**Effect of 30% copper alloying on electro-catalytic activity of nickel for ethanol oxidation in alkaline media**

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**Abstract**

In this research, nickel-copper (70/30) alloy was investigated for its possible redox process and electro-catalytic activity towards oxidation of ethanol, in alkaline solutions. For this purpose, cyclic voltammetery, chronoamperometry and impedance spectroscopy were employed. According to the cyclic voltammetery studies, NiCu alloy can demonstrate a significantly higher response for ethanol oxidation, compared to pure nickel. So that, enhancement of the anodic peak current corresponding to oxidation of nickel hydroxide was accompanied with attenuated cathodic current, in the presence of ethanol. The anodic peak currents depended on square root of scan rates, linearly, which is characteristic of diffusion controlled processes. Based on the chronoamperometry measurements, the reaction exhibited a Cottrellian behavior and the coefficient of ethanol diffusion was found to be 1.26×10-5 cm2 s-1. Further, impedance spectroscopy declared electro-catalytic behavior of NiCu electrode for oxidation of ethanol and showed that charge transfer resistance will decrease if ethanol concentration be increased.

**Keywords:** Electro-catalytic Activity; Nickel-copper Alloy; Ethanol; Impedance.

**1. Introduction**

Recently, direct ethanol fuel cells (DEFCs) have attracted much interest for different applications.1,2 The reason is that they can provide convenient operation, storage and distribution. However, DEFCs require further development compared to hydrogen based fuel cells3, as one of the unresolved problems of DEFCs is slow anodic rate of ethanol oxidation.4 In this respect, considerable researches have been devoted to studying ethanol electro-oxidation at high pH values. Utilizing alkaline solutions has many advantages, in fuel cells. For example, alkalinity can enhance fuel cell efficiency, reduce corrosion, enable application of many electrode materials, promote efficiency of the processes taking place at both the anode and cathode, eliminate sensitivity to the surface structure and decrease poisoning effects.5-8

In electrochemical oxidation of ethanol, selection of an appropriate material for the anode is very crucial if high efficiency of the electro-catalyst is concerned. Some studies have reported significant increase of fuel utilization and power density through optimizing different factors related to fuel cells.9,10 For the electrode, different materials have been employed to catalyze electrochemical oxidation of ethanol.11,12 One of the well-established electrode materials is nickel, which poses proper surface oxidation properties. Nickel and nickel complexes have been commonly applied to electro-catalysis to proceed both anodic and cathodic reactions in water electrolysis and organic synthesis.13-17 One of the remarkable applications of nickel is catalysis of ethanol oxidation. Several studies regarding electro-oxidation of alcohols by Ni have been reported, e.g. Refs. 18-20.

To benefit from properties of the other metals in electrodes, along with Ni, and anticipate a synergistic electro-catalytic system, nickel alloys specifically nickel copper can be employed.21-23 In addition, alloy electrodes can offer further advantages, such as long-term stability and ease of preparation, compared with other electro-catalyst electrodes. The positive point about nickel-copper alloys is that the crystal structures of pure Ni and Cu metals are similar, i.e. they possess face-centered cubic structures with similar lattice parameters. Therefore, it is possible to make a wide range of NiCu alloy compositions.24-27

The present work aims to study electrochemical oxidation of ethanol on NiCu alloy (70/30) electrode in an alkaline solution of 1 M NaOH and compare its catalytic activity with pure Ni electrode. With this purpose, electrochemical methods of cyclic voltammetery, chronoamperometry and impedance spectroscopy were used.

