

Electrochemical Study of Ethanol Oxidation on Nickel in Alkaline Media

A.J. Motheo*, S.A.S. Machado, F.J.B. Rabelo and J.R. Santos Jr.¹

Instituto de Química de São Carlos, Universidade de São Paulo, C.P. 780,
13560-970 São Carlos - SP, Brazil

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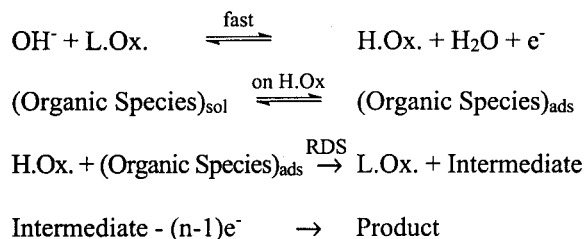
O mecanismo da oxidação de etanol sobre níquel em soluções de hidróxido de potássio é discutido em termos da formação de óxidos de níquel de valência superior. Na primeira etapa deste estudo foi utilizado voltametria cíclica e foram encontradas evidências para um processo de intermediação envolvendo o óxido superior e a molécula orgânica. Posteriormente foram feitas medidas de impedância a.c. nos potenciais de 0,45, 0,6 e 1,0 V, e os ajustes destes resultados, utilizando um circuito equivalente que inclui elementos de fase constante, indicam o mecanismo no qual o óxido superior tem um papel importante como o mais apropriado.

The mechanism of the oxidation of ethanol on nickel in potassium hydroxide solutions is discussed in terms of the formation of higher valence nickel oxides. The first step of this study was performed using cyclic voltammetry and showed evidence of a process of mediation involving the higher oxides and the organic molecule. To confirm these conclusions, a.c. impedance measurements were done at potentials of 0.45, 0.6 and 1.0 V vs. Hg/HgO, and the fittings of these results, using an equivalent circuit which included constant phase elements, indicated that the mechanism involving higher oxides is the most appropriate.

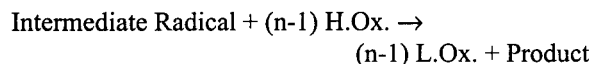
Keywords: ethanol oxidation, nickel electrodes, impedance

Introduction

The oxidation of organic molecules promoted by an unstable metal oxide of higher valence is a well established process for several systems^{1,2}. In the particular case of the electrochemical oxidation of alcohols on NiO_x, Fleischmann *et al.*³ proposed a simple mechanism involving the mediation of a "superior oxide", assumed to be Ni³⁺ (or β-NiOOH). This generic proposition is composed of the following pathways³:



or



where L.Ox. and H.Ox. are the lower and higher oxide, respectively, and the main product was identified as acetic acid³. This mechanism was analyzed by Robertson⁴, who postulated its validity only for high OH⁻ concentrations.

A major problem related to this mechanism is the adsorption of organic molecules on a surface which is not very active for this kind of interaction. On platinum, where the adsorption of organic molecules is highly enhanced, Snell and Keenan⁵ observed three anodic peaks, including one in the cathodic sweep. These peaks were associated with the oxidation of CH₃C(Pt)HOH, CH₃CH₂OH_{ads} and CH₃CH₂OH reacting with Pt and PtOH.

Although the adsorbed species are questionable on Ni surfaces, another possibility must be examined. As stressed by Lu and Srinivasan⁶, according to thermodynamic data the highest oxidation state of Ni is hydrated NiO₂, although the authors noted that its formation occurs only in the oxygen evolution potential region. As shown by Pigeaud⁷, in alkaline solutions of pH 14, NiO₂ must be stable at potentials more positive than *ca.* - 0.20 V vs. Hg/HgO. It should be evident that the redox couple Ni(OOH)/NiO₂

¹ - Permanent Address: Universidade Federal do Piauí, Dept. Química, CCN - Teresina, 64050 - PI, Brazil

must be more active to intermediate organic molecules oxidation than the $\text{Ni}(\text{OH})_2/\text{Ni}(\text{OOH})$ proposed by Fleischmann *et al.*³. Recently, Comninellis² grouped the "higher oxides" as a species having a high concentration of "oxygen vacancies", which can favor the selective oxidation of organics. In a previous study, we postulated that the participation of these higher valence oxides are fundamental for the oxidation of ethanol⁸.

