

# The role of a bimetallic catalyst in enhancing the electro-catalytic activity towards methanol oxidation

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## Abstract

Nickel and ruthenium dispersed on graphite electrode showed a catalytic activity towards methanol oxidation in KOH solution. Various modified graphite electrodes of different Ni–Ru ratios were prepared by the electro-deposition of Ni and Ru from their salt solutions by changing the relative concentration of each metal ion in the deposition bath. Results of the electrochemical measurements revealed that simultaneous deposition of the binary metals is the best method to prepare the catalyst. The relative distribution of Ni–Ru deposits on the graphite electrode depends on the method of deposition as shown by optical microscope analysis. The catalytic activity of the bimetallic catalyst C/(Ni–Ru) towards methanol oxidation was found to vary with the amount of electrodeposited Ni and Ru. However, the catalytic activity increases with increasing the Ni content relative to Ru in the electrode. The dependence of the oxidation current on methanol concentration and the upper- and lower-potential limits was discussed. It was concluded from the electrochemical measurements that methanol oxidation begins at the potential value of NiOOH production with the formation of intermediate products. The presence of perruthenate species on the electrode surface is responsible for the complete oxidation of the intermediate species.

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## 1. Introduction

Direct methanol fuel cell (DMFC) is considered one of the promising systems for power generation in electric vehicles [1]. Methanol, as a fuel, is a relatively highly active and easily transported and converted into energy from the liquid state. Platinum has been recognized as an important electro-catalyst in the direct oxidation of small organic compounds [2]. Numerous modifications of Pt electrodes have been carried out in order to enhance the electro-catalytic oxidation process. This was achieved using various metals either by alloying, novel immersion techniques [3], or underpotential deposition [4]. One of the impeding problems in the commercialization in DMFCs is perhaps the high over potential associated with the direct electro-oxidation of methanol [5]. Although electro-catalysts based on Pt [6] and Pt–Ru alloys [7,8] have been developed and indeed exhibit good activities, high costs of these materials are often very prohibitive. A great deal of interest has recently been cen-

tered on the choice of materials cheaper than platinum. Several trials have used less expensive materials, for example: Co [9], Pd [10], Fe [11], Ni [12,13], and on TiO<sub>2</sub> [14] and Ti coated with oxides of Fe, Co, Ni, Mo, Mn, Cr, Cu, and Hg or their combinations: Sb–Sn, Co–Mn, Ni–Si, Ni–Cr–Mo, and Fe–Cr [15].

The heterogeneous catalytic oxidation of organic substances by redox catalysis was previously explored [16]. For this type of redox reactions, nickel was found to be a good catalyst [16–18]. It was commonly used as an electro-catalyst for both anodic and cathodic reactions in organic synthesis and water electrolysis [19,20]. RuO<sub>2</sub> was also reported to effectively catalyze the electro-oxidation of alcohols [21], both in acidic [22] and in alkaline solutions [23]. Modification of the nickel surface by the addition of RuO<sub>2</sub> seems to enhance the electro-catalytic activity towards the oxidation of ethanol [24] compared to the bulk metal oxide electrodes [25]. This enhancement was attributed to the excellent corrosion resistance and the high electro-catalytic activity of the RuO<sub>2</sub>-coated electrodes. In addition, the presence of the mixed oxides serves as good electron transfer mediators for the oxidation process. These mixed oxides involve the redox couple of nickel, i.e., nickel

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hydroxide Ni(OH)<sub>2</sub>/nickel oxyhydroxide NiOOH, and that of ruthenium, i.e., ruthenate Ru(VI)/perruthenate Ru(VII).

The purpose of the present work is to study the electro-catalytic oxidation of methanol at graphite electrodes modified with nickel–ruthenium deposits in alkaline solution, aiming to have a less expensive electro-catalyst in the DMFC.

## 2. Experimental techniques

Electrochemical measurements were performed on spectroscopically pure crystalline graphite disc electrodes of apparent surface area of 0.37 cm<sup>2</sup> modified by simultaneously electrodeposited nickel–ruthenium. Before the electro-deposition process, the graphite electrode was mechanically polished by using metallurgical papers of various grades, then it was subsequently degreased with acetone, rinsed with distilled water, and dried with a soft tissue paper. The electrode surface was activated via the potentiostatic polarization at 1400 mV for 5 min followed by polarization in a cyclic mode from the H<sub>2</sub> evolution potential (−800 mV) to a potential beyond O<sub>2</sub> evolution (1400 mV) in 1 M H<sub>2</sub>SO<sub>4</sub> at a scan rate of 50 mV s<sup>−1</sup> for 50 cycles. The apparent surface area was calculated from geometrical appearance and the current density is referred to this area. Hg/HgO/1.0 M NaOH (MMO) and Hg/HgSO<sub>4</sub>/1.0 M H<sub>2</sub>SO<sub>4</sub> (MMS) are used as reference electrodes 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 °C ± 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 and ruthenium was performed simultaneously using the potentiostatic and the galvanostatic methods from solutions composed of 1 × 10<sup>−3</sup> M RuCl<sub>3</sub> with different concentrations of NiSO<sub>4</sub> ranging from 1 to 1.6 × 10<sup>−2</sup> M in 1.0 M H<sub>2</sub>SO<sub>4</sub> solution. The potentiostatic deposition method is carried out at −1000 mV versus (MMS) while the galvanostatic method is at 0.1 and 1.0 mA cm<sup>−2</sup>. After the preparation of the nickel–ruthenium deposits on the graphite electrodes, no further pretreatment of the electrode was necessary to avoid any changes in the substrate surface.

The electrochemical measurements were performed by the cyclic voltammetric technique. Details of the electrochemical equipments as well as the electrolytic cell were described elsewhere [26].

