

SKELETAL NICKEL ELECTRODE WITH CATALYTIC EFFECT FOR ETHANOL ELECTROOXIDATION IN ALKALINE MEDIA

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Abstract

The aim of this investigation is to examine ethanol anodic oxidation on a skeletal nickel electrode in aqueous alkaline solution ($1 \text{ mol L}^{-1} \text{ NaOH}$). Electrocatalytic activity for ethanol anodic oxidation 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. Electrochemical behavior has been studied by cyclic and linear voltammetry.

Introduction

Alkaline fuel cells (AFCs) commonly use a potassium hydroxide aqueous solution as electrolyte [1]. Also, sodium hydroxide can be used but has a disadvantage because of sodium carbonate lower solubility, obtained as secondary product, compared to potassium carbonate [1]. Compared to AFCs which use H_2/O_2 , direct alcohol fuel cells (DAFCs) are more compact without the heavy and bulky external fuel reformer and can be used to power electric vehicles [2]. Liquid fuels, such as small alcohols from C1 - C3 group, featuring higher volumetric and gravimetric energy densities and better energy efficiency, are easily handled, stored and transported in comparison with gaseous fuels [2].

Ethanol can be produced on a massive scale from biomass feed stocks originating from agriculture (first-generation bioethanol), forestry and urban residues (second-generation bioethanol) [3,4]. The advantage of using ethanol as fuel consists in a large volume energy capacity of 6.3 kWh/L , which is higher than of hydrogen (2.6 kWh/L) or methanol (4.8 kWh/L) [5].

A significant challenge in the development of direct ethanol fuel cells (DEFCs) technologies is the manufacture of highly active catalysts for ethanol oxidation reaction (EOR). Platinum is the most commonly used catalytic metal in DEFCs because has excellent properties in ethanol adsorption and dissociation [3]. However, the cost of platinum is a major impediment in DEFCs commercialization [3]. Pd has similar catalytic properties with Pt, making it very attractive for long-term industrial applications. In this series, other tested catalysts were Pt-M and Pd-M binary or ternary alloys obtained by adding metallic elements such as: Ru, Sn, Ir, Bi, Rh, Mo, Fe, Co, Cu, Ni, Au, Ag, etc [3]. Since 1970, nickel and nickel-based electrodes have been used in fundamental and practical studies for the small alcohols oxidation in alkaline media [6]. Nickel based electrocatalysts are considered low-cost materials and making the DEFC a potentially low cost technology compared to fuel cells with platinum or platinum based catalysts [7].

In this paper, a skeletal nickel electrode was used as electrocatalyst for ethanol oxidation in alkaline media.

Experimental

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 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 0.2 cm^2 . All potentials are given versus the reference electrode ($E_{\text{ref}} = 0.197 \text{ V}$ vs SHE). Different concentrations of ethanol (0.125, 0.25, 0.5, 1 and 2 mol L^{-1}) were added in 1 mol L^{-1} NaOH electrolyte solution.

Results and discussion

Cyclic voltammograms recorded in alkaline solutions, in the absence and presence of ethanol, in a wide range of potential (from -1.20 to $+0.75 \text{ V}$), at 500 mV s^{-1} are presented in figure 1. Starting from open circuit potential (OCP) towards anodic polarisation it is observed an anodic plateau associated with EOR. When the electrode potential is over $+0.60 \text{ V}$, oxygen evolution reaction (OER) on skeletal nickel surface can be observed. On the backward scan, a pronounced cathodic peak associated with adsorbed oxygen reduction or reduction of ethanol oxidation products, was recorded. At more negative than -1.10 V electrode potential values, hydrogen evolution reaction (HER) occurs.

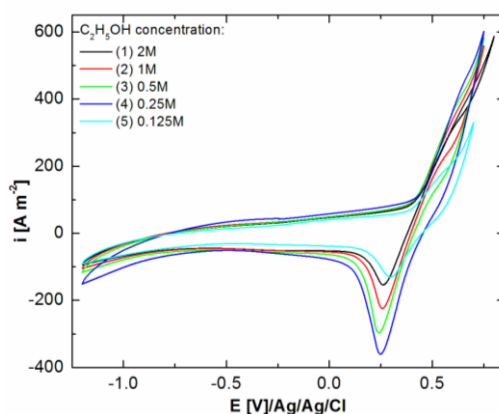


Figure 1. CVs recorded on Ni_{sk} electrode in 1 mol L^{-1} NaOH without and with different concentration of ethanol, scan rate: 500 mV s^{-1} .

