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Electrochemical Oxidation of Sulphite in Neutral Media on Platinum Anode

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In this paper, electrochemical behavior of sulphite ions on platinum in neutral solution (1 mol L^{-1} Na_2SO_4) has been studied in order to identify the relationship between the sulphite concentration in the electrolyte solution (10^{-3}, 10^{-2}, 10^{-1}, $5\cdot10^{-1}$ and 1 mol L^{-1}) and kinetic parameters of the anodic process. Electrochemical behavior of sulphite in the test solutions has been studied by linear and cyclic voltammetry. More information regarding the studied process occurring at electrode/electrolyte interface and kinetic parameters (current density i_0 and anodic transfer coefficient α) were obtained by Tafel plots method. Further, electrochemical impedance spectroscopy was carried out to confirm obtained data on platinum electrode. As well, chrono-electrochemical methods (chronoamperometry, chrono-potentiometry, chronocoulometry) were chosen in order to achieve the optimum parameters (current density, oxidation potential characteristic for sulphite electrooxidation and transformation degree of SO_3^{2-} in the test solution).

Keywords: sulphite anodic oxidation, Tafel plots method, electrochemical impedance spectroscopy, chrono-electrochemical methods

1. INTRODUCTION

Fuel cells are still considered promising alternative energy source with wide prospects of practical use. Throughout time, various types of fuel cells equipped with platinum catalysts have been developed, due to the high catalytic activity of this noble metal. Even of their large applications in various fields, including electronic and automotive industry, the high cost is a serious impediment to widespread commercialization [1-7]. Consequently, numerous researches have been focused not only on the development of new catalysts, but as well on the identification of new cheaper fuels. In this respect, recently, a special attention has been paid to sulphur compounds: hydrogen sulphide, alkaline sulphides, sulphur dioxide and sulphites. Their electrochemical behavior recommends them as possible combustible in fuel cells [8-10].

Electrochemical behavior of SO_2 and SO_3^{2-} has been a subject of several studies [8, 9], especially on electrodes made of noble metals, due to their electrocatalytic properties. In this case, it is necessary to take into account that in aqueous solution equilibrium between chemical species $SO_{2(aq)}$, HSO_3^- and SO_3^{2-} is established depending on *pH*. In a solution at *pH* = 7, practically only HSO_3^- and SO_3^{2-} coexist [11]. Although, in recent years, a lot of studies on the sulphur dioxide/sulphite anodic oxidation in both acid and alkaline media have been carried out, the oxidation process is not clear, still being considered a complex transformation [11-14]. It is generally accepted that direct anodic oxidation of sulphite in neutral or alkaline solutions occurs according equations (1) and/or (2), having as a result the decrease of the *pH*.

$$\mathrm{SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + 2H^+ + 2e^-} \quad (1)$$

$$\mathrm{HSO_3^- + H_2O \rightarrow SO_4^{2-} + 3H^+ + 2e^-} \quad (2)$$

The main aim of the paper is to present a study on the electrochemical behavior of sulphite in neutral solutions and to identify the favorable conditions to reuse sulphites resulting as a byproduct in many industrial chemical processes as fuel in Na_2SO_3/O_2 cell. The rate determining step will be revealed in the electrode potential range in which the main process is the sulphite oxidation. As well, kinetic parameters for the anodic reaction will be evaluated. Further, the investigation can be extended in a study of SO_2/O_2 fuel cell which can produce both electricity and H_2SO_4 [15].

2. MATERIALS AND METHODS

A three-electrode undivided cell connected to SP 150 Bio-Logic potentiostat/galvanostat was used during all measurements. The working electrode was a smooth platinum plate having 0.5 cm^2 active area, two graphite roads were used as counter electrode and Ag/AgCl as reference electrode. The electrochemical cell was equipped with a nitrogen purging system in order to deaerate the solution before each measurement.

Electrochemical experiments were carried out in 1 mol L^{-1} Na_2SO_4 solution in the absence and presence of different sulphite concentrations (10^{-3}, 10^{-2}, 10^{-1}, $5\cdot10^{-1}$ and 1 mol L^{-1}). Reagents Na_2SO_4 (p. a., ≥ 99%, Merck) and Na_2SO_3 (p. a., ≥ 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}, while linear polarization curves have been drawn using low scan rate (1 mV s^{-1}) in order to ensure quasi-stationary.

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 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 circuit (EEC) by CNLS Levenberg – Marquardt method using ZView – Scribner Associates Inc. software.