## 3. Results and discussion

The modified C/(Ni–Ru) electrode was prepared electrochemically by the co-deposition of nickel and ruthenium from a solution composed of 0.008 M NiSO<sub>4</sub> + 0.001 M RuCl<sub>3</sub> in 1.0 M H<sub>2</sub>SO<sub>4</sub> via potentiostatic technique at

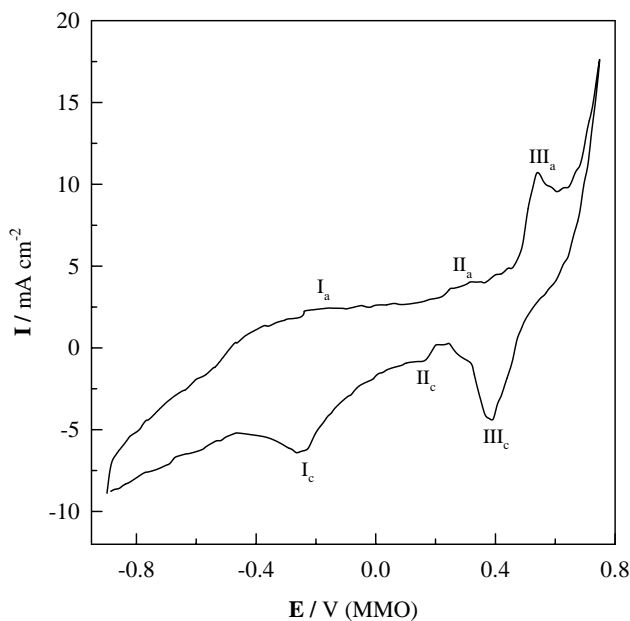
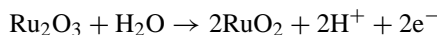
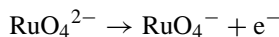


Fig. 1. Cyclic voltammogram of C/(Ni–Ru) electrode in 1.0 M KOH. Potential was scanned at 10 mV s<sup>−1</sup> from −900 to +750 mV. (Ni and Ru were simultaneously deposited from their salt solutions of molar ratio 8:1).

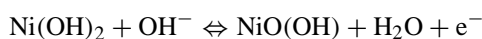
−1000 mV versus (MMS) for 1 h. Fig. 1 represents the cyclic voltammetric behaviour of this electrode in 1.0 M KOH at a scan rate of 10 mV s<sup>−1</sup> in the potential range from −900 to +750 mV. Three redox couples are observed in the voltammogram; the first appears at potential values of −200 and −250 mV (I<sub>a</sub> and I<sub>c</sub>), the second at +280 and +150 mV (II<sub>a</sub> and II<sub>c</sub>) while the third appears at +550 and +400 mV (III<sub>a</sub> and III<sub>c</sub>). The first and second redox couples represent, respectively, the formation of Ru<sub>2</sub>O<sub>3</sub> [Ru(III)] and RuO<sub>2</sub> [Ru(IV)] according to the following equilibria [27]:



The higher oxidation states of ruthenium Ru(IV)/Ru(VI) and ruthenate [Ru(VI)]/perruthenate [Ru(VII)] are believed to be formed at potential values above 1.05 V (RHE) [21] as represented in the following reactions:



In the present work, these higher oxidation states of ruthenium cannot be easily detected in the voltammogram of Fig. 1 as oxygen gas evolution starts at about +650 mV (MMO). The third redox couple, observed in Fig. 1 (III<sub>a</sub> and III<sub>c</sub>), represents the oxidation of Ni(OH)<sub>2</sub> to NiOOH in accordance with the reaction [12,28]:



The electro-oxidation of 0.5 M methanol at the C/(Ni–Ru) electrode was studied at a scan rate of 10 mV s<sup>−1</sup> in the po-

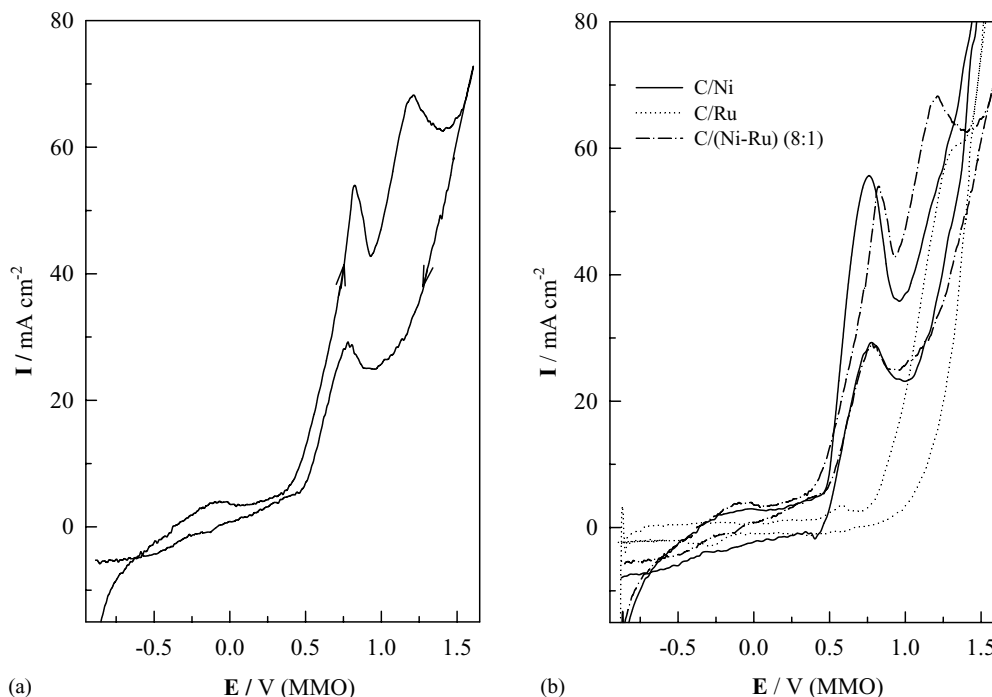
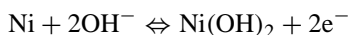
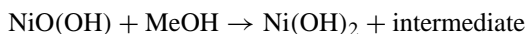


Fig. 2. (a) Cyclic voltammogram of C/(Ni-Ru) electrode in 0.5 M MeOH + 1.0 M KOH solution. Potential was scanned at  $10 \text{ mV s}^{-1}$  from  $-900$  to  $+1600$  mV. (b) Comparison between the cyclic voltammetric behaviour of C/Ni, C/Ru, and C/(Ni-Ru) electrodes at a scan rate of  $10 \text{ mV s}^{-1}$  in 0.5 M MeOH + 1.0 M KOH solution. (Ni and Ru were simultaneously deposited from their salt solutions of molar ratio 8:1).

