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VOLTAMMETRIC STUDIES OF ETHANOL ELECTROOXIDATION IN ALKALINE MEDIA ON SKELETAL NICKEL ELECTRODE

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Abstract

In this paper, new aspects of ethanol electrocatalytic oxidation on skeletal nickel electrode in aqueous alkaline solution was investigated by cyclic voltammetry and linear polarization techniques. Nickel and its alloys are commonly catalytic materials used as anode for alcohols dissociation. Electrocatalytic activity for ethanol oxidation reaction (EOR) becomes a serious issue, especially due to the utilization of skeletal nickel electrodes in fuel cells. In order to understand the oxidation mechanism on the surface of these types of electrodes, comprehensive researches were necessary. The used electrode has a high surface area and increased catalytic activity for EOR in alkaline media. Also, comparative cyclic and linear voltammetric studies on skeletal and smooth nickel electrodes are shown.

Key words: skeletal nickel electrode, ethanol electrooxidation reaction, voltammetric studies.

INTRODUCTION

In different industrial and domestic applications, fuel cells are widely used as attractive devices whitch obtain directly electric energy by chemical products combustion (Antolini E. et al, 2007). Also, fuel cells offer an alternative of clean and sustainable power generation (Goel J. et al, 2012, Bayer D. et al, 2011). Among many types of fuel cells, alkaline fuel cells (AFCs) are the most developed and extensively studied since the 1960s (Antolini E. et al, 2010).

Low molecular weight alcohols used as liquid fuels in AFCs, can be handled, stored and transported easily and this represents a several advantages compared to pure hydrogen (Sheikh A.M. et al, 2010). Direct alcohol fuel cells (DAFCs) are a sub-category of AFCs, which uses a hydroxide ion-based alkaline electrolyte (Nash S. et al, 2014, Antolini E. et al, 2010). DAFCs shows a high potential as power supply for mobile, stationary, and portable applications (Bayer D. et al, 2011). Primary alcohols and mainly methanol (Hogarth M.P. et al, 1996), ethanol (Kamarudin M.Z.F. et al, 2013) and propanol (Anis A. et al, 2012) were confirmed as possible fuels in DAFCs.

Among various alcohol fuels, ethanol is less toxic and can be massively produced from agricultural products or biomass and the theoretical mass energy density is rather high 8.0 kWh kg^{-1} (Li Y.S. et al, 2011, Rousseau S. et al, 2006). The use of bioethanol as a fuel will not change the natural balance of carbon dioxide in the atmosphere (Rousseau S. et al, 2006).

The ethanol complete oxidation to CO_2 is difficult because involves 12 electrons and breaking of C-C bond (Tayal J. et al, 2010). The formation of CO intermediates as partial oxidation byproducts has a negative effect by poisoning of platinum anode catalysts (Goel J. et al, 2012).

Acetaldehyde, acetate and CO are considered as reaction intermediates in alkaline media. Ethanol oxidation reaction (EOR) mechanism involving a reaction of the adsorbed intermediates and adsorbed OH^- on anode surface. The abundance of adsorbed hydroxyl groups (HO^-) at the catalyst surface will accelerate the anodic reactions (Moraes L.P.R. et al, 2016). Yet, the final product of EOR in alkaline media is not clearly defined.

The catalytic activity of an anode used in ethanol oxidation depends on the size distribution and dispersion of the catalyst, relatively large surface area, good electrical conductivity and an accessible porosity (Goel J. et al, 2012). Pt is known as the most active material for ethanol electro-oxidation in both acid and alkaline media inducing C-C bond breaking (Doan N. et al, 2016). Ni-based electrocatalysts have potential to replace Pt at the anode due to its higher catalytic properties in alkaline media and to the lower cost. Nickel and skeletal nickel have been reported to be an efficient electrodes for various inorganic and organic compounds electrooxidation and for oxygen evolution reaction (OER) (Huang J.J. et al, 2009, Enache A.F. et al, 2016).

However, apart from all the advantages of using ethanol in alkaline medium as fuel in DEFCs , its anodic catalytic oxidation in fuel cells is still subject to many research (Bayer D. et al, 2011). The main problems that may arise are catalyst poisoning and membrane damage in the fuel cell.

In this paper, skeletal nickel electrode electocatalytic activity was evaluated by performing EOR in alkaline medium using cyclic and linear voltammetry.