Based on the fact that the continuous change in the valence states of the surface must promote the formation of oxide films with different conductivity, the objective of this paper is to associate the results obtained using cyclic voltammetry with the analysis of ac faradaic impedance in stationary current conditions.

Experimental

Electrode preparation

The working electrode was prepared by mounting a nickel rod (VARIAN 99,98%) onto a Teflon holder, leaving a single face with a geometric area of 0.78 cm^2 exposed to the electrolyte. For the first mechanical treatment applied to the face of the electrode emery paper (from grid 320 to 1500) was used and before each experiment the electrode was polished with 1500 grid emery paper. Between each step of this treatment the electrode was cleaned in an ultrasonic bath. The counter electrode was a platinum foil with a total area of 3 cm^2 . The reference electrode was a $\text{Hg} / \text{HgO} / \text{KOH} 0.1 \text{ M}$ prepared as described elsewhere⁹.

Solution preparation

Potassium hydroxide (Merck p.a.) was recrystallized from water, redissolved and submitted to a 72 h pre-electrolysis using two platinum electrodes in a single compartment cell. After this treatment the solution was standardized using oxalic acid and kept in a sealed plastic flask at around 10°C . Before each experiment, a portion of this solution was used to prepare the working solution of 0.1 M KOH . Ethanol (Merck 99.5%) was distilled and its purity checked by infrared spectroscopy. The water used in this work was provided by a Milli-Q purification system (Millipore).

Electrochemical measurements

A glass (Pyrex) cylindrical cell was used to carry out the voltammetric and spectroscopic a.c. impedance experiments. The cyclic voltammetry analysis was performed using an EG&G/PARC Potentiostat / Galvanostat Model 273A controlled by EG&G/PARC software Model M270. The a.c. impedance measurements were made using the same Potentiostat coupled with a Frequency Response Analyzer from Solartron, Model 1255, and controlled by EG&G/PARC software, Model M388, in the frequency range of 10^{-3} Hz to 50 kHz . The analysis of these experi-

mental results was carried out using EQUIVCRT¹⁰ software. Before each set of a.c. impedance measurements, the electrode potential was held at the corresponding value for 4 h, in order to reach a stationary steady state current. All experiments were carried out at room temperature.

Results and Discussion

Cyclic voltammetry

The electro-oxidation of ethanol on Ni electrodes in aqueous KOH solutions begins at slightly less positive potentials than those corresponding to the transformation of $\beta\text{-Ni}(\text{OH})_2$ to $\gamma\text{-Ni}(\text{OOH})$. This can be seen in Fig. 1 which shows the stabilized voltammograms for Ni in 0.1 M KOH (solid line) and $0.1 \text{ M KOH} + 1 \text{ M ethanol}$ (dashed line) solutions at 0.10 V/s in a de-oxygenated electrolyte. The oxidation peak occurs at 0.84 V , and is followed by a sharp decrease in the current and the oxygen evolution reaction. In the reverse scan, at 0.80 V the current rises anodically again, almost overlapping the one observed in the direct scan. This behavior is usually attributed to a regeneration of the active sites on the surface which were blocked by the reaction products.

The strong dependence of this electrochemical reaction on the state of oxidation of surface oxides is shown in Fig. 2. The solid lines numbered 1 to 5 represent, respectively,