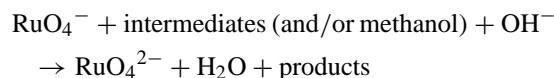
tential range from  $-900$  to  $+1600$  mV in 1.0 M KOH solution. The result is represented in Fig. 2a that showed the presence of two anodic peaks, the first one at  $+840$  mV, while the second one at  $+1210$  mV. In presence of methanol,  $\text{O}_2$  evolution is observed at more positive potentials than in its absence (see Fig. 1). It naturally appears after the second anodic peak at a potential value of about  $+1450$  mV, as the oxidation of methanol represents a predominant reaction than the  $\text{O}_2$  evolution one. By comparing the cyclic voltammograms of C/Ni, C/Ru, and C/(Ni-Ru) modified electrodes in the same solution (Fig. 2b), it was concluded that the first oxidation peak might correspond to the contribution of nickel in the methanol oxidation process, while the second one corresponds to that of ruthenium. On the basis of these results, one may suggest a mechanism for the oxidation of methanol at the modified C/(Ni-Ru) electrode as follows: during potential scanning in the anodic direction, nickel (and ruthenium) will undergo anodic oxidation with the formation of their respective oxides. With respect to nickel, the hydroxide and then the oxyhydroxide species are formed at potential values up to  $+840$  mV (MMO) according to the following reactions [12,28]:



Once NiOOH is formed, methanol oxidation begins at this potential value, according to the following reaction:



This suggestion was mainly based on the experimental observations reported by Fleischmann et al. [12,13]. They found that, alcohols and other organic compounds were oxidized at a potential value that coincided exactly with that at which NiOOH was produced. Therefore, according to the above reaction, it is assumed that methanol is oxidized by the reduction of NiO(OH) to Ni(OH)<sub>2</sub> with the formation of intermediate products. Accordingly, it is expected to obtain a cyclic voltammogram free from the NiOOH reduction peak in the cathodic sweep (see Figs. 1 and 2a). With respect to ruthenium and during potential scanning in the anodic direction, the various ruthenium oxides are formed until a potential value of  $+1210$  mV (MMO) at which the perruthenate species is formed. The presence of the perruthenate species on the electrode surface is possibly responsible for the second anodic peak that appears in Fig. 2a which corresponds to the oxidation of the intermediate species (and/or methanol) according to the following reaction:



Due to the excellent stability and reversibility of the redox couple ruthenate Ru(VI)/perruthenate Ru(VII), it can act as a suitable heterogeneous electron transfer mediator [24]. The high catalytic activity of C/(Ni-Ru) electrode is thus attributed to the presence of more than one active metal oxide represented by the nickel redox couple Ni(OH)<sub>2</sub>/NiOOH and the ruthenium redox couple Ru(VI)/Ru(VII). These

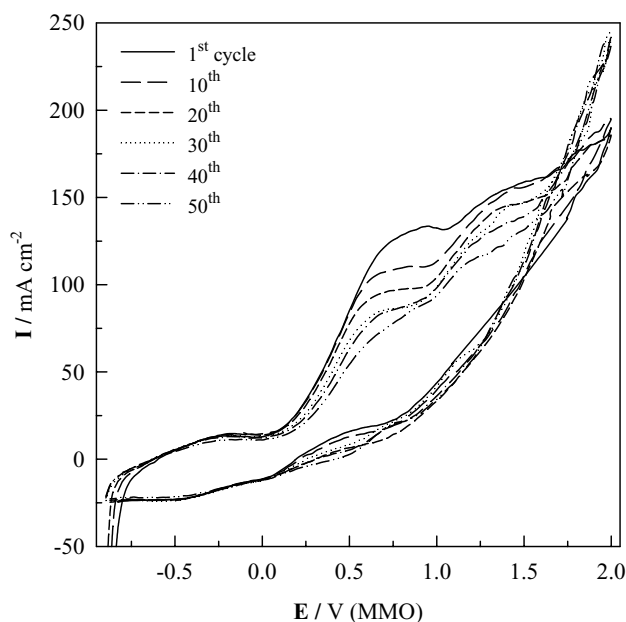


Fig. 3. Repeated cyclic voltammograms of methanol oxidation at C/(Ni–Ru) electrode. Potential was scanned at  $50 \text{ mV s}^{-1}$  from  $-900$  to  $+2000 \text{ mV}$ . (Ni and Ru were simultaneously deposited from their salt solutions of molar ratio 8:1).

mixed nickel–ruthenium oxides act as good electron transfer mediators for the methanol oxidation process [24,29].

Stability of the modified C/(Ni–Ru) electrode was examined by cycling the potential during methanol oxidation in  $1.0 \text{ M KOH}$  in presence of  $0.5 \text{ M MeOH}$  at a scan rate of  $50 \text{ mV s}^{-1}$  in the potential region from  $-900$  to  $2000 \text{ mV}$  (MMO). The results are represented in Fig. 3 that shows a decrease in the height of the two oxidation peaks by potential cyclization. After 50 cycles, the height of the first oxidation peak decreases to 62.4% of its value at the first cycle while the height of the second oxidation peak decreases to 71.9%. The decrease of the peak current density of methanol oxidation by potential cyclization could be possibly attributed to the activity loss of the nickel and ruthenium oxides. With respect to nickel, the formation of irreducible  $\beta\text{-Ni(OH)}_2$  or  $\text{NiO}_2$  at potentials above  $-0.5 \text{ V}$  (MMO) [20,30] could explain this activity loss. This passive oxide film blocks the electrode surface due to its compactness and poor conducting behaviour that electrically isolate the active material from the reaction zone [31]. The flaking off of nickel oxide from the electrode surface could also be considered another possible explanation for the decrease of the peak height. In addition, the high  $\text{NiO(OH)}$  thickness after several cycles might act as a barrier inhibiting the charge transfer process for methanol oxidation. On the other hand, the activity loss with respect to ruthenium may be attributed to the mechanical removing of some Ru oxide surface layers during prolonged cyclization [32] or to the dissolution of the Ru oxide layer to form  $\text{RuO}_4^{2-}$  [33], and  $\text{RuO}_4^-$  [34] as soluble species at higher potentials. The formation of a thick hydrous oxide layer all over the potential range [35] could represent another pos-

sible explanation for this activity loss. These hydrous oxides are susceptible to dissolution or they rearrange readily, with expulsion of water, to yield a more stable and compact surface layer [36]. In another opinion, the decrease of the peak height of methanol oxidation is due to the poisoning effect by the diffusion of the oxidation products into the inner pores of the passive Ni and Ru oxide films [29], hence reducing the number of the catalytically active sites for the oxidation process [21].

A set of experiments was carried out to study the effect of methanol concentration. Cyclic voltammograms at a scan rate of  $10 \text{ mV s}^{-1}$  for methanol concentrations ranging from  $0.30$  to  $1.50 \text{ M}$  in  $1.0 \text{ M KOH}$  were recorded in Fig. 4. It was observed that at lower methanol concentrations, up to  $0.75 \text{ M}$ , the two anodic oxidation peaks are sharp and well defined (Fig. 4a) and the peak heights increase with the increase of methanol concentration. Above  $0.75 \text{ M}$  the oxidation peaks become broad with a slight increase in current density (Fig. 4b). As methanol concentration increases, more nickel oxyhydroxide and perruthenate species will be consumed, and it was suggested that the rate of the formation of a complex between nickel oxyhydroxide as well as perruthenate and the alcohol is faster than that of its decomposition producing the oxidation products, thus, the broadening of the alcohol oxidation peaks at higher concentrations is expected [30]. The height of the two oxidation peaks increases linearly with methanol concentration up to  $1.0 \text{ M}$ , however, it deviates from linearity at higher concentrations (Fig. 5a). The deviation from linearity at high concentrations is probably due to the absorption of oxidation products at the electrode surface that retards the oxidation process. On the other hand, almost constant values of the oxidation peak potential are observed independent of the methanol concentration.

