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Anodic Oxidation of Sulphite in Alkaline Solutions on Skeletal Nickel Electrode

II. Chrono – Amperometric, Potentiometric, Coulometric and Electrochemical Impedance Studies

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Abstract: In this paper, anodic oxidation of sulphite ions on skeletal nickel electrode in aqueous alkaline solution was investigated in order to find the relationship between the sulphite concentration added in solution, oxidation potential, current density and oxiditation efficiency. Both for a complete characterization of sulphite oxidation on skeletal nickel electrode in alkaline medium, and to demonstrate that in the chosen potential range only the studied process occurs, electrochemical impedance spectroscopy has been performed.

Keywords: skeletal nickel, sulphite anodic oxidation, chronoamperometry, chronopotentiometry, chronocoulometry, electrochemical impedance spectroscopy.

1. Introduction

A fuel cell is a device that converts the chemical energy from a fuel into electricity through a chemical reaction with oxygen or another oxidizing agent [1].

The electrolyte is essential for a fuel cell to work properly the electrochemical oxidation of sulphite ions has been topic of great relevance in relation to possible use of SO_3^{2-} as an alkaline electrolyte in fuel cells [2]. Anodic oxidation of sulphite ions can lead to a variety of products: elemental sulfur, polysulfide, thiosulphates and sulphates.

Electrochemical oxidation of sulphite catalyzed by copper ion, using potential step chronoamperometry and potentiometry has been studied for the fist time by A. Katagiri et al [3].

Nickel, his alloys and nickel oxide are good electrocatalysts for oxygen evolution in alkaline media due to their relatively low overvoltage, high corrosion stability and reasonable cost price [4-6]. Also, nickel is frequently used as a reference anode material for comparison with new electrode materials for oxygen evolution reaction (OER) in alkaline solutions [4]. Sulphite electrochemical oxidation and OER are very sensitive to the nature and structure of the anodic materials [5].

Skeletal nickel electrode (SNE) as catalyst for anodic reaction was first introduced in 1924 and due to its geometry and porous structure it can play a double role: as electrode and electrocatalys. Consequently, SNE is suitable as anode in fuel cells [7].

The aim of this work is the study of the electrochemical oxidation process of sulphite ions in alkaline media on skeletal nickel electrode using chronoamperometry, chronopotentiometry, chronocoulometry and electrochemical impedance spectroscopy. Further, efficiency of the oxidation process as a function of the electrode potential and sulphite concentrations added in test solution has been determined.

2. Experimental

Electrochemical tests were performed at room temperature using a SP-150 potentiostat/galvanostat (Bio-Logic, SAS, France). A typical glass cell was equipped with three electrodes: working electrodes consisting of skeletal nickel samples, Ag/AgCl reference electrode and two graphite rods used as counter electrodes. For performed experiments, the exposed surface of working electrode was 0.8 cm^2.

The sulphite oxidation efficiency was determined using specific methods: chronoamperometry, chonopotentiometry and chronocoulometry.

Electrochemical impedance spectroscopy (EIS) measurements were carried out 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.

During all electrochemical studies 1 mol L^{-1} NaOH solution has been used as supporting electrolyte. Concentrations of sulphite added in the supporting electrolyte were: 10^{-3}, 10^{-2} si 10^{-1} mol L^{-1}. All reactives used: NaOH and Na_2SO_3 where Sigma-Aldrich pro analysis quality.

3. Results and Disscusion

3.1. Linear voltammetry studies

From voltametric studies already published [8], it was revealed that at the interface of skeletal nickel - alkaline solution, in the presence of sulphite, the anodic processes which occur are oxidation of sulphite ions to sulphate and anodic oxygen evolution (OER), described by equations (1) and (2):

$$SO_3^{2-} + 2HO^- \rightarrow SO_4^{2-} + 2H_2O + 2e^- \qquad (1)$$

$$4HO^- \rightarrow O_2 + 2H_2O + 4e^- \qquad (2)$$

As well, it can be reminded the metal oxidation processes which take place at the surface of skeletal nickel, but they do not influence significantly the development of the studied process. The reactions are presented as general mechanisms in a previous paper [8].

The initial purpose to determine parameters which characterize the electrochemical oxidation of sulphite on skeletal nickel was to identify the optimum potential at which only the reaction (1) is carried out on the working electrode.

Correlating information obtained by linear and cyclic voltammetry previously presented [8], it was observed that the range +0.50 ÷ + 0.75 V is the optimum domain for chronoamperometric and cronocoulometric determinations. Figure 1 shows linear voltammograms on skeletal nickel electrode plotted on a small polarization rate of 1 mV s^{-1} in 1 mol L^{-1} NaOH solution in which different concentrations of sulphite ions were added.