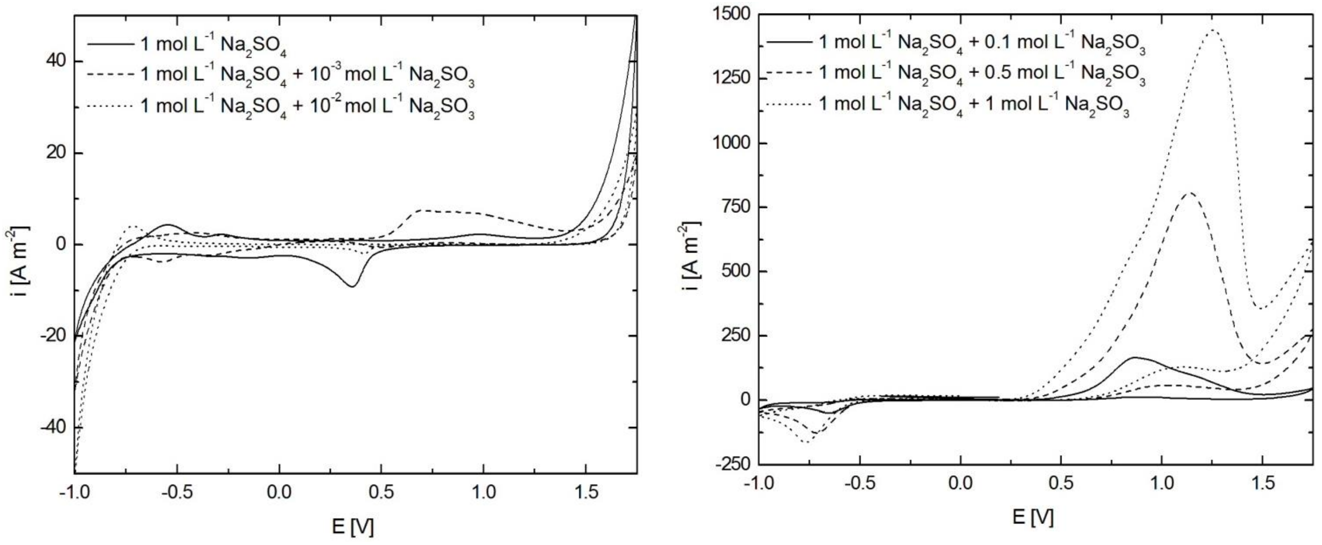
Chronoamperometry, chronocoulometry and chronopotentiometry methods were applied in order to determine the sulphite oxidation efficiency at six oxidation potential values.

3. RESULTS AND DISCUSSION

3.1. Cyclic voltammetry

Cyclic voltammograms were recorded in above-mentioned solutions in order to identify the processes occurring at the electrode/electrolyte interface. The voltammograms presented in Fig. 1a and 1b indicate that, at cathodic polarization, the peak assigned to the oxygen reduction reaction is revealed only in the absence of sulphite ions. That means, the entire amount of oxygen anodically formed has been consumed in a chemical reaction with sulphite ions. Furthermore, at advanced cathodic polarization, it can be seen that only hydrogen evolution reaction takes place.

To better highlight the electrochemical reactions on working electrode, cyclic voltammograms are represented at a higher resolution for low sulphite concentrations (10^{-3} and 10^{-2} mol L^{-1}) than the resolution for moderate sulphite concentrations (0.1, 0.5 and 1 mol L^{-1}).



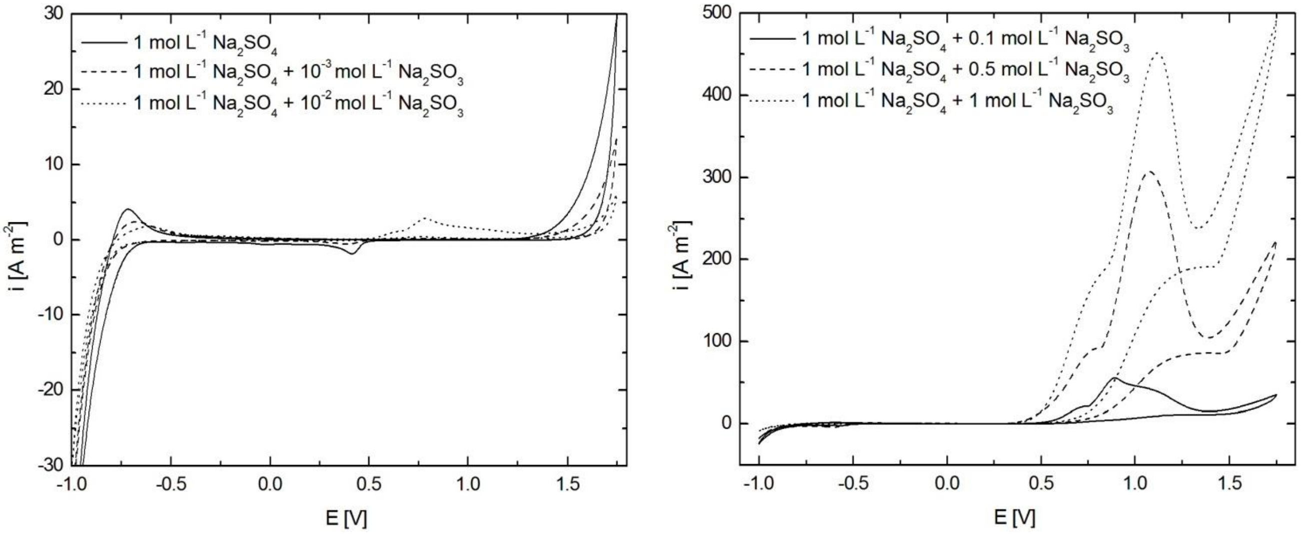
a) b)

Figure 1. Cyclic voltammograms recorded on Pt electrode in 1 mol L^{-1} Na_2SO_4 solution without and with different sulphite concentrations, scan rate 100 mV s^{-1}.