The logarithmic plot of the peak current density of methanol oxidation at the C/(Ni–Ru) electrode with its bulk concentration up to a value of  $1.0 \text{ M}$  produces straight line relations (see Fig. 5b). The slope of these straight lines is equal to the order of the reaction with respect to methanol according to the relations:

$$\text{Rate} \equiv I = kC^n$$

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

where  $I$  is the peak current density,  $k$  is the reaction rate constant,  $C$  is the bulk concentration of methanol, and  $n$  is the reaction order. Values of  $0.5$  and  $0.2$  were estimated for the order of the reaction at the Ni and Ru deposits, respectively. The value obtained at Ni in this case is comparable to that obtained at the C/Ni modified electrode. On the other hand, the value obtained at Ru is relatively smaller than that obtained at Ni which leads to the conclusion that the oxidation of the intermediate products rather than methanol takes place on.

Extending the upper-potential limit beyond  $+1600 \text{ mV}$  was found to affect both the height and the potential values of the two anodic peaks of methanol oxidation (Fig. 6).

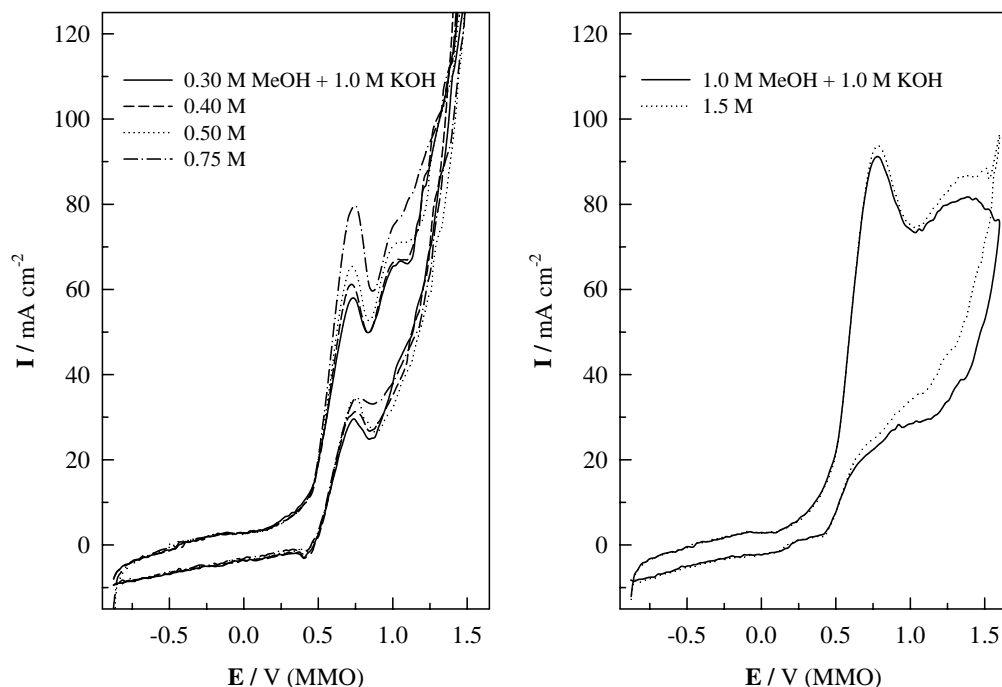


Fig. 4. Cyclic voltammograms of methanol oxidation at C/(Ni-Ru) electrode in various methanol concentrations. Potential was scanned at  $10 \text{ mV s}^{-1}$  from  $-900$  to  $+1600 \text{ mV}$ . (Ni and Ru were simultaneously deposited from their salt solutions of molar ratio 8:1).

The experimental procedure followed up throughout this study compels the modified electrode to spend much more time in the oxygen evolution region as extending the higher-potential limit to higher values. In the oxygen gas evolution region, a complete oxidation of methanol and in-

termediate products could possibly take place in addition to the stabilization of the mixed nickel oxyhydroxide and per-ruthenate species. This could enhance the rate of methanol oxidation at C/(Ni-Ru) electrode in the subsequent cycles. The complete oxidation of methanol and intermediate

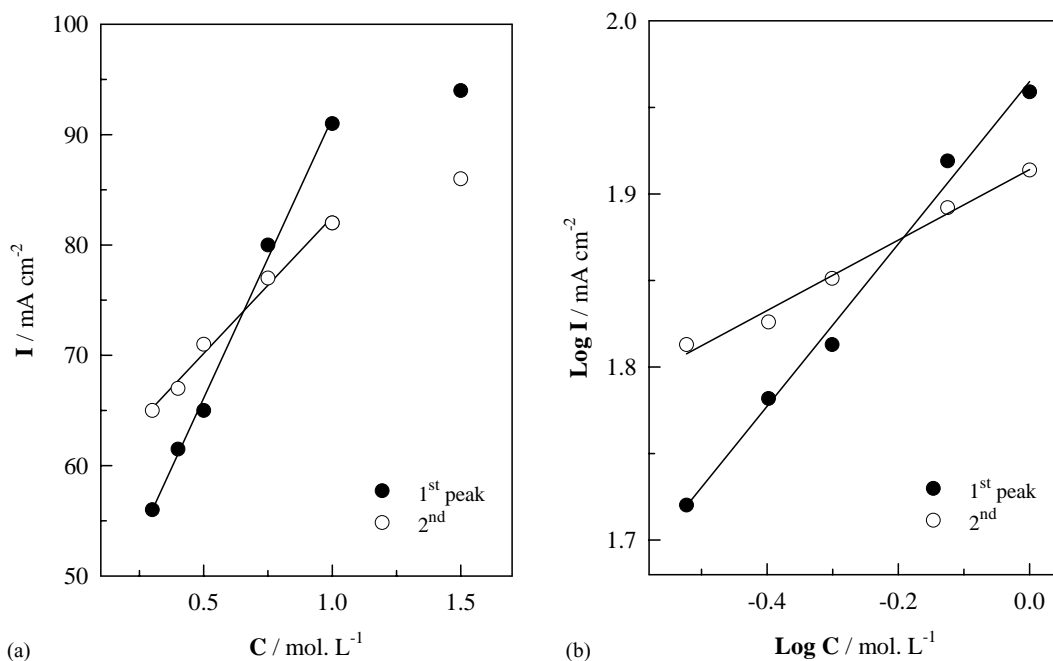


Fig. 5. (a) Variation of the first and the second peak current density of methanol oxidation at C/(Ni-Ru) electrode with its concentration. (b) Variation of the logarithm of methanol oxidation peak current density at the C/(Ni-Ru) electrode with the logarithm of methanol bulk concentration. (Ni and Ru were simultaneously deposited from their salt solutions of molar ratio 8:1).

