New Electrodes Based on Pt-Co Alloys Used as Anodic Materials for Sulphite Oxidation in Alkaline Fuel Cells

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Abstract. In this paper, electrooxidation of sulphite ions on Cu/Pt-Co electrodes in alkaline media (1 mol L^{-1} NaOH) has been investigated in order to establish the mechanism and to determine optimal parameters of the anodic process. Electrochemical behavior of sulphite ions on Cu/Pt-Co electrodes in alkaline solutions has been studied by voltammetric techniques (cyclic and linear), and kinetic parameters (current density i_o and anodic transfer coefficient α) have been determined by Tafel plots method. Furthermore, electrochemical impedance spectroscopy was carried out to confirm the sulphite oxidation mechanism on this type of electrode. Chrono-electrochemical techniques have been applied in order to determine the optimum characteristic parameters: current density, oxidation potential for sulphite electrooxidation and transformation degree of SO_3^{2-} ions in the anodic process at different electrolysis times.

1. Introduction

Among noble metals tested in order to obtain appropriate anodes for both alkaline and acid media, platinum exhibits the highest catalytic activity [1]. Limited resources and high cost of Pt are considered significant impediments for a wide commercialization of fuel cells. Pt-Co alloys represent an attractive challenge in the development of advanced electrocatalysts, which would considerable decrease not only the content of Pt, but would also enhance the catalytic activity and durability [2]. Alloying Pt in the form of nanoparticles with 3d transition metals (Fe, Co, and Ni) has shown much more potential in tailoring the atomic and electronic structures of catalytically active materials than any other approach [3].

Several anodes made of metal oxides, as well as electrodes with modified surface have been used throughout time in order to study the electrochemical oxidation of sulphite ions (SO_3^{2-}) and sulphur dioxide dissolved in water ($SO_{2(aq)}$) [4-6]. Much attention was paid to the oxidation of sulphite and sulphur dioxide on the electrodes based of noble metals (Pt, Au, Pd) due to their high catalytic activity [7-11]. The oxidation rate of tetravalent sulphur compounds was noticed to be strongly dependent on the electrode material nature, electrocatalytic properties of electrode, active electrode surface, state of metal surface and specific potential range for electrooxidation process. For noble metals these effects are related mainly to the influence of adsorbed sulphur species [12, 13] on the kinetics of the electrode process. However, the oxidation rate of sulphur dioxide and sulphite ions might also be influenced by oxidation processes on the surface of noble metals [14, 15].

The general purpose of this study is to obtain an alloy catalyst with increased selectivity and activity, low energy consumption and long lifetime, operable in a SO_3^{2-} / O_2 fuel cell. As well, its aim is to reduce the amount of noble metal by obtaining nanometric particles, thus increasing the active electrodes surface, improving electrochemical reactivity and reducing process costs.

2. Experimental part

Working electrode has been obtained by electrodeposition of Pt-Co on a smooth copper disc with 1.2 cm^2 surface. The electrodeposition of Pt-Co alloy catalyst by the pulsed current plating method was done into an acidic solution, platinum ions coming from K_2PtCl_4 solution and cobalt ions from $CoCl_2 \cdot 6H_2O$ solution. The molar ration between Pt^{2+} and Co^{2+} ions in electrolyte solution was 1:20. 1 M KCl and 0.5 M H_3BO_3 were added into solution in order to achieve optimum conductivity and pH stabilization. The pulsed current deposition parameters were t_{on} = 20 ms, t_{off} = 100 ms, i = 250 A m^{-2} and 20000 cycles. These are the optimum values in order to obtain Pt-Co alloy catalyst particles with size distribution in the nanometric range on copper support.

For sulphite anodic oxidation in alkaline media, a three-electrode undivided cell connected to SP 150 BioLogic potentiostat/galvanostat was used during all measurements. Pt-Co alloys prepared catalysts were used as working electrode with 0.8 cm^2 active surface. Also, two graphite roads - counter electrodes and Ag/AgCl - reference electrode, equipped the electrolysis cell. A nitrogen purging system was used to de-aerate the solution before each electrochemical measurement.

Electrochemical experiments were carried out in 1 mol L^{-1} NaOH solution in the absence and presence of different sulphite concentrations (10^{-3}, 10^{-2}, 10^{-1}, $5 \cdot 10^{-1}$ and 1 mol L^{-1}). Reagents NaOH and Na_2SO_3 (p.a., $\geq$ 98%, Merck) were used in order to prepare the test solutions.

Cyclic voltammograms have been recorded at different scan rates, between 5 - 500 mV s^{-1} and linear polarization at low scan rate (1 mV s^{-1}) in order to ensure quasi-stationary conditions.