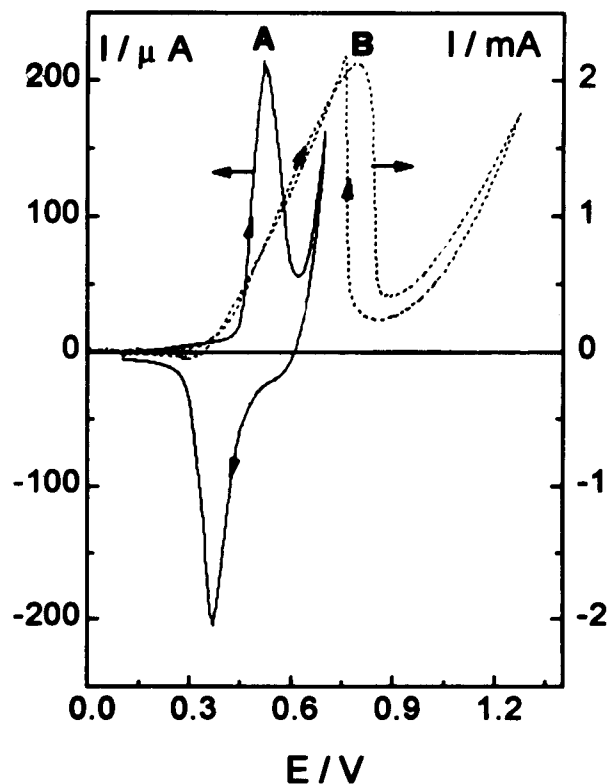


Figure 1. Cyclic voltammograms for: (A) 0.1 M KOH , and (B) $0.1 \text{ M KOH} + 1 \text{ M ethanol}$ on a nickel working electrode (geometrical area of 0.78 cm^2) at 25°C . Scan rate = 0.10 V s^{-1} .

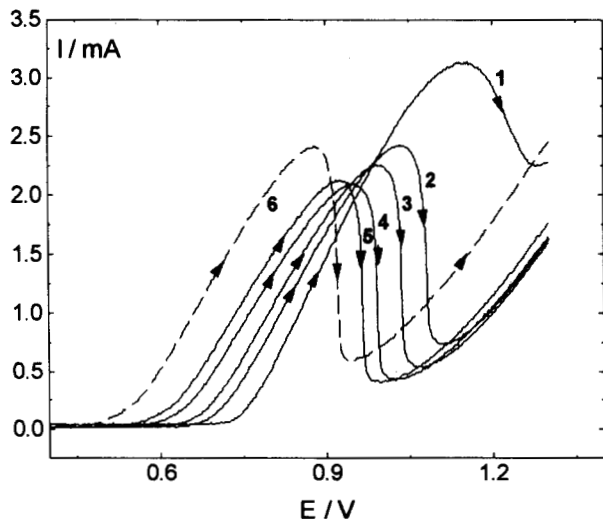


Figure 2. The anodic branch of cyclic voltammograms for successive cycles on nickel in 0.1 M KOH + 1 M ethanol at 0.10 V s^{-1} . Curves: (1) first, (2) 5th, (3) 10th, (4) 20th, (5) 30th cycles, and (6) after pre-passivation of the surface in the electrolyte without ethanol.

the first, fifth, tenth, twentieth and thirtieth cycles of voltammograms performed under the same conditions as those shown in Fig. 1. Curve 6 (dashed line) corresponds to a first cycle voltammogram on a pre-passivated surface (cycled twenty times between 0.10 and 0.70 V before the addition of ethanol in the electrolyte) under the same conditions as curve 1. The effect of these two procedures on the oxidation peak is the same, i.e., to reduce the peak current from 3.13 mA to 2.14 mA and to shift the peak potentials from 1.14 V to 0.94 V. It is clear that the oxidation of the organic compound responds to the formation of a special kind of oxide on the Ni surface, that is not $\gamma\text{-Ni(OOH)}$, since it is already formed in the first cycle on the non-pre-passivated surface¹¹. This special oxide inhibits the peak current and promotes a cathodic shift in the reaction potentials which, together with the magnitude of currents shown in Figs. 1 and 2 for the oxidation of ethanol, strongly suggests a highly catalytic process occurring between ethanol and the oxides in a superior state of oxidation on the Ni surface.