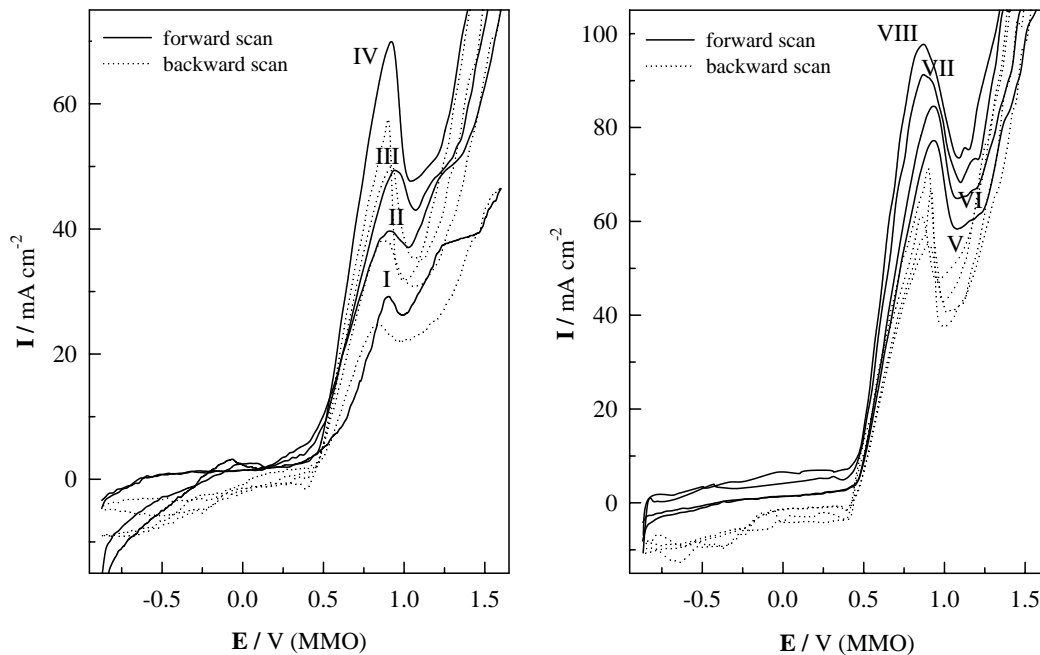


Fig. 6. Effect of increasing the upper-potential limit on the cyclic voltammograms of methanol oxidation at C/(Ni–Ru) electrode at a scan rate of  $10 \text{ mV s}^{-1}$ . Potential scanning was started from  $-900 \text{ mV}$  to: I,  $+1600$ ; II,  $+1800$ ; III,  $+2000$ ; IV,  $+2200$ ; V,  $+2400$ ; VI,  $+2600$ ; VII,  $+2800$ ; and VIII,  $+3000 \text{ mV}$  (Ni and Ru were simultaneously deposited from their salt solutions of molar ratio 8:1).

products tends to reduce the poisoning effect at the electrode surface. However, the mixed oxides stabilization reduces the overvoltage, hence it is expected to get oxidation peaks at less positive potential values as the higher-potential limit moves inside the oxygen gas evolution region. Furthermore,

reaching higher-potential limits enables the oxidation peak height to increase leading to the merge of the second oxidation peak with the oxygen evolution. On the other hand, Fig. 7 represents the effect of extending the lower-potential limit towards more positive values. In this figure, as start-

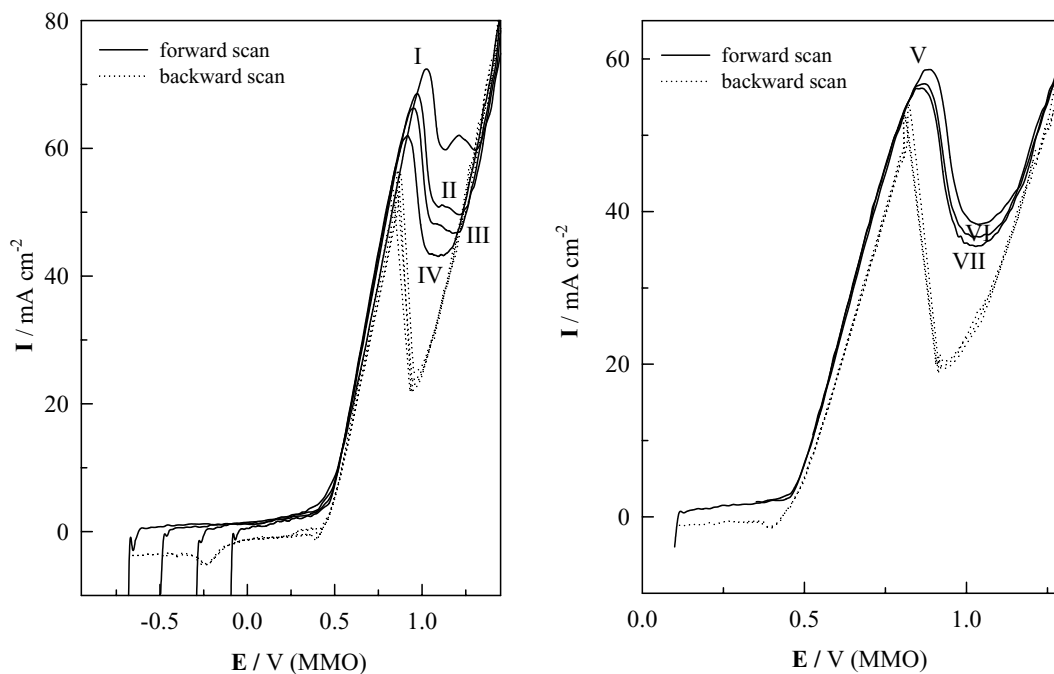


Fig. 7. Effect of extending the lower-potential limit towards more positive values on the cyclic voltammograms of methanol oxidation at C/(Ni–Ru) electrode at a scan rate of  $10 \text{ mV s}^{-1}$ . Potential scanning was started from: I,  $-700$ ; II,  $-500$ ; III,  $-300$ ; IV,  $-100$ ; V,  $+100$ ; VI,  $+300$ ; and VII,  $+500$  to  $+1600 \text{ mV}$ . (Ni and Ru were simultaneously deposited from their salt solutions of molar ratio 8:1).

ing the polarization from more positive potential values than  $-900$  mV, the following observations are recorded:

- a decrease in the height of the first oxidation peak;
- a decrease in the height of the second oxidation peak until a starting potential value of  $-300$  mV above which it completely disappears;
- the potential of the two oxidation peaks are shifted towards lower values.