MATERIAL AND METHOD

Skeletal nickel electrode was prepared using thermal arc spraying technique. For skeletal Ni electrodes preparation Ni (Fluka, 99.2%) and Al (Fluka, 99.5%) have been used as anode, respectively as cathode. During the thermal spray the arc current and voltage were set to 200 A and 30 V. In order to remove Al from the coating, the samples were submitted to alkaline leaching in 1 M NaOH solution at about 80°C, for 2 h (Kellenberger A. et al, 2007). Finally, the electrodes were cleaned for 15 minutes in an ultrasonic bath using distilled water. The chemical reaction of Al dissolution is (Trefilov M.I. et al, 2007):

$$2(Al\text{-}Ni)_{(s)} + 2OH^- + 6H_2O \rightarrow 2Ni + 2Al(OH)_4{}^-{}_{(aq)} + 3H_{2(g)} \qquad (1)$$

Electrochemical tests were performed at room temperature using a SP-150 potentiostat/galvanostat (Bio-Logic, SAS, France). A 100 mL typical glass cell was equipped with three electrodes: samples of skeletal or smooth nickel as working electrodes, Ag/AgCl reference electrode and two graphite rods as counter electrodes. For performed experiments, the exposed surface of working electrode was 1 cm^2. All potentials are given versus the reference electrode (E_{ref} = 0.197 V vs SHE). Different concentrations of ethanol (0.125, 0.25, 0.5, 1 and 2 M) were added in 1 M NaOH electrolyte solution.

Table 1 presents the values of conductivity for electrolyte solutions used in experimental data. Conductivity measurements were performed with ProLab2000 (Schott Instruments, Germany)

Table 1

Conductivity of different electrolytes used in experimental studies:

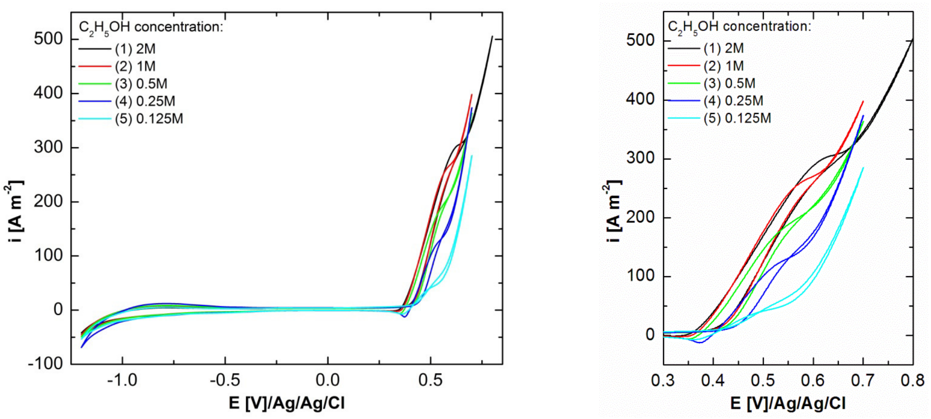
Electrolyte	**Conductivity [S m^{-1}]**
Distilled water	$2.25\cdot10^{-6}$
EtOH 99,8%	$3.16\cdot10^{-6}$
NaOH 1M (BS)	$160.7\cdot10^{-3}$
BS + EtOH 0.125 M	$156.2\cdot10^{-3}$
BS + EtOH 0.25 M	$152.6\cdot10^{-3}$
BS + EtOH 0.5 M	$147.0\cdot10^{-3}$
BS + EtOH 1 M	$134.3\cdot10^{-3}$
BS + EtOH 2 M	$112.2\cdot10^{-3}$

Analysing data from table 1, it can be noticed the decrease of the conductivity along with the increasing of ethanol concentration. In electrochemical measurements, the effect of these values on EOR has been observed.

Cyclic voltammetry and linear polarization were used in order to emphasize the electrocatalytic activity of skeletal nickel electrode for EOR in alkaline media. Cyclic voltammograms (CVs) were recorded at different scan rate, between 5 and 500 mV s^{-1}. Linear polarization curves were registered potentiostatically with 1 mV s^{-1} scan rate.