On the other hand, at anodic polarization, the sulphite oxidation (Eq. 1 and 2) occurs simultaneously with atomic oxygen formation (Eq. 3), as it has been featured in previous papers. The small peak (at about +1 V) on the voltammogram drawn in the absence of sulphite (Fig. 1a) can be assigned to the reaction (3) [15, 16].

$$3H_2O \rightarrow O + 2H_3O^+ + 2e^- \qquad (3)$$

These considerations are valid for cyclic voltammograms drawn at high scan rate (100 mV s^{-1}). At low scan rate (Fig. 2a and 2b), as expected, the anodic current peaks are smaller, but an obvious wave can be observed on the left size of the main anodic peak, proving that two electrochemical reactions occur on the electrode, the smaller wave can be assigned to the direct anodic oxidation of sulphite. At more positive potential values molecular oxygen is the reaction product, but the rate of sulphite chemical oxidation with atomic or molecular oxygen formed on the anode becomes appreciable, taking into account that the cathodic oxygen reduction peak is not present at the reverse shifting of the electrode potential.



a) b)

Figure 2. Cyclic voltammograms recorded on Pt electrode in 1 mol L^{-1} Na_2SO_4 solution without and with different sulphite concentrations, scan rate 5 mV s^{-1}.

3.2. Linear voltammetry

In order to provide quasi-stationary conditions at the electrode, linear voltammetry has been applied at low scan rate. The analysis of the linear voltammograms, recorded at 1 mV s^{-1} in neutral media (Fig. 3), revealed the specific potential range of the sulphite oxidation on platinum in the presence of SO_3^{2-} ions at different concentrations in the electrolyte solutions. It can be seen that at low concentration of sulphite (10^{-3} and 10^{-2}), the amount of SO_3^{2-} ions reaching the interface metal-electrolyte solution is insignificant, and as a consequence oxidation current is not distinguishable. As it was shown before, the peaks at about +1 V are assigned to the atomic oxygen formation, whereas the related waves appear due to the direct anodic oxidation of sulphite. The higher is the sulphite concentration, the more pronounced is the anodic peak. That proves that at the anode a chemical reaction between atomic oxygen and sulphite occurs simultaneously with electrochemical ones. In this circumstances, the rate of the atomic oxygen generation is a measure of sulphite oxidation. These considerations are valid at moderate anodic polarization, whereas at low anodic one the main reaction is the direct oxidation of sulphite to sulphate.

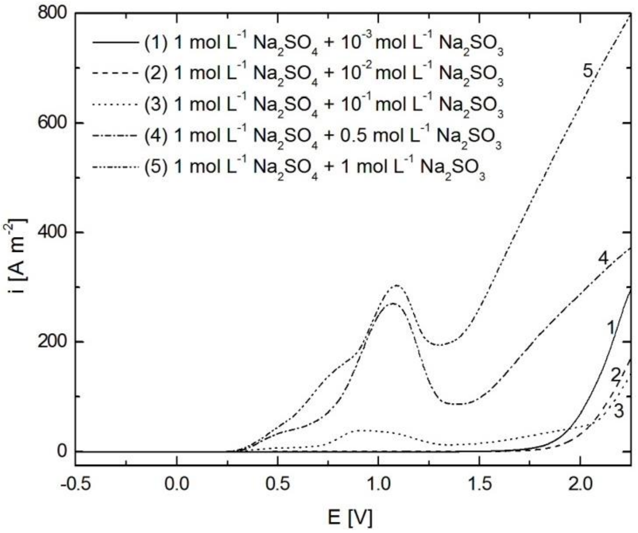


Figure 3. Linear voltammograms recorded on Pt electrode in 1 mol L^{-1} Na_2SO_4 solution with different sulphite concentrations, scan rate 1 mV s^{-1}.

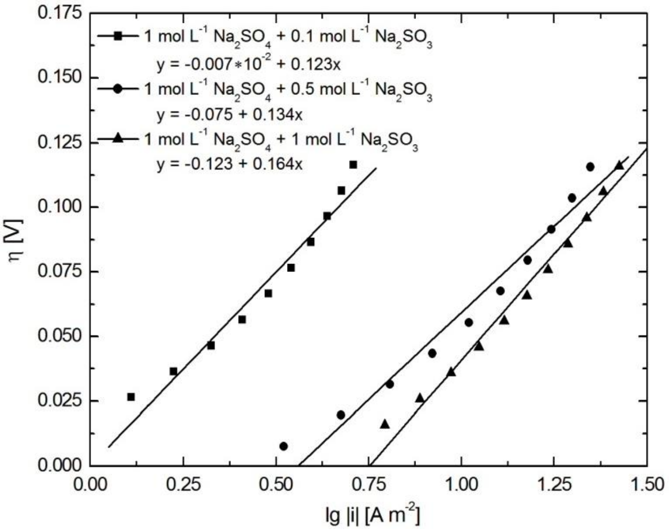


Figure 4. Tafel plot for sulphite anodic oxidation on Pt electrode in Na_2SO_4 solution with different sulphite concentrations.

Furthermore, kinetic parameters (anodic transfer coefficient α and exchange current density i_o) for electrochemical process (3) have been determined in 0.1, 0.5 and 1 mol L^{-1} sodium sulphite solutions, using Tafel plots method (Fig. 4). The calculated kinetic parameters are presented in Table 1. Tafel slope values are close to the theoretical one (+0.118 V) for one-electron charge transfer process and consequently the anodic charge transfer coefficient α is close to 0.5 [15, 16]. High values of exchange current density are obtained, characteristic for fast charge transfer processes. In these circumstances, it can be appreciated that the rate determining step for the atomic oxygen generation (Eq. 3) is controlled by charge transfer step. The diminution of the charge transfer coefficient α with the increase of the sulphite concentration is equivalent with the shifting of the reaction plane (inner Helmholtz plane) towards electrolyte solution [17-19]. This effect is due to sulphite competitive adsorption onto the electrode surface, compensated by the consistent increase of the exchange current density $i_{o.}$