Electrochemical impedance spectroscopy (EIS) studies were performed using the SP-150 impedance module, in frequency range 0.1 Hz - 100 kHz and alternative 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 have been fitted to the electrical equivalent circuits (EECs) by CNLS Levenberg – Marquardt method using ZView – Scribner Associates Inc. software.

Chronoamperometry, chronocoulometry and chronopotentiometry methods were applied in order to determine the sulphite electrooxidation process parameters as: current density, potential range, and transformation degree, at five oxidation potential values.

3. Results and discussion

3.1. Cyclic voltammetry. Cyclic voltamograms (CVs) have been recorded in alkaline solution in order to identify the processes occurring at the Pt-Co alloys electrode/alkaline electrolyte interface.

In Figure 1 the CVs registered for three types of electrodes (Pt, Cu, Cu/Pt-Co) in presence of 10^{-1} mol L^{-1} sulphite are shown. On the curves drawn for the electrodes containing copper (Cu and Cu/Pt-Co), the appearance of a pick can be observed at approximately -0.25 $\div$ +0.25 V corresponding to the copper oxidation process. At advanced anodic polarization, on the three electrodes the peak specific to sulphite ions oxidation appears at +0.50 $\div$ +0.75 V.

In Figure 2 the CVs ploted on Cu/Pt-Co electrode in alkaline solution with and without sulphite ions are presented. CVs recorded on Pt electrode are represented at a higher resolution than for Cu and Cu/Pt-Co electrodes in order to highlight the electrochemical reactions occuring at electrode/electrolyte interfaces. It can be observed that, at cathodic polarization, the peak assigned to the oxygen reduction reaction is revealed only in the absence of sulphite ions. That means, the oxygen anodically formed has been consumed for sulphite ions oxidation in a chemical reaction.
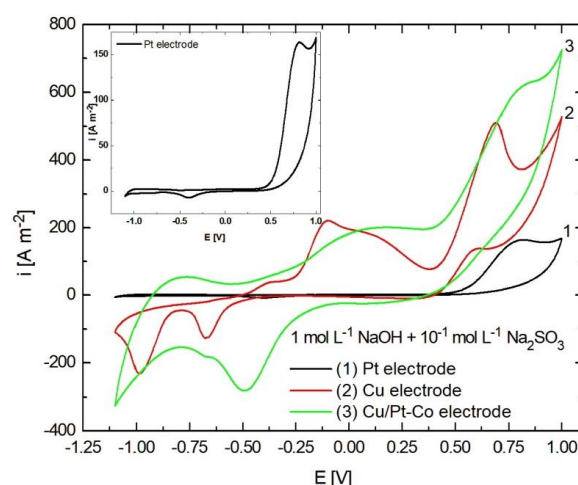
Figure 1. CVs recorded on different electrodes in alkaline solution in presence of 10^{-1} mol L^{-1} Na_2SO_3, scan rate 500 mV s^{-1}.

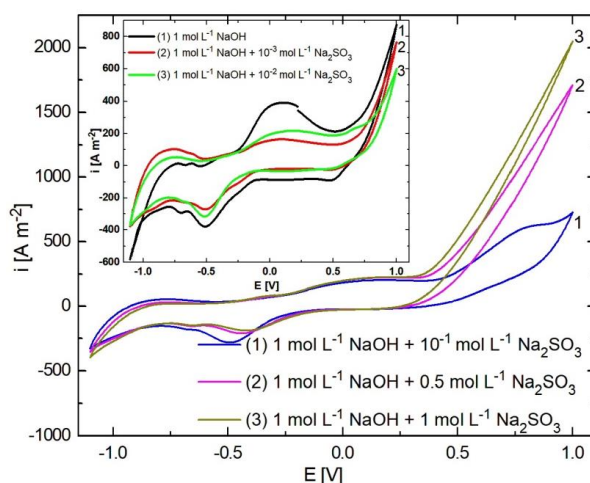At advanced cathodic polarization, it can be seen that only hydrogen evolution reaction (HER) takes place.

Figure 2. CVs recorded on Cu/Pt-Co electrode in alkaline solution with and without Na_2SO_3, scan rate 500 mV s^{-1}.

As well, at anodic polarization, the sulphite oxidation (Eq. 1) occurs simultaneously with atomic oxygen formation (Eq. 2), as it has been shown in previous papers [16-18].

$$SO_3^{2-} + 2HO^- \rightarrow SO_4^{2-} + H_2O + 2e^- \tag{1}$$

$$2HO^- \rightarrow O + H_2O + 2e^- \tag{2}$$

3.2. Linear voltammetry. Linear voltammograms (LVs) have been drawn at low scan rate (1 mV s^{-1}) in order to provide quasi-stationary conditions at the electrode.