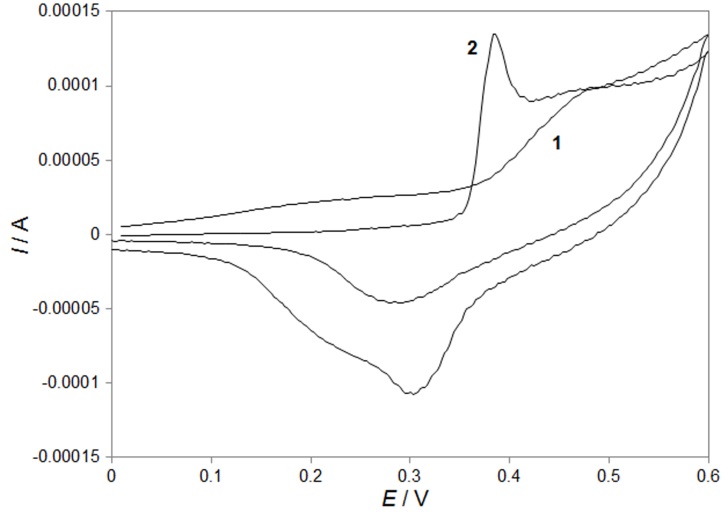
**2. Experimental**

Analytical grade sodium hydroxide and ethanol were purchased from Merck and used without further purification. Double distilled water was employed to prepare the solutions. The electrochemical measurements were conducted in a three-electrode cell, which was powered by a Metrohm-Autolab potentiostat/ galvanostat (model 302N). A 1 cm2 area disk of NiCu alloy (70/30) was used as the working electrode. Before each measurement, the bare electrode was polished with 1000 grit emery paper and rinsed in double distilled water and acetone. The counter and reference electrodes were made of platinum and KCl-saturated Ag/AgCl (Metrohm), respectively. All the electrochemical studies were completed at 22 ± 1 °C.

The electrochemical impedance spectroscopy experiments were carried out in the frequency range of 100 kHz to 0.01 Hz, at AC open circuit potential of 10 mV amplitude. The experimental impedance spectroscopy data were fitted to the proposed equivalent circuit using a home written least square software. This software was programmed according to the method of Marquardt for optimization of functions and Macdonald weighting for the real and imaginary parts of the experimental impedance data.28,29

**3. Results and discussion**

Figure 1 displays consecutive cyclic voltammograms of the NiCu electrode in 1 M NaOH solution recorded at 100 mV s-1 potential scan rate, after 50 cycles. All following peak positions are reported with respect to Ag/AgCl reference electrode. Upon the first scan, a pair of redox peaks was observed at 463 and 295 mV, which are attributed to the Ni2+/Ni3+ redox couple. In the subsequent cycles, the peaks shift to negative direction and stabilize at 378 and 310 mV, respectively. The observed behavior is consistent with the data reported in previous electrochemical studies related to formation and inter-conversion of α-Ni(OH)2 and ß-phases, conversion of Ni(OH)2 to NiOOH and enrichment of Ni3+ species around the surface of the electrode.30,31 During the next cycles, negative shift of the anodic peaks and their stabilization are evident, which refer to higher potential energies required for NiOOH nucleation, in the first cycle. Increased base line current, compared to the first cycle, corresponds to oxidation of Ni to Ni2+. Intensification of the current with the number of potential scan runs demonstrates continuous enrichment of Ni2+ and Ni3+ electroactive species that are accessible by the electrode’s surface.

