

ANODIC OXIDATION OF SULPHITE IN ALKALINE MEDIA ON PLATINUM NANOPARTICLES MODIFIED NICKEL ELECTRODE

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Abstract. In this paper, anodic oxidation of sulphite ions on platinum nanoparticles modified nickel electrode (Ni–Pt NPs) in aqueous alkaline solution was investigated in order to establish the relationship between kinetic parameters and sulphite concentration. The purpose of this research is both to clarify the oxidation mechanism and to find optimal parameters for sulphite oxidation process using various electrochemical methods. Cyclic voltammetry and linear polarization have been applied to investigate the electrochemical behaviour of sulphite ions and Tafel plots method has been used in order to determine kinetic parameters. To confirm the anodic oxidation mechanism, electrochemical impedance spectroscopy studies have been performed. Furthermore, chrono-electrochemical methods (chronoamperometry, chronopotentiometry, chronocoulometry) have been used in order to obtain more information on sulphite electrooxidation process.

Keywords: sulphite anodic oxidation, smooth nickel, platinum nanoparticles, chrono-electrochemical methods.

Received: 31 March 2017/ Revised final: 16 May 2017/ Accepted: 30 May 2017

Introduction

Researches regarding the use of hydrogen sulphide and sodium hydrosulphide as a fuel in ion-exchange membrane fuel cells have led to the idea of using other sulphur compounds, such as those recovered in oil refineries. The interest of researchers has been focused on the use of sulphites as fuel in alkaline fuel cells, taking into account that they result as waste in SO₂ removal processes from fossil fuel combustion gases [1,2].

Platinum and nickel are commonly metallic materials used to obtain catalysts for anodic reactions. Since the 70's, the anodic behaviour of nickel in alkaline solution has been the subject of many studies, especially for the reactions that take place in nickel-alkaline battery [3].

It is well known that sulphur oxides (SO_x) and hydrogen sulphide (H₂S) are considered noxious impurities in many fuel cells. Sulphur compounds poison the anodic materials with the formation of conventional bulk metal sulphides (e.g. Ni₂S₃ - if anode is nickel based) [4] or can be physically absorbed into membrane decreasing its conductivity [5]. The results will be an adverse effect on performances and lifetimes of fuel cell devices.

In order to improve the anodic catalytic activity, platinum nanoparticles were deposited on smooth nickel substrate by spray-pyrolysis

method [6,7]. Nickel based electrocatalysts present high corrosion stability in contact with sulphur compounds and their cost price is reasonable.

The process of sulphite oxidation in alkaline media is very complex. There are two possible mechanisms according to the study achieved by Skavas *et al.* [8,9]. Despite of investigations conducted until now, the mechanism of sulphite electrooxidation is not clear.

In the present paper, a series of electrochemical methods (linear and cyclic voltammetry, Tafel plots method, electrochemical impedance spectroscopy and chrono-electrochemical measurements) were applied to obtain additional information about anodic oxidation of sulphite to sulphate in alkaline media. The main purpose of this work is to evaluate the possibility of using alkaline solutions containing sulphites as fuel in a SO₃²⁻/O₂ AFC in order to reduce the pollution by harnessing the sulphites resulting from industry, this way obtaining energy, water and Na₂SO₄ as products in a manner that will not affect the environment. Further, researches can be extended on the electrochemical behaviour of sulphur dioxide in order to use it in a SO₂/O₂ fuel cell, which can produce both electricity and sulphuric acid.

Experimental

Platinum nanoparticles (Pt NPs) deposition was achieved on smooth nickel electrode substrate by spray-pyrolysis technique, using an ultrasonic nebulizer SONO-TEK Corporation Exacta Coat, from a fixed quantity of mixture consisting of chloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) and isopropanol (Sigma-Aldrich, 99.7%). The samples have been heated at 350°C , for 30 minutes, to obtain platinum nanoparticles [6,7]. One layer platinum nanoparticles is defined as the amount deposited on smooth nickel substrate during one complete cycle: spray-pyrolysis - thermal treatment. Finally, an active electrode surface composition with about 1.2% Pt and 98.8% Ni weight percentage has been obtained. Ni-Pt NPs electrode has been realized by the deposition of six successive layers in order to obtain a sufficient concentration of platinum nanoparticles, as set out in a previous paper [6].

A three-electrode undivided electrochemical cell connected to SP 150 Bio-Logic potentiostat/galvanostat was used for electrochemical measurements. Ni-Pt NPs electrode with 0.5 cm^2 active surface was used as working electrode, two graphite rods placed symmetrically to the working electrode as counter electrodes, and Ag/AgCl as reference electrode. Standard cell used for experiments was equipped with Luggin capillary in order to avoid the potential drop through the electrolyte solution between working and reference electrodes.