RESULTS AND DISCUSSION

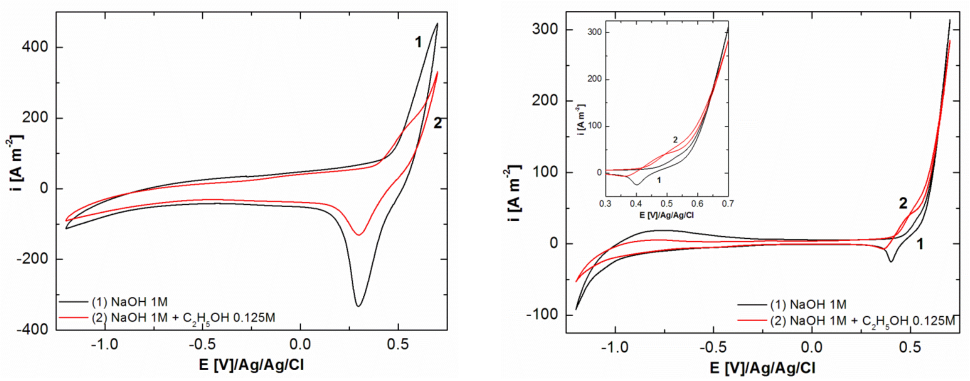
CVs recorded in alkaline solutions with different ethanol concentration, in a wide range of potential (from -1.20 to +0.75 V), at low scan rate, 5 mV s^{-1} are depicted in figure 1. Starting from open circuit potential (OCP) towards anodic polarisation it is observed an anodic plateau associated with EOR. The potential range for EOR is specific for every concentration. At positive potential values then EOR, OER on skeletal nickel electrode can be noticed. On the backward scan, a low intensity cathodic peak associated with adsorbed oxygen reduction or reduction of ethanol oxidation products, was recorded. At more negative electrode potential values than -1.00 V, hydrogen evolution reaction (HER) appears.



a) b)

Fig. 1. Cyclic voltamograms (a) and anodic domain (b) recorded on Ni_{sk} electrode in 1 M NaOH without and with different concentration of ethanol at 5 mV s^{-1}scan rate

For better identification of EOR characteristic potential domain, figure 2 presents CVs plotted on skeletal nickel electrode in 1 M NaOH without and with 0.125 M ethanol (minimum concentration used in experimental tests), at 500 (a) and 5 mV s^{-1} (b) scan rate. Also, it can be observed that the ethanol addition in alkaline electrolyte confers an inhibitory effect for HER and OER on this type of electrode.



a) b)

Fig. 2. Cyclic voltamograms recorded on Ni_{sk} electrode in 1 M NaOH without and with 0.125 M ethanol at 500 (a) and 5 mV s^{-1} (b) scan rate.

LVs recorded at 1 mV s^{-1} scan rate in 1 M NaOH solution without and with different ethanol concentrations are shown in figure 3.

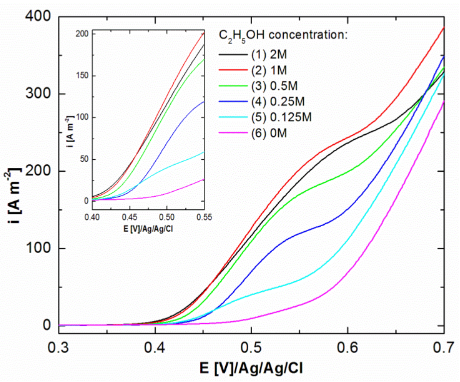


Fig. 3. Linear voltammograms recorded on skeletal nickel electrode in 1M NaOH solution with different ethanol concentrations, at 1 mV s^{-1} scan rate

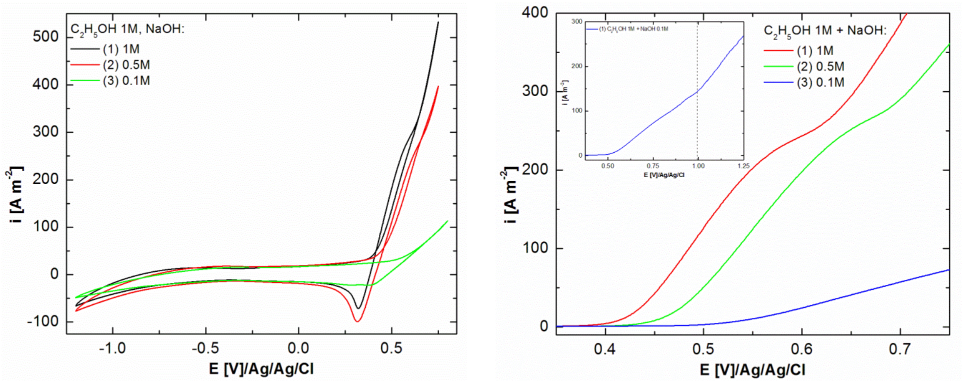
The curves shape indicates only one oxidation process on skeletal nickel electrode surface.

