak current density, k the reaction rate constant, C the bulk concentration and n is the reaction order. A value of 0.5 was calculated for the reaction order in agreement with the values obtained by other authors [47,48].

Fig. 9 represents cyclic voltammograms of methanol oxidation (0.5 M) at different scan rates ($v = 75, 50, 30, 20$ and 10 mV s⁻¹) in 1.0 M KOH at C/Ni electrode. With increasing the scan rate the height of the oxidation peak of methanol increases and a potential shift towards higher

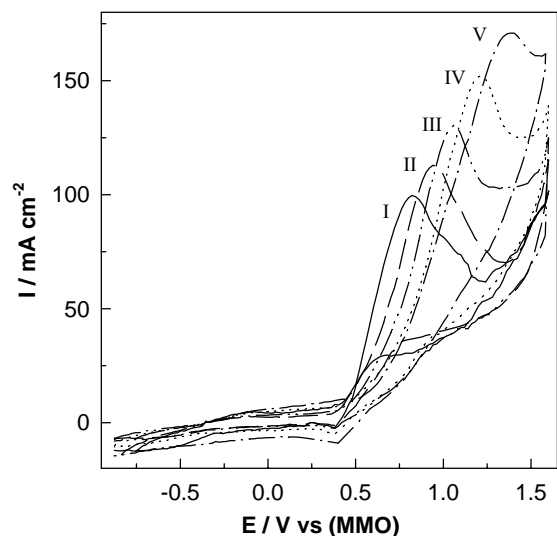


Fig. 9. Cyclic voltammograms of methanol oxidation (0.5 M) in 1.0 M KOH at C/Ni electrode at different scan rates: (I) 10 mV s⁻¹; (II) 20 mV s⁻¹; (III) 30 mV s⁻¹; (IV) 50 mV s⁻¹; (V) 75 mV s⁻¹.

Table 1

Values of the weight of nickel theoretically and experimentally measured, the amount of charge (Q) and the deposition efficiency for the potentiostatic deposition of Ni on graphite electrode

Time of deposition (s)	Q (C)	$W_{t.theo.}$ (μg)	$W_{t.exp.}$ (μg)	Deposition efficiency
300	0.1990	59.80	34.80	58.19
600	0.2587	77.74	52.20	67.15
900	0.3403	102.27	63.80	62.38
1200	0.4565	137.79	87.00	63.14
1500	0.5190	155.97	92.80	59.50

Ni was deposited from an acidic nickel sulphate solution for various times at -1000 mV (MMS).

potential values was observed. The shift of the peak potential to higher values is possibly due to the IR drop generated at high current density values.

In order to investigate the effect of the amount of nickel deposited and the method of deposition on methanol oxidation, nickel was electro-deposited using the potentiostatic and the galvanostatic techniques at various times of deposition. In the potentiostatic method, nickel was deposited on the mechanically treated graphite electrode by applying a constant potential step of -1000 mV to the working electrode for different times: 300, 600, 900, 1200 and 1500 s. During each potentiostatic experiment the amount of charge consumed was simultaneously measured. Using the amount of charge measured assuming 100% efficiency the weight of nickel deposited was calculated ($W_{t.theo.}$). After electro-deposition, the weight of nickel deposited was then experimentally determined ($W_{t.exp.}$) by using the complexometric method. This was carried out in order to determine the exact efficiency of the potentiostatic deposition method. Data of the theoretical and experimental weight of deposited nickel as well as the current efficiency are tabulated in Table 1. From this table one can deduce the average efficiency for the potentiostatic nickel deposition as 62.1%.

Fig. 10 shows the effect of the weight of Ni deposited by the potentiostatic and galvanostatic methods on the current density of methanol oxidation at the C/Ni electrodes. In these experiments methanol oxidation was carried out by the potentiostatic polarization in a solution composed of 0.5 M MeOH + 1.0 M KOH for 1 h at 1200 mV (MMO) (the value corresponding to the methanol oxidation peak potential (see Fig. 3)). Variation of the steady state current density with the deposition time indicates that certain low quantities of deposits show a high catalytic activity. Fig. 10a shows that the highest catalytic effect in case of potentiostatic deposition was observed at deposited nickel layers of weight 68 and $180 \mu\text{g cm}^{-2}$. However, for relatively thick layers a low catalytic effect was observed. At a higher time of deposition, it is expected to have high nickel oxide films that can act as a barrier for methanol oxidation as reported above. The same procedure was applied in the galvanostatic method wherein nickel was deposited at a constant current of 0.1 and 0.2 mA cm^{-2} for different times. The results are represented

