

SKELETAL NICKEL BASED 6 LAYERS PLATINUM NANOPARTICLES ELECTRODE WITH CATALYTIC EFFECT FOR ANODIC OXIDATION OF SULPHITE IN ALKALINE SOLUTION

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Abstract

In this paper, anodic oxidation of sulphite ions on skeletal nickel based 6 layers platinum nanoparticles electrode ($\text{Ni}_{\text{sk}} - \text{Pt}_{6\text{layers}}$) in aqueous alkaline solution was investigated by cyclic voltammetry and linear polarization. The present research is essential to understand the mechanism of reaction on this electrode.

The preliminary results presented in experimental part confirm the high catalytic activity of $\text{Ni}_{\text{sk}} - \text{Pt}_{6\text{layers}}$ for sulphite electrooxidation process and offer the possibility to use this type of electrodes in alkaline fuel cells.

Introduction

Since the 1990s, nanocatalysis emerged as one area at the interface between homogeneous and heterogeneous catalysis, which provide unique solutions to fulfill the conditions required for process improvement [1, 2].

Lately, the attention of researchers was directed towards the nanostructured materials for innovative applications in energetic industry. These materials possess promising properties for energy harvesting, conversion and storage [3].

Currently, nanoparticles represent key components in the development of energy technologies, which play an important role in replacing fossil fuels by renewable energy resources. It is therefore necessary to grow techniques for preparing larger volume of nanoparticles, that would be advantageous in terms of costs and considering that performance and commercialization of fuel cells depends on electrode material properties [4].

Nanoparticles are used as electrocatalysts in fuel cells and other electrochemical converters. The desire is to increase activity per unit area and to reduce the required amount of catalyst material whose cost is high. Performance and commercialization of fuel cell depend on electrode materials [4].

Electrochemical oxidation of sulphite in aqueous solution became an important subject for industry and environment. This process has been investigated throughout time and it has gained further interest recently due to the participation of this reaction in the Hybrid Sulfur (HyS) cycle for hydrogen production [5–9].

In this paper, cyclic voltammetry and linear polarization techniques have been used in order to describe the sulphite anodic oxidation mechanism in alkaline solutions on skeletal nickel based 6 layers platinum nanoparticles electrode.

Experimental

Electrode preparation

Chloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) and isopropanol (Sigma-Aldrich, 99.7%) were used for preparation of platinum salt precursor solution.

Platinum nanoparticles were deposited on skeletal nickel substrate by spray-pyrolysis technique using an ultrasonic nebulizer SONO-TEK Corporation Exacta Coat. After

deposition, the samples were heated at 350°C for 30 minutes to obtain the platinum nanoparticles [10].

Electrochemical measurements

SP 150 Bio-Logic potentiostat/galvanostat in a three-electrode electrochemical were used for electrochemical measurements. The cell consists of $\text{Ni}_{\text{sk}} - \text{Pt}_{6\text{layers}}$ as working electrode with 0.5 cm^2 active surface area, two graphite rods as counter electrodes placed symmetrically to the working electrode and Ag/AgCl as reference electrode.

Electrochemical experiments were performed in 1 mol L^{-1} NaOH solution (prepared using Merck NaOH, p.a. min. 99.8%) in the absence and presence of Na_2SO_3 (Merk, p.a. min. 98%). Na_2SO_3 concentrations added were: 10^{-3} , 10^{-2} and $10^{-1} \text{ mol L}^{-1}$.

Cyclic voltammograms were plotted at different scan rate between 5 and 500 mV s^{-1} . Linear polarization curves were registered at 1 mV s^{-1} scan rate.

Results and discussion

Cyclic voltammetry studies

Cyclic voltammograms plotted with high scan rate (500 mV s^{-1}) on $\text{Ni}_{\text{sk}} - \text{Pt}_{6\text{layers}}$ electrode in alkaline electrolyte with different amounts of sodium sulphite are shown in Figure 1.

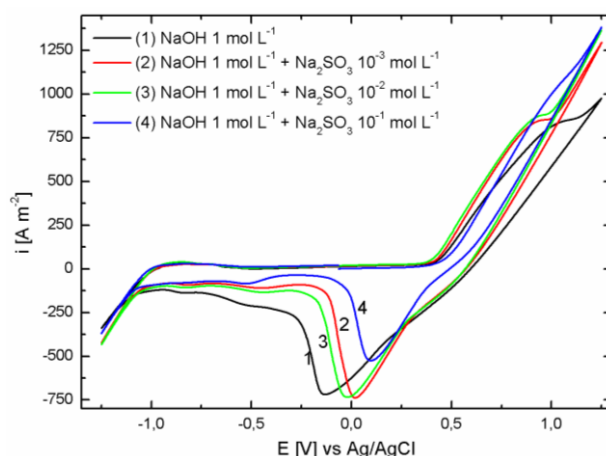


Figure 1. Cyclic voltammograms recorded on $\text{Ni}_{\text{sk}} - \text{Pt}_{6\text{layers}}$ electrode in 1 mol L^{-1} NaOH without/with different concentration of Na_2SO_3 at 500 mV s^{-1} .

