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Cobalt Layered Perovskite Type $Y_{0.5}Ca_{0.5}BaCo_4O_7$ as Anodic Material for Sulphite Oxidation in Neutral Media

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Abstract. In this paper, the behaviour of an anodic catalyst made by calcium doped cobalt layered perovskite type 114 electrode ($Y_{0.5}Ca_{0.5}BaCo_4O_7$) has been investigated for the electrooxidation process of sulphite ions in neutral media (1 mol L^{-1} Na_2SO_4). This research is necessary to understand the oxidation mechanism on the surface of this type of electrode. Voltammetric techniques (cyclic and linear) have been applied in order to describe the electrooxidation mechanism and to find the optimum parameters for sulphite anodic oxidation. Kinetic parameters for the process occurring on the working electrode surface have been determined by Tafel plots method. Further, electrochemical impedance spectroscopy was performed to confirm the sulphite oxidation mechanism on $Y_{0.5}Ca_{0.5}BaCo_4O_7$ electrode. Optimum characteristic parameters, such as current density, oxidation potential range for sulphite electrooxidation and SO_3^{2-} ions transformation degree in test solutions, have been obtained by chrono-electrochemical methods (chrono -amperometry, -potentiometry, -coulometry).

1. Introduction

In the last years, the applications of metal and metal oxide nanostructures have attracted the interest of researchers. The modified electrodes have become the materials more and more used in the studies of the electrocatalytic oxidation and reduction kinetics of many important redox systems [1, 2].

$Y_{0.5}Ca_{0.5}BaCo_4O_7$ layered perovskite was defined as semiconductor material [3]. One of the most investigated transitional metals mixed oxides is 114 cobalt perovskites family due to their structural, magnetic and electrochemical properties. Experimental researches have shown that there is a correlation between compound structure and his properties, especially due to the variable cobalt ions oxidation number [4, 5].

Modified electrodes have a wide range of applications, especially in electrochemical technology, energy conversion and storage systems, information storage, electrochromic and display devices, as well in electroanalysis [6-9].

Electrochemical behaviour of $Y_{0.5}Ca_{0.5}BaCo_4O_7$ has been studied both in alkaline and neutral solutions and had as starting point the electrochemical intercalation of oxygen inside of transitional metal oxide network as well as the experimental results regarding the electrochemical behaviour of cobalt studied by voltammetric techniques and electrochemical impedance spectroscopy [10-15]. Based on the electrochemical properties, especially its uncommon oxygen intake-release capability, these layered cobalt perovskite type 114 may be proposed for use as anodic materials with electrocatalytic properties in different fuel cells with alkaline or neutral electrolyte.

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Anodic oxidation of SO_2 is a component of the hybrid sulphur cycle for hydrogen production, being also used for fuel gas desulfurization [16]. The composition and concentrations of the compounds with S(IV) in aqueous solutions depend on pH value. In solutions having pH < 1.8 sulphur dioxide predominates and when pH > 7.2 mainly sulphite ions are present in solution [17, 18]. It was found that oxidation rate is strongly dependent on the nature of electrode materials, porosity and active surface of electrodes. These effects are explained by the influence of adsorption of Sulphur chemical species [17]. Also, the potential range for sulphite anodic oxidation is depending on the chosen anodic material, the type of electrolyte (acid, neutral or alkaline) and the sulfite ions concentration added in the solution.

The general aim of this study is to identify the suitable conditions for the recycling of sulphites resulting as byproducts in many industrial processes. This research on electrochemical behaviour of sulphite ions will allow its use in a Na_2SO_3/O_2 fuel cell operable in order to produce green energy from waste materials.

2. Experimental part

The $Y_{0.5}Ca_{0.5}BaCo_4O_7$ perovskite has been prepared using solid state reaction, by mixing Y_2O_3 (Aldrich 99,99%), $CaCO_3$ (Aldrich 99,99%), $BaCO_3$ (Aldrich 99,99%) and $CoO_{1.38}$ (99,99% Normapur) according to the stoichiometric cation ratio. The powder has been reground after decarbonation at 600°C, fired in air for 48 hours at 1100°C and then removed rapidly from furnace. The mixture was then reground and pressed into discs of 1 cm^2 and sintered in air for 24 hours at 1100°C. The structure of obtained $Y_{0.5}Ca_{0.5}BaCo_4O_7$ perovskite has been checked by X-Ray powder diffraction.