Table 1. The kinetic parameters for sulphite oxidation in Na_2SO_4 solutions

Na_2SO_3 conc. [mol L^{-1}]	***b*** **[mV dec^{-1}]**	α	**i_o [A m^{-2}]**
0.1	123	0.48	1.00
0.5	134	0.44	1.75
1	164	0.36	2.12

Similarly, for the direct oxidation of sulphite, the main anodic process at low anodic polarization, the rate determining step is the charge transfer given by Eq. (4) [14].

$$\mathrm{SO_{3\,(ads)}^{2-}} \rightarrow \mathrm{SO_{3\,(ads)}^{\bullet-}} + \mathrm{e^-} \qquad (4)$$

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

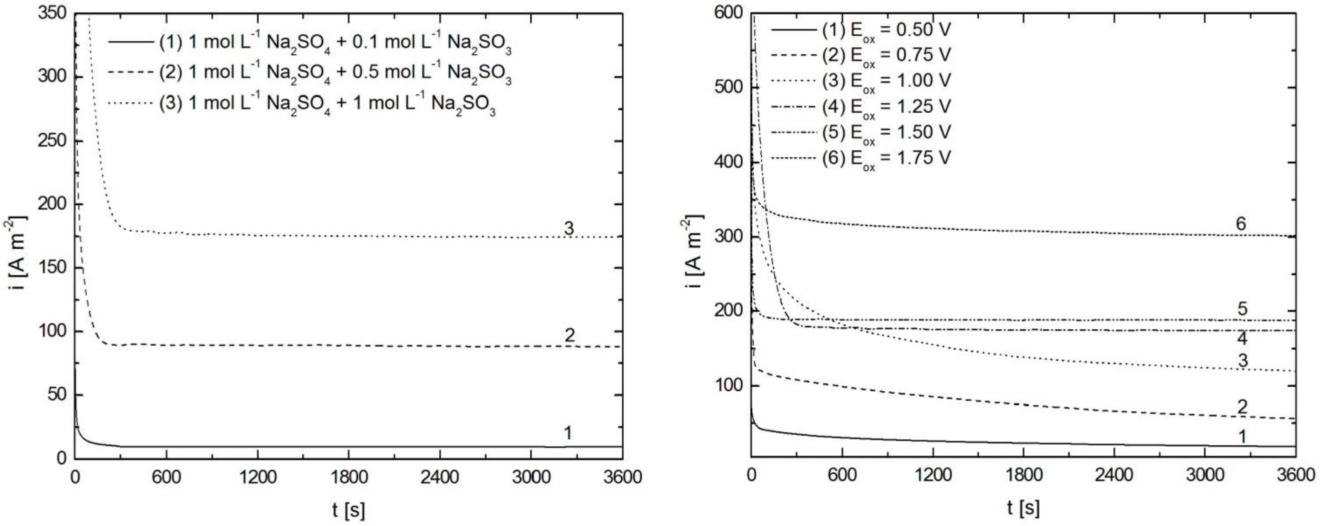
Taking into account that on the electrode, in the potential range of sulphite oxidation, two parallel processes occur (direct sulphite oxidation and atomic oxygen generation), the values determined for α and i_o are just apparent. In a previous paper, on platinum nanoparticles modified nickel electrode, in 1 mol L^{-1} NaOH electrolyte-support solution, a value of 169 mV dec^{-1} was reported [16]. As well, on the platinum rotating disk electrode, in alkaline solution ($pH = 11$), Skavas et al. have been obtained higher Tafel slope values (between 172 and 219 mV dec^{-1}), which correspond to much smaller transfer coefficients than 0.5 [14]. On the other hand, on graphite rotating disk electrode, in 0.25 mol L^{-1} NaOH solution, J.Lu et al. have been obtained unexpected very low Tafel slopes (0.59 – 0.066) for low potential range, and normal values (0.19 – 0.22) for high potential range [13].

3.3. Chronoamperometric studies

Chrono-electrochemical measurements had as a starting point the linear voltammograms shown in Fig. 3. Analyzing these curves, six potential steps were chosen (+0.50, +0.75, +1.00, +1.25, +1.50 and +1.75 V) to highlight the anodic processes that occur at the electrode surface. The first five values correspond to the sulphite direct or indirect oxidation in test solutions and the last one (+1.75 V) is assigned to the oxygen evolution reaction (OER).

Chronoamperometric curves, relating to sulphite oxidation, for 60 minutes, on working electrode in neutral solutions, with different sulphite ions concentrations, at a potential value of +1 V are presented in Fig. 5a.

In the Fig. 5b, the variation of the current density in time registered on Pt electrode in 1 mol L^{-1} Na_2SO_4 solution containing also 1 mol L^{-1} Na_2SO_3 is presented, for all six potential values at which the experiments have been carried out.



a) b)

Figure 5. Current-time curves for Pt electrode in 1 mol L^{-1} Na_2SO_4 solution with different sulphite concentrations at +1 V (a) and in 1 mol L^{-1} Na_2SO_4 + 1 mol L^{-1} Na_2SO_3 solution (b).

Based on chronoamperometric data the following conclusions may be drawn:

i) characteristic potential range for SO_3^{2-} oxidation in neutral solution, between +0.5 and +1.25 V, does not depend on the sulphite concentration;

ii) at more positive potential values, SO_3^{2-} oxidation and oxygen evolution reaction occur simultaneously;

iii) current densities recorded for all test solutions increase with the increasing sulphite concentration.

