

ANODIC OXIDATION OF SULPHITE IONS ON SMOOTH NICKEL BASED 1 LAYER PLATINUM NANOPARTICLES IN ALKALINE SOLUTION

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Abstract

In this paper, nickel based 1 layer platinum nanoparticles electrode (Ni-Pt_{1layer}), prepared by spray-pyrolysis technique, it has been tested in order to obtain a complete characterization for the process of anodic oxidation of sulphite to sulphate in alkaline media. This process was investigated by cyclic voltammetry technique and linear polarization. The present study concerns the preliminary evaluation of electrocatalytic properties for this type of electrode toward the electrochemical oxidation of sulphite.

Introduction

In a world with limited resources, the dominant model for economic growth based on rising resource consumption and pollutants emission, no longer tenable [1]. In this context, the concept of "green economy" has offered the opportunity to change the way society handles the interaction between environmental and economic areas. To enable the society to build and sustain a green economy concept associate " green nanotechnology " aims to exploit innovations in materials science and engineering to develop products and processes that are energy efficient as well as economically and environmentally sustainable [1].

Nanotechnology has a significant impact in fuel cells domain, which are devices able to convert chemical energy into electrical one [2]. Nanomaterials can be very efficient electrocatalysts for oxidation / reduction reactions in fuel cells because of high active surface area [3, 4]. Platinum nanoparticles have been considered as the best catalyst for application in fuel cells [5]. Nanomaterials containing platinum alloys have been the subject of research because of high electrocatalytic activity and chemical resistance [6]. Platinum is one of the rarest and most expensive metals. It has high corrosion resistance and numerous catalytic applications including automotive catalytic converters and petrochemical cracking catalysts. Platinum nanoparticles are used to reduce the amount of metal needed for various applications.

Electrochemical oxidation of sulphite in aqueous solution is an important issue for the industrial sector. The mechanism for this reaction has been extensively studied for application to the hybrid sulfur cycle (Hys), also known as Westinghouse cycle, for hydrogen production [7, 8], this process being also applied to remove the sulphite from exhaust gases (flue gas desulfurization) [9, 10], electrogenerative oxidation [11] and the analytical determination of sulfur compounds concentrations [12]. Many aspects of this reaction have also interest in fundamental electrocatalysis [13].

Sulphur dioxide - oxygen fuel cells present an important role due to the possibility to produce both electric energy and sulphuric acid.

In this paper, cyclic voltammetry and linear polarization techniques were used in order to characterize the sulphite anodic oxidation in alkaline solutions on skeletal nickel based platinum nanoparticles electrode.

Experimental

Electrode preparation

Platinum salt precursor solution used for platinum nanoparticles deposition has been prepared with chloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) and isopropanol (Sigma-Aldrich, 99.7%).

Platinum nanoparticles were deposited on smooth nickel substrate by spray-pyrolysis technique using an ultrasonic nebulizer SONO-TEK Corporation Exacta Coat. After deposition, the electrodes were heated at 350°C during 30 minutes to obtain the platinum nanoparticles [14].

Electrochemical measurements

Electrochemical measurements were performed with a SP 150 Bio-Logic potentiostat/galvanostat in a three-electrode electrochemical cell consisting of Ni-Pt_{1layer} as working electrode with surface area of 0.5 cm^2 . Two graphite rods were used as counter electrodes placed symmetrically to the working electrode and Ag/AgCl as reference electrode. Electrochemical experiments were carried out in 1 mol L^{-1} NaOH solution (prepared with Merck NaOH, p.a.) with and without Na_2SO_3 (Merk, p.a. 98%). Electrolyte solutions with different concentrations of Na_2SO_3 were prepared, as follow: 10^{-3} , 10^{-2} and $10^{-1} \text{ mol L}^{-1}$.

Cyclic voltammograms have been registered with $5 - 500 \text{ mV s}^{-1}$ scan rate. Linear polarization curves have been recorded with 1 mV s^{-1} scan rate.

Results and discussion

Cyclic voltammetry studies

A typical cyclic voltammograms recorded on Ni-Pt_{1layer} electrode in alkaline solution with different concentration of Na_2SO_3 are presented in Figure 1.

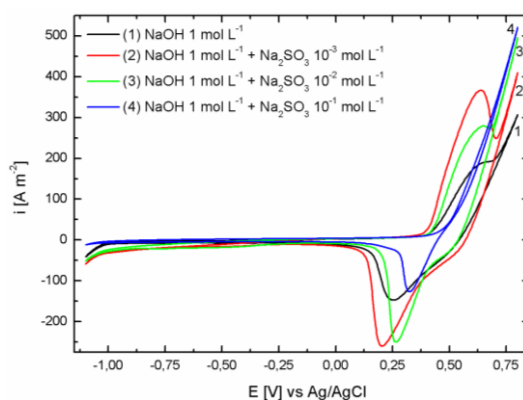


Figure 1. Cyclic voltammograms recorded on Ni-Pt_{1layer} electrode in 1 mol L^{-1} NaOH without/with different concentration of Na_2SO_3 at 500 mV s^{-1} .