A three-electrode undivided cell connected to SP 150 Bio-Logic potentiostat/galvanostat was used during all measurements. Two graphite roads were used as counter electrode and Ag/AgCl as reference electrode. Test solution was deaerate before each measurement using a nitrogen purging system.

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}). Test solutions were prepared from Na_2SO_4 and Na_2SO_3 reagents (p.a. ≥ 98%, Merck).

Cyclic voltammograms have been recorded at different scan rates (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) has been performed using the SP-150 impedance module, in frequency range between 100 kHz and 10 mHz. An alternative voltage amplitude of 10 mV was applied. 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.

Chrono-amperometry, -coulometry and -potentiometry techniques were applied in order to determine the transformation degree of sulphite to sulphate at six potential values betweend -0.25 and 1.00 V.

3. Results and discussion

3.1. Cyclic voltammetry

Cyclic voltammograms (CVs) recorded at 50 mV s^{-1} scan rate, on $Y_{0.5}Ca_{0.5}BaCo_4O_7$ compound in neutral solution without and with different sodium sulphite concentrations, are presented in Figure 1a. It can be observed that in the absence of sulphite ions at anodic polarization a distinctive peak appears at approximate +1 V potential value, which is associated with Co(II) to Co(III) oxidation inside of perovskite structure. At more positive potential oxygen evolution reaction (OER) is unfolding. In test solutions containing different concentration of sulphite ions, the characteristic potential for OER on the electrode surface is shifted to more positive values, respectively the potential of hydrogen evolution reaction is shifted to more negative ones.

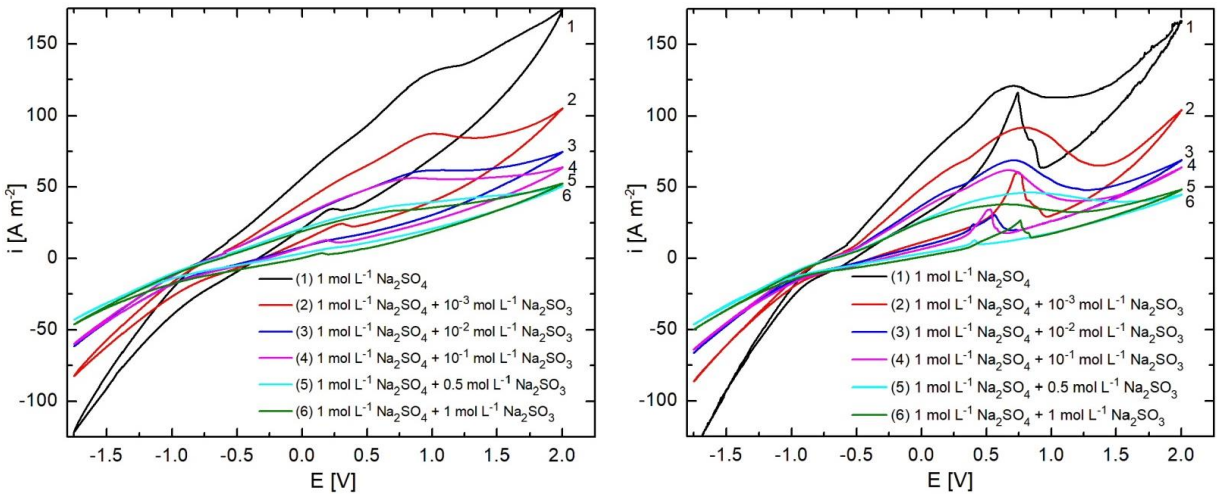


Figure 1. CVs recorded on $Y_{0.5}Ca_{0.5}BaCo_4O_7$ electrode in neutral solution in presence of different concentrations of Na_2SO_3, scan rate 50 mV s^{-1} (a) and 5 mV s^{-1} (b).