If the electrode potential is shifted to more positive values that +0.5 V a concomitant development of two anodic processes will carry out. Oxygen evolution on the electrode surface will have a negative effect for electrochemical oxidation of sulphite due to the direct chemical reaction between oxygen molecules formed and sulphite ions into the bulk of solution, according to equation:

$$2\,SO_3^{2-} + O_2 \rightarrow 2\,SO_4^{2-} \qquad (3)$$

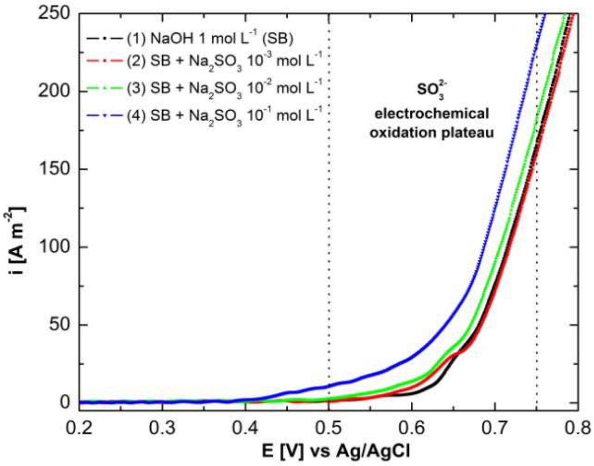
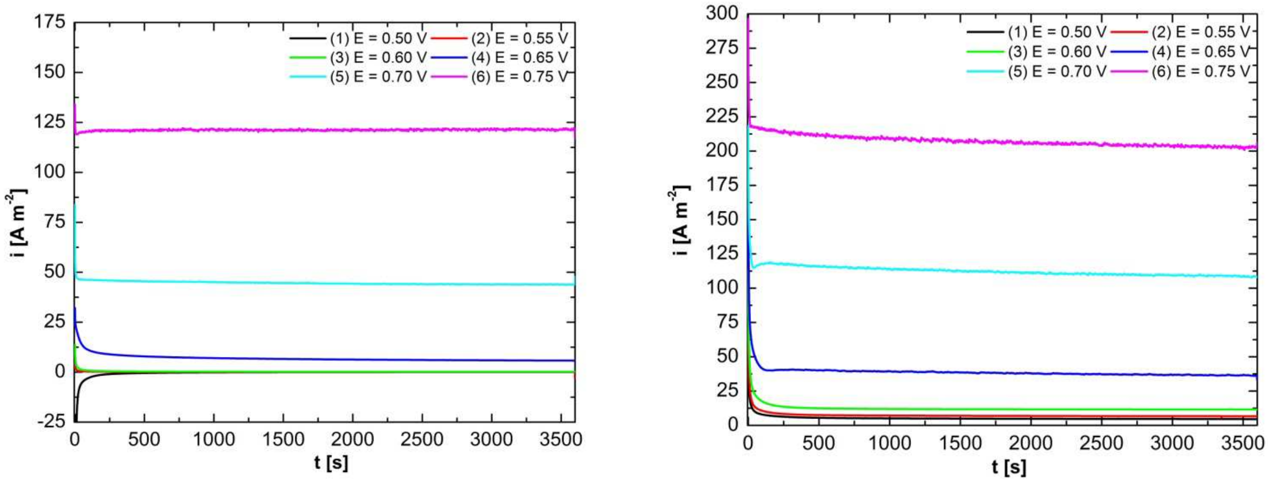


Figure 1. Linear voltamograms recorded on skeletal nickel electrode in 1 mol L^{-1} NaOH wihout/with different concentrations of Na_2SO_3 at 1 mV s^{-1}

3.2. Chronoamperometric and chropotentiometric studies

Chronoamperometric and cronopotentiometric studies had as a starting point the linear voltamograms shown in Figure 1. Analyzing these curves, six potential values corresponding to the sulphite oxidation plateau were chosen in order to carry out the chronoamperometric measurements: 0.50, 0.55, 0.60, 0.65, 0.70 and 0.75 V/Ag/AgCl.

The results are presented in Figures 2 a and b for chronoamperometric measurements in 1 mol L^{-1} NaOH without and with 10^{-1} mol L^{-1} Na_2SO_3.



a) b)

Figure 2. Chronoamperometric measurements on skeletal nickel electrode in 1 mol L^{-1} NaOH without (a) and with 10^{-1} mol L^{-1} Na_2SO_3 solution for electrochemical oxidation at different potential values

Also, the values obtained at four oxidation time-frames (15, 30, 45 and 60 minutes) are shown in Table 1.