Electrochemical experiments were performed in alkaline media, 1 mol L^{-1} NaOH solution in the absence and presence of sulphite ions. Sodium sulphite concentrations added were: 10^{-3} , 10^{-2} and $10^{-1}\text{ mol L}^{-1}$. Used reagents NaOH and Na_2SO_3 , were Sigma-Aldrich pro analysis quality. All measurements were carried out in solutions purged with high purity nitrogen.

Cyclic voltammograms were registered at different scan rate, between 5 and 500 mV s^{-1} . Linear polarization curves were recorded with 1 mV s^{-1} scan rate. Electrochemical impedance spectroscopy (EIS) studies were performed using the impedance module of SP-150, in the frequency range from 0.1 Hz to 100 kHz and AC voltage amplitude of 10 mV. For each spectrum, 60 points were collected, with a logarithmic distribution of 10 points per decade. The experimental EIS data were fitted to the electrical equivalent circuit by CNLS Levenberg – Marquardt procedure using ZView – Scribner Associates Inc. software. Sulphite oxidation efficiency has been determined by

chronoamperometry, chronocoulometry and chronopotentiometry methods.

Results and discussion

Cyclic voltammetry

Cyclic voltammograms were recorded in 1 mol L^{-1} NaOH in the absence and presence of various concentrations of sodium sulphite (10^{-3} , 10^{-2} , and respectively $10^{-1}\text{ mol L}^{-1}$) in order to identify the processes that take place at the electrode/electrolyte interface. The voltammograms presented in Figure 1 indicate that at anodic polarization the sulphite oxidation occurs simultaneously with atomic oxygen formation.

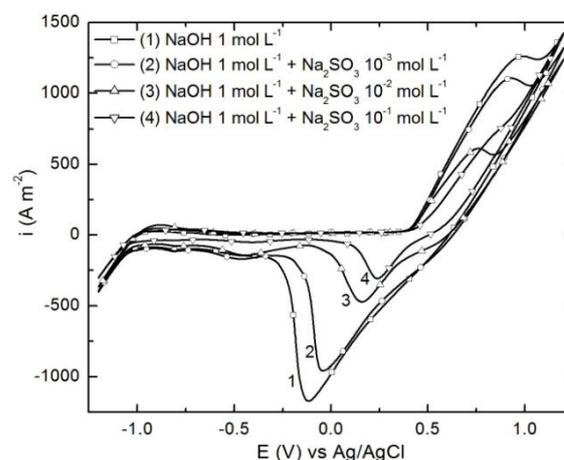
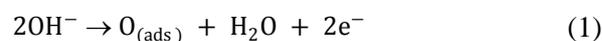


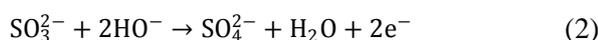
Figure 1. Cyclic voltammograms recorded on Ni – Pt NPs electrode in 1 mol L^{-1} NaOH solution without and with different sulphite concentrations, at 500 mV s^{-1} .

As it can be seen, at advanced cathodic polarization only hydrogen evolution reaction (HER) takes place. On the other hand, in the anodic domain between $0.5\div 0.8\text{ V}$, in the absence of sulphite ions (curve 1), a peak attributed to the formation of adsorbed atomic oxygen, according to the Eq.(1), can be observed [9].



In the presence of a small amount of sulphite, the peak decreases proportionally to the concentration of sulphite ions in test solutions as a result of the SO_3^{2-} ions adsorption on the electrode surface. At higher sulphite concentrations ($\geq 10^{-1}\text{ mol L}^{-1}$), the peak disappears due to sulphite oxidation reaction, probably carried out directly on the electrode surface, as specified by other researchers [8,9]. At advanced anodic polarization, the mediated oxidation of sulphite takes place simultaneously with the direct oxidation according to Skavas, E. and

Hemmingsen, T. [9], followed by oxygen evolution reaction, as it is highlighted on the cyclic voltammograms recorded at 50 mV s⁻¹ (Figure 2). Cyclic voltammograms recorded on working electrode in alkaline solution without and with different SO₃²⁻ concentrations are presented in Figure 2, at 50 mV s⁻¹ scan rates. The shape of curves is characteristic for smooth nickel electrode in alkaline media. Starting from open circuit potential (OCP), at anodic polarization, only an oxidation peak has been observed at more positive potential values than +0.40 V. In the presence of different concentrations of SO₃²⁻ ions, the oxidation peak is characteristic for sulphite anodic oxidation, described by the Eq.(2):



Recorded anodic peaks, characteristic for sulphite oxidation, are more prominent on the Ni-Pt NPs than on smooth Ni [10], due to the catalytic effect of platinum nanoparticles deposited on the nickel surface.