Figure 3 shows the dependence of the voltammograms on the variation in ethanol concentration. These voltammograms correspond to 0.1 M KOH aqueous solutions, containing 0.05 M (1), 0.5 M (2) and 1 M (3) of ethanol. It can be seen that while the alcohol concentration increases by ten times between curves 1 and 2, the anodic peak currents vary only by a factor of three times in the same potential. Although the ethanol concentration doubles between curves 2 and 3, the peak current increases only from 10.6 to 13.1 mA, but with a shift in the peak potentials from 0.66 V to 0.8 V. This potential shift can be associated with the need for oxide formation to perform the ethanol oxidation. When the ethanol concentration increases too much all of the oxide is consumed and it is

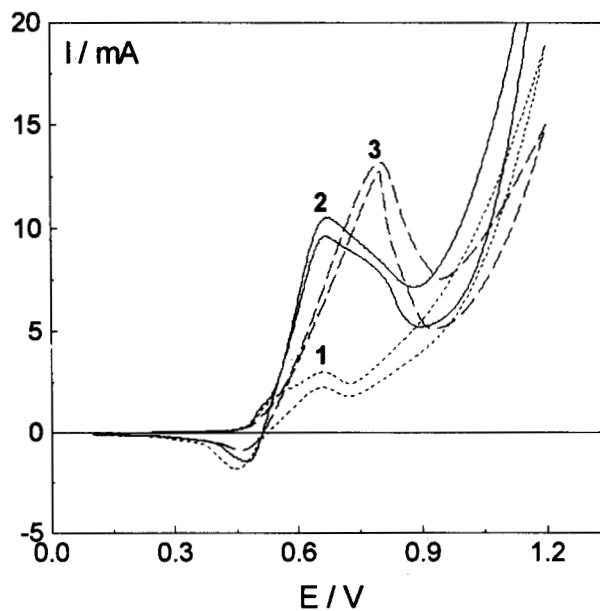


Figure 3. Cyclic voltammograms for nickel in 0.1 M KOH and different ethanol concentrations: (1) 0.05 M, (2) 0.5 M, and (3) 1 M ethanol. Scan rate = 0.1 V s^{-1} .

necessary to go to more positive potentials to regenerate the superior oxide on the surface.

Finally, Fig. 4 shows the absolutely abnormal behavior of the peak currents with the potential scan rate. The initial sharp increase is almost proportional to v , but at 0.10 V/s there is an abrupt decrease, and the currents, after passing through a minimum, become almost independent of the scan rate. This unusual dependence suggests a mechanism for the reaction that does not follow any traditional diagnostic criterion, not even for catalytic reactions¹². This behavior can be interpreted as an occurrence of a non-vol-

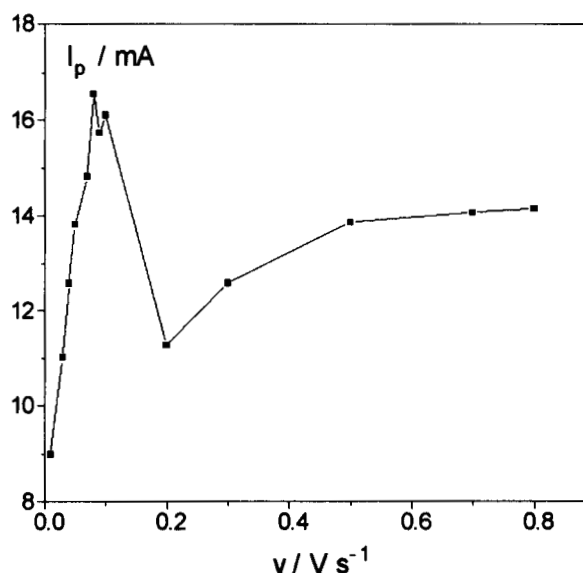


Figure 4. The dependence of the peak current on the scan rate for the oxidation of ethanol under the same conditions as Fig. 1.

tammetric current maximum due to the mediation of higher surface oxides in ethanol oxidation.