Analyzing graphical data, we can conclude the following aspects:

- between +0.50 and +0.70 V/Ag/AgCl the only process that occurs in the system is SO_3^{2-} electrochemical oxidation;

- if chronoamperometric measurements are carried out at +0.75 V/Ag/AgCl, on the skeletal nickel electrode surface unfolds simultaneously both oxidation processes: SO_3^{2-} oxidation and OER; the shape of curve 6 (Figure 2b) indicates that gas evolution reaction occurs and consequently current density increases to about 100 A m^{-2};

- if the concentration of sulphite added in alkaline electrolyte is 10^{-3} mol L^{-1}, electrochemical oxidation process takes place in the range of +0.55 - +0.70 V/Ag/AgCl. At the potential of +0.50 V, only initially is noted the appearance of a low intensity cathodic current due to the cathodic processes on the electrode surface;

- approximately + 0.70 V/Ag /AgCl is the maximum limit of the potential until the only process that takes place on the electrode is the oxidation of sulphite, fact confirmed by electrochemical impedance spectroscopy;

- values of current densities characteristic for studied oxidation process are significantly influenced by both the potential value at which the process is led and the concentration of sulphite in the electrolyte.

- comparing the values of current densities obtained for the four solutions used in experimental studies confirmed that these increase with the increasing of the amount of sulphite added in alkaline electrolyte. Correlating these values with the results obtained in voltametric studies when a shift of characteristic OER potential to negative values was observed, we conclude that the amount of sulphite added in alkaline electrolyte stimulates OER even at low concentrations.

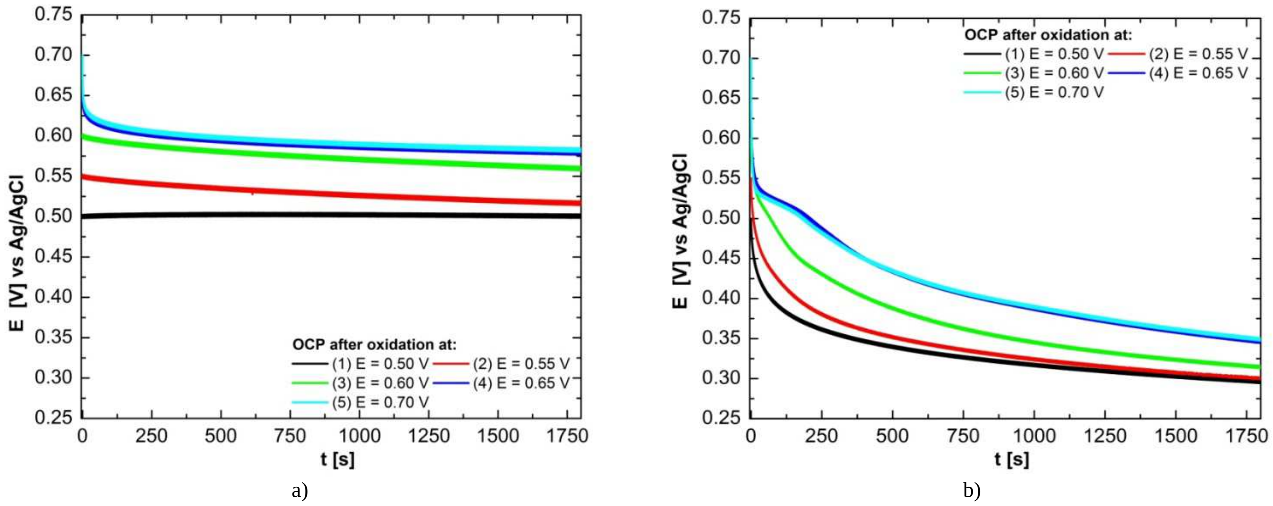
3.3. Chropotentiometric studies

Electrochemical sulphite oxidation process by chronoamperometry was followed by cronopotenţiometry at $I = 0$ A. Chronoamperometric measurements were performed for 60 minutes. In chronopotentiometric measurements a 30 minutes timeframe was chosen. The aim of these studies was to observe the variation of OCP (open circuit potential) values before and after oxidation process. Initial values of OCP were: +0.561, +0.555, +0.515 and +0.276 V/Ag/AgCl for following SO_3^{2-} concentrations added in alkaline solution: 0, 10^{-3}, 10^{-2} and 10^{-1} mol L^{-1}.

Figure 3 presents cronopotentiometric data recorded after carrying out the oxygen evolution process (Figure 3a), respectively electrochemical oxidation of sulphite (Figure 3b) on skeletal nickel electrode in alkaline electrolyte without and with the highest amount of SO_3^{2-} ions.