As well, on the voltammograms anodic branch at more positive potentials than the open circuit potential (OCP) no additional oxidation peak is registered, the only one present being the peak specified for the solution without sulphite ions. This is the first important information about the mechanism of sulphite electrochemical oxidation on layered cobalt perovskite electrodes in neutral media. The intensity of the anodic peak that appears in the range of +0.50 ÷ +1.25 V decreases more and more with the addition of a higher sulphite concentration.

Figure 1b presents the cyclic curves plotted for same test solutions at low scan rate (5 mV s^{-1}). Decreasing the scan rate provides the possibility to accurately identify the peaks corresponding to the oxidation processes that take place on $Y_{0.5}Ca_{0.5}BaCo_4O_7$ electrode, Co(II) to Co(III) inside to perovskite and SO_3^{2-} to SO_4^{2-} on electrode surface.

In neutral media, electrochemical behaviour of $Y_{0.5}Ca_{0.5}BaCo_4O_7$ perovskite can be described by the reversible reaction (Eq. 1).

$$Y_{0.5}Ca_{0.5}BaCo_4O_7 + \delta H_2O \leftrightarrow Y_{0.5}Ca_{0.5}BaCo_4O_{7+\delta} + 2\delta H^+ + 2\delta e^- \quad (1)$$

Due to the structure flexibility, $Y_{0.5}Ca_{0.5}BaCo_4O_7$ can realise an excess or deficit of oxygen ions (δ) into its structure, property common to 114 layered cobalt perovskite family [10]. After the electrode preparation step, using the method described previous, in the structure of $Y_{0.5}Ca_{0.5}BaCo_4O_{7\pm\delta}$ value of δ is 0 and cobalt average oxidation number is +2.375, being present both Co(II) and Co(III) ions.

The sulphite oxidation process are mediated by Co(II)/Co(III) redox couple, the diminution of oxygen content by electrochemical reduction in neutral media would favour the processes occurring on the perovkite electrode surface by decreasing the cobalt average oxidation number.

3.2. Linear voltammetry

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

The analysis of LVs shown in Figure 2, specific potential ranges of both oxidation processes that occur at the interface perovskite electrode/neutral electrolyte were identified in all test solutions with different sulphite ions concentrations. One can be distinguished two oxidation domains:

I - potential values between -0.25 and +1.25 V characteristic for Co(II) to Co(III) oxidation inside to perovskite structure for all test solutions and SO_3^{2-} to SO_4^{2-} oxidation on perovskite electrode surface for solution with sulphite ions;

II - OER on anode surface at potential values higher than +1.25 V described by Eq. (2).

$$2H_2O \leftrightarrow O_2 + 4H^+ + 4e^- \quad (2)$$

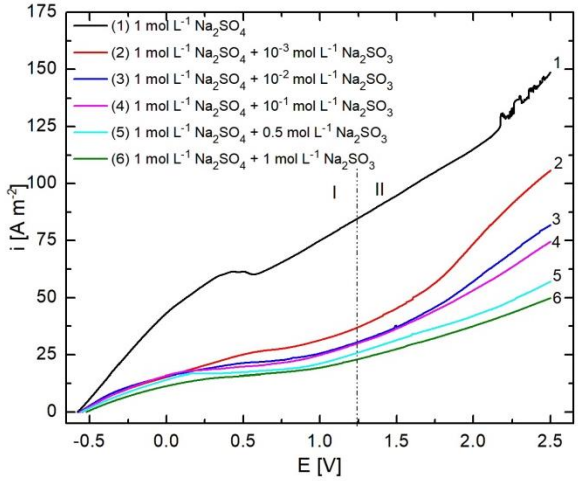


Figure 2. LVs recorded on $Y_{0.5}Ca_{0.5}BaCo_4O_7$ electrode in neutral solution in absence and presence of different concentrations of Na_2SO_3, scan rate 1 mV s^{-1}.

Based on LVs, kinetic parameters (anodic transfer coefficient α and exchange current density i_o) for electrochemical oxidation of sulphite to sulphate in neutral solution on $Y_{0.5}Ca_{0.5}BaCo_4O_7$ electrode have been calculated for each electrolyte solution using Tafel plots method (Figure 3). The kinetic parameters values are presented in Table 1.