In Figure 3 the LVs plotted for 3 different electrodes containing (Pt, Cu, Cu/Pt-Co) in presence of 10^{-1} mol L^{-1} Na_2SO_3 are presented. The electrochemical processes which take place on all 3 electrodes have been highlighted by the occurrence of peaks at different potential values. Thus, a peak at about -0.30 V appears as a result of copper oxidation and at approximately +0.40 V the sulphite oxidation occurs followed by oxygen evolution reaction (OER).
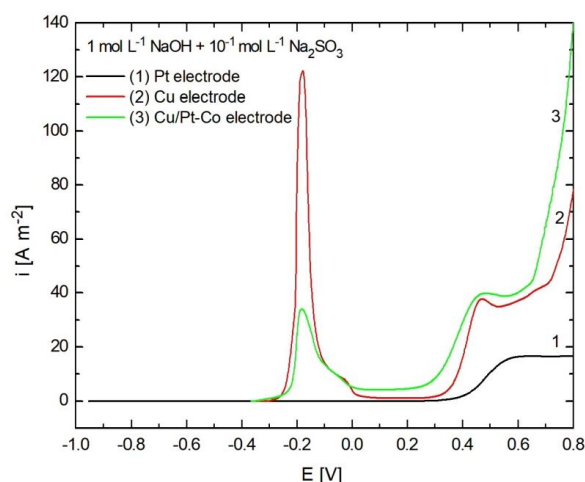
Figure 3. LVs recorded on different electrodes in alkaline solution in presence of 10^{-1} mol L^{-1} Na$_2$SO$_3$, scan rate 1 mV s^{-1}.

Analyzing the LVs recorded in alkaline media in presence of different concentrations of sulphite (Figure 4), it can be seen that sulphite oxidation current increases with the sulphite concentration added in electrolyte. That proves that at the anode a chemical reaction between atomic oxygen and sulphite occurs simultaneously with electrochemical ones. The oxidation current for low concentration of sulphite (10^{-3} and 10^{-2} mol L^{-1}) is almost indistinguishable due to an insignificant amount of SO$_3^{2-}$ ions in the solution at electrode/electrolyte interface.
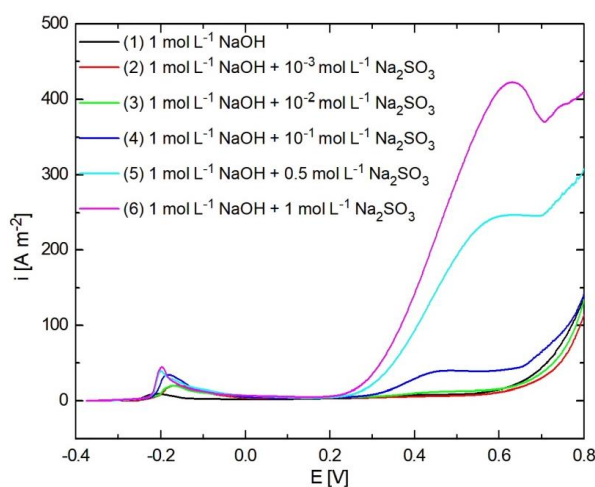

Figure 4. LVs recorded on Cu/Pt-Co in alkaline solution with and without Na$_2$SO$_3$, scan rate 1 mV s^{-1}

In order to determine the kinetic parameters (transfer coefficient α and exchange current density i_o) for anodic oxidation of sulphite Tafel plots method presented in Figure 5 has been applied.

The calculated kinetic parameters are presented in Table 1. Obtained high values of exchange current density are characteristic for fast charge transfer processes. In these circumstances, it can be appreciated that the rate determining step for the atomic oxygen generation (Eq. 2) is controlled by charge transfer step.
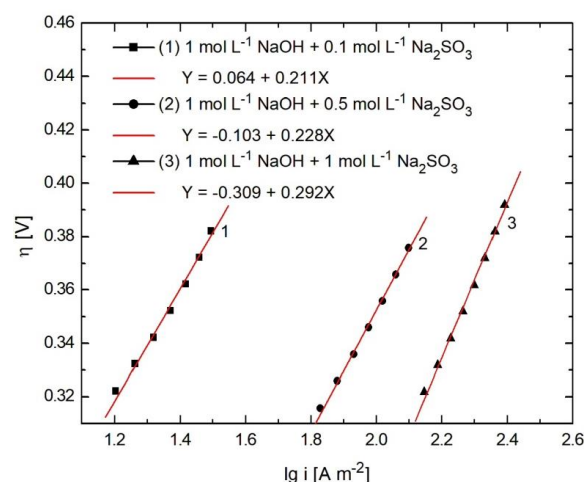
Figure 5. Tafel plots for sulphite oxidation on Cu/Pt-Co electrode in alkaline solution with different concentrations of Na$_2$SO$_3$.