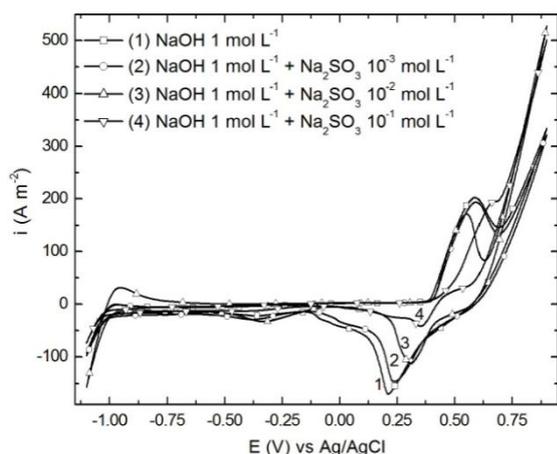
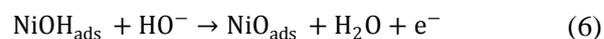
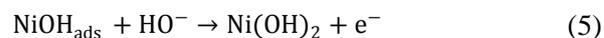
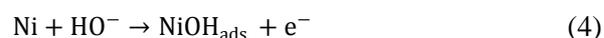
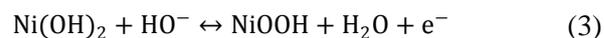


Figure 2. Cyclic voltammograms recorded on Ni-Pt NPs electrode in 1 mol L⁻¹ NaOH solution without and with different sulphite concentrations, at 50 mV s⁻¹.

It is necessary to take into account that on the working electrode surface there are sites of nickel uncovered with platinum particles, so at higher current densities other processes are possible.

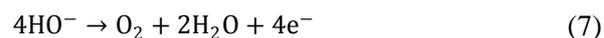
The limiting current plateau recorded in the absence of sulphite ions corresponds to Ni(II)/Ni(III) oxidation during the reversible transformation Ni(OH)₂/NiOOH according to Eq.(3), this reaction being a final step in a complex mechanism characteristic for electrochemical behaviour of nickel in alkaline media. Initially, at low anodic current, metallic nickel is oxidized to Ni(II) in two steps, following

the Eqs.(4) and (5). The intermediate NiOH_{ads} can participate in other oxidation reaction as shown in Eq.(6) [11,12]:



The anodic process of sulphite oxidation is mediated by Ni(OH)₂/NiOOH redox couple or NiOH_{ads}/NiO_{ads} formed on the active surface site of working electrode. As well, on platinum nanoparticles layers, sulphite oxidation occurs according to Eq.(2) by intermediate species as sulphite radical (SO₃^{•-}) or dithionate ions (S₂O₆²⁻) [13].

At more positive potential, simultaneously with sulphite oxidation processes, oxygen evolution reaction (OER) occurs on electrode surface, according to Eq.(7).



On the cathodic branch of cyclic voltammograms it is recorded a pronounced peak assigned to the reduction of superficial residual oxygen on Ni-Pt NPs electrode surface or NiOOH reduction. Further, at more negative potentials than -1.0 V, HER occurs on electrode surface.

On cyclic voltammograms plotted at 50 mV s⁻¹ shown in Figure 2, the peak corresponding to sulphite electrooxidation is sharper than on the curves traced in the same solutions at 500 mV s⁻¹.

Cyclic voltammograms traced at 5 mV s⁻¹ are presented in Figure 3, only oxidation peak of SO₃²⁻ on anodic branch and superficial remnant oxygen or NiOOH reduction processes on cathodic branch being highlighted. The cathodic peak registered on curve 4 is less intense because SO₃²⁻ ions present at electrode/electrolyte interface in higher concentration (10⁻¹ mol L⁻¹) will consume the most part of the oxygen generated on anodic plateau, thus the number of oxygen molecules remaining adsorbed on the electrode surface is very small.

Linear voltammetry

The initial aim to determine optimum parameters that characterize the sulphite oxidation was to identify the range potential in which only the studied process is carried out on Ni-Pt NPs electrode. Linear voltammetry was applied in

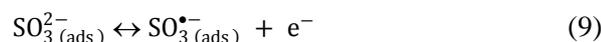
order to obtain the variation of current density as a function of electrode potential on anodic domain, at low scan rate. The curves recorded at 1 mV s^{-1} in alkaline media in the presence of different concentration of SO_3^{2-} ions are shown in Figure 4.

From the analysis of linear voltammograms, specific potential ranges of sulphite oxidation process on Ni–Pt NPs electrode versus sulphite concentration in alkaline electrolyte, have been highlighted. Further, kinetic parameters (transfer coefficient α and exchange current density i_0) for electrochemical oxidation of SO_3^{2-} to SO_4^{2-} ions in alkaline solution have been calculated for the highest sulphite concentration, using Tafel plots method, shown in Figure 5. The calculated kinetic parameters are presented in Table 1. The obtained values for the transfer coefficient α and anodic slope b indicate an one-electron charge transfer process.