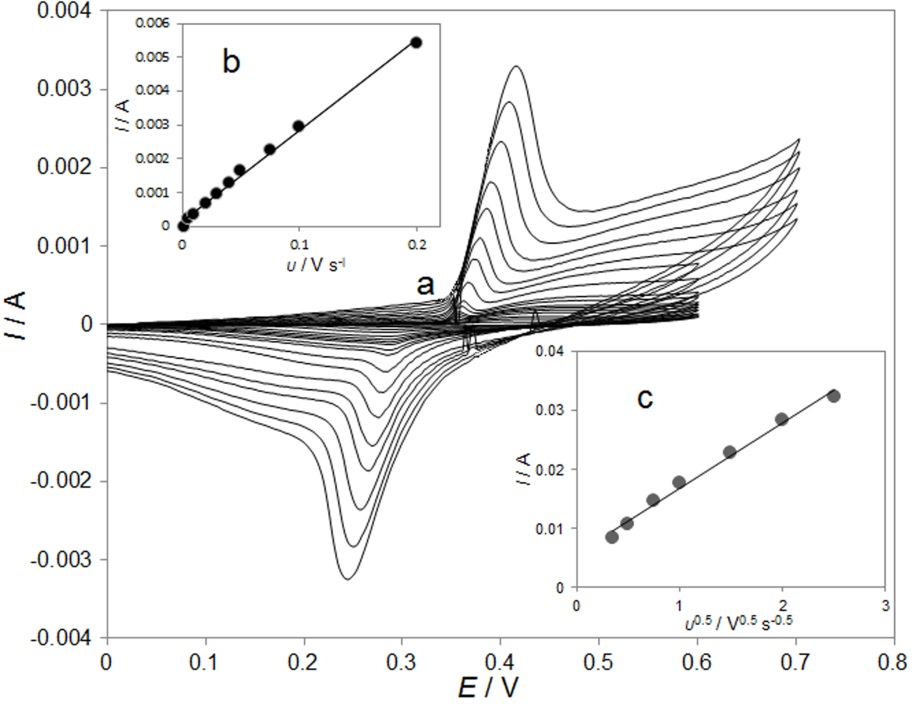


**Figure 1.** Consecutive cyclic voltammogram of NiCu electrode oxidation in 1 M NaOH composed of (1) first and (2) fiftieth cycle at a scan rate of 100 mV s-1. The potential is against the Ag/AgCl reference electrode.

Figure 2a illustrates typical CVs of a NiCu electrode at various scan rates from 2 mV s-1 to 2500 mV s-1, in 1 M NaOH solution. Figure 2b exhibits dependency of the anodic peak currents to lower voltammetry scan rates. Based on this figure, the peak currents increase proportional to the scan rate values (2–200 mV s-1). Such behavior should be expected for electrochemical activity of surface redox couples that their voltammetric responses are sensitive to small concentrations of surface-confined electroactive species.32 Surface coverage of the redox species, , can be calculated according to the slope of the lines shown in Figure 2b:33

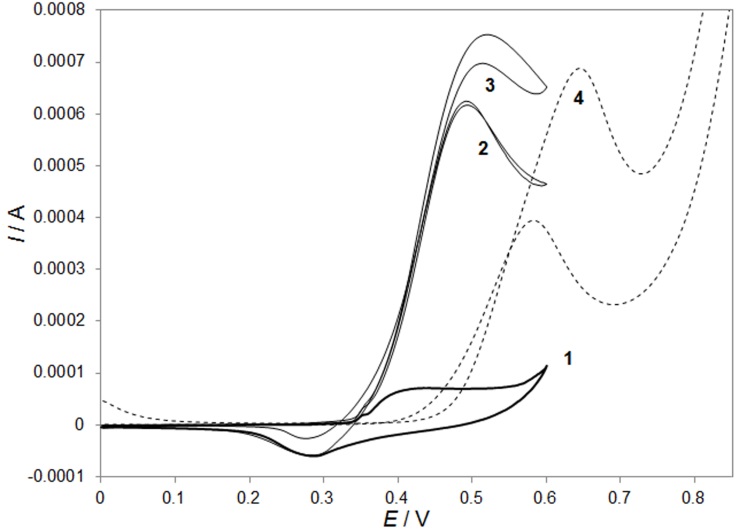
 (1)

Here,  is the potential scan rate. The  value is averaged over both cathodic and anodic results and is calculated to be about 8.15×10-8 mol cm-2, which is associated with the presence of ca. 80 monolayers of surface species for the alloy. Figure 2c presents proportionality of peak currents at the anode to square root values of higher scan rates (350 to 2500 mV s-1). It outlines dominance of a diffusion controlled process in higher scan rate, at the anode.



**Figure 2.** (a) Typical cyclic voltammograms of a NiCu electrode in 1 M NaOH in different scan rates of 2–2500 mV s-1. (b) the dependency of anodic peak currents to the scan rate at lower values (2–200 mV s-1). (c) The proportionality of anodic peak currents to the square roots of scan rate at higher values (350–2500 mV s-1).