Table 1. Kinetic parameters for sulphite oxidation in alkaline solution.

Na$_2$SO$_3$ conc. (mol L^{-1})	b (mV dec^{-1})	α	i_o (A m^{-2})
0.1	211	0.28	0.74
0.5	228	0.26	1.57
1	292	0.20	2.88

Similarly, for the direct oxidation of sulphite, the rate determining step is the charge transfer given by Eq. (3) [19].

$$SO_{3\,(ads)}^{2-} \rightarrow SO_{3\,(ads)}^{\bullet -} + e^- \tag{3}$$

In case of reduced sulphite concentrations (10^{-3} and 10^{-2} mol L^{-1}), the diffusion of sulphite ions from the bulk of solution to the electrode becomes the determining step.

Taking into account that on the electrode/electrolyte interface, in the potential range of sulphite oxidation, two parallel processes occur (direct sulphite oxidation and atomic oxygen generation), the values determined for α and i_o are just apparent.

3.3. Chronoamperometric studies. Analyzing the LVs from Figure 4, five potential steps were chosen (+0.35, +0.45, +0.55, +0.65 and +0.75 V) to highlight the anodic processes that occur at electrode/electrolyte interface. The first four values correspond to the sulphite direct/indirect oxidation in test solutions and the last one is assigned to OER.

In Figure 5a are presented the chronoamperometric curves, relating to sulphite oxidation, for 60 minutes, on working electrode in alkaline solutions, with different sulphite concentrations, at a potential value of +0.55 V.

In Figure 6b, the variation of current density in time registered on Cu/Pt-Co electrode in alkaline solution containing 1 mol L^{-1} Na$_2$SO$_3$ is presented for all five potential values at which the experiments have been carried out.

Based on chronoamperometric data it can be observed that the characteristic potential range for SO$_3^{2-}$ oxidation in alkaline solution, between +0.35 and +0.65 V, does not depend on the sulphite concentration, but the current density increase with the increasing of sulphite concentration. At more positive potential values, SO$_3^{2-}$ oxidation and OER occur simultaneously.
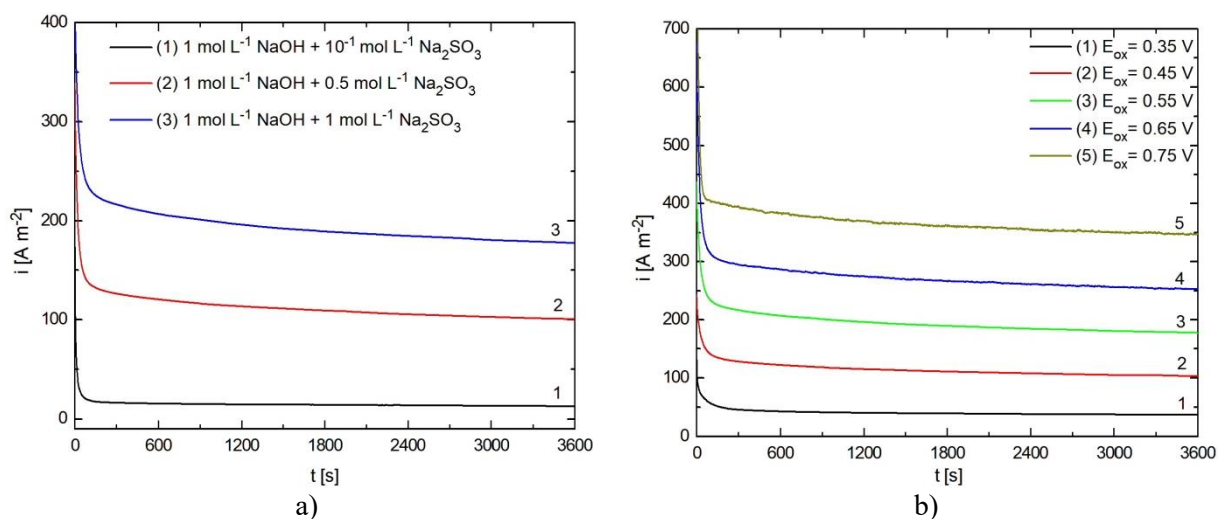
Figure 6. Current-time curves for Pt electrode in 1 mol L^{-1} Na$_2$SO$_4$ solution with different sulphite concentrations at +1 V (a) and in 1 mol L^{-1} Na$_2$SO$_4$ + 1 mol L^{-1} Na$_2$SO$_3$ solution (b).

