

**SULPHITE ELECTROOXIDATION IN ALKALINE MEDIA
ON SKELETAL NICKEL BASED 3 LAYERS PLATINUM
NANOPARTICLES ELECTRODE
I. VOLTAMMETRIC STUDIES**

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Abstract

In this paper, anodic oxidation of sulphite ions on skeletal nickel based platinum nanoparticles electrode (3 layers) in aqueous alkaline solution was investigated in order to find the relationship between kinetic parameters and sulphite concentration. The purpose of this research is both to understand the oxidation mechanism and to determine optimal parameters for studied process. Electrochemical behavior of sulphite ions has been studied by cyclic voltammetry and linear polarization. Tafel method was used in order to determine kinetic parameters.

Key words: skeletal nickel, platinum nanoparticles, sulphite anodic oxidation, cyclic voltammetry, linear polarization.

INTRODUCTION

The energy amount from renewable sources worldwide is expected to grow with 38% in the next 20 years. Consequently, getting energy from renewable sources will go toward new alternative energy conversion, storage and process management being required. Hydrogen production by water electrolysis, enable the possibility for a high capacity of production and management without greenhouse emissions (Kjartansdóttir, 2013).

Tacking into account platinum high price, nanoparticles are used to reduce the amount of metal required in various applications. It has high corrosion resistance and numerous catalytic applications including automotive catalytic converters and petrochemical cracking catalysts.

Due to their chemical and physical properties, platinum nanoparticles are used in present for a wide variety applications, including electronics and optics (Giancaterini et. al, 2015), enzyme immobilization (Chauhan et. al, 2013), catalysts for many reactions, including hydrogen evolution reaction used in fuel cells (Sanap et. al, 2014), for proton exchange membrane fuel cell (PEMFC) (Reddington et. al, 1998), for nitric acid synthesis (Williams et. al, 1997), reduction of exhaust gases from vehicles (Bell, 2003) and as catalytic nucleating agents for magnetic nanoparticles synthesis (Sun et. al, 2000).

Sulfur is found in natural gas, petroleum and coal. These raw materials are valuable fuels for powering and energy supply to the world. Use of these materials individually (vehicles, oil furnaces) and at industrial level (power plants, refineries, foundries) causes the release of sulfur dioxide into environment.

A possibility of pollution abatement is to absorb sulfur dioxide in basic solutions and use them as fuel in an alkaline fuel cell. In order to oxidize sulphite to sulphate in alkaline media, materials such as graphite (Hunger et. al, 1991, Lu et. al, 1999), calcium doped cobalt layered perovskite type 114 electrode (Enache et. al, 2015), skeletal nickel (Dan et. al, 2016, Enache et. al, 2016) were tested.

In this paper, cyclic voltammetry and linear polarization techniques were used in order to find optimum parameters for sulphite anodic oxidation in alkaline media on skeletal nickel based 3 layers platinum nanoparticles electrode.

MATERIALS AND METHODS

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 electrodes were heated at 350°C for 30 minutes to remove the solvent and to obtain the Pt nanoparticles (Iacob et. al, 2015).

Electrochemical measurements

Electrochemical measurements were performed with a SP 150 Bio-Logic potentiostat/galvanostat in a three-electrode electrochemical cell consisting of skeletal nickel based platinum nanoparticles ($\text{Ni}_{\text{sk}} - \text{Pt}_3 \text{ layers}$) as working electrode with a geometric area of 0.5 cm^2 , two graphite rods as counter electrodes placed symmetrically to the working electrode and Ag/AgCl as reference electrode. All potentials are presented versus this reference electrode ($E_{\text{Ag/AgCl}} = +0.197 \text{ V vs. SHE}$).

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

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

The research presented in this paper has been conducted during PhD studies (2015-2016) in Laboratory of Electrochemistry, Corrosion and Electrochemical Engineering, Faculty of Industrial Chemistry and Environmental Engineering, University Politehnica Timisoara, Romania.

RESULTS AND DISCUSSION

Cyclic voltammetry studies

A typical cyclic voltammograms recorded on $\text{Ni}_{\text{sk}} - \text{Pt}_3$ layers electrode in alkaline solution are presented in figure 1.

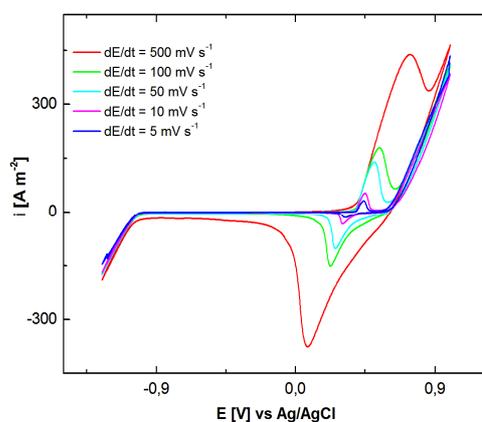


Fig. 1. Cyclic voltammograms recorded on $\text{Ni}_{\text{sk}} - \text{Pt}_3$ layers electrode in $1 \text{ mol L}^{-1} \text{ NaOH}$ at different polarization rate

Comparing obtained curves plotted at different scan rates in alkaline solution without sulphite ions, hydrogen evolution reaction (HER) is the only visible process on the cathodic domain. Sweeping the electrode potential towards anodic polarization, between $+0.45 - +0.80 \text{ V}$ a pick appears that may be associated with the formation of an oxid layer on the electrode surface, followed by sulphite oxidation and oxygen evolution reaction (OER) at more positive values.