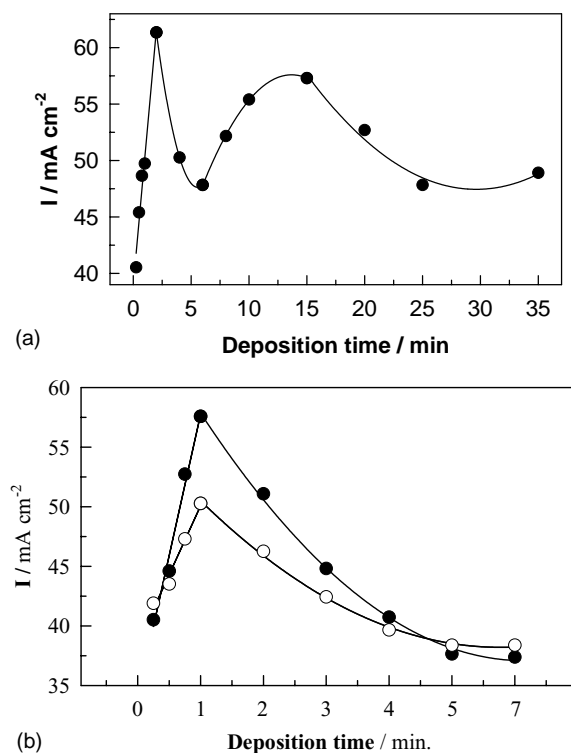


Fig. 10. (a) Variation of the steady state current density of methanol oxidation with the time of Ni deposition. (Ni was deposited by the potentiostatic method). (b) Variation of the steady state current density of methanol oxidation with the time of Ni deposition. Ni was deposited by the galvanostatic method at: (●) 0.1 mA cm^{-2} ; (○) 0.2 mA cm^{-2} .

in Fig. 10b that shows, for both current density values, that the current of methanol oxidation increases with the increase of the amount of nickel deposited (or the amount nickel oxide) on the electrode surface up to a certain thickness thereafter it decreases and finally reaches almost a constant val-

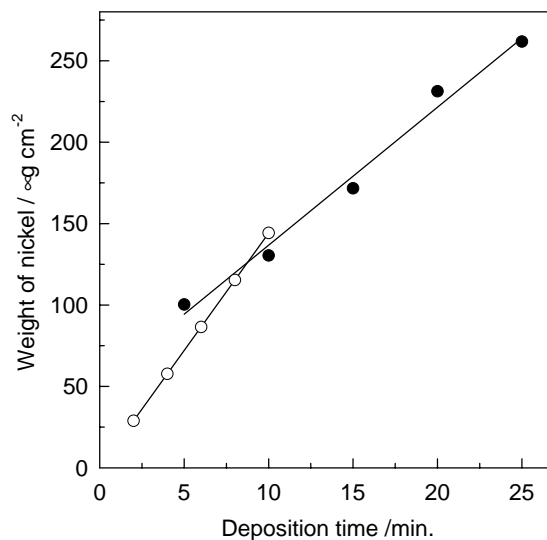


Fig. 11. Variation of the weight of nickel deposited on graphite electrode with the time of deposition: (●) potentiostatic deposition; (○) galvanostatic deposition.

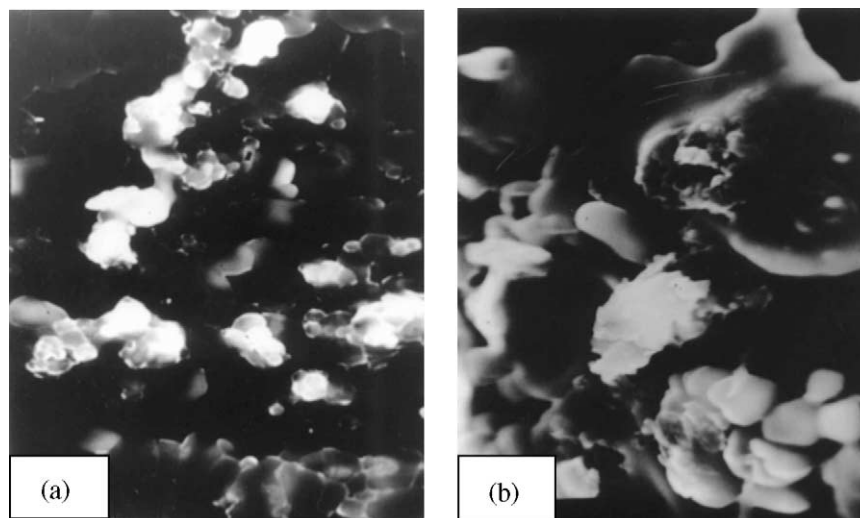


Fig. 12. Scanning electron micrograph of C/Ni electrode (All $\times 1000$): (a) potentiostatic deposition at -1000 mV (MMS) for 30 min; (b) galvanostatic deposition at 0.1 mA cm^{-2} for 6 min.