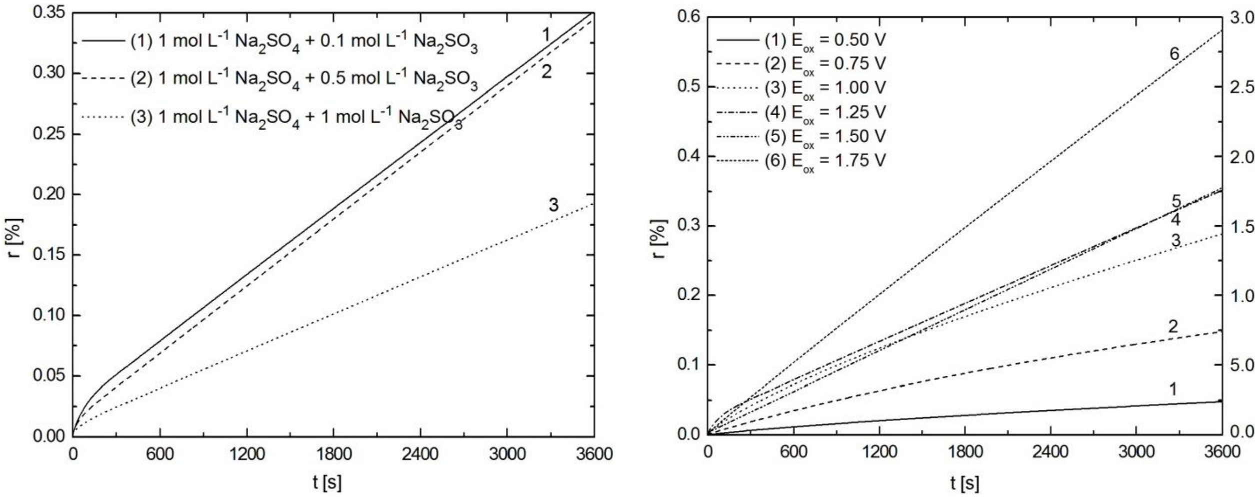
Correlating these values with cyclic and linear voltammetric data, it can be established that the amount of sulphite added in neutral solutions stimulates the first stage of OER, emphasized by the shift of characteristic potential to more negative values.

3.4. Chronocoulometric studies

The amount of electricity consumed for electrooxidation of sulphite ions in the characteristic potential range for each test solution has been measured by chronocoulometric technique.

Sulphite transformation degree during anodic oxidation as a function of time and sulphite concentration added in solution, when the electrochemical process is carried out at +1 V potential value, is shown in Fig. 6a. The highest values of the transformation degree have been obtained for the test solution containing the lowest concentration of sulphite (0.1 mol L^{-1}) in the electrolyte solution.

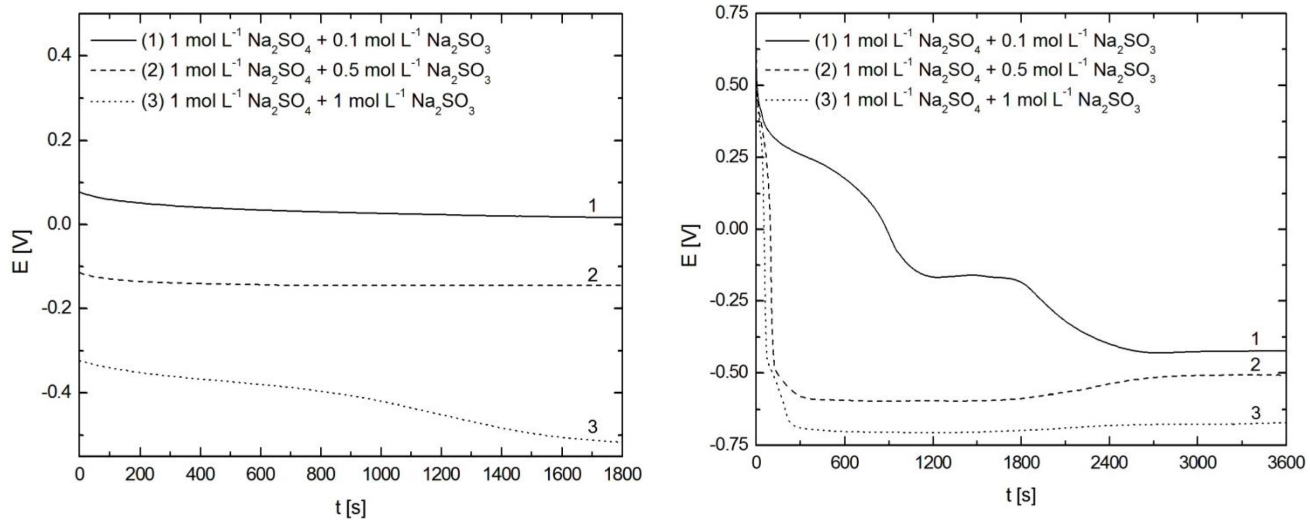
Based on chronocoulometric data, the assessment of a number of sulphite moles changed in the anodic reaction (δ) and electrochemical transformation degree (r) of sulphite to sulphate has been possible applying Faraday's laws [13]. The results for 1 mol L^{-1} sulphite added in neutral solution at all six potentials are presented in Fig. 6b.



a) b)

Figure 6. Chronocoulometric curves for Pt electrode in 1 mol L^{-1} Na_2SO_4 solution with different sulphite concentrations at 1 V (a) and in 1 mol L^{-1} Na_2SO_4 + 1 mol L^{-1} Na_2SO_3 solution (b).