The obtained value for Tafel slope ($+0.169 \text{ V}$) is close to the theoretical one, $+0.118 \text{ V}$ for one-electron charge transfer process and the anodic charge transfer coefficient α is close to 0.5. A high value of exchange current density is determined (1.88 A m^{-2}), that is characteristic for fast charge transfer processes. In these circumstances, it can appreciate that the rate determining step for the formation of atomic oxygen is the charge transfer process leading to the formation of HO radical adsorbed on electrode surface, according to the Eq.(8) [9]:



Similarly, for the direct oxidation of sulphite, the rate determining step is the charge transfer given by Eq.(9).



Taking into account that on the electrode, in the potential range of SO_3^{2-} oxidation to SO_4^{2-} , two parallel processes occur, the values determined for α and i_0 are just apparent.

Chronoamperometric studies

Chrono-electrochemical measurements had, as a starting point the linear voltammograms shown in Figure 4. For the analysis of these curves, six potential steps were chosen (0.40, 0.45, 0.50, 0.55, 0.60 and 0.65 V) to highlight the anodic processes that occur at electrode/electrolyte interface. From these values, the first four ones correspond to the sulphite oxidation plateau in alkaline solutions and the last two (0.60 V and 0.65 V) is assigned to the OER.

In Figure 6(a) the results for sulphite oxidation during 60 minutes on working electrode in alkaline solutions with different sulphite ions concentrations at $+0.55 \text{ V}$ are presented.

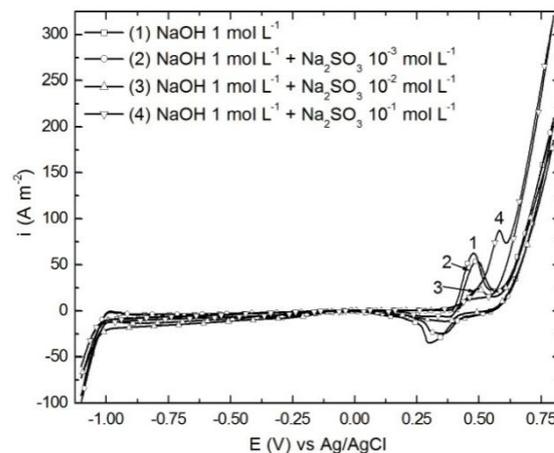


Figure 3. Cyclic voltammograms recorded on Ni–Pt NPs electrode in 1 mol L^{-1} NaOH solution without and with different sulphite concentrations, at 5 mV s^{-1} .

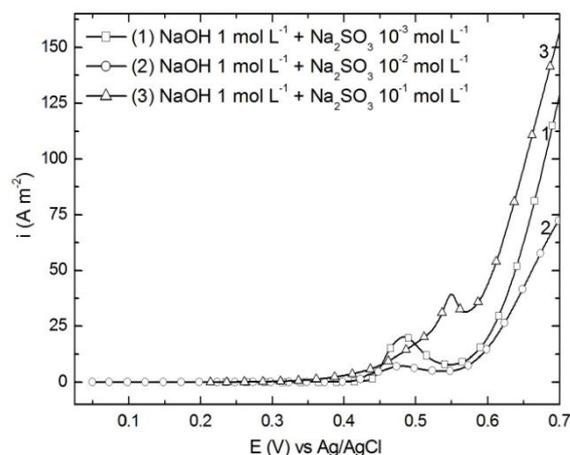


Figure 4. Linear voltammograms recorded on Ni–Pt NPs electrode in 1 mol L^{-1} NaOH solution with different sulphite concentrations, at 1 mV s^{-1} .

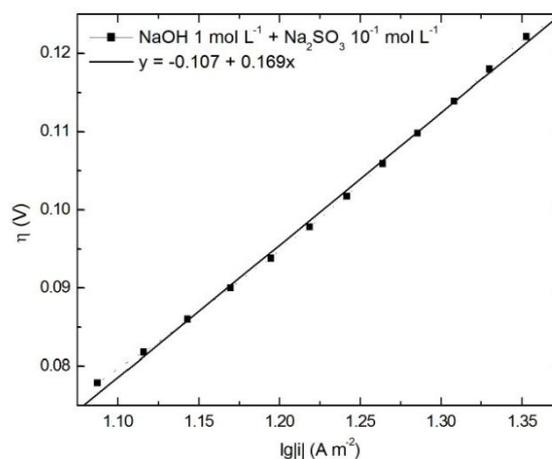


Figure 5. Tafel plot for sulphite oxidation on Ni–Pt NPs electrode in alkaline solution with $10^{-1} \text{ mol L}^{-1}$ sodium sulphite.