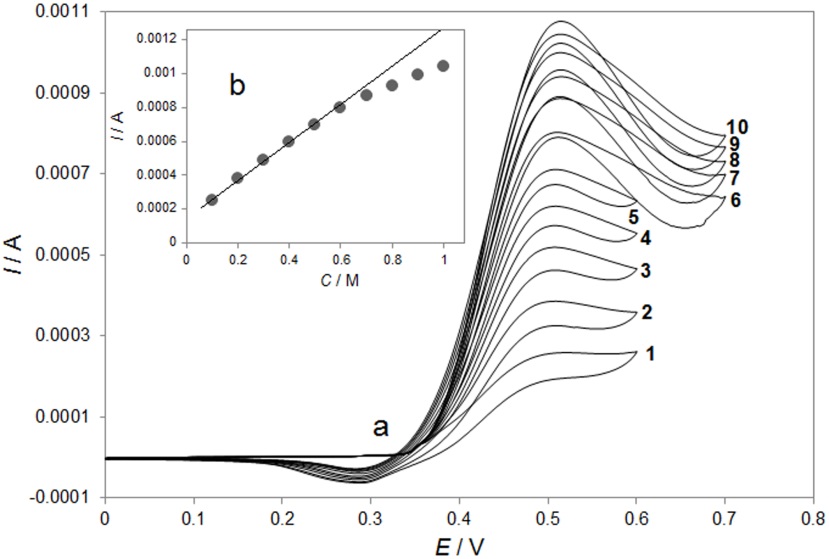
Figure 3 depicts cyclic voltammograms of pure Ni and NiCu electrodes at a scan rate of 10 mV s-1, in a solution of 1 M NaOH and 0.5 M ethanol. As observed, the NiCu electrode provides a higher current density for ethanol electro-oxidation, in NaOH solution. The reason can be related to higher atomic radius of Cu compared with Ni, which can enhance ethanol adsorption. Furthermore, electro-catalytic activity of Cu for ethanol oxidation is high, but at higher anodic overpotentials. As it can be seen, the measured oxidation potentials for application of NiCu and Ni electrodes are the same. Consequently, Cu’s high electro-catalytic activity is responsible for electro-catalytic activity of NiCu electrode, which does not increase the over-potential.



**Figure 3.** Cyclic voltammograms (1) in the absence and (2) the presence of 0.5 M of ethanol on Ni, (3) NiCu (4) Cu electrode in 1 M NaOH solution. Scan rate: 10 mV s-1.

Figure 4 exhibits the cyclic voltammograms of NiCu electrode at a scan rate of 10 mV s-1, in a solution of 1 M NaOH and various concentrations of ethanol. It is declared that the oxidation of ethanol on NiCu alloy electrode is a typical electro-catalytic response. The anodic current increases around 350 mV and ethanol oxidation starts parallel to oxidation Ni2+ to Ni3+. The anodic to cathodic charge ratio in the presence of 0.5 M ethanol is obtained to be 92/8 while it equal to 55/45 in the absence of ethanol. The charge values are calculated through integrating the background corrected anodic and cathodic peaks.