Correlating these values with cyclic and linear voltammetric data, it can be established that the amount of sulphite added in alkaline solutions stimulates the first stage of OER.

3.4. Chronocoulometric studies. Chronocoulometric technique has been applied in order to determine the amount of electricity consumed for electrooxidation of sulphite ions in the characteristic potential range for each test solution.
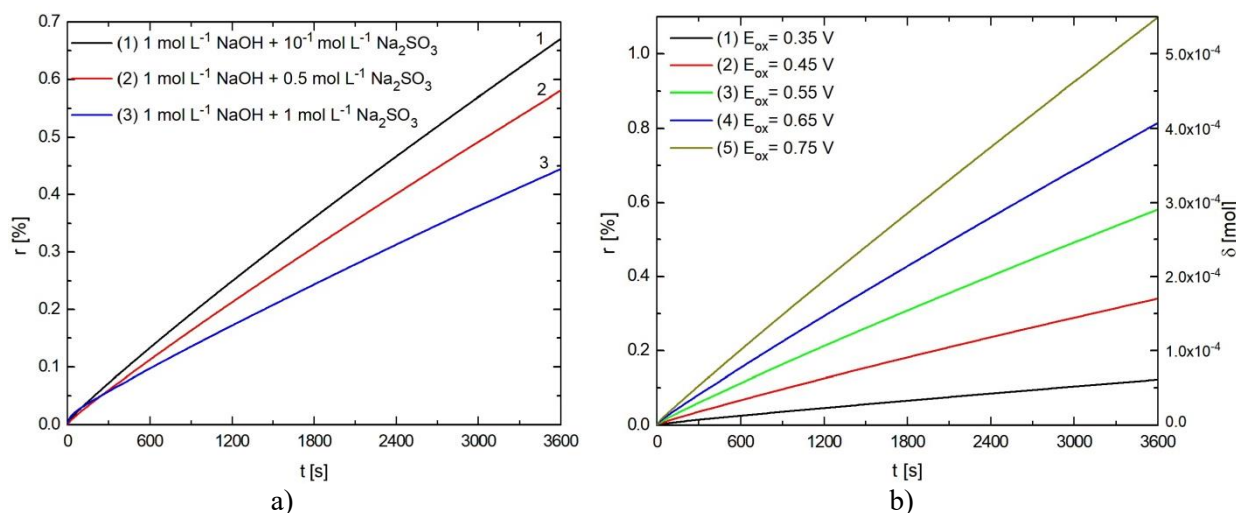

Figure 7. Chronocoulometric curves for sulphite electrooxidation on Cu/Pt-Co electrode in 1 mol L^{-1} Na$_2$SO$_4$ solution with different sulphite concentrations at 1 V (a) and in 1 mol L^{-1} Na$_2$SO$_4$ + 1 mol L^{-1} Na$_2$SO$_3$ solution (b).

Figure 6a presents the sulphite transformation degree during anodic oxidation as a function of time and sulphite concentration, when the electrochemical process is carried out at +0.55 V. Sulphite concentration is inversely proportional to the transformation degree, so the highest value of the transformation degree has been obtained for the test solution containing the lowest concentration of sulphite (0.1 mol L^{-1}).

Based on chronocoulometric data, the evaluation of number of sulphite moles changed in the anodic reaction (δ) and transformation degree (r) of sulphite to sulphate has been possible using Faraday's laws [20]. The results for 1 mol L^{-1} sulphite added in alkaline solution at all five potentials are presented in Figure 6b.