ues at high oxide thickness. The highest catalytic effect was observed at 15 $\mu\text{g cm}^{-2}$. Data of the theoretical and experimental weight of deposited nickel as well as the efficiency are tabulated in Table 2 from which the average efficiency for the galvanostatic nickel deposition was deduced. A value of 80.0% was obtained in this case.

From the above results and after deducing the efficiency in both the potentiostatic and the galvanostatic methods of deposition, the exact weight of nickel deposited can be plotted as a function of the time of deposition. Fig. 11 shows this relation for both methods from which the rate of deposition can be estimated. Values of 8.47 and 14.43 $\mu\text{g cm}^{-2} \text{min}^{-1}$ were obtained for the deposition rate in case of the potentiostatic and the galvanostatic methods, respectively.

The increase in the current density of methanol oxidation with the small amount of nickel deposited at the first few seconds is attributed to the increase in the catalytic surface area of the electrode available for the reaction. However, for a relatively thick layer, a low catalytic effect is observed, where an increased amount of NiOOH would be produced with its inhibiting action towards methanol oxidation [37].

Table 2

Values of the weight of nickel theoretically and experimentally measured, the amount of charge (Q) and the deposition efficiency for the galvanostatic deposition of Ni on graphite electrode

Time of deposition (s)	Q (C)	$W_{\text{theo.}}$ (μg)	$W_{\text{exp.}}$ (μg)	Deposition efficiency
120	0.12	13.34	11	82.46
240	0.24	26.69	20.9	78.31
360	0.36	40.03	31.9	79.69
480	0.48	53.37	43.5	81.51
600	0.60	66.72	52.2	78.24

Ni was deposited from an acidic nickel sulphate solution for various times at 1.0 mA cm^{-2} .

In another opinion, these dense layers may approach the behaviour of the massive nickel electrode, which is not a good catalyst for methanol oxidation as the dispersed form [32]. In the galvanostatic deposition method, increasing the rate of the deposition (the constant current density at which the galvanostatic deposition is carried out) causes a decrease in the resulting current density of methanol oxidation (see Fig. 10b). Applying higher current densities in the galvanostatic technique accelerates the rate of the deposition process resulting in the formation of thicker and larger sized nickel crystals with a lower catalytic action towards methanol oxidation. This explanation was confirmed by observing the difference in the scanning electron micrographs of the C/Ni samples prepared by both the potentiostatic (see Fig. 12a) and the galvanostatic (see Fig. 12b) techniques. Deposits of a larger particle size are observed using the galvanostatic technique. In addition, the deposition rate in the case of the potentiostatic and the galvanostatic methods estimated from a relation between the time of the nickel deposition and its corresponding deposited weight (Fig. 11) supports this opinion. The rate of the nickel deposition by using the galvanostatic method (14.43 $\mu\text{g cm}^{-2} \text{min}^{-1}$) is higher than that by using the potentiostatic one (8.47 $\mu\text{g cm}^{-2} \text{min}^{-1}$). This relatively higher rate of nickel deposition in the galvanostatic method than in the potentiostatic one forced us to reduce the rate of deposition when studying the effect of nickel amount on methanol oxidation. This was achieved by applying a much less current density value, ca. 0.1 mA cm^{-2} for the galvanostatic electro-deposition of nickel.

4. Conclusion

The unmodified graphite electrode shows no activity for methanol oxidation reaction in 1.0 M KOH. However, the

nickel-modified graphite electrodes are good catalysts for this reaction and high current densities (over 150 mA cm^{-2}) can be reached. During the electro-chemical oxidation of methanol the modified electrodes suffer from loss of catalytic activity which can be improved by periodic reactivation of the electrode in the hydrogen evolution potential region. The height of the oxidation peak of methanol increases with increasing the alcohol concentration. For concentrations higher than 0.5 M , no appreciable change in the oxidation peak height was observed. The results indicate that the reaction of the electro-oxidation of methanol is activation controlled proceeding by direct chemical reaction with NiO(OH) for thin nickel oxides and by charge transfer with the electrode for thick oxides. Certain amount of nickel deposits, either prepared by the potentiostatic or the galvanostatic technique, exhibits a high catalytic activity otherwise the catalytic activity is poor.

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