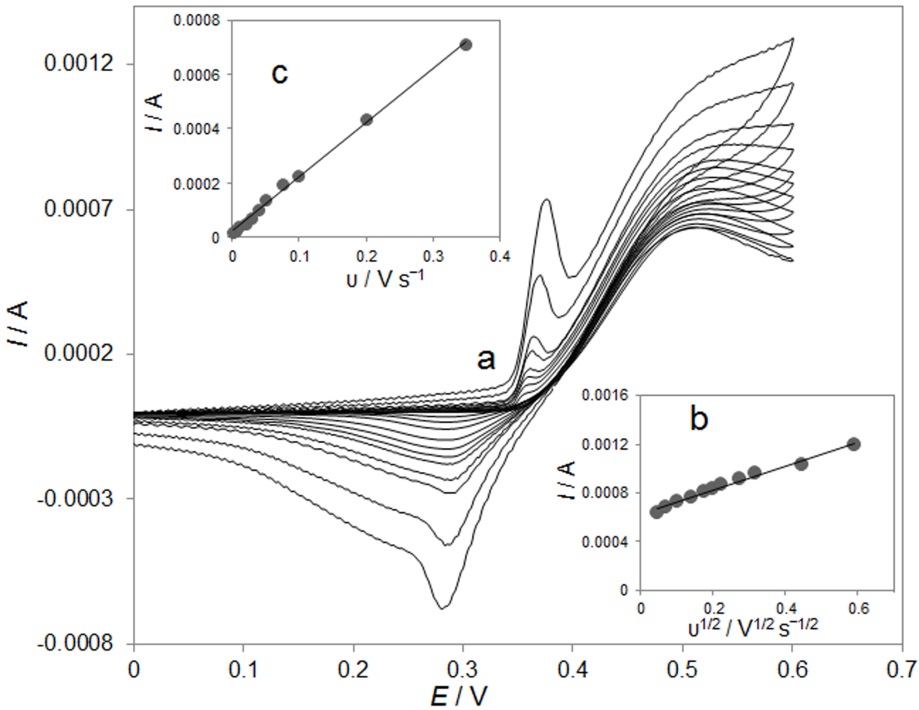
In the positive sweep, the measured anodic current is proportional to the bulk concentration of ethanol. Elevation of ethanol concentration caused an almost proportional linear promotion of the anodic current up to 0.6 M (Figure 4b). Based on these evidences, catalytic electro-oxidation of ethanol on NiCu electrode is confirmed.



**Figure 4.** (a) Cyclic voltammograms of the NiCu electrode in 1 M NaOH solution in the presence of (1) 0.1, (2) 0.2, (3) 0.3, (4) 0.4, (5) 0.5, (6) 0.6, (7) 0.7, (8) 0.8, (9) 0.9 and (10) 1 M of ethanol. Scan rate: 10 mV s-1. (b) Dependency of the anodic peak current on the concentration of ethanol.

The attenuated cathodic current, that occurs in the reverse cycle of the oxidation process, verifies involvement of ethanol in the rate determining step. It also indicates that the process is incapable of reducing all high valence nickel species that have formed in the oxidation cycle. Parallel to oxidation of the Ni2+ species to Ni3+, the adsorbed ethanol molecules oxidize on the surface, at higher overpotentials. The products or intermediates of the reaction poison electrode surface and reduces the number of available sites for ethanol adsorption. Consequently, the overall rate of ethanol oxidation would decrease and moreover, the anodic current approaches a maximum when the potential is swept, anodically. Electro-catalytic oxidation of ethanol also proceeds to the initial stage of the cathodic half cycle. During the reverse half cycle, the oxidation process continues and its associated current tends to a maximum since some active sites for adsorption of ethanol regenerate due to removal of the adsorbed intermediates and products. According to the signified anodic current, when the sweeping cycle reaches unfavorable cathodic overpotentials, ethanol oxidation declines, in the cathodic half cycle.

Cyclic voltammograms of NiCu electrode corresponding to various potential scan rates (from 2 mV s-1 to 350 mV s-1) in the presence of 0.5 M ethanol and scan rate proportionality of the anodic peak currents are presented in Figured 5a to 5c, respectively. The principal anodic peak appears at 0.5 V is a result of ethanol oxidation on the Ni sites. The anodic peak currents vs. the square root of scan rate values provide a linear relationship, what remarks that overall oxidation of ethanol on NiCu electrode is controlled by diffusion of ethanol from the solution to the redox sites accessible on the electrode’s surface (Figure 5b). Though, the cathodic peak of Ni3+ reduction is negligible at low scan rates, it appears during application of increased scan rates. This observation implies that electro-oxidation of nickel species is much faster than catalytic oxidation of ethanol, at higher potential scan rates. Therefore, oxidation of ethanol on nickel surface can be inspected as a slow process.