In Figure 6(b), the variation of current density in time registered on Ni–Pt NPs electrode in 1 mol L⁻¹ NaOH solution with 10⁻¹ mol L⁻¹ Na₂SO₃ is presented, for all six values of potential at which the experiments have been carried out.

Based on chronoamperometric data we can conclude the following aspects:

- potential range characteristic for SO₃²⁻ oxidation process in alkaline solution is independent of sulphite concentration added in electrolyte, it being placed between 0.40÷ 0.55 V;
- at more positive values of potential, SO₃²⁻ oxidation and OER occur simultaneously on the electrode/electrolyte interface, this fact being demonstrated by the shape of current-time curve recorded at E_{ox} = +0.65 V;
- current densities recorded for all test solutions intensify with the increasing of sulphite concentration added in electrolyte.

Correlating these values with cyclic and linear voltammetric data, we can conclude that the amount of sulphite added in alkaline electrolyte stimulates the first stage of OER, emphasized by the shift of characteristic potential to more negative values.

Chronocoulometric studies

Simultaneously with chronoamperometric studies, the amount of electricity consumed for electrooxidation of sulphite ions in the characteristic potential range for each test solution were measured by chronocoulometric technique.

Based on the shape of chronoamperometric curves 5 and 6 depicted in Figure 6(b), we can affirm that OER is carried out on working electrode at E_{ox} = +0.60 V and it is intensely carried out at E_{ox} = +0.65 V.

Sulphite transformation degree during anodic oxidation as a function of time and

sulphite ions concentration added in electrolyte, when the electrochemical process is conducted at +0.55 V potential value, is shown in Figure 7(a). The highest values of the transformation degree were obtained for the alkaline solution containing the lowest concentration of sulphite (10⁻³ mol L⁻¹) added to electrolyte.

Based on chronocoulometric data, the assessment of a number of sulphite moles changed in the anodic reaction (δ) and electrochemical transformation degree (r) of sulphite to sulphate was possible by applying Faraday's laws [14]. The results are presented in Figure 7(b) versus time and potential values for 10⁻¹ mol L⁻¹ sulphite ions added in alkaline solution.

Chronopotentiometric studies

Chronopotentiometric measurements at zero current were performed on Ni–Pt NPs electrode in alkaline solutions in presence of all Na₂SO₃ concentrations used in test solutions before and after electrochemical sulphite oxidation at maximum potential value (E_{ox} = +0.55 V) for 30 minutes. The aim of these studies was to follow the variation of OCP in time. In Figure 8, the curves obtained for all sulphite concentrations added in alkaline solution are presented. Analysis of the graphical results shows that E_{OCP} recorded before and after oxidation has approximately same values, meaning that a sufficiently high concentration of sulphite ions was provided in the test solutions, so that the processes occurring at the electrode/electrolyte interface have been emphasized.

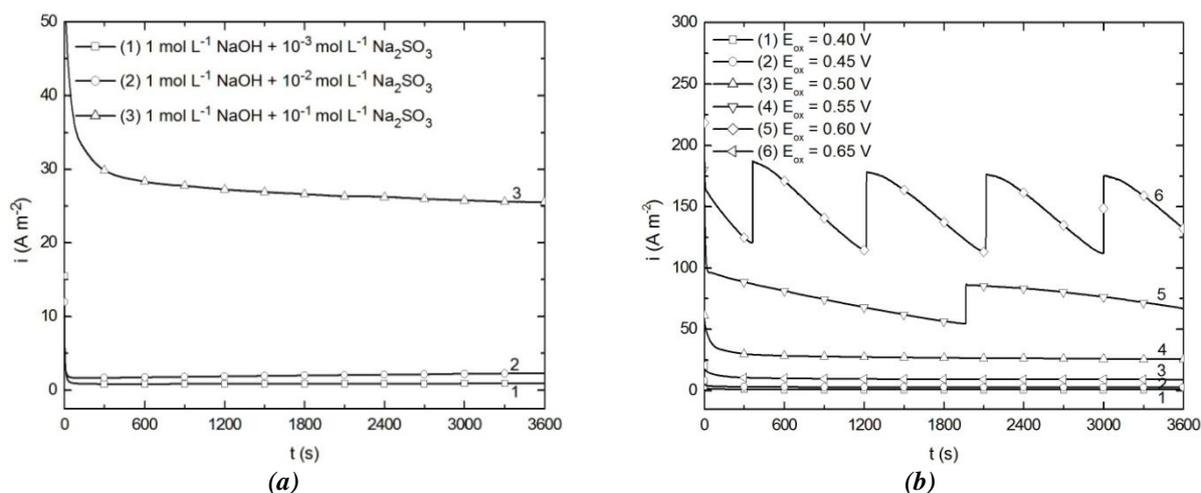
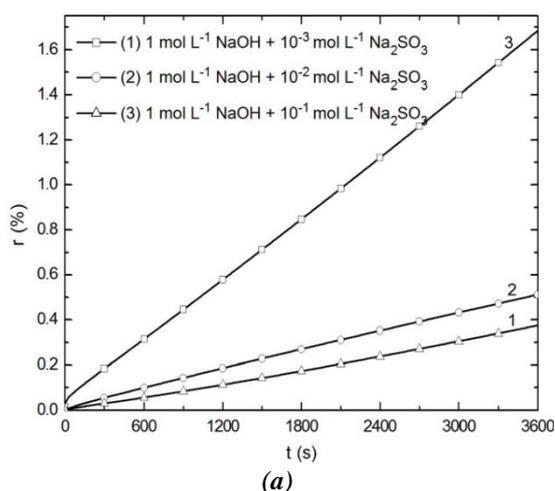