TABLE 1. Chronoampetrometric measurements on skeletal nickel electrode in 1 mol L^{-1} NaOH solution without and with different Na_2SO_3 concentrations

E [V]	NaOH 1 mol L^{-1} (SB)				SB + SO_3^{2-} 10^{-3} mol L^{-1}				SB + SO_3^{2-} 10^{-2} mol L^{-1}				SB + SO_3^{2-} 10^{-1} mol L^{-1}			
	Oxidation time [min]															
	15	30	45	60	15	30	45	60	15	30	45	60	15	30	45	60
0.50	-0.19	-0.05	0.00	0.02	-0.20	-0.04	0.00	0.02	0.37	0.33	0.37	0.41	5.11	4.79	4.67	4.53
0.55	0.09	0.08	0.08	0.07	0.11	0.10	0.09	0.09	0.61	0.57	0.52	0.50	7.14	6.89	6.72	6.65
0.60	0.24	0.19	0.17	0.16	0.33	0.25	0.23	0.21	1.62	1.40	1.29	1.26	12.0	11.7	11.6	11.6
0.65	7.13	6.38	6.00	5.75	10.2	9.11	8.57	8.26	26.4	24.3	22.8	21.5	39.5	38.0	37.0	36.3
0.70	45.3	44.3	44.0	43.9	52.5	51.9	51.8	51.7	85.9	83.7	82.1	80.8	114	111	109	108
0.75	121	120	121	122	132	132	132	132	169	167	165	165	209	207	204	203



a) b)

Figure 3. Chronopotentiometric measurements on skeletal nickel electrode in 1 mol L^{-1} NaOH without (a) and with 10^{-1} mol L^{-1} Na_2SO_3 solution after electrochemical oxidation at different potential values

From the analysis of diagrams presented in Figure 3 it is observed that after the oxidation step, the value electrode potential does not change significantly in electrolyte solution without Na_2SO_3. The form of the curves from Figure 3b is explained by the fact that near the electrode sulphite ions concetration decreases due to their oxidation, the values of potential being initialy (in the first moments of determination) close to those of Figure 3a, then it decreases to baseline OCP due to the homogenization of the solution by migration of sulphite ions from the bulk of solution to the interface.

Simultaneously with chronoamperometric measurements, chronocoulometric data were recorded in skeletal nickel/1 mol L^{-1} NaOH + Na_2SO_3 system, measuring accurately the consumed electricity amount in anodic sulphite oxidation between +0.50 V and +0.70 V/Ag/AgCl potential values, when the only process occurring in system is SO_3^{2-} oxidation.

Based on these results, using Faraday's laws, it has been possible to evaluate the sulfate ions number of moles changed into the anodic reaction (δ) and sulphite electrochemical oxidation process efficiency.

Figure 4 presents the variation of the sulphite moles number oxidized and efficiency of sulphite oxidation process to sulphate versus time and potential for the case in which in alkaline electrolyte was added 10^{-1} mol L^{-1} sodium sulphite, the maximum concentration used in experimental studies.

Figure 5 presents the variation of the anodic oxidation efficiency of sulphite in alkaline medium by time and concentration of sulphite ions added, when the electrochemical process has led at a potential of 0.65V/Ag /AgCl. Maximum values of efficiency for the oxidation process were obtained for the solution with the lowest concentration of sulphite added to the electrolyte.

It can be observed that the efficiency is significantly influenced by the potential at which anodic oxidation process is driven.

Table 2 shows the values of efficiency for electrochemical oxidation of sulphite in alkaline medium at four values of electrolysis time versus potential and sulphite concentration in electrolyte solution.

3.4. Electrochemical impedance spectroscopy studies

EIS spectra for the skeletal nickel electrode in 1 mol L^{-1} NaOH solution without and with different concentration of SO_3^{2-} successively recorded in direction of the increasing potential are presented in the Nyquist complex plane representation in figures 6-9. Also, was represented Bode plots for each case studied. AC impedance measurements were performed in the range of 0.50 - 0.75 V/Ag/AgCl with an amplitude of 10 mV over the frequency range of 100 kHz–10 mHz.