It is believed that, maintaining the electrode potential for a long time at the region of oxide formation tends to increase the produced amount of such oxide. As a result, it is expected to have higher amounts of oxide as the starting potential commences at more negative values. For this reason, the methanol oxidation peak height decreases with moving the starting potential towards less negative values. However, if the starting potential value was  $-100$  mV and more positive, the second methanol oxidation peak disappears (see Fig. 7). This means that ruthenium oxides did not form on the modified electrode. Referring to Fig. 1, it is noted that ruthenium began to be oxidized at a potential value of  $-200$  mV with the formation of  $\text{Ru}_2\text{O}_3$ . Therefore, with a value of  $-100$  mV and higher as a starting potential, the presence of only nickel oxides will affect the methanol oxidation at the modified electrode. On the other hand, various amounts of oxides will also affect the peak potential, where the higher amount of oxides will increase the oxidation peak height and in turns generates IR drop at higher current values leading, finally, to a positive potential shift.

The effect of the amount of nickel and ruthenium electrodeposited simultaneously was studied by varying the time of deposition and also by changing the relative concentration of their salts in the deposition bath. In this study, the potentiostatic technique was employed for metals deposition at various time intervals. Different modified electrodes of various Ni–Ru ratios were prepared from solutions of molar ratios 1:1, 8:1, and 16:1, respectively. The efficiency of the deposition process of both Ni and Ru was estimated by comparing the weight of deposited material calculated using the amount of charge consumed in the deposition process and that calculated using complexometric and spectroscopic methods [37]. From these measurements the average

efficiency for the potentiostatic deposition of nickel and ruthenium were found to be 62.1 and 56.7%, respectively. The estimation method depends on dissolving the deposited Ni–Ru in 1.0 M  $\text{H}_2\text{SO}_4$  followed by determining the concentration of dissolved Ni through titration with standard EDTA solution and then the weight of deposited Ni. On the other hand, the concentration of dissolved Ru was estimated using a calorimetric technique, due to the ability of Ru ions to form soluble blue coloured complex when treating their solutions with 1.0 M thiourea in hot alcoholic 1.0 M HCl. Using these chemical analyses, one can estimate the exact Ni–Ru ratios deposited on the modified electrode surface in each case after dissolution. Data of the experimental weights of the deposited nickel and ruthenium as well as their corresponding deposited weight ratios were tabulated in Table 1. From this table, it is shown that the weight ratios of Ni and Ru deposited from their solutions molar ratios 1:1, 8:1, and 16:1 are, respectively, about 1:1, 1.9:1, and 2.4:1.

Fig. 8 represents the dependence of the oxidation peak heights on the deposition time for modified electrodes prepared at nickel to ruthenium weight ratios of 1:1 and 1.9:1. It is noted from this figure that the height of both the first and the second oxidation peaks increases with increasing the deposition time up to 60 min with respect to the first peak and up to 40 min with respect to the second, after which a slight decrease in the peak height is observed. Increasing the deposition time leads to an increase in the amount of nickel and ruthenium deposits. This leads consequently to an increase in the number of the active sites that enhance the electro-catalytic activity and an increase in the oxidation rate of methanol is expected. At higher-deposition times, the presence of relatively thick layers of the nickel and the ruthenium oxides can act as a barrier for methanol oxidation and thus low catalytic activity was observed. For the C/(Ni–Ru) electrode prepared in the Ni–Ru weight ratio of 1.9:1, it is noted that increasing the nickel content leads to an increase in the height of the second oxidation peak. This confirms the above proposed mechanism that Ru oxides enhance the complete oxidation of intermediate products produced as a result of methanol oxidation at Ni oxide. The presence of Ni in the modified electrode facilitates the job of Ru oxide as an electro-catalyst. In other words, if the ox-

Table 1

Values of the weight of nickel and ruthenium, deposited on the graphite electrode, experimentally measured using chemical analyses as well as the deposited weight ratios

Molar ratios of Ni–Ru in the deposition bath	Time of deposition (min)	Experimental weight ( $\mu\text{g}$ )		Deposited weight ratios
		Ni	Ru	
1:1	30	26.10	28.88	0.90:1
	60	43.50	49.09	0.89:1
8:1	30	60.90	31.76	1.92:1
	60	126.16	66.42	1.90:1
16:1	30	104.40	43.32	2.41:1
	60	210.84	86.63	2.43:1

Ni and Ru were simultaneously deposited from their salt solutions in acidic medium using the potentiostatic technique at  $-1000$  mV (MMS).