On the cathodic plateau the only process visible is the hydrogen evolution reaction (HER) according to the equation (1):



Sweeping the potential in the anodic region, at potential range between $0.35 - 0.70 \text{ V}$ vs. Ag / AgCl it was observed a pick that can be associated with the formation of an oxide on the electrode surface followed by oxidation of sulphite and oxygen evolution reaction.

The most generally accepted mechanisms for oxygen evolution reaction (OER) on various electrodes, including nickel based platinum nanoparticles, involve reactions with one of the electron charge transfer steps rate-determining [15]:





Cyclic voltammograms plotted with high scan rate (50 mV s^{-1}) on Ni-Pt_{1layer} electrode in alkaline electrolyte with different amounts of Na₂SO₃ are shown in Figure 2.

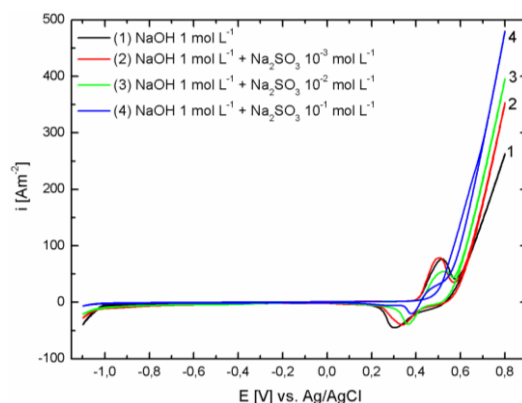


Figure 2. Cyclic voltammograms recorded on Ni-Pt_{1layer} electrode in 1 mol L^{-1} NaOH without/with different concentration of Na₂SO₃ at 50 mV s^{-1} .

On cyclic curves plotted at 50 mV s^{-1} shown in Figure 2 for 1 mol L^{-1} NaOH solutions in the absence and presence of different concentrations of Na₂SO₃ it can be observed the OER potential value is shifted to more negative potentials in the presence of SO₃²⁻ ions.

The decrease of scan rate from 500 mV s^{-1} at 50 mV s^{-1} provides the opportunity to point out the identification of the SO₃²⁻ ions oxidation processes occurring at the interface working electrode/electrolyte solution in the potential range between +0.5 and +0.7 V vs. Ag/AgCl.

Linear voltammetry studies

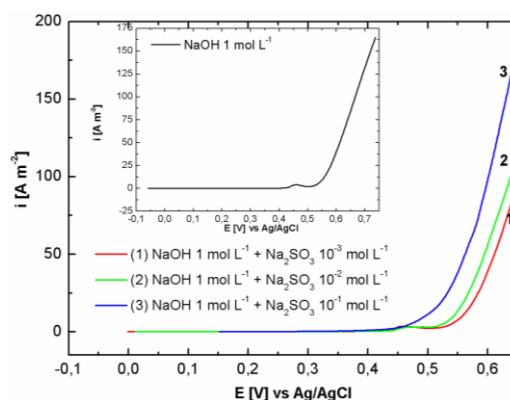


Figure 3. Linear voltammograms recorded on Ni-Pt_{1layer} electrode in 1 mol L^{-1} NaOH with different concentration of Na₂SO₃ at 1 mV s^{-1} ; linear voltammograms in 1 mol L^{-1} NaOH inserted.

Linear voltammetry technique was applied to validate the results presented above. Curves registered at low scan rate (1 mV s^{-1}) in alkaline media with different concentrations of SO₃²⁻ ions are shown in Figure 3. From the analysis of linear voltammograms, specific potential ranges of oxidation processes that occur at the interface electrode/electrolyte solution (SO₃²⁻ ions oxidation and OER) have been emphasized. The electrochemical oxidation of sulphite to sulphate ions in alkaline media can occur following two possible mechanisms, presented by

Skavas [16] where sulphite anion is oxidized to sulphate in two successive steps, each implying one electron transfer or sulphite anion is oxidized to sulphite radical which can interact and form dithionate ions $S_2O_6^{2-}$. Finally, these ions disproportionate in SO_4^{2-} and SO_3^{2-} .

The OER mechanism on Ni-Pt_{1layer} electrode takes place following reactions (2) – (5) and SO_3^{2-} ions oxidation is conducted directly in alkaline electrolyte by a chemical irreversible process when the molecular oxygen was produced on electrode surface.

Conclusion

Ni-Pt_{1layer} electrode prepared by spray-pyrolysis technique has been characterized by different techniques in order to its applicability as an electrocatalytic material in fuel cells for the oxidation of sulphite ions in alkaline solution. The insertion of platinum nanoparticles has a significant effect on the activity of the studied reaction and the experiments presented have confirmed the possibility to oxidize electrochemically SO_3^{2-} to SO_4^{2-} on smooth nickel based platinum nanoparticles electrode.

Acknowledgements

This work was partially supported by Politehnica University Timisoara in the frame of PhD studies.

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