In previous studies, several mechanisms for OER on the surface of various electrodes in alkaline solution have been proposed (Damjanovica et. al, 1966, Iwakura et. al, 1976).

The most generally accepted mechanisms on various electrodes involve reactions with one of the electron transfer steps rate-determining (Akano, 1980):



It has been pointed out that the most probable path for OER on platinum in alkaline solution are the above steps and reaction 2 is rate-determining at lower overpotentials, while reaction 1 is rate-determining at higher potentials.

Cyclic voltammograms drawn with high scan rate (500 mV s^{-1}) on $\text{Ni}_{\text{sk}} - \text{Pt}_3$ layers electrode in alkaline electrolyte with different amounts of sodium sulphite are shown in figure 2.

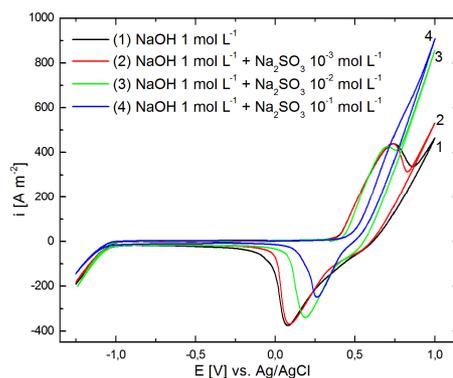


Fig. 2. Cyclic voltammograms recorded on $\text{Ni}_{\text{sk}} - \text{Pt}_3$ layers electrode in 1 mol L^{-1} NaOH without/with different concentration of Na_2SO_3 at 500 mV s^{-1}

On cyclic curves plotted at 100 mV s^{-1} shown in figure 3 for 1 mol L^{-1} NaOH solutions in absence and presence of $10^{-1} \text{ mol L}^{-1}$ Na_2SO_3 it can be observed the OER potential value is shifted to more negative values in the presence of ions SO_3^{2-} . Most probably this is the effect of atomic oxygen involved in the oxidation of sulphite to sulphate in the anodic branch.

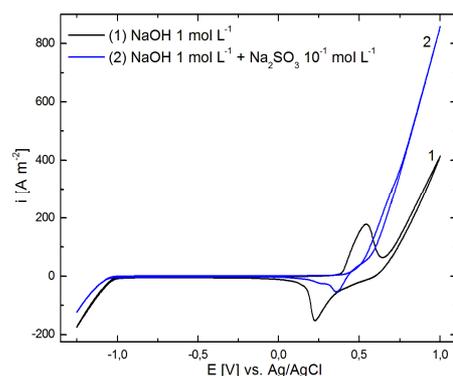


Fig. 3. Cyclic voltammograms recorded on $\text{Ni}_{\text{sk}} - \text{Pt}_3$ layers electrode in 1 mol L^{-1} NaOH without/with $10^{-1} \text{ mol L}^{-1}$ Na_2SO_3 at 100 mV s^{-1}

Decreasing the scan rate at 10 mV s^{-1} (figure 4) provides the opportunity to make a first identification of the SO_3^{2-} ions oxidation

processes occurring at the interface working electrode/electrolyte in potential range between +0.4 and +0.6 V.

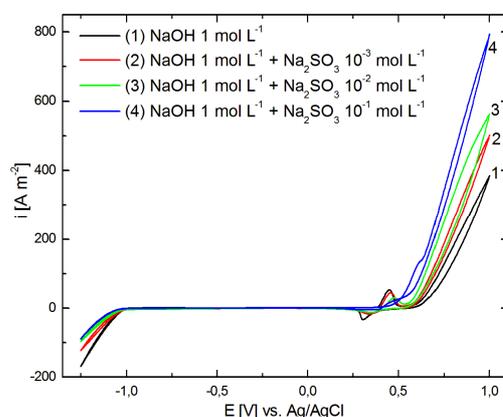


Fig. 4. Cyclic voltammograms recorded on $\text{Ni}_{\text{sk}} - \text{Pt}_3$ layers electrode in 1 mol L^{-1} NaOH without/with different concentration of Na_2SO_3 at 10 mV s^{-1}

Linear voltammetry studies

Linear voltammetry technique was applied to obtain the dependence of current versus electrode potential for anodic plateau at low scan rate. The curves obtained at 1 mV s^{-1} in alkaline media in presence of SO_3^{2-} ions are shown in figure 5.