3.5. Chronopotentiometric studies



a) *b)*

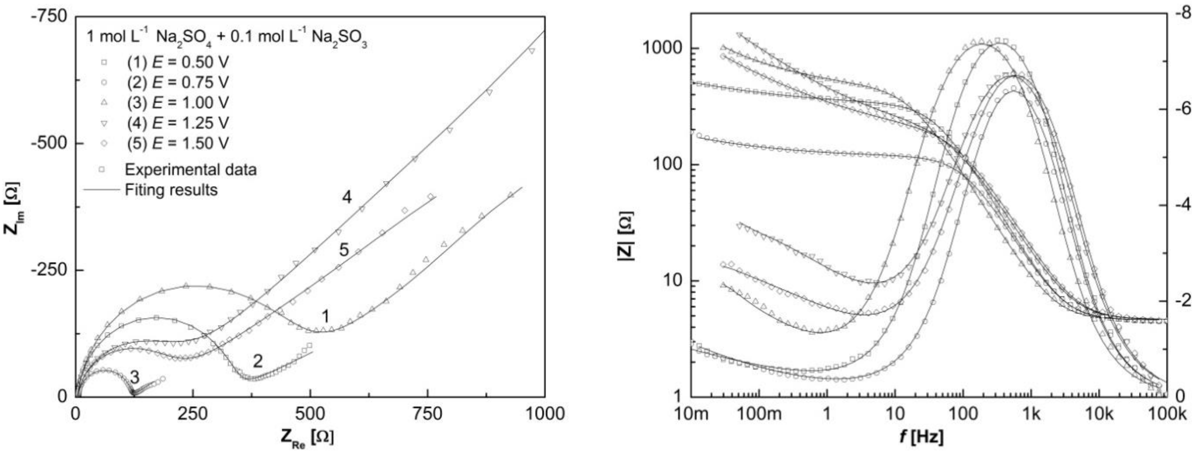
Figure 7. OCP curves for Pt electrode in 1 mol L^{-1} Na_2SO_4 solution with different sulphite concentrations before (a) and after (b) oxidation.

Chronopotentiometric measurements at zero current were performed on Pt electrode in neutral solutions in the presence of all Na_2SO_3 concentrations added in test solutions, before and after electrochemical sulphite oxidation during an hour at potential value of +1 V, for 30, respectively 60 minutes. The aim of this study was to follow the variation of the open circuit potential (OCP) in time. The curves obtained for all cases are presented in Fig. 7.

Analyzing the graphical results, E_{OCP} recorded before and after oxidation has approximately same values, it means that a sufficient high concentration of sulphite was provided in the test solutions, so that the processes occurring at the electrode surface could be highlighted.

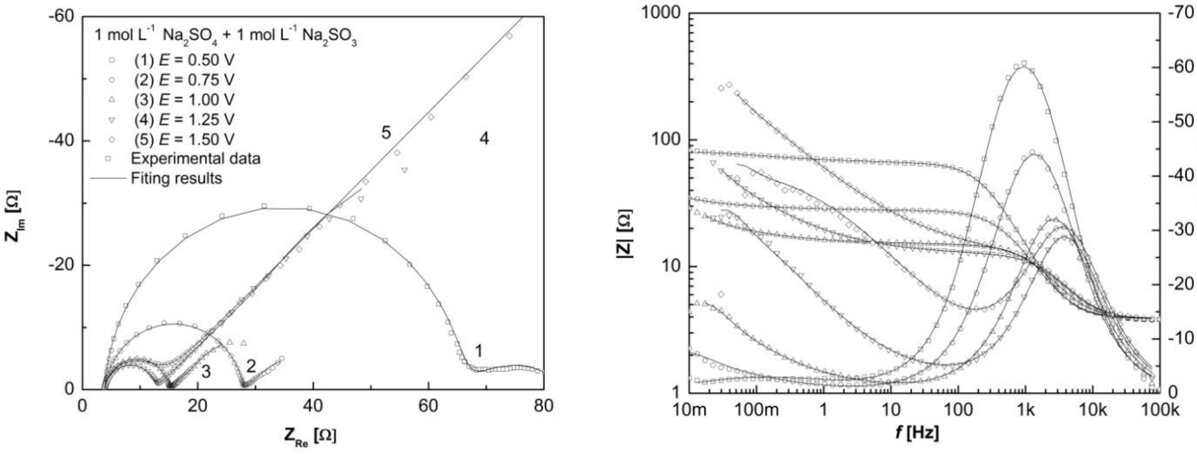
The potential-time curves show a pronounced decrease of E_{OCP} value in the first 600 s for 1 and 0.5 mol $\mathrm{L^{-1}}$ sulphite, respectively 2400 s for 0.1 mol $\mathrm{L^{-1}}$, mainly caused by sulphite ions deficiency at the proximity of the interface. If the solution is homogenized by sulphite ions migration / diffusion from the bulk of solution towards the electrode, the value E_{OCP} stabilizes very close to the initial one.