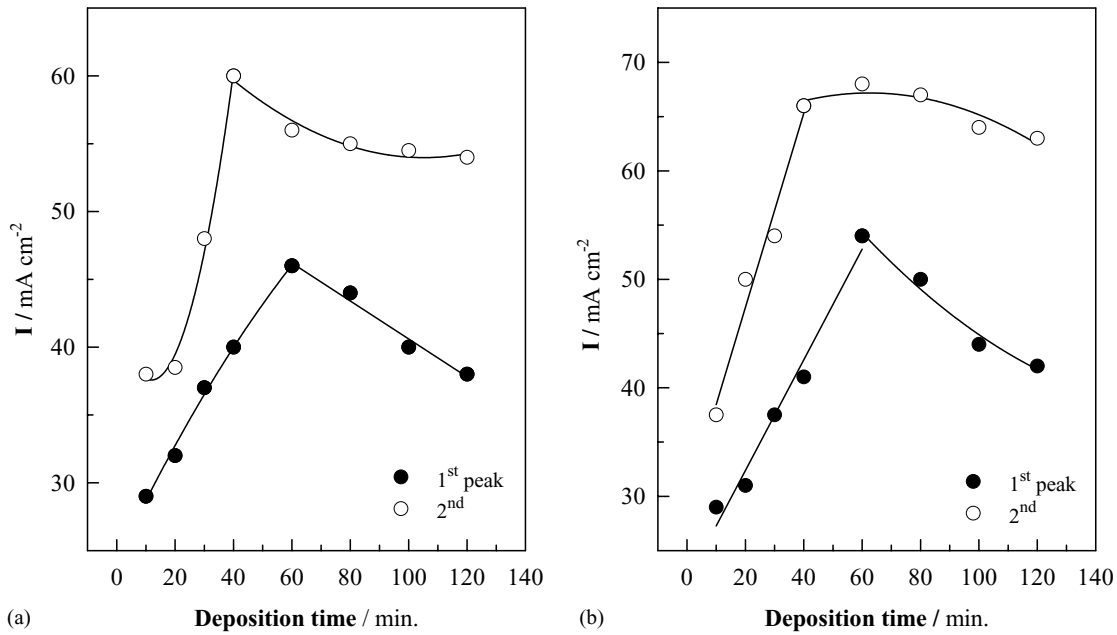


Fig. 8. Variation of the current density of the two anodic peaks of methanol oxidation with the deposition time at C/(Ni-Ru) electrodes prepared potentiostatically at  $-1000\text{ mV}$  in the weight ratio of 1:1 (a) and 1.9:1 (b).

oxidation of methanol takes place at Ru oxide in several steps, the presence of Ni oxide could possibly reduce these steps, thus facilitating the oxidation process. A further increase in the ratio of nickel deposits in the modified electrode (Ni:Ru in the weight ratio of about 2.4:1, respectively) leads to approaching the behaviour of nickel alone.

Increasing the ruthenium content in the deposition bath was found to affect the oxidation process. The results are rep-

resented in Fig. 9 which showed that the presence of higher amount of ruthenium lowers the oxidation current density of methanol. This could prove that the presence of nickel in a higher content than ruthenium enhances the electro-catalytic activity of ruthenium (see Fig. 10). Increasing the ruthenium content, starting from low-deposition time, increases the number of active sites on the catalyst surface and hence the catalytic activity of the oxidation process would increase

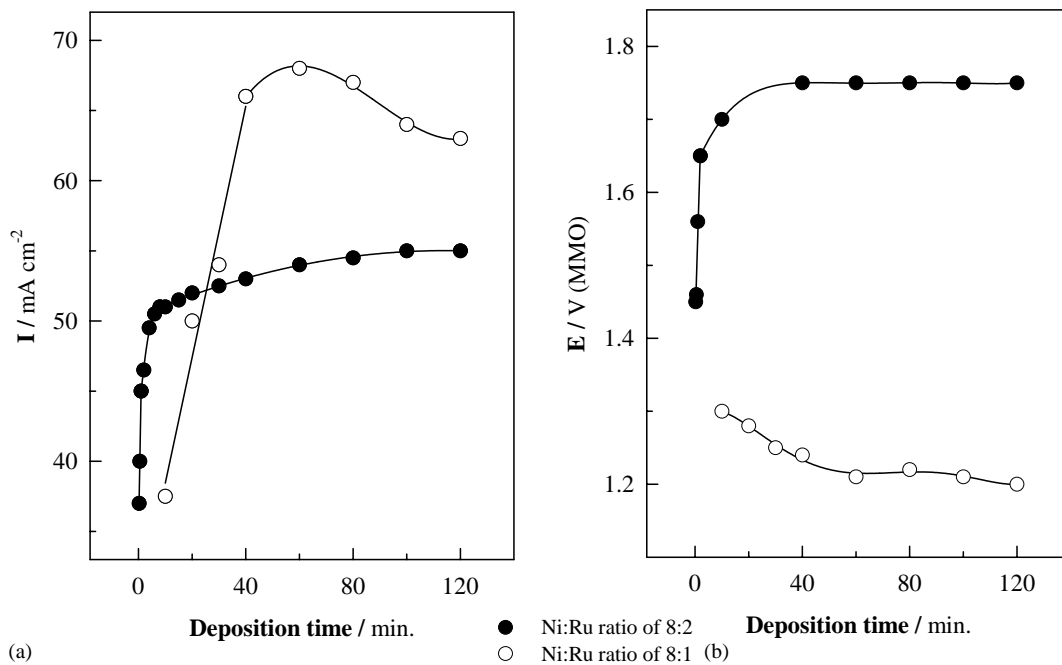


Fig. 9. Variation of the peak current density (a) and the peak potential (b) of methanol oxidation at C/(Ni-Ru) electrode prepared potentiostatically at  $-1000\text{ mV}$  from salt solutions in the molar ratios of 8:1 and 8:2 with deposition time.



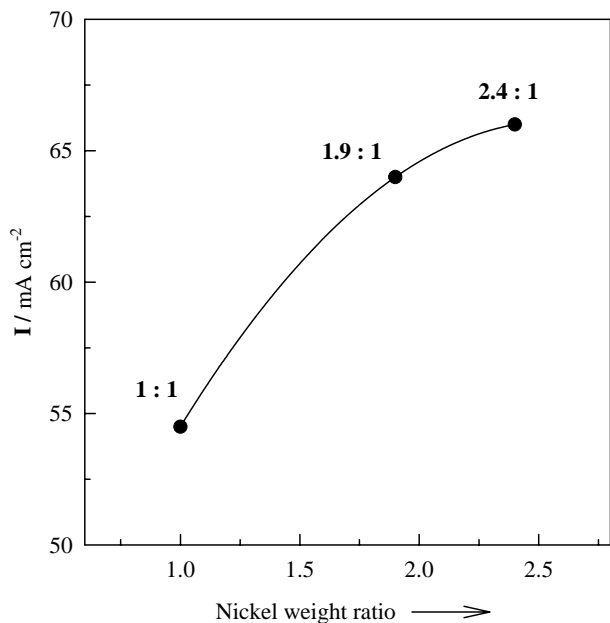


Fig. 10. Effect of increasing the Ni weight ratio in the catalyst on the current density of the second methanol oxidation peak at C/(Ni–Ru) electrodes.

[38]. Continuing the deposition process, higher amounts of  $\text{RuO}_2$  produced and tend to saturate the electrode surface approaching the behaviour of pure  $\text{RuO}_2$  [32,39].