Applying electrical current through electrode/electrolyte solution system, hydrogen evolution reaction (HER) is the only process visible on the cathode plateau. Sweeping potential to more positive values, within a range between $+0.45 \div +1.15 \text{ V vs. Ag / AgCl}$ can be seen a pick that may be associated with the formation of an oxid layer on the electrode surface followed by sulphite oxidation and oxygen evolution reaction (OER).

First identification of SO_3^{2-} ions oxidation process occurring at the interface working electrode/electrolyte was possible when the scan rate was decreased at 50 mV s^{-1} (Figure 2).

On cyclic curves registered at 50 mV s^{-1} in 1 mol L^{-1} NaOH solutions without and with Na_2SO_3 it can be observed in characteristic potential range for anodic oxidation of sulphite ions between $+0.45$ and $+0.75 \text{ V vs. Ag/AgCl}$. It can be also noted that OER potential value is shifted to more negative values in solutions with SO_3^{2-} ions.

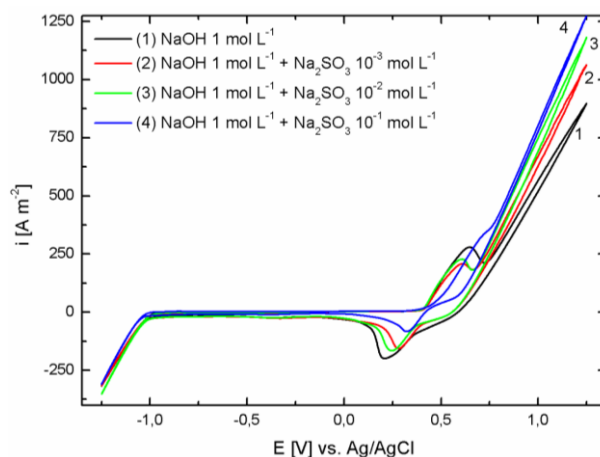


Figure 2. Cyclic voltammograms recorded on $\text{Ni}_{\text{sk}} - \text{Pt}_{6\text{layers}}$ electrode in 1 mol L^{-1} NaOH without/with different concentration of Na_2SO_3 at 50 mV s^{-1} .

Linear voltammetry studies

Linear voltammetry technique was applied to obtain the dependence of current density versus electrode potential for anodic plateau at low scan rate (1 mV s^{-1}) in alkaline solutions with and without SO_3^{2-} (Figure 3).

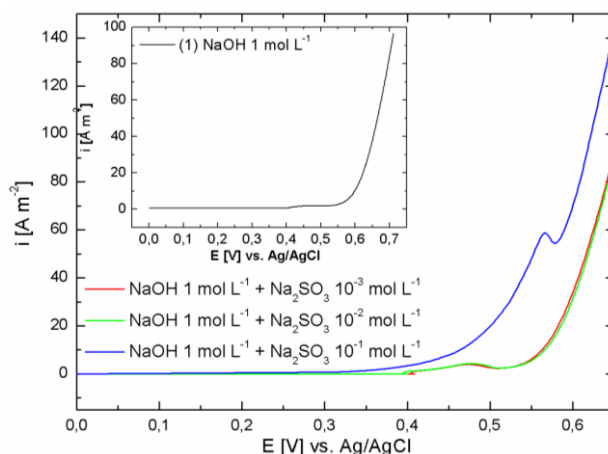


Figure 3. Linear voltammograms recorded on $\text{Ni}_{\text{sk}} - \text{Pt}_{6\text{layers}}$ electrode in 1 mol L^{-1} NaOH without/with different concentration of Na_2SO_3 at 1 mV s^{-1} ; linear voltammograms in 1 mol L^{-1} NaOH inserted.

From linear voltammograms analysis, potential ranges of both oxidation processes that occur on anodic plateau (SO_3^{2-} ions oxidation and OER) have been highlighted. The curves shape indicates only one oxidation process on electrode surface.

Skavas [11] described two possible mechanisms for electrochemical oxidation of sulphite to sulphate ions in alkaline media. According to this mechanism, sulphite anion is oxidized to sulphate in two successive steps, each implying one electron transfer.

On the other hand, sulphite anion is oxidized to sulphite radical which can interact forming dithionate ions $\text{S}_2\text{O}_6^{2-}$. Consecutively these ions disproportionate in sulphate and sulphite ions.

Conclusion

Ni_{sk} – Pt_{6layers} electrodeprepared by spray-pyrolysis technique has proved to be a promising catalyst for sulphite anodic oxidation. The platinum nanoparticles insertion has a significant effect on the studied process. The experiments presented have confirmed the possibility to oxidize electrochemically SO₃²⁻ to SO₄²⁻ on this type of electrode.

The possibility to oxidize sulphite ions provides a very good reason to continue studies regarding the use of Ni_{sk} – Pt_{6layers} as catalyst in alkaline fuel cells.

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