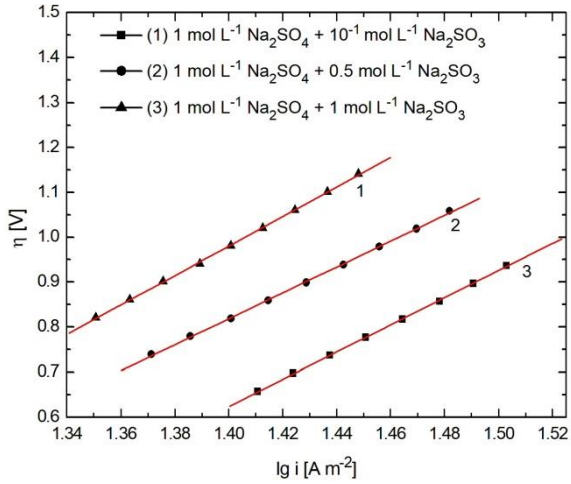


Figure 3. Tafel plots for sulphite oxidation on $Y_{0.5}Ca_{0.5}BaCo_4O_7$ electrode in neutral solution with different concentrations of Na_2SO_3.

Table 1. Kinetic parameters values for sulphite oxidation in neutral solution.

Na_2SO_3 conc. (mol L^{-1})	α	i_o (A m^{-2})
0.1	0.021	3.05
0.5	0.020	3.30
1	0.018	3.01

Transfer coefficient values prove the complexity of the anodic mechanisms for sulphite ions in neutral solution on this layered cobalt perovskite electrode.

High values obtained for exchange current density are characteristic for fast charge transfer processes. In these situation, it can be appreciated that the rate determining step is the charge transfer given by Eq. (3) similarly for the direct oxidation of sulphite [19].

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

Taking into account that on the electrode surface, in the potential range of sulphite oxidation at higher than +1.00 V, two parallel processes occur (direct sulphite oxidation and atomic or molecular oxygen generation), the values obtained for kinetic parameters α and i_o are just apparent.

3.3. Chronoamperometric studies

Analyzing the LVs from Figure 2, six potential values were chosen (-0.25, 0.00, +0.25, +0.50, +0.75 and +1.00 V) to highlight the sulphite direct/indirect oxidation processes that occur at electrode/electrolyte interface.

Figure 4a shows the chronoamperometric curves, relating to sulphite oxidation, for 60 minutes, on working electrode in neutral solutions, with different sulphite concentrations, at a potential value of +0.75 V.

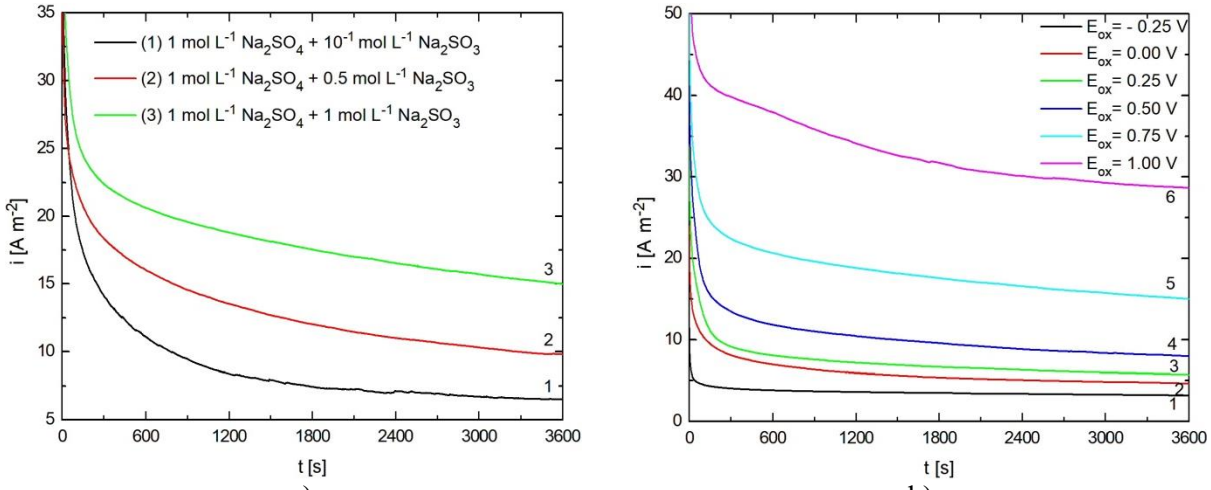


Figure 4. Current-time curves for sulphite electrooxidation process on $Y_{0.5}Ca_{0.5}BaCo_4O_7$ layered perovskite electrode in 1 mol L^{-1} Na_2SO_4 solution with different sulphite concentrations at +0.75 V (a) and in 1 mol L^{-1} Na_2SO_4 + 1 mol L^{-1} Na_2SO_3 solution (b).