For better identification of EOR characteristic potential domain, figure 2 presents the anodic plateau of cyclic voltammograms recorded on skeletal nickel electrode in 1 mol L^{-1} NaOH with different concentrations of ethanol, at 500 mV s^{-1} scan rate.

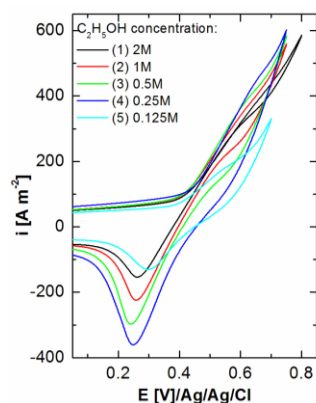


Figure 2. CVs (anodic domain) recorded on Ni_{sk} electrode in 1 mol L^{-1} NaOH without and with different concentrations of ethanol, scan rate: 500 mV s^{-1} .

Scan rate influence on cyclic curves shape plotted on skeletal nickel electrode in 1 mol L^{-1} NaOH solution with 1 mol L^{-1} ethanol are depicted in figure 3.

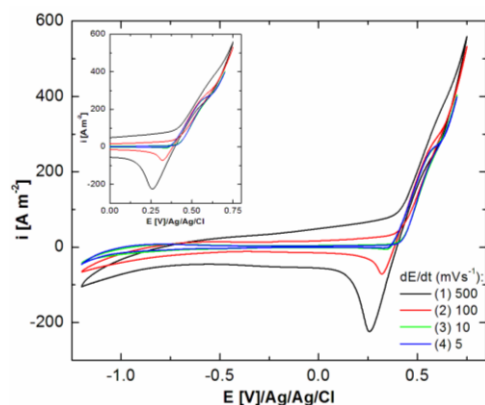


Figure 3. CVs recorded on Ni_{sk} electrode in 1 mol L^{-1} NaOH with 1 mol L^{-1} ethanol at different scan rates.

Cyclic voltammograms recorded at 100 mV s^{-1} scan rate on skeletal and smooth nickel electrodes in 1 mol L^{-1} NaOH with 0.25 mol L^{-1} ethanol solution are presented comparatively in figure 4.

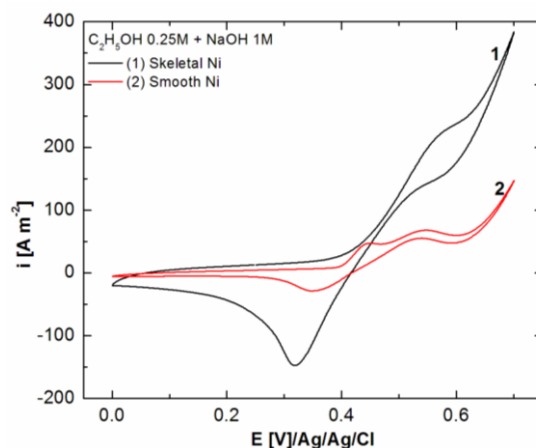


Figure 4. CVs recorded on Ni_{sk} and Ni electrodes in 1 mol L^{-1} NaOH with 0.25 mol L^{-1} ethanol, scan rate: 100 mV s^{-1} .

Other electrochemical experimental technique which confirmed the advantage of skeletal nickel electrode compared to smooth nickel electrode as catalyst for EOR is linear voltammetry recorded at very low scan rate (1 mV s^{-1}). Obtained curves are shown in figure 5. The curves shape indicates only one oxidation process on both electrodes surface. Specific parameters (oxidation range potential and limiting current density) for are presented in table 1.

Table 1. Electrochemical parameters from EOR:

Electrode	$E_{\text{ox range}}$ [V]	$i_{\text{lim,ox}}$ [A m^{-2}]
Skeletal nickel	$0.42 \div 0.57$	135
Smooth nickel	$0.44 \div 0.60$	23

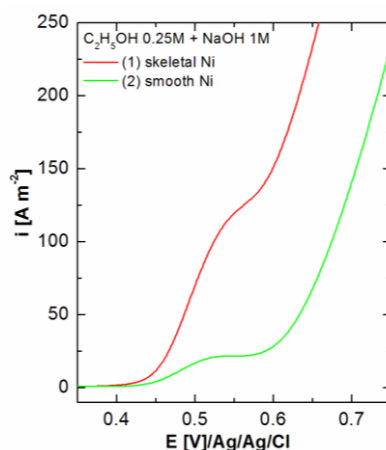


Figure 5. LVs (anodic domain) recorded on Ni_{sk} and Ni electrodes in 1 mol L⁻¹ NaOH with 0.25 mol L⁻¹ ethanol, scan rate: 1 mV s⁻¹.

Conclusion

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.

Acknowledgements

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