In the above work, simultaneous electro-deposition of nickel and ruthenium was chosen as the deposition technique. Therefore, it is interesting to investigate the action of the deposition of various ruthenium amounts over a constant amount of nickel, and vice versa, on the methanol oxidation

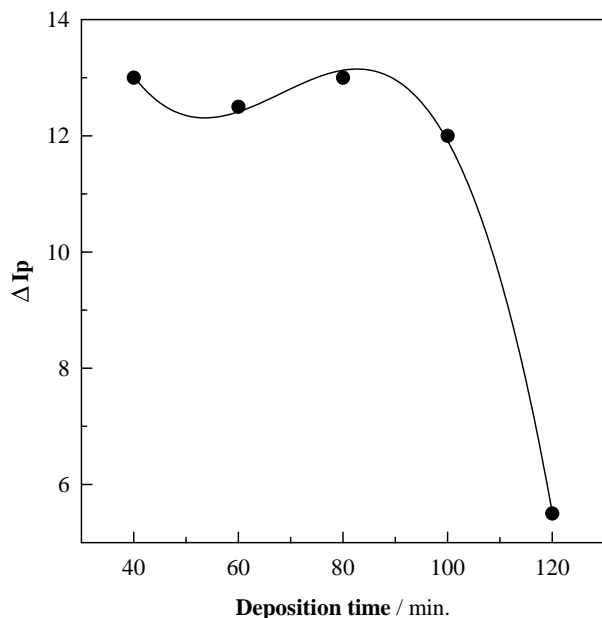


Fig. 11. Variation of the difference between the height of the first and the second methanol oxidation peak with the deposition time of Ru over a constant Ni content.

reaction. The first study involves the effect of varying the deposited amount of ruthenium, on constant nickel content, on the oxidation of 0.5 M methanol in 1.0 M KOH solution. At first, the C/Ni electrode was prepared by the potentiostatic deposition of nickel on the graphite electrode at  $-1000$  mV (MMS) for 2 min from a solution composed of 1.0 M  $\text{NiSO}_4$  in 1.0 M  $\text{H}_2\text{SO}_4$ . Then, the resulting electrode was removed from the deposition bath, washed with distilled water, and then introduced into another electrolytic cell containing the ruthenium salt. Ruthenium was thus deposited by the potentiostatic technique at  $-200$  mV (MMS) from a solution composed of 0.001 M  $\text{RuCl}_3$  in 1.0 M  $\text{H}_2\text{SO}_4$  for various deposition times. The results revealed that as the deposition time of ruthenium increases, the height of both anodic oxidation peaks decreases. Fig. 11 shows that, by increasing the deposition time of ruthenium the difference between the height of the first and the second oxidation peaks decreases indicating a deposition of Ru over parts of the surface cov-

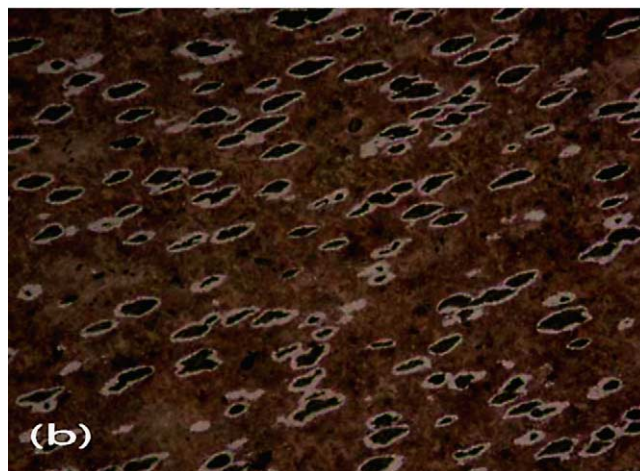
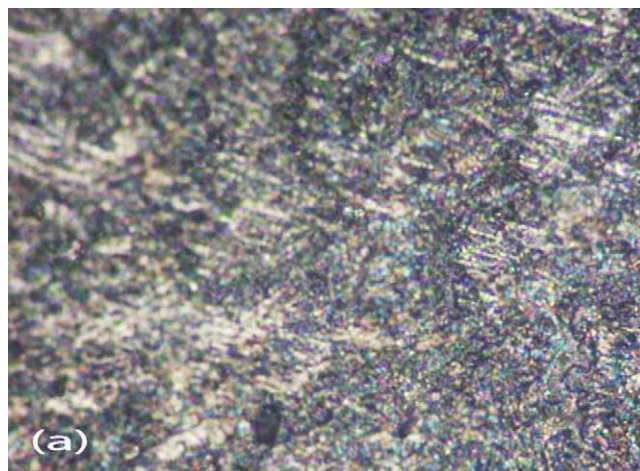


Fig. 12. (a) Optical microscope photograph recorded for the C/(Ni–Ru) electrode after simultaneous deposition of Ni and Ru on graphite electrode. (b) Optical microscope photograph recorded for the C/(Ni–Ru) electrode after deposition of Ru over Ni deposited on graphite electrode. (Deposition of both Ni and Ru was carried out electrochemically.)

ered with nickel. At the relatively low ruthenium deposition time, both nickel and ruthenium exist on the electrode surface at which Ru will cover parts of the surface covered by Ni. As a result, the height of the first oxidation peak decreases. With increasing the deposition time of ruthenium, the relative amount of nickel to ruthenium will decrease and thus a regular decrease in the first oxidation peak height was observed. The decrease in the current density of the second oxidation peak with ruthenium deposition time may be attributed to the formation of thick hydrous oxide layers [35], which are susceptible to dissolution, or they rearrange readily, with expulsion of water, to yield a more stable and compact surface layer [36]. The second study involved the effect of varying the nickel content over constant ruthenium deposit on the graphite electrode. The results showed that this method of deposition leads to the formation of a surface layer of nickel parting the action of ruthenium away from the reaction surface zone.

The above results revealed that the simultaneous deposition of nickel and ruthenium is the best method to prepare the modified C/(Ni–Ru) electrode. Photographs recorded for some C/(Ni/Ru) electrodes using an optical microscope showed that the method of nickel and ruthenium deposition on the graphite surface, either simultaneous deposition or not, affect their relative distribution (see Fig. 12). Relative distribution of nickel and ruthenium on the catalyst surface seems to be an important feature in determining the catalytic activity of such electro-catalysts.

#### 4. Conclusion

Electrochemical measurements revealed that binary Ni–Ru deposits dispersed on graphite electrode are good electro-catalysts for methanol oxidation in KOH solution. The method of electro-deposition as well as the Ni–Ru ratios was found to affect the catalytic activity. Increasing the amount of Ni relative to that of Ru increases the catalytic activity of the catalyst. On the other hand, extending the upper or the lower-potential limit was found to affect the rate of methanol oxidation. Values of 0.5 and 0.2 were deduced for the reaction order with respect to methanol bulk concentration on Ni and Ru, respectively. From these values, it is concluded that the oxidation of methanol takes place on Ni, however, the oxidation of the intermediate products rather than methanol takes place on Ru.

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