3.6. Electrochemical impedance spectroscopy



a) b)

Figure 8. Nyquist and Bode plots for sulphite oxidation on Pt electrode in 1 mol $\mathrm{L^{-1}}$ $\mathrm{Na_2SO_4}$ solution with 10^{-1} mol $\mathrm{L^{-1}}$ $\mathrm{Na_2SO_3}$ at different potential values.



a) b)

Figure 9. Nyquist and Bode plots for sulphite oxidation on Pt electrode in 1 mol $\mathrm{L^{-1}}$ $\mathrm{Na_2SO_4}$ solution with 1 mol $\mathrm{L^{-1}}$ $\mathrm{Na_2SO_3}$ at different potential values.

Based on cyclic and linear studies, confirmed by chronoamperometric data, electrochemical impedance spectra were recorded on Pt electrode in neutral media for all Na_2SO_3 concentrations from test solutions, at 5 potential values between +0.50 and +1.50 V. The recorded results are shown in Nyquist and Bode complex plane representation given in Fig. 8 for 0.1 mol L^{-1} Na_2SO_3 and Fig. 9 for 1 mol L^{-1} Na_2SO_3.

The Nyquist plots consist of one semicircle which can be attribute to sulphite oxidation process at the interface followed by the component owed to the sulphite diffusion from solution to the interface. The first process is controlled by one charge transfer step and the second one by mass transfer. The experimental impedance data were fitted to the electrical equivalent circuit presented in Fig. 10, using a complex non-linear least squares (CNLS) procedure. This EEC was the one that provided the lowest relative errors (Chi square, in Table 2) amongst other tested circuits.

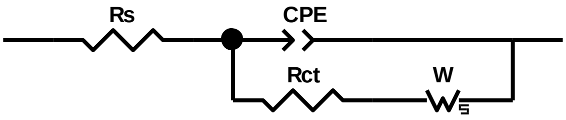


Figure 10. Equivalent electrical circuit for modelling sulphite anodic oxidation in neutral solution on Pt electrode.

The EEC used to analyze the impedance data for sulphite oxidation on platinum electrode in neutral solution is the Randles circuit for semi-infinite linear diffusion R_s (CPE ($R_{ct}W_s$)) [14]. It consists in a solution resistance R_s which represents the uncompensated solution resistance, bound in series with a parallel connection between a constant phase element (CPE) and a charge transfer resistance R_{ct} in series with a Warburg element (W_s) characteristic of diffusion. In the real electrochemical systems, *CPE* element characterized more precisely double layer capacity (C_{dl}) for real electrochemical system thus replacing the ideal capacitor (C). CPE impedance can be describe by equation:

$$CPE = \frac{1}{T(j\omega)^n}$$

where T is *CPE* capacity element, ω – the angular frequency, j – the imaginary vector unit and n – CPE exponent. If $n = 1$, then CPE element act as pure capacitor (C_{dl}) and when $n = 0.5$ it means a pure diffusion. The Warburg element, typical to describe the mass diffusion process, has a similar expression for impedance as CPE, but with three components W_R - resistive part, W_T - inductive part and W_P - exponent [20].

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 decrease significantly with the increase of sulphite concentration, indicating that the sulphite anodic oxidation 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 decreases with the increasing of polarization.

As well, based on the variance of resistive component values of the Warburg element which is describing the sulphite diffusion from the electrolyte to the electrode, it can be observed that if the process is conducted at low potential values, from the potential range in which the experiments were performed (which coincides with a low anodic polarization and thus a lower current density), the process is mostly controlled by the charge transfer step and less by the diffusion of the sulphite ions to the electrode/electrolyte interface. For the described case, it can be observed that at the potential values of 0.5, 0.75 and 1.00 V only for the concentration of 0.1 mol L^{-1} sulphite, the value of W_R parameter is with an order of magnitude higher than its values recorded for the other potential values.

For the same sulphite concentration added in the neutral electrolyte, the value of the charge transfer resistance decrease with increasing polarization until a minimum value, after which it increases as a result of the development of oxygen evolution reaction on the electrode surface simultaneously with the studied process.

Table 2. Calculated data of the circuit elements and experimental errors (between brackets).

SO_3^{2-} conc. (M)	E (V)	R_s (Ω cm^2)	$T \cdot 10^5$ (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})	$Chi^2 \cdot 10^3$
0.10	0.50	4.61	1.50	0.97	496	881	278	0.28	1.29	0.69
	0.75	4.61	1.88	0.95	362	111	60.2	0.38	1.47	0.75
	1.00	4.63	2.70	0.94	126	1629	48.5	0.43	1.93	0.85
	1.25	4.64	1.81	0.93	198	2314	45.7	0.46	1.14	0.39
	1.50	4.66	1.47	0.94	175	4034	129	0.37	0.98	0.47
0.50	0.50	4.10	1.43	0.97	87.6	53.9	112	0.22	1.20	0.79
	0.75	4.04	2.68	0.94	32.4	36.5	96.4	0.41	1.47	0.47
	1.00	4.04	2.75	0.91	19.3	142	68.3	0.45	1.28	0.33
	1.25	4.06	1.87	0.92	19.6	1328	247	0.49	0.95	0.40
	1.50	4.06	1.82	0.94	21.2	3496	309	0.48	0.87	0.78
1.00	0.50	3.90	1.43	0.97	59.8	20.0	9.08	0.27	1.18	0.87
	0.75	3.86	2.61	0.94	23.8	14.9	80.1	0.42	1.42	0.64
	1.00	3.84	2.39	0.92	10.2	21.5	42.8	0.45	1.12	0.35
	1.25	3.86	1.73	0.93	8.6	100	29.3	0.47	0.88	0.25
	1.50	3.87	1.47	0.94	11.2	402	13.0	0.47	0.80	0.33

4. CONCLUSIONS

Experimental results have shown that in neutral media, on platinum electrode, SO_3^{2-} ions are easily oxidized, either directly on the electrode or indirectly with the atomic or molecular oxygen electrochemically generated.