**Figure 5.** (a) Typical cyclic voltammograms of the NiCu in 1 M NaOH in the presence of 0.5 M ethanol at various scan rates of 2, 5, 10, 20, 30, 40, 50, 75, 100, 200 and 350 mV s-1. (b) Dependence of anodic peak current at 530 mV on the square roots of scan rate. (c) Dependence of anodic peak current at 370 mV on scan rate.

At higher scan rates, the peak specific to oxidation of Ni(OH)2 to NiOOH rises at potentials that are considerably more negative than the potential of ethanol oxidation (370 mV). This peak is insignificant at low scan rates but enhances at higher scan rate values. Figure 5c illustrates a linear dependency for the current relating to this peak on the sweeping scan rate, which proposes presence of surface-confined electroactive species. With respect to the high current density observed in presence of ethanol and also appearance of two oxidation peaks for Ni2+ and ethanol, one part of the anodic current can be attributed to the oxidation of ethanol by NiOOH since the NiOOH reduction peak disappears during the negative sweep. The other part can be assigned to direct electro-oxidation of ethanol on the surface of the oxide layer.

The following redox transition of the nickel species is expected:

 (2)

while ethanol oxidizes on the alloy electrode through the following reaction:

 (3)

 (4)

The Ni sites can be regenerated by the power source or via direct electro-oxidation on Ni oxide surface:

 (5)

 (6)

In Eqs. (5) and (6), Ni provides an active site for direct ethanol oxidation. Eqs. (2), (5) and (6) refer to the two anodic peaks of Ni2+ and ethanol oxidation.

Figure 6a displays the choronoamperograms recorded for NiCu in 0.0 M to 0.8 M ethanol upon application of 500 mV potential step. Figure 6b identifies a linear behavior for net current changes, i.e. after removal of the background current, vs. inverse square root of time. Evidently, a diffusion controlled process is dominant in this electrochemical process. If the slope of this line be implemented in Cottrell equation33 (Eq. (7)),

 (7)

then diffusion coefficient of ethanol will be 1.26×10-5 cm2 s-1.

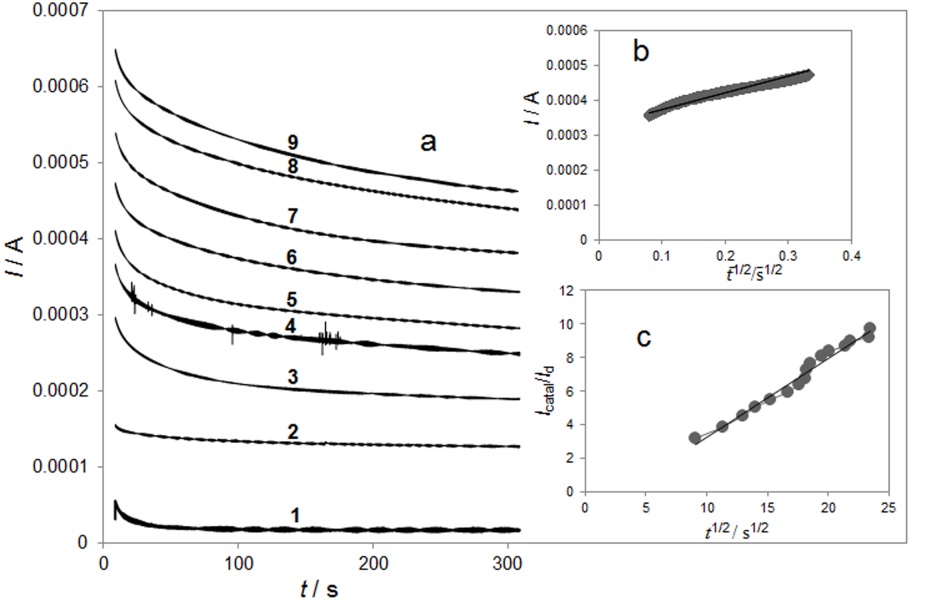
Further, the choronoamperometry results can help evaluating the corresponding catalytic rate constant of ethanol oxidation on NiCu alloy according to Eq. (8), which is introduced by Pariente et al:34