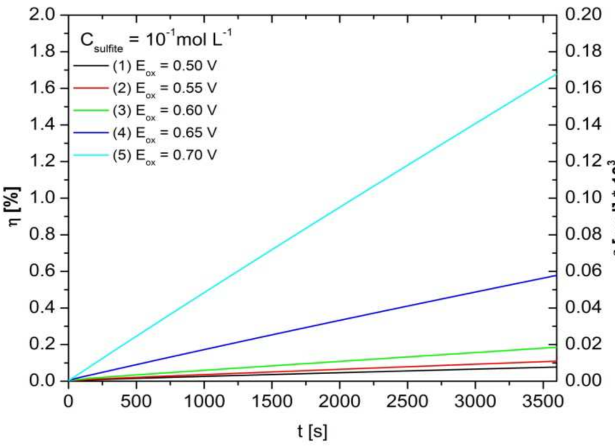


Figure 4. Sulphite anodic oxidation results

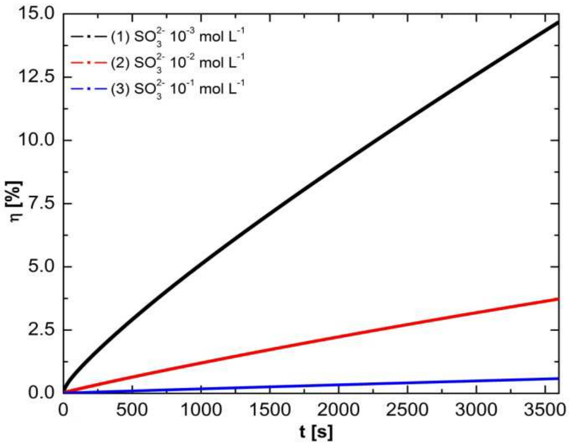
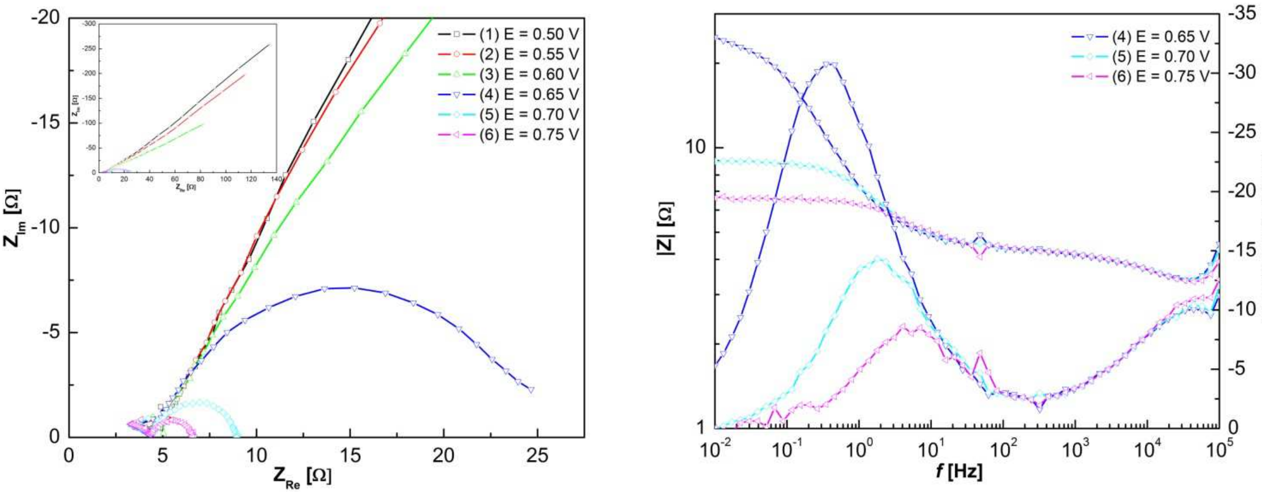


Figure 5. Sulphite electrochemical oxidation process efficiency at E=0.65V/Ag/AgCl

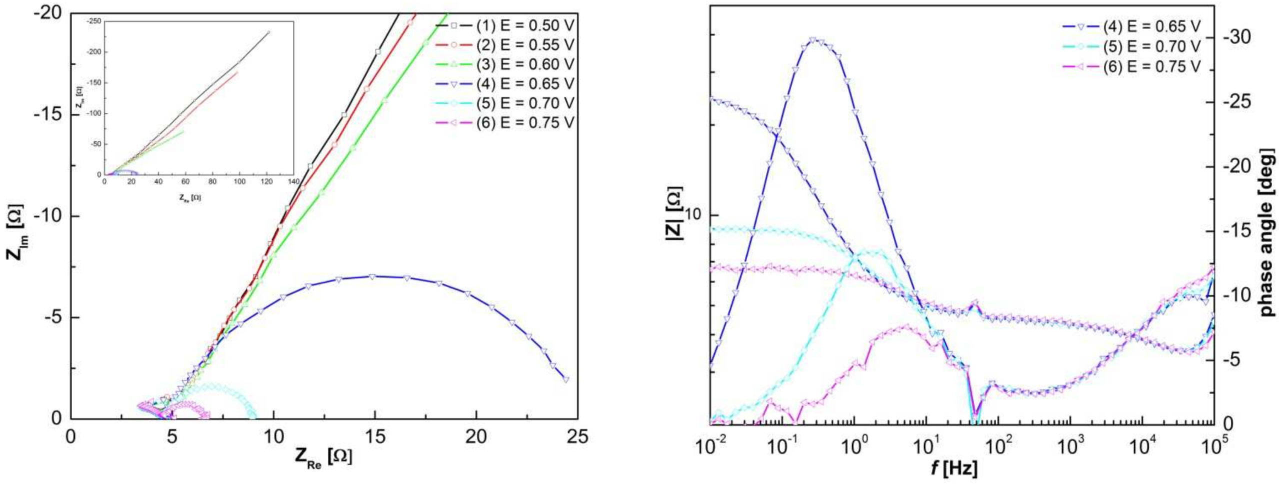
TABLE 2. The sulphite electrochemical oxidation process efficiency in test solutions