3.5. Electrochemical impedance spectroscopy. Based on cyclic and linear voltammetry confirmed by chronoamperometric data, the non-destructive experimental method electrochemical impedance spectroscopy (EIS) was used to obtain specific information for sulphite oxidation in alkaline media on Cu/Pt-Co electrode. EIS data weere recorded in test solutions with sulphite concentration between 10^{-3} and 1 mol L^{-1} at 4 oxidation potential values in the range +0.35 and + 0.65 V. The obtained results are shown in Nyquist and Bode complex plane representation given in Figure 8 for 0.5 mol L^{-1} Na_2SO_3 added in alkaline solution and Figure 9 for all test solution at same oxidation potential value, +0.45 V.
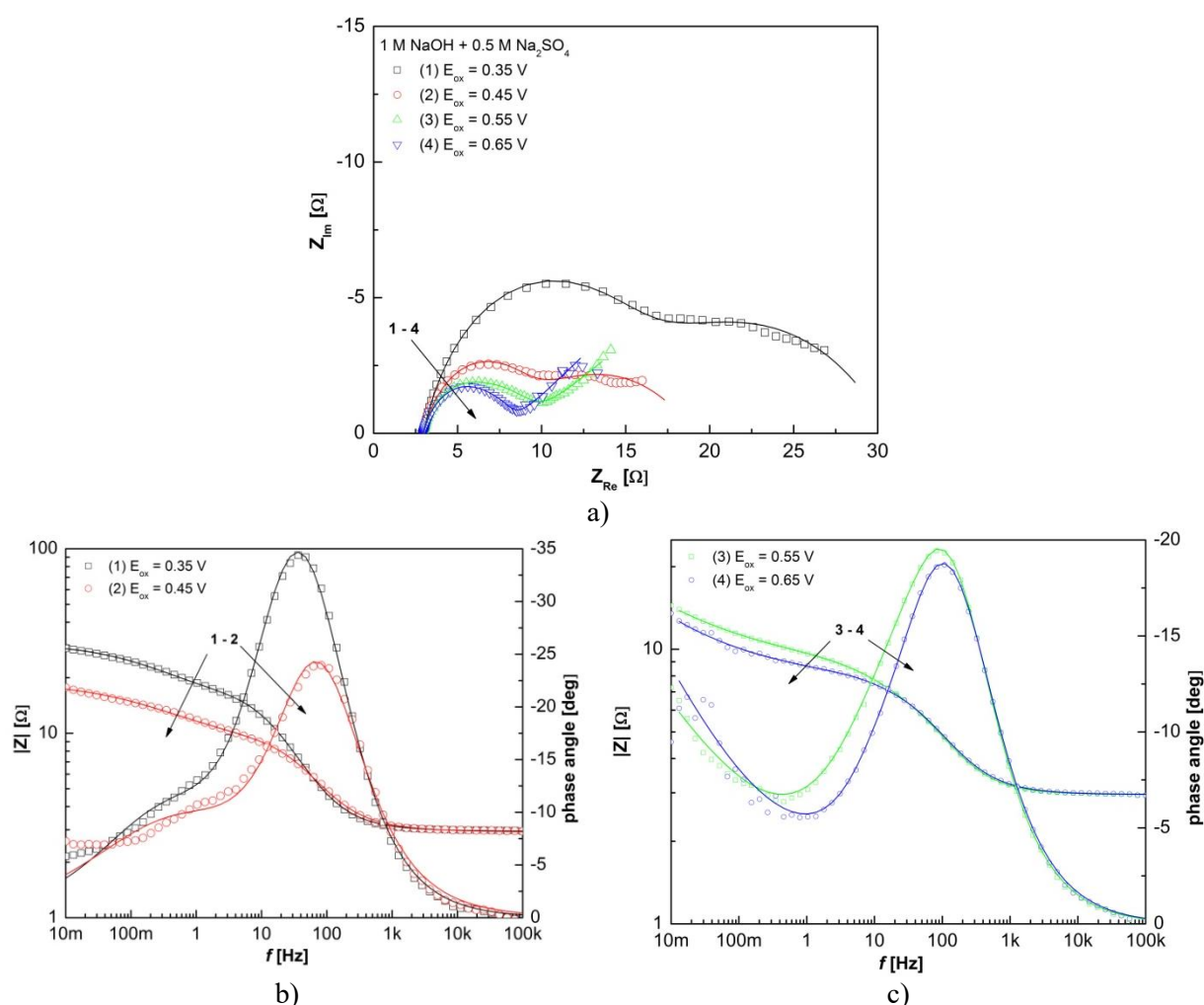