 (8)

where *I*cat and *I*L stand for NiCu electrode currents in the presence and absence of ethanol, respectively.  is the related error function, in which *k* is the catalytic rate constant, *C* is concentration of bulk ethanol and *t* is the elapsed time. When ,  equals to unity, approximately, and Eq. (8) simplifies to:

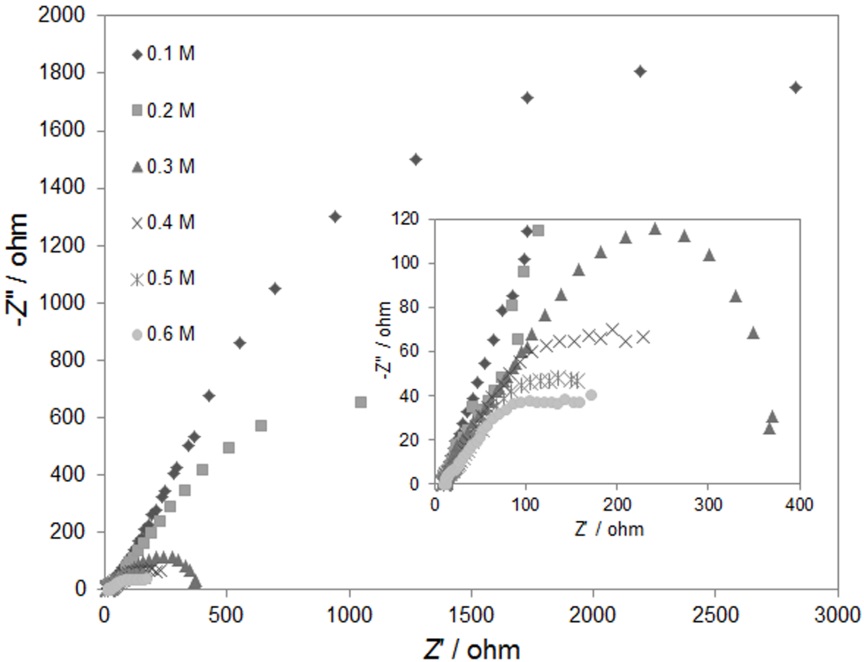
 (9)

Based on the slope of *I*cat/*I*L vs. *t*1/2 plot, the obtained mean catalytic rate constantis 865.5 cm3 mol-1 s-1 for 0.1 M to 0.8 M ethanol (Figure 6c).



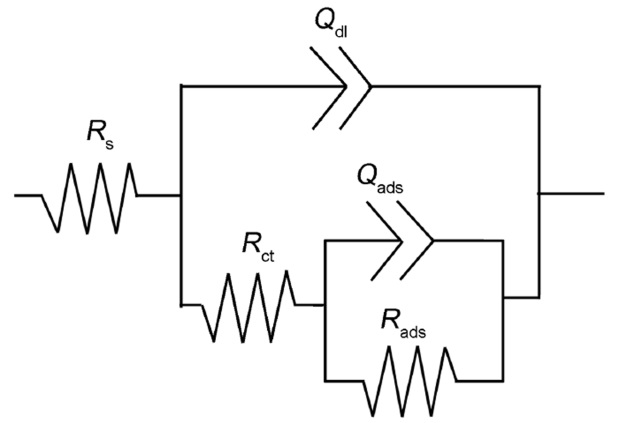
**Figure 6.** (a) Chronoamperograms of NiCu electrode in 1 M NaOH solution with different concentrations of ethanol: (1) blank, (2) 0.1, (3) 0.2, (4) 0.3, (5) 0.4, (6) 0.5, (7) 0.6, (8) 0.7 and (9) 0.8 M at potential step of 500 mV. (b) Dependency of transient current on *t-*1/2. (c) Dependence of *I*catal/*I*L on *t*1/2 derived from the data of chronoamperograms.