E [V]	SB + SO_3^{2-} 10^{-3} mol L^{-1}				SB + SO_3^{2-} 10^{-2} mol L^{-1}				SB + SO_3^{2-} 10^{-1} mol L^{-1}			
	Electrochemical oxidation efficiency [%]											
	15	30	45	60	15	30	45	60	15	30	45	60
0.50	-	-	-	-	0.02	0.03	0.04	0.06	0.02	0.04	0.06	0.08
0.55	0.09	0.13	0.16	0.19	0.04	0.06	0.08	0.10	0.03	0.06	0.08	0.11
0.60	0.30	0.41	0.50	0.58	0.10	0.16	0.21	0.27	0.05	0.10	0.14	0.19
0.65	4.68	8.24	11.5	14.7	1.10	2.03	2.91	3.72	0.16	0.30	0.44	0.58
0.70	19.8	39.4	58.8	78.1	3.33	6.50	9.58	12.6	0.44	0.86	1.27	1.68



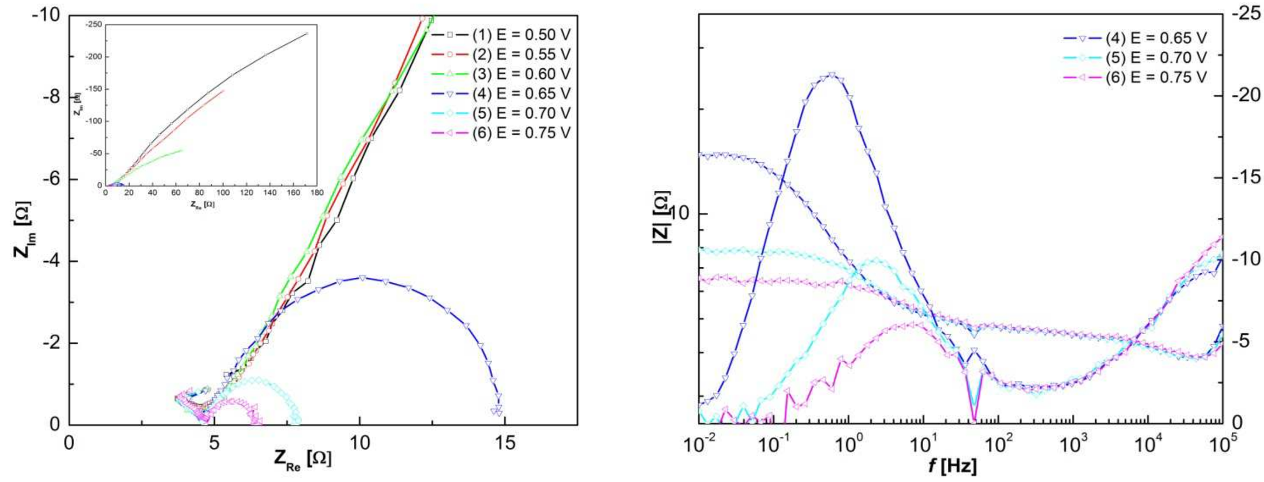
a) b)

Figure 6. Experimental Nyquist (a) and Bode (b) plots recorded for OER on skeletal electrode at different potential in 1 mol L^{-1} NaOH solution