Figure 6. Current-time curves for Ni – Pt NPs electrode in 1 mol L⁻¹ NaOH solution with different sulphite concentrations, at E_{ox} = +0.55 V (a) and in 1 mol L⁻¹ NaOH + 10⁻¹ mol L⁻¹ Na₂SO₃ solution (b).

The potential-time curves shape drawn by chronopotentiometric measurements show a pronounced decrease of E_{OCP} value in first 600 s for 10^{-3} and 10^{-2} mol L $^{-1}$ sulphite ions, respectively 1200 s for 10^{-1} mol L $^{-1}$, mainly caused by sulphite ions deficiency at a proximity of the interface. While the solution is homogenized by sulphite ions migration/diffusion from the bulk of the solution to the electrode, the value stabilizes. The potential value stabilizes very close to the initial one as much as sulphite ions from the solution reach by diffusion or migration in the solution around the electrode where a shortage exists, so that their concentration homogenizes.

Electrochemical impedance spectroscopy studies

Based on cyclic and linear voltammograms, confirmed by chronoamperometric data, electrochemical impedance spectra were recorded on Ni-Pt NPs electrode at specific oxidation potential values for each sulphite ions added in test solutions.



For 10^{-3} and 10^{-2} mol L $^{-1}$ Na $_2$ SO $_3$, impedance measurements are conducted at 0.45, 0.50 and 0.55 V. When sulphite concentration increases to 10^{-1} mol L $^{-1}$, 0.40 V potential value has been included for EIS test, because the potential range specific for this concentration is wider. The recorded results are presented in the Nyquist complex plane representation in Figure 9.

AC impedance measurements were performed with amplitude of 10 mV over the frequency range of 100 kHz–10 mHz.

The Nyquist plots consist of one semicircle which confirms that the sulphite oxidation process is controlled by one charge transfer step. The experimental impedance data were fitted to the electrical equivalent circuit (EEC) presented in Figure 10, using a complex non-linear least squares (CNLS) procedure. The EEC consists in a solution resistance R_s which represents the uncompensated solution resistance, bound in series with a parallel connection between a charge transfer resistance R_{ct} and a constant phase element (CPE).

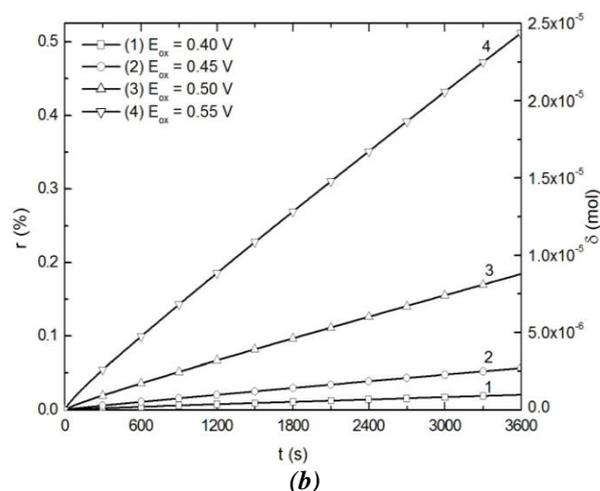


Figure 7. Chronocoulometric curves for Ni-Pt NPs electrode in 1 mol L $^{-1}$ NaOH solution with different sulphite concentrations, at $E_{ox}=+0.55$ V (a) and in 1 mol L $^{-1}$ NaOH + 10^{-1} mol L $^{-1}$ Na $_2$ SO $_3$ solution (b).