Figure 8. Nyquist (a) and Bode plots (b, c) recorded for sulphite electrooxidation on Cu/Pt-Co electrode from 1 mol L^{-1} NaOH + 0.5 mol L^{-1} Na_2SO_3 solution at different potential values.
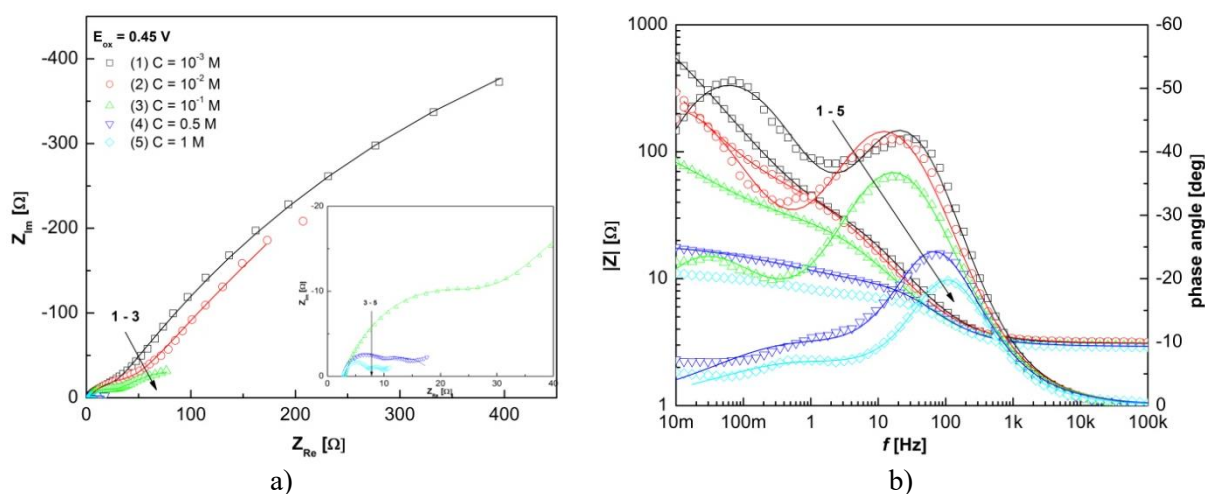
Figure 9. Nyquist (a) and Bode plots (b, c) recorded for sulphite electrooxidation on Cu/Pt-Co electrode from 1 mol L^{-1} NaOH + 0.5 mol L^{-1} Na$_2$SO$_3$ solution at different potential values.

The equivalent electrical circuits (EEC) shown in Figure 10a was used to fit the impedance data obtained for sulphite eletrooxidation in alkaline solution with Na$_2$SO$_3$ concentration between 10^{-3} and 10^{-1} mol L^{-1} in potential range +0.35 ÷ +0.65 V. Also, the same EEC was used in the case of more concentrated Na$_2$SO$_3$ solutions, 0.5 and 1 mol L^{-1}, at oxidation potential values up to +0.45 V. This EEC consists in a solution resistance Rs in series with a two parallel connections of the type (CPE - R). In first one, a constant-phase element (CPE_e) and resistor (R_e) was necessary to fit impedance data recorded at the high frequency values, which are attributed to a charge-transfer process at the outermost surface of Cu/Pt-Co electrode [21,22]. In the second connection, (CPE_{dl}) is the electric double-layer capacitance used instead of an ideal capacitor to characterize the Pt alloys catalysts behaviour in electrooxidation process and resistance (R_{ct}) is the charge transfer resistance [21,22].
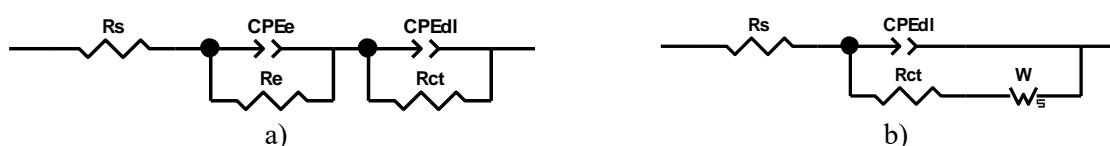

Figure 10. EECs used for modelling sulphite electrooxidation process on Cu/Pt-Co electrode in 1 mol L^{-1} NaOH solution with different sulphite concentration at different potential values.

EEC from Figure 10b has a single parallel connection ($CPE_{dl}(R_{ct}W_s)$) in which the charge transfer resistance R_{ct} is in series with a Warburg element (W_s) characteristic of sulphite ions diffusion from alkaline electrolyte to the Cu/Pt-Co electrode surface. A similar EEC was used to fit the EIS data obtained for sulphite oxidation on Pt electrodes in neutral solution [18].

The Bode diagrams shape confirms the choice of the two EECs for sulphite oxidation process fitting on this type of electrode, depending on the SO$_3^{2-}$ ions concentration added to the alkaline electrolyte and the oxidation potential value.

The fitting results for sulphite oxidation on Cu/Pt-Co electrode are shown as continuous line in graphical EIS sprectra and the corresponding values of EEC elements are shown in Tables 2 and 3. Also, the double layer capacity (C_{dl}) values have been calculated for each studied electrode/electrolyte interface.