Table 2

Electrochemical parameters characteristic for EOR from linear voltammograms

Electrolyte	**E_{ox} range [V]**	**$i_{lim.ox}$ [A m^{-2}]**
BS + EtOH 0.125 M	+0.43 ÷ +0.56	50
BS + EtOH 0.25 M	+0.43 ÷ +0.60	110
BS + EtOH 0.5 M	+0.42 ÷ +0.63	200
BS + EtOH 1 M	+0.42 ÷ +0.63	255
BS + EtOH 2 M	+0.42 ÷ +0.65	250

Specific parameters (oxidation range potential and limiting current density) for EOR on this type of electrode are shown in table 2. For ethanol oxidation limiting current density variation versus concentration added in alkaline electrolyte it can observe the same principle as for conductivity values variation presented in table 1.

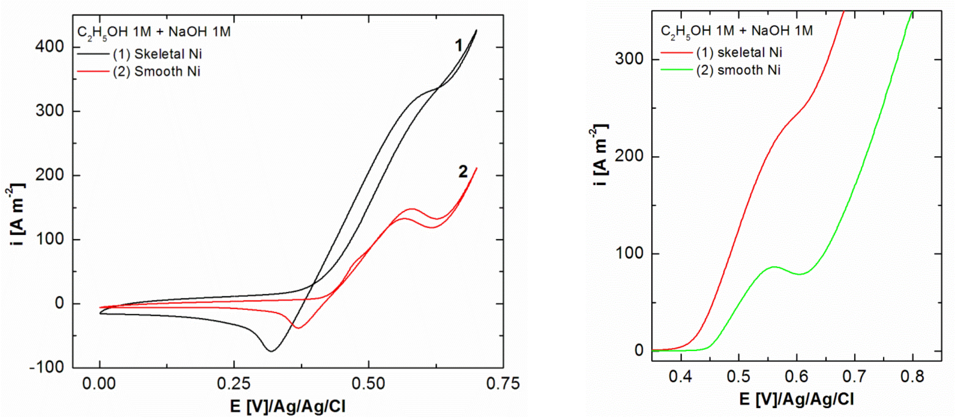


a) b)

Fig. 4. Cyclic (a) and linear (b) voltamograms recorded on Ni$_{sk}$ electrode 1 M ethanol added in different NaOH solutions. Scan rate 100 (a) and 1 mV s^{-1} (b)

Alkaline media influence on EOR was studied using cyclic and linear voltammetry methods. CVs and LVs plotted on skeletal nickel electrode in 1 M ethanol added in NaOH solution with different concentrations (0.1, 0.5 and 1 M) are depicted in figure 3. Cyclic curves shape (fig. 3a) and especially oxidation range potential and limiting current density for EOR from LVs confirm necessity of using an alkaline electrolyte with minimum 1 M concentration. Although, the EOR specific potential range increases, corresponding current density values decrease significantly.

CVs recorded 100 mV s^{-1} and LVs plotted at 1 mV s^{-1} scan rate on skeletal and smooth nickel electrodes in 1 M NaOH with 1 M ethanol solution are presented comparatively in figure 5. Also, oxidation range potential and limiting current density for EOR on both electrodes are shown in table 3. From CVs and LVs shape and specific parameters shown in figure 5 it can be observed an intensification of the electrocatalytic effect for EOR when using skeletal nickel electrode.



a) b)

Fig. 5. Cyclic (a) and linear (b) voltamograms recorded in 1 M NaOH with 1 M ethanol on smooth and skeletal electrodes at 100 (a) and 1 mV s^{-1} (b) scan rate.

Table 3

Electrochemical parameters for EOR from smooth and skeletal nickel electrodes:

Electrolyte	Electrode	E_{ox} range [V]	$i_{lim.ox}$ [A m^{-2}]
BS + EtOH 1 M	Skeletal nickel	+0.42 ÷ +0.63	255
	Smooth nickel	+0.46 ÷ +0.63	75

CONCLUSIONS

In this paper, new aspects of ethanol oxidation reaction on skeletal nickel electrode are presented. The used electrode has a high surface area and increased catalytic activity for EOR in alkaline media. Also, comparative cyclic and linear voltammetric studies on skeletal and smooth nickel electrodes are shown.

A thoroughgoing study is necessary for EOR complete characterization by chronoamperometric method and electrochemical impedance spectroscopy. Furthermore, EOR optimum characteristic parameters will be accessible.

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