Nyquist diagrams of NiCu electrode recorded at the oxidation peak potential as the dc-offset for different ethanol concentrations are presented in Figure 7. These diagrams contain two slightly depressed capacitive semicircles that are overlapped, in the high and low frequency regions of the spectrum for all ethanol concentrations. The high frequency depressed semicircle can correspond to a combination of resistance against charge transfer and capacitance of the double layer whereas the low frequency semicircle can be an outcome of reaction intermediate adsorption on the surface of CuNi electrode.35,36



**Figure 7.** Nyquist diagrams of nickel-copper electrode in different concentration of ethanol at applied anodic potential of 500 mV. (Inset: high frequency part of the Nyquist diagram.)

Figure 8 shows the equivalent circuit in the presence of ethanol, which is compatible with Nyquist diagram. In order to achieve a satisfying impedance simulation of electrochemical ethanol oxidation, the capacitor *C* of the equivalent circuit should be replaced with a constant phase element (CPE), *Q*. The most credited explanation for observation of CPE behavior and depressed semicircles on solid electrodes is microscopic roughness. Microscopic roughness causes inhomogeneous distribution in the solution resistance and the double-layer capacitance.37,38 In the electrically equivalent circuit of figure 8, *Rs*, *Qdl* and *Rct* are resistance of the solution, a constant phase element related to capacitance of the double layer and charge transfer resistance, respectively. Also, *Qads* and *Rads* represent the electrical elements corresponding to adsorption of reaction intermediates. In this circuit, the concept of resistance against charge transfer during the electrode reaction is physically simple and can be interpreted as how fast charge transfers during electro-oxidation of ethanol at the surface of the electrode.



**Figure 8.** Equivalent circuit compatible with the experimental impedance data in Figures 4 and 5 for ethanol electro-oxidation on nickel-copper electrode.

The experimental data were fitted to equivalent circuit to corroborate the equivalent circuit and obtain the circuit elements. Table 1 reports parameters of the equivalent circuit for impedance spectra of ethanol oxidation. Diameter decrease with ethanol concentration can be seen for the two semicircles, which means that ethanol electro-oxidation enhances using higher ethanol concentrations. It also approves catalytic activity of NiCu alloy for ethanol oxidation.

**Table 1.** Equivalent circuit parameters of electro-oxidation of ethanol on NiCu electrode in NaOH solution.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| *Concentration*  / M | *Rs*  */* Ω | *R1*  / Ω | *Q1*  / F | *n1* | *R2*  / Ω | *Q2*  / F | *n2* |
| 0.1 | 11.9 | 105 | 0.0018 | 0.79 | 4224 | 0.008 | 0.9 |
| 0.2 | 11.5 | 78 | 0.0024 | 0.79 | 1671 | 0.018 | 0.75 |
| 0.3 | 11.7 | 45 | 0.0026 | 0.77 | 361 | 0.018 | 0.68 |
| 0.4 | 10.3 | 21 | 0.0025 | 0.67 | 274 | 0.02 | 0.56 |
| 0.5 | 10.5 | 19 | 0.003 | 0.66 | 196 | 0.025 | 0.58 |
| 0.6 | 10.9 | 18 | 0.003 | 0.67 | 181 | 0.03 | 0.57 |

**4. Conclusions**

In this study, a nickel oxide film was formed on the surface of nickel-copper alloy, electrochemically, in a cyclic voltammetry regime. The film was applied to electro-oxidation of ethanol in alkaline solution. The results confirmed that NiCu alloy is electro-catalytically active for ethanol oxidation at around 500 mV/Ag,AgCl. To be more specific, the response obtained for electro-oxidation of ethanol on NiCu electrode is greater than the response observed for pure nickel, noticeably. The anodic peak currents for ethanol oxidation on the alloy electrode are proportional to square root of the scan rates, linearly. Choronoamperograms of the alloy revealed dominance of a diffusion controlled process, in presence of ethanol. In this respect, a diffusion coefficient equal to 1.26×10-5 cm2 s-1 was calculated for ethanol. Moreover, charge transfer resistance for various concentrations of ethanol was evaluated and highlighted effective catalytic activity of NiCu alloy for oxidation of ethanol, in alkaline solutions.

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