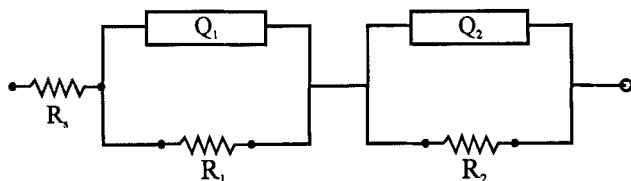
A.C. impedance measurements

The usual treatment of impedance data obtained using an interface consisting of a solid electrode takes into account a constant phase element (CPE). The admittance expression of the CPE, using a very general dispersion formula, is given by¹⁰:

$$Y^*(\omega) = Y_0(j\omega)^n = Y_0\omega^n \cos(n\pi/2) + jY_0\omega^n \sin(n\pi/2) \quad (1)$$

where Y_0 is an adjustable parameter containing the diffusion coefficient, ω is the angular frequency ($\omega = 2\pi f$), and n is a parameter related to the phase angle shift. When $n = 0$ the formula represents a resistance with $R = Y_0^{-1}$, for $n = 1$ a capacitance with $C = Y_0$, for $n = 0.5$ it represents a Warburg element, and when $n = -1$ it represents an inductance with $L = Y_0^{-1}$ ¹⁰.

The impedance measurements were obtained for different d.c. potentials applied to the electrode. In the systems without ethanol the following d.c. potentials were chosen: 0.45 and 0.6 V. The first value corresponds to the steady-state condition potentials corresponding to that in the passivated voltammetric region just before the peak of γ -Ni(OOH) formation. The second potential value corresponds, in voltammetric conditions, to the region slightly more positive than that where the peak of γ -Ni(OOH) formation occurs. In the presence of ethanol, the same potentials were studied, plus 1 V which corresponds to the peak of organic oxidation. The electrode response was allowed to stabilize for 4 h prior to the impedance measurement to assure a stationary state current condition. The analysis of these experimental data was performed using an equivalent circuit represented by



where Q represents a CPE.

In solutions without ethanol at 0.45 V the Nyquist diagram presents linear behavior with a phase angle shift, and at 0.6 V the result is a single semi-circle. In the presence of ethanol, at 0.45 V, the resulting Nyquist diagram is a single semi-circle. Under the same conditions, at 0.6 and 1.0 V, the corresponding experimental data and the simulated values obtained by using the equivalent circuits given above are shown in Fig. 5. The margin of error obtained with the fitting procedure in the imaginary and real part of the impedance was always less than 5%. The fitting parameters obtained for both systems studied are presented in

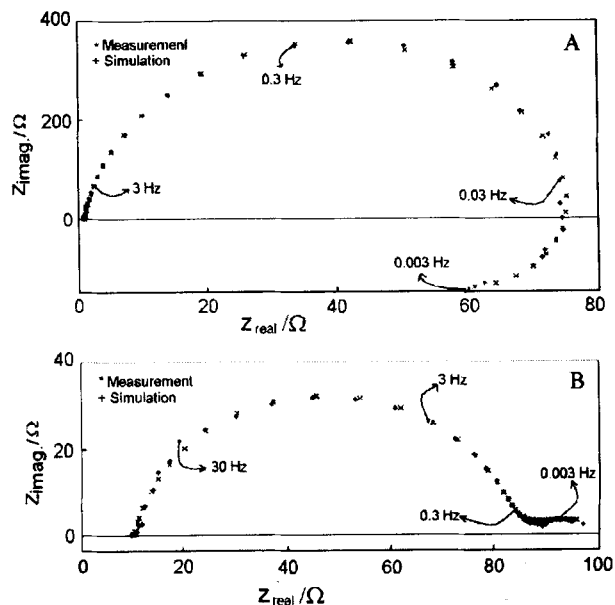


Figure 5. Nyquist diagram for the interface of nickel with an aqueous solution of 0.1 M KOH + 1 M ethanol at 0.6 (a) and 1.0 V (b). A.C. potential of 10 mV p.p. and a frequency range of 10^{-3} Hz to 50 kHz.

Table 1, where it is possible to observe that the value of the solution resistance (R_s) is practically constant in all situations. The elements corresponding to the first block of the general circuit have the following behavior: the resistance R_1 decreases when the potential is more positive and also decreases with the presence of ethanol, Q_1 has a value on the same order of magnitude in all situations, and n_1 has a value around 0.9 which corresponds to a capacitive behavior of this CPE. On the other hand, the second block of the circuit appears only for the potentials of 0.6 and 1.0 V in the presence of ethanol, and the values are indicative of an inductive behavior at 0.6 V and a Warburg element at 1.0 V.