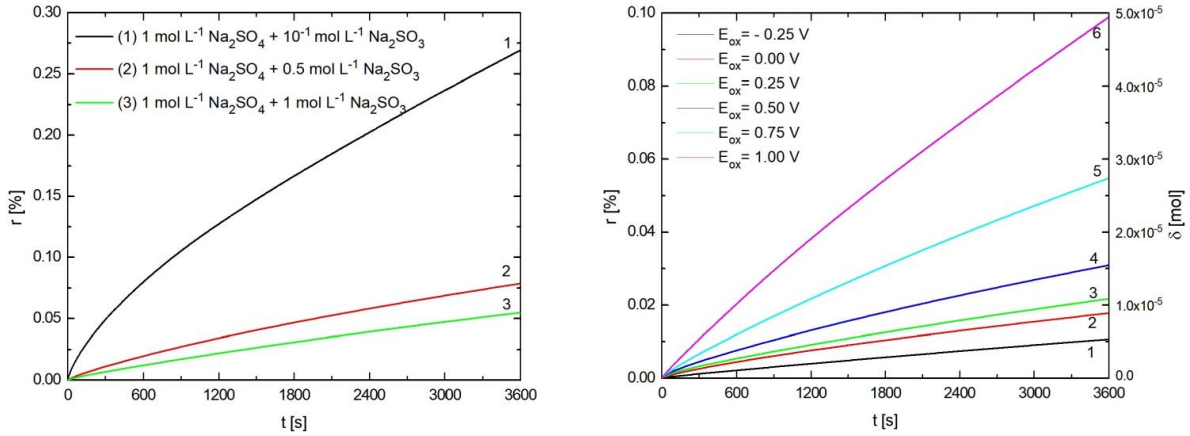
In Figure 4b, the variation of current density in time registered on $Y_{0.5}Ca_{0.5}BaCo_4O_7$ electrode in neutral solution containing 1 mol L^{-1} Na_2SO_3 is presented for all six potential values at which the experiments have been carried out.

It can be observed that in the characteristic potential range for sulphite electrooxidation in neutral solution, current densities are strongly dependent on anodic potential and SO_3^{2-} ions concentration in electrolyte. The increase of sulphite concentration from 10^{-1} to 1 mol L^{-1} has a result in an increase of about 150% of the current density when oxidation process is carried out at E_{ox} = +0.75 V, Also, at same SO_3^{2-} concentration (1 mol L^{-1}) the current density increases from 2.5 A m^{-2} for E_{ox} = -0.25 V to 27.5 A m^{-2} for E_{ox} = 1.00 V. The approximate constant value of current densities in time during chronoamperometric tests in neutral solution on $Y_{0.5}Ca_{0.5}BaCo_4O_7$ electrode confirms that sulphite ions concentration used in experimental studies is high enough, its slightly decrease is depending on the decrease of SO_3^{2-} ions concentration near the interface.

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 determinated by chronocoulometry.

In Figure 5a the sulphite transformation degree during anodic oxidation as a function of time for different sulphite concentration is presented, when the electrochemical process is carried out at +0.75 V. The highest value of the transformation degree has been obtained for the test solution containing the lowest concentration of sulphite (10^{-1} mol L^{-1}).