Table 2. Calculated parameters of EEC elements from figure 9a for sulphite oxidation in alkaline media

SO_3^{2-} conc. (M)	E (V)	R_s (Ω cm^2)	CPE_e $T \cdot 10^5$ (F cm^{-2} s^{n-1})	n	R_e (Ω cm^2)	CPE_{dl} $T \cdot 10^4$ (F cm^{-2} s^{n-1})	n	R_{ct} (Ω cm^2)	$C_{dl} \cdot 10^6$ (F cm^{-2})	Chi^2 $\cdot 10^3$
10^{-3}	0.35	3.09	3.17	0.77	24.8	1.05	0.65	1300	1.30	1.81
	0.45	3.09	2.75	0.78	22.7	0.91	0.67	1164	1.77	1.38
	0.55	3.10	2.46	0.78	21.3	0.90	0.71	837	3.16	1.59
	0.65	3.15	1.93	0.88	20.4	0.86	0.72	56.4	3.80	1.76
10^{-2}	0.35	3.11	4.46	0.70	45.4	0.74	0.61	1179	2.88	1.76
	0.45	3.10	4.05	0.72	37.2	2.42	0.62	997	3.02	1.72
	0.55	3.13	3.27	0.74	32.7	2.39	0.63	480	3.60	1.83
	0.65	3.18	1.19	0.84	28.5	2.16	0.65	26.5	4.37	1.33
10^{-1}	0.35	2.94	5.50	0.69	38.3	2.00	0.66	209	5.97	0.59
	0.45	2.92	4.66	0.70	24.3	6.93	0.58	124	7.92	0.51
	0.55	2.94	3.15	0.72	21.6	6.70	0.60	85.3	1.08	0.35
	0.65	3.00	2.20	0.77	15.2	6.64	0.61	19.5	15.1	2.53
0.5	0.35	2.94	2.41	0.80	12.0	9.88	0.48	15.7	2.36	0.61
	0.45	2.91	2.05	0.83	5.43	9.21	0.56	10.7	10.8	1.72
1	0.35	2.88	1.80	0.85	8.05	15.50	0.47	8.28	5.13	0.21
	0.45	2.88	1.43	0.87	3.52	13.0	0.54	5.23	23.4	0.35

Table 3. Calculated parameters of EEC elements from figure 9b for sulphite oxidation in alkaline media

SO_3^{2-} conc. (M)	E (V)	R_s (Ω cm^2)	CPE_{dl} $T \cdot 10^4$ (F cm^{-2} s^{n-1})	n	R_{ct} (Ω cm^2)	W_R (Ω cm^2)	W_T (H cm^2)	W_p	$C_{dl} \cdot 10^5$ (F cm^{-2})	Chi^2 $\cdot 10^3$
0.5	0.55	2.93	3.05	0.73	5.44	24.1	186	0.17	3.16	0.47
	0.65	2.95	2.68	0.75	5.06	8.58	48.9	0.37	3.44	0.67
1	0.55	2.88	3.46	0.76	3.29	22.2	245	0.26	7.84	0.70
	0.65	2.85	3.03	0.78	2.97	5.19	89.8	0.37	9.64	0.55

Analyzing the results from Tables 2 and 3, it can be observed that transfer resistance values (R_{ct}) decrease significantly with the increase of sulphite concentration added in alkaline solution, indicating that the sulphite anodic oxidation occurs with higher rate, confirming voltammetric and kinetic data. For the same sulphite concentration used in experimental studies, the value of the charge transfer resistance decrease with increasing polarization, the minimum values being recorded for an oxidation potential value of +0.65 V. Also, the double layer capacity (C_{dl}) have been calculated and, as expected, values of this parameter increases with the increasing of anodic potential value at which the sulphite ion oxidation process is carried out. The order of 10^{-3} for chi-square values indicate very good correlation between the experimental EIS data and the chosen EEC model values.

4. Conclusions

Experimental results have shown that SO_3^{2-} ions can be easily oxidized on Cu/Pt-Co electrode, in alkaline media, either directly on the electrode or indirectly with the atomic oxygen electrochemically generated.

The obtained data showed that the potential range at which the electrode processes are carried out does not depend on the sulphite concentration and the increase of the sulphite concentration stimulates the atomic and molecular oxygen generation reactions. As expected, the degree of sulphite transformation depends on the electrolysis time and sulphite concentration in the electrolyte solution.

The electrochemical behavior of SO_3^{2-} suggest that type of electrode can be used as anodic material for sulphite electrooxidation, especially in a SO_3^{2-} / O_2 alkaline fuel cell.

5. References

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