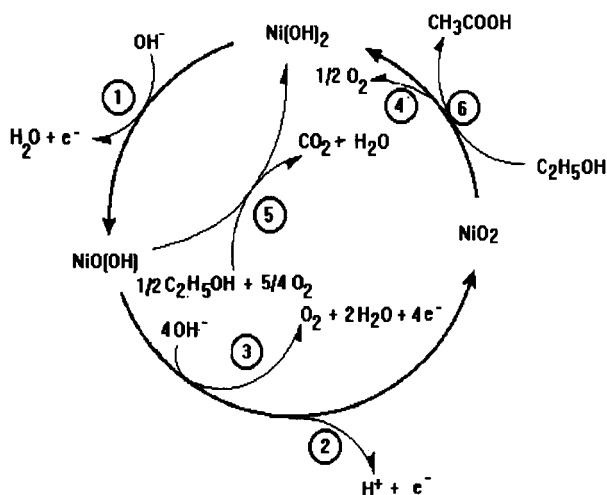
Conclusions

The voltammetric results indicate that the oxidation of ethanol should occur in a mechanism which includes the participation of the higher valence surface oxides, as al-

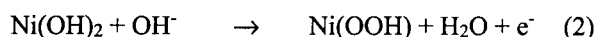
Table 1. Parameters obtained from the impedance fitting using the equivalent circuit presented in the text.

	without EtOH		with EtOH		
	0.45	0.6	0.45	0.6	1.0
R_s/Ω	9.22	9.39	11.03	8.65	9.60
R_1/Ω	2.3×10^6	2300	41000	800	75
Q_1	3.6×10^{-4}	8.5×10^{-4}	5.5×10^{-4}	7.2×10^{-4}	2.4×10^{-4}
n_1	0.85	0.92	0.87	0.89	0.89
R_2/Ω	—	—	—	401	16
Q_2	—	—	—	-6.1×10^{-2}	0.3
n_2	—	—	—	-0.79	0.50

ready observed³. The magnitude of the oxidation currents observed in the presence of ethanol suggests a catalytic mechanism. A good possibility for explaining such behavior is the Comninellis model² correlated to the mechanism of Fleischmann *et al.*³. Such a mechanism may be represented by the following cycle:



In the first step of this mechanism, OH^- in alkaline solution is discharged and the oxidation state of nickel changes from +2 to +3, according the equation:

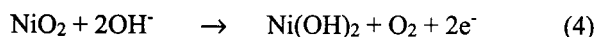


Before this reaction, the surface is totally passivated with $\beta\text{-Ni(OH)}_2$, so it can be expected that such behavior is associated with the impedance spectra obtained at 0.45 V in solutions without ethanol, where only a straight line was observed due to the double layer charging.

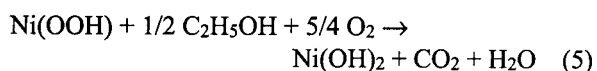
In a second step, the oxy-hydroxide may be oxidized to a valence of +4, forming a higher oxide on the surface:



This unstable oxide decomposes to generate oxygen, creating an equilibrium on the surface and justifying the semi-circle obtained at 0.6 V in the absence of alcohol. This reaction can be associated with:



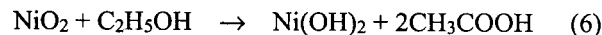
In the presence of ethanol it appears that a combustion reaction may occur as follows:



Such reactions, which Comninellis² associated with the presence of adsorbed OH on the surface, are possible in the range of 0.45 V (where the surface is totally covered by

$\beta\text{-Ni(OH)}_2$), and may be associated with the semi-circle observed.

In the region where the surface is covered with NiO_2 , the ethanol can undergo a selective oxidation by the following reaction, suggested by Fleischmann *et al.*³:



which generates the lower oxide Ni(OH)_2 on the surface and furnishes a reagent for a new lap in the circle. This reaction is highly complex and the flux of electrons between the inner layers of oxide, the surface and the organic molecule, which are processes having different relaxation times, can justify the inductive loop in the impedance spectra obtained at 0.60 V. Finally, the spectra at 1.0 V show a Warburg component that can be associated with the oxygen evolution reaction which is highly enhanced at these potentials.

Acknowledgments

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