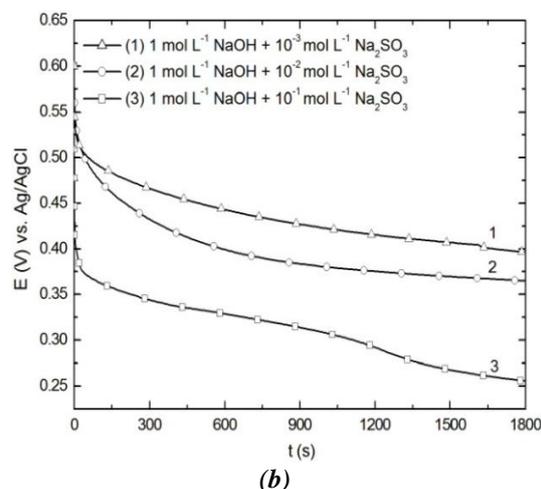
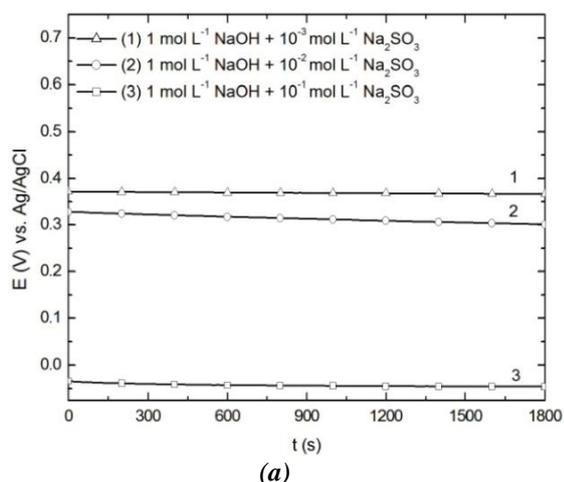


Figure 8. OCP curves for Ni-Pt NPs electrode in 1 mol L $^{-1}$ NaOH solution with different sulphite concentration before (a) and after (b) oxidation.

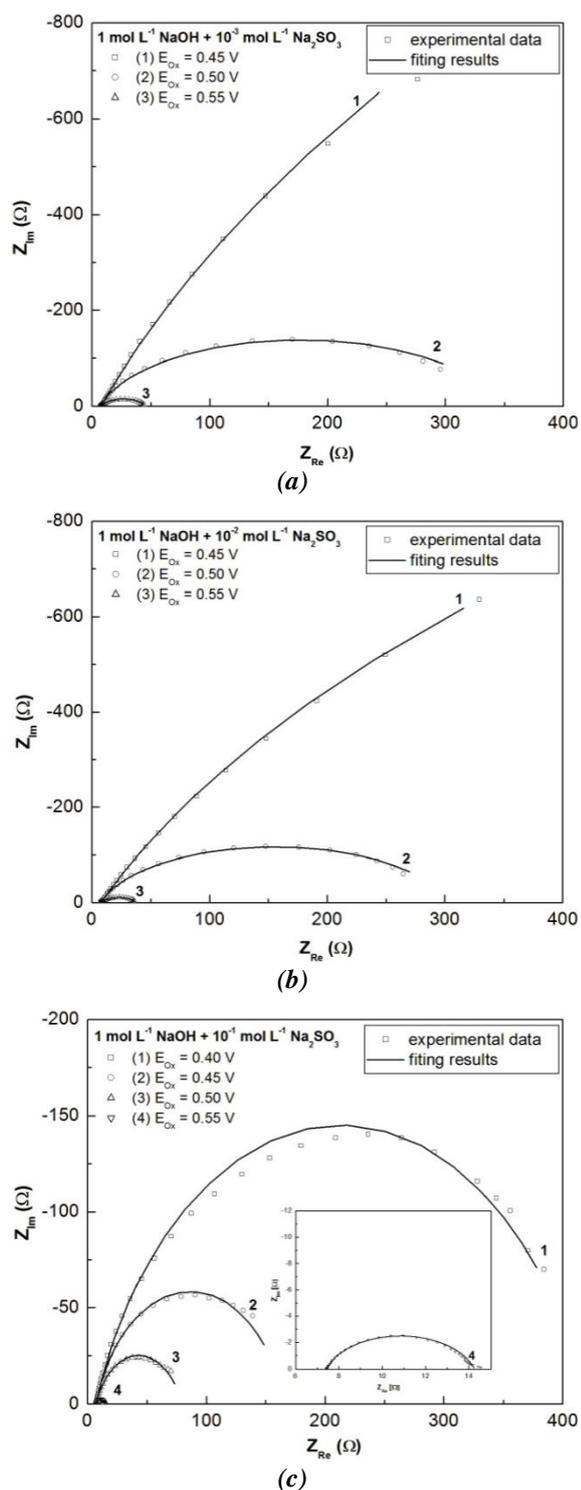


Figure 9. EIS spectra (Nyquist plots) for sulphite oxidation on Ni-Pt NPs electrode in 1 mol L⁻¹ NaOH solution with: 10⁻³ (a), 10⁻² (b) and 10⁻¹ mol L⁻¹ (c) at different potential values.