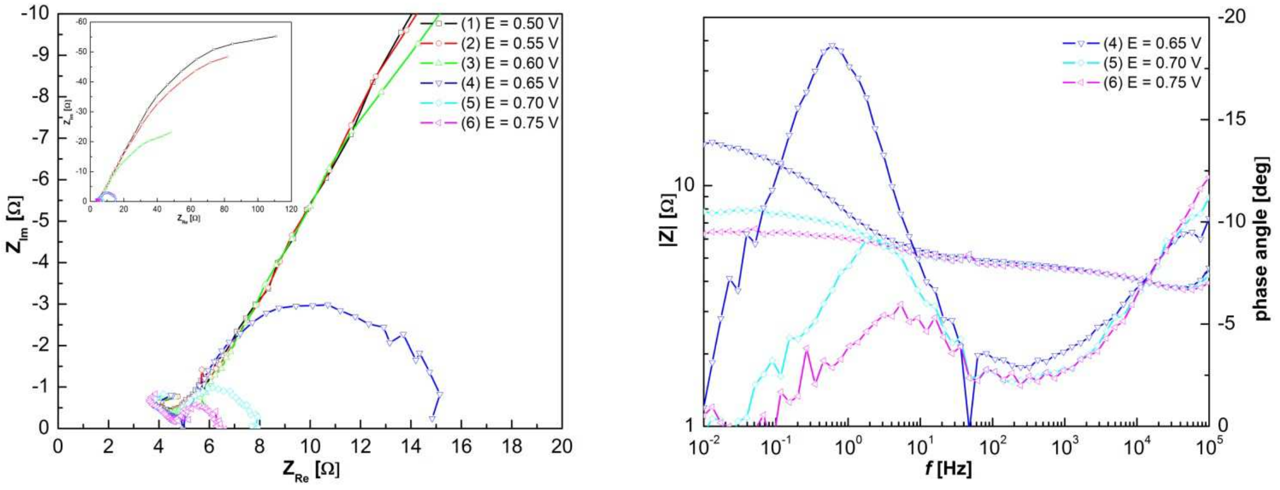
a) b)

Figure 7. Experimental Nyquist (a) and Bode (b) plots recorded for SO_3^{2-} anodic oxidation on skeletal electrode at different potential in 1 mol L^{-1} NaOH with 10^{-3} mol L^{-1} Na_2SO_3 solution



a) b)

Figure 8. Experimental Nyquist (a) and Bode (b) plots recorded for SO_3^{2-} anodic oxidation on skeletal electrode at different potential in 1 mol L^{-1} NaOH with 10^{-2} mol L^{-1} Na_2SO_3 solution



a) b)

Figure 9. Experimental Nyquist (a) and Bode (b) plots recorded for SO_3^{2-} anodic oxidation on skeletal electrode at different potential in 1 mol L^{-1} NaOH with 10^{-1} mol L^{-1} Na_2SO_3 solution

The Nyquist plots consist of two distorted semicircles. The experimental Nyquist and Bode plots for the EIS data, recorded similarly in 1.0 mol L^{-1} NaOH without and with different concentration of Na_2SO_3 at potentials associated with significant SO_3^{2-} oxidation current densities, show a typical shape for oxygen evolution on nickel electrode [4, 9].

Due to graphic shapes of spectra impedance and similarity of sulphite anodic oxidation and OER mechanisms carried on skeletal nickel, the determinating rate of reaction being the electric charge transfer, it is recommended to use the same electrical circuit equivalent shown in Figure 10 for fitting data impedance.

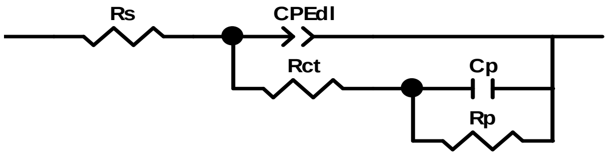


Figure 10. Electrical equivalent circuit used for simulating the impedance spectra of SO_3^{2-} oxidation and OER on skeletal nickel electrode in alkaline media

This model is often called the Armstrong - Henderson equivalent circuit [10] and has been used for characterization of OER in different systems: platinum electrode, cobalt oxide electrodeposited on nickel and platinum electrodes and cobalt and nickel midex oxides on a nickel subtrate, all in 1 mol L^{-1} NaOH solution [4, 9, 11-13].

Analyzing the circuit shown in Figure 10 it can observe two overlapping capacitive loops: one of them required to characterize the interface double-layer capacitance C_{dl}, in parallel with the oxidation process (SO_3^{2-} oxidation or OER) charge transfer resistance R_{ct}, the other one describing C_p and R_p. R_{ct} represent charge transfer resistance of the electrode reaction and it is the only circuit element which describes how fast the rate of charge transfer during the followed oxidation process.

In Figure 11a-c are shown Nyquist diagrams recorded on skeletal nickel in four test solutions at three significant potential values.

From the study of Nyquist diagrams it appears that oxidation of sulphite ions is dependent on both electrode potential and concentration of these ions in alkaline electrolyte. As it was specified above, the determining rate is the charge transfer which means low values of R_{ct} (charge transfer resistance). The value of this parameter is correlated with the size of the second semi-circle from Figure 11 a-c. It can be seen that low values of R_{ct} are achieved for sulphite concentrations over 10^{-2} mol L^{-1} at potential values in the range of 0.65 - 0.70 V/Ag/AgCl.