Cyclic voltammograms drawn in cvasi-stationary conditions have revealed that at low anodic polarization sulphite ions are directly oxidized according to Eq. (1) or (2). The peaks intensification of atomic oxygen formation (Eq. 3), at about + 1 V, proportional with the sulphite concentration in the electrolyte solution, demonstrates that, at this potential value, sulphite ions react with the atomic oxygen. Furthermore, the absence of the molecular oxygen reduction peak shows that SO_3^{2-} ions react with all amount of the molecular oxygen produced on the platinum surface.

Kinetic parameters determined by Tafel plots method emphasize a significant increase of the exchange current density i_o in the presence of sulphite. Simultaneously, the decrease of the charge transfer coefficient α is noted due to the concurrent adsorption of sulphite ions at the metal - electrolyte interface, equivalent the shifting of the reaction plane (inner Helmholtz plane) towards the electrolyte solution. At a moderate anodic polarization, the oxidation process occurs having as a determining rate step the atomic oxygen formation (Eq. 3), for which kinetic parameters have been determined using Tafel plots method. Consequently, the rate of the anodic process (Eq. 3) is a measure of the overall reaction (Eq. 1).

Chronoelectrochemical data showed that the potential at which the electrode processes are carried out does not depend on the sulphite concentration, and at advanced polarization, sulphite oxidation occurs both directly and indirectly with atomic or molecular oxygen generated at the anode. 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. On the other hand, the evolution of OCP after a certain oxidation time indicates an important diminution of the sulphite ions concentration in the proximity of the anode, which is why the global process is also controlled by the diffusion step of the sulphite from the solution to the electrode.

Electrochemical impedance spectroscopy confirmed the effect of the sulphite concentration on the oxidation process rate given by the anodic current density. The occurrence of the Warburg resistive component shows that, at advanced anodic polarization, the process is also influenced by the slow diffusion of sulphite ions. The electrochemical behavior of SO_3^{2-}, especially its oxidation susceptibility in neutral media, suggest that this chemical species can be used as a fuel in Na_2SO_3 (aq) / O_2 (air) fuel cell.

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References

1. H-W. Hu, *Appl. Energy*, 165 (2016) 81.
2. M. Winter and R. J. Brodd, *Chem.Rev.*, 104 (2004) 4245.
3. N. Doan, M. C. Figueiredo, C. Johans and T. Kallio, *Int. J. Electrochem. Sci.*, 11 (2016) 7631.
4. H. Gasteiger, J. Panels and S. Yan, *J. Power Sources*, 127 (2004) 162.
5. G. H. El-Nowihy, A. M. Mohammad, M. M. H. Khalil and M. A. Sadek, *Int. J. Electrochem. Sci.*, 12 (2017) 62.
6. T. Sutharssan, D. Montalvao, Y. K. Chen, W-C. Wang, C. Pisac and H. Elemara, *Renew. Sustain. Energy Rev.*, 11 (2007) 1720.
7. O. Scialdone, *Electrochim. Acta*, 54 (2009) 6140.
8. D. Uzun, E. Razkazova-Velkova, K. Petrov and V. Beschkov, *J. Appl. Electrochem.*, 46 (2016) 943.
9. V. Beschkov, D. Yankov, I. Angelov, E. Razkazova-Velkova and M. Martinov, *Chemical Problems*, 1 (2017) 9.

10. G. Pchelarov, D. Uzun, E. Razkazova-Velkova, O. Dimitrov, S. Vassilev and K. Petrov, *Bulg. Chem. Commun.*, 49 (2017) 218.
11. J.A. O'Brien, J.T. Hinkley, S.W. Donne and S-E. Lindquist, *Electrochim. Acta*, 55 (2010) 573.
12. E. Skavas, A. Adriaens and T. Hemmingsen, *Int. J. Electrochem. Sci.*, 1 (2006) 414.
13. J. Lu, D.B. Dreisinger and W.C. Cooper, *J. Appl. Electrochem.*, 29 (1999) 1161.
14. E. Skavas and T. Hemmingsen, *Electrochim. Acta*, 52 (2007) 3510.
15. A. Enache, M. Dan, A. Kellenberger and N. Vaszilcsin, *Bulg. Chem. Commun.*, 49 (2017) 139.
16. A.F. Enache, M. L. Dan and N. Vaszilcsin, *Chem. J. Mold.*, 12 (2017) 102.
17. M. Bonnemay, G. Bronoel and M. Savy, *Electrochim. Acta*, 13 (1968) 659.
18. H. H. Bauer, *Electroanal. Chem. Interfacial Electrochem.*, 16 (1968) 419.
19. R. Creţu, A. Kellenberger and N. Vaszilcsin, *Int. J. Hydrogen Energy,* 38 (2013) 11685.
20. J.P. Diard, B. Le Gorrec, C. Montella, *The handbook of electrochemical impedance spectroscopy*, ER@SE/LEPMI, Hosted by Bio-Logic, 2013.
21. M.E. Orazem and B. Tribollet, *Electrochemical Impedance Spectroscopy*, John Wiley & Sons, Hoboken, New Jersey, 2008.