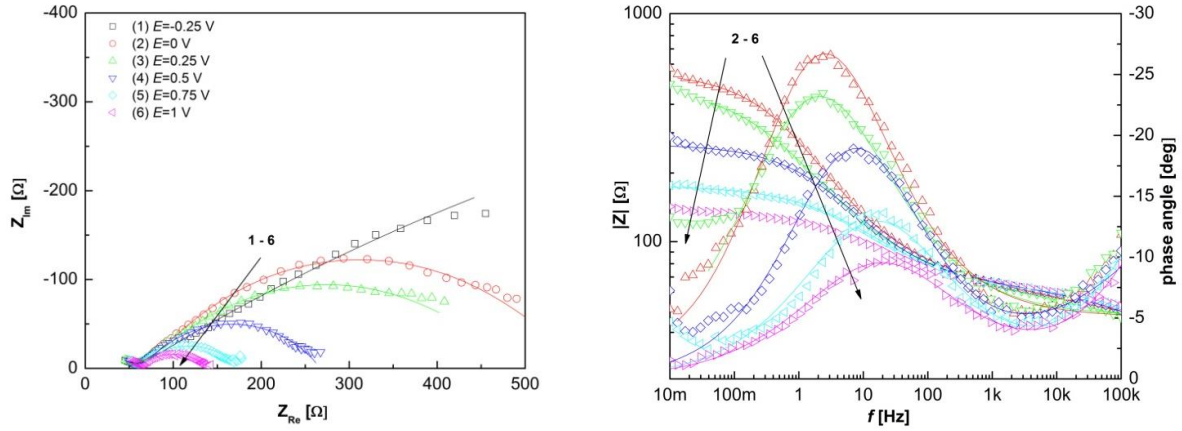
a) b)

Figure 5. Chronocoulometric curves for sulphite electrooxidation process on $Y_{0.5}Ca_{0.5}BaCo_4O_7$ electrode in neutral solution with different sulphite concentrations at +0.75 V (a) and in 1 mol L^{-1} Na_2SO_4 + 1 mol L^{-1} Na_2SO_3 solution (b).

Based on these 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 neutral solution at all six potentials are presented in Figure 5b.

3.5. Electrochemical impedance spectroscopy

Based on the studies presented above cyclic and linear voltammograms, Tafel plots method and chrono-electrochemical data, EIS was used to obtain specific information for sulphite ions oxidation on $Y_{0.5}Ca_{0.5}BaCo_4O_7$ electrodes in Na_2SO_4 solution with different Na_2SO_3 concentrations between 10^{-3} and 1 mol L^{-1} at 6 oxidation potential values in the range -0.25 and + 1.00 V.



a) b)

Figure 6. Nyquist (a) and Bode plots (b) recorded for sulphite electrooxidation on $Y_{0.5}Ca_{0.5}BaCo_4O_7$ electrode from 1 mol L^{-1} Na_2SO_4 + 1 mol L^{-1} Na_2SO_3 solution at different potential values.

The obtained results presented in form of Nyquist and Bode complex plane representation are shown in Figure 6 for 1 mol L^{-1} Na_2SO_3 added in neutral solution.

The equivalent electrical circuit (EEC) shown in Figure 7 was used to fit the impedance data obtained for sulphite electrooxidation on layered cobalt perovskite electrode in 1 mol L^{-1} Na_2SO_4 with all Na_2SO_3 concentrations used in electrochemical studies in the potential range between -0.25 and +1.00 V. The EEC consists in a solution resistance *R*s in series with two parallel connections with a constant-phase element and a resistor (*CPE* - *R*). First one (CPE_{el} - R_{el}) was used to fit impedance data recorded at the high frequency values, which are attributed to a charge-transfer process at the layered cobalt perovskite electrode surface. The second connection was necessary to fit EIS data specific to the lower frequency values being composed of CPE_{ox} element for characterization of $Y_{0.5}Ca_{0.5}BaCo_4O_7$ electric double-layer capacitance in sulphite oxidation process and the charge transfer resistance (R_{ct}).

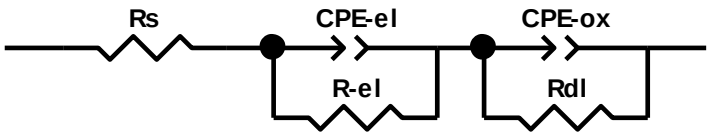


Figure 7. EECs used for modelling sulphite oxidation process on $Y_{0.5}Ca_{0.5}BaCo_4O_7$ electrode from 1 mol L^{-1} Na_2SO_4 solution with different sulphite concentration at different potential values.