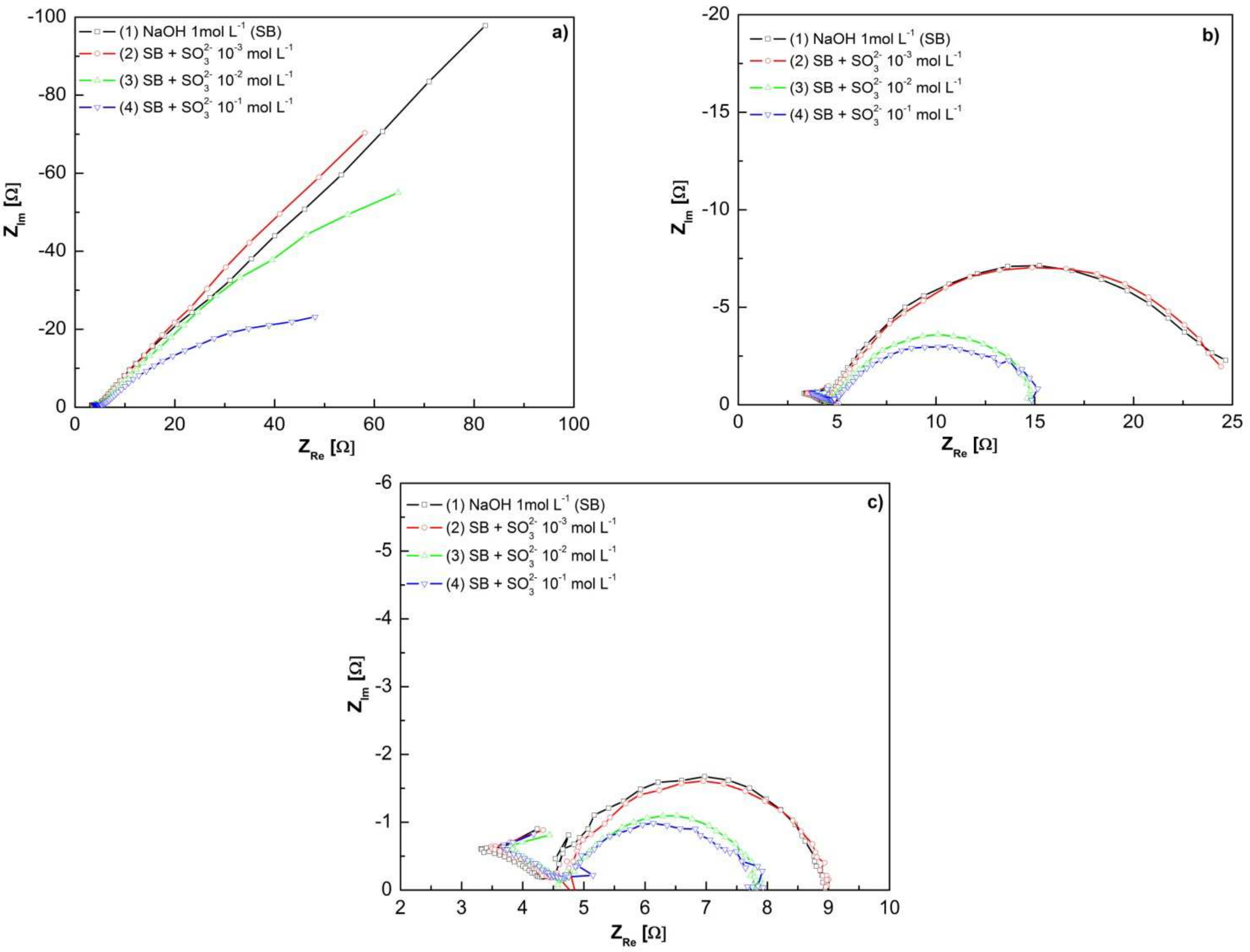


Figure 11. Experimental Nyquist plots recorded for SO_3^{2-} anodic oxidation on skeletal electrode in test solutions at different potential values (E_{ox}): (a) 0.60V, (b) 0.65V and (c) 0.70V/Ag/AgCl

4. Conclusions

The results presented in this paper represents a full characterization of electrochemical oxidation process of sodium sulphite in alkaline media on skeletal nickel electrodes, correlating cyclic and linear voltammetry data, kinetics data of electrode process obtained from Tafel method and EIS with chronoamperometry, cronopotentiometrie and cronocoulometrie data. It has been found that the efficiency of oxidation process depends on the potential value at which this process is conducted and the concentration of sulphite ions in the electrolyte. The optimum potential is +0.65 - 0.70 V/Ag/AgCl for sulphite concentrations higher than 10^{-2} mol L^{-1} added in alkaline media.

At potential values higher than +0.70 V/Ag/AgCl both sulphite ions oxidation and OER take place simultaneously on the electrode, and efficiency of electrochemical oxidation process of sulphite ions will decrease due to their chemical oxidation with oxygen molecules released on the surface of skeletal nickel electrode.

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