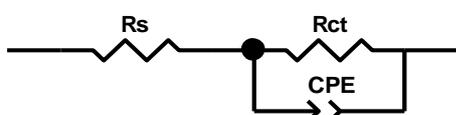


Figure 10. Equivalent electrical circuit for modeling sulphite oxidation on Ni-Pt NPs electrode in alkaline media.

In the real electrochemical systems, CPE element characterized more precisely double layer capacity (C_{dl}) thus replacing the ideal capacitor (C). The obtained fitting results are shown as continuous line in graphical EIS data and the corresponding values of EEC elements are shown in Table 2. Analyzing the results from Table 2, it can be observed that R_{ct} values significantly decrease with the increase of both potential and sulphite concentration, indicating that the sulphite electrooxidation takes place with higher rate, confirming voltammetric data. Also, the values for double layer capacity (C_{dl}) have been calculated. As expected, the double layer capacity increases with the polarization increasing. As well, the accumulation of a larger amount of sulphite in solution near the electrode increases the double layer capacity.

Conclusions

Studied electrodes, obtained by spray-pyrolysis technique, contain a small amount of platinum deposited as nano layers on nickel, and consequently have a considerable reduced costs. The catalytic effect of the new electrodes has been studied for sulphite oxidation in alkaline solution using various electrochemical methods: cyclic and linear voltammetry, chronoamperometry and electrochemical impedance scanning results obtained being encouraging.

Although the electrooxidation of sulphite is a complex process whose mechanism can be considered complicated, by specified electrochemical methods the characteristic range of optimal potential, for each sulphite concentration added in the alkaline electrolyte solution, has been identified and current densities specific for sulphite oxidation and the transformation degrees depending on the electrolysis time have been determined. As well, kinetic parameters (α and i_0) have been computed, showing that the overall process is controlled by the charge transfer step. It was confirmed by EIS studies, based on which charge transfer resistance (R_{ct}) and double-layer capacity (C_{dl}) were calculated for different potential values of the chosen range and for each sulphite concentration used in the experimental tests. The significant value of exchange current i_0 (1.88 A m⁻²) emphasizes an important catalytic effect of the electrode achieved for sulphite oxidation.

Studied electrodes, based on platinum nanoparticles layers supported on smooth nickel, can be used as prospective anodic material for sulphite electrochemical oxidation, especially in a new SO₃²⁻/O₂ alkaline fuel cell.

Table 2

Calculated values of the circuit elements for modeling sulphite oxidation.

Na_2SO_3 conc. ($mol L^{-1}$)	E (V)	R_s (Ωcm^2)	$T \cdot 10^5$ ($F cm^{-2} s^{n-1}$)	n	R_{ct} (Ωcm^2)	$C_{dl} \cdot 10^5$ ($F cm^{-2}$)	Chi^2 10^3
10^{-3}	0.45	7.57 (0.32 %)	8.15 (0.45 %)	0.85 (0.27 %)	5800 (3.71 %)	7.17	12.3
	0.50	7.56 (0.28 %)	12.5 (0.50 %)	0.86 (0.27 %)	338 (0.92 %)	7.46	7.37
	0.55	7.59 (0.15 %)	18.8 (0.67 %)	0.87 (0.28 %)	37.6 (0.32 %)	9.11	2.20
10^{-2}	0.45	7.56 (0.19 %)	12.0 (0.37 %)	0.82 (0.16 %)	3640 (2.30 %)	10.0	3.23
	0.50	7.56 (0.16 %)	20.5 (0.31 %)	0.85 (0.17 %)	295 (0.50 %)	12.5	2.16
	0.55	7.91 (0.11 %)	51.9 (0.64 %)	0.87 (0.24 %)	29.4 (0.24 %)	28.5	1.23
10^{-1}	0.40	7.16 (0.77 %)	35.4 (2.33 %)	0.78 (0.54 %)	412 (1.48 %)	20.6	4.81
	0.45	7.28 (0.45 %)	42.0 (1.96 %)	0.81 (0.43 %)	158 (0.01 %)	22.2	2.25
	0.50	7.26 (0.40 %)	63.3 (2.28 %)	0.86 (0.52 %)	71.5 (0.91 %)	38.2	2.13
	0.55	7.42 (0.13 %)	96.4 (2.28 %)	0.88 (0.64 %)	6.85 (0.44 %)	49.6	1.86

Acknowledgment

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

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