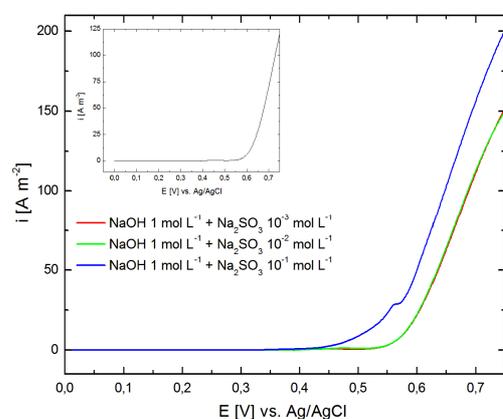
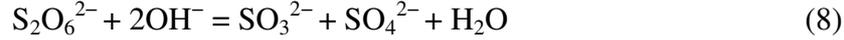
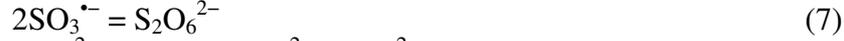
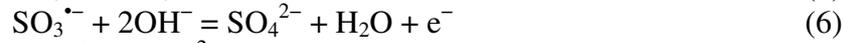


Fig. 5. Linear voltammograms recorded on $\text{Ni}_{\text{sk}} - \text{Pt}_3$ layers electrode in 1 mol L^{-1} NaOH with different concentration of Na_2SO_3 at 1 mV s^{-1} ; linear voltammograms in 1 mol L^{-1} NaOH inserted

Inserted linear voltammograms offer the possibility to analyze the specific potential ranges for oxidation processes that occur at the interface electrode/electrolyte (SO_3^{2-} oxidation and OER).

The electrochemical oxidation of sulphite to sulphate ions in alkaline media has been described by Skavas (Skavas et. al, 2007) using two possible

mechanisms. According to the first one, sulphite anion is oxidized to sulphate in two successive steps, each implying one electron transfer:



In the second mechanism, sulphite anion is oxidized to sulphite radical (reaction 5). In next step two sulphite radicals can interact forming dithionate ions $\text{S}_2\text{O}_6^{2-}$ (reaction 7). Finally, these ions consecutively disproportionate in sulphate and sulphite ions (reaction 8).

In the potential range between +0.5 – +0.75 V from figure 5 the OER on $\text{Ni}_{\text{sk}} - \text{Pt}_3 \text{ layers}$ electrode takes place according to reactions (1) – (4) and SO_3^{2-} ions oxidation occurs by a chemical irreversible process in which the adsorbed atomic oxygen produced on electrode surface in OER oxidizes sulphite to sulphate (reaction 9):



Based on Tafel plots $\eta = f(\log i)$ shown in figure 6, transfer coefficient and exchange current density for electrochemical oxidation of sulphite to sulphate in alkaline solution on $\text{Ni}_{\text{sk}} - \text{Pt}_3 \text{ layers}$ electrode have been calculated. The values of kinetic parameters are presented in Table 1.

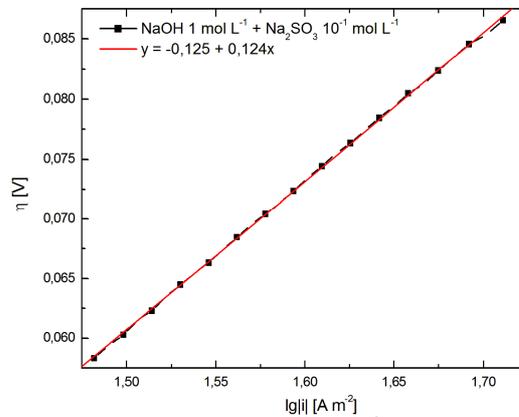


Fig. 6. Tafel slope for electrochemical oxidation of SO_3^{2-} oxidation in alkaline media

Table 1

The kinetic parameters for sulphite oxidation in alkaline solutions

Na_2SO_3 concentration [mol L ⁻¹]	b [mV dec ⁻¹]	α	i_o [A m ⁻²]
10 ⁻¹	124	0.48	2.74

It can be noticed that the slope value obtained is 124 mV dec^{-1} , which is close to the theoretical one (118 mV dec^{-1}). Also, it can be observed a considerable current exchange value.

CONCLUSIONS

Skeletal nickel based platinum nanoparticles (3 layers) electrode prepared by spray-pyrolysis technique has been characterized by cyclic voltammetry techniques and linear polarization in order to use this type of material in fuel cells in alkaline solution. The data presented in this paper have confirmed the possibility to oxidize electrochemically to SO_4^{2-} on skeletal nickel based 3 layers platinum nanoparticles electrode.

Kinetic parameters values show that SO_3^{2-} oxidation reaction to SO_4^{2-} is fast, this process taking place at low polarization. This is an essential premise for using SO_3^{2-} as fuel in an alkaline fuel cell.

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