The Bode diagrams shape confirm the chosen EEC for fitting EIS data obtained for sulphite electrooxidation process on $Y_{0.5}Ca_{0.5}BaCo_4O_7$ electrode in neutral solution. The fitting results for sulphite oxidation on this type of electrode are plotted as continuous line in graphical EIS sprectra and the corresponding values of EEC elements are shown in Tables 2. On the other side, the double layer capacity (C_{dl}) values have been calculated for each studied layered cobalt perovskite electrode/neutral electrolyte interface.

Analyzing the results from Table 2, it can be observed that transfer resistance values (R_{ct}) decrease significantly with the increase of sulphite concentration in neutral solution, especially if the process is led to an oxidation potential value higher than + 0.50 V, indicating that the sulphite anodic oxidation occurs with higher rate, confirming chrono -amperometric and -coulometric data. For the same sulphite concentration used in experimental studies, the charge transfer resistance decreases with the polarization increasing, the minimum values being recorded for an oxidation potential of +1.00 V. As well, the double layer capacity (C_{dl}) have been calculated and, as expected, values of this parameter increase with the oxidation potential at which the electrolysis process is carried out. The order of $10^{-3} \div 10^{-4}$ for chi-square values indicate an excellent correlation between the experimental electrochemical impedance data and the chosen EEC model.

Table 2. Calculated parameters of EEC elements for sulphite electrooxidation in neutral solution on layered cobalt perovskite electrode

SO_3^{2-} conc. (M)	*E* (V)	R_s (Ω cm^2)	CPE_{el}		R_e (Ω cm^2)	CPE_{ox}		R_{ct} (Ω cm^2)	$C_{dl}\cdot10^5$ (F cm^{-2})	$Chi^2\cdot10^3$
			$T\cdot10^4$ (F cm^{-2} s^{n-1})	n		$T\cdot10^4$ (F cm^{-2} s^{n-1})	n			
10^{-3}	-0.25	3.78	6.90	0.25	44.7	1.37	0.52	1609	3.48	1.18
	0.00	3.88	5.38	0.27	46.5	1.58	0.54	1170	3.69	0.84
	0.25	3.50	4.02	0.30	49.3	1.88	0.56	680	3.75	0.50
	0.50	3.48	1.81	0.32	55.9	2.32	0.57	393	3.81	0.88
	0.75	4.09	1.00	0.34	59.9	2.57	0.59	286	4.19	0.53
	1.00	4.44	0.75	0.36	61.6	2.66	0.60	252	4.40	0.28

SO_3^{2-} conc. (M)	E (V)	R_s (Ω cm^2)	CPE_{el} $T\cdot10^4$ (F cm^{-2} s^{n-1})	CPE_{el} n	R_e (Ω cm^2)	CPE_{ox} $T\cdot10^4$ (F cm^{-2} s^{n-1})	CPE_{ox} n	R_{ct} (Ω cm^2)	$C_{dl}\cdot10^5$ (F cm^{-2})	$Chi^2\cdot10^3$
10^{-2}	-0.25	3.19	8.33	0.26	61.9	1.44	0.54	1488	3.89	4.50
	0.00	3.23	6.26	0.29	64.5	1.64	0.55	1094	4.07	0.42
	0.25	3.59	6.44	0.31	65.6	1.96	0.57	654	4.24	1.70
	0.50	3.75	4.47	0.34	67.9	2.35	0.59	376	4.47	1.06
	0.75	3.87	2.49	0.37	74.4	2.67	0.60	269	4.54	0.32
	1.00	3.62	2.25	0.41	81.2	2.87	0.61	228	4.91	1.42
10^{-1}	-0.25	3.59	9.42	0.34	85.3	1.61	0.54	1336	4.26	0.66
	0.00	4.26	9.10	0.36	94.5	1.83	0.55	956	4.48	0.63
	0.25	4.30	8.36	0.39	101	2.04	0.58	635	4.74	1.00
	0.50	4.01	6.47	0.40	105	2.76	0.59	305	4.97	4.50
	0.75	4.01	4.84	0.43	108	3.00	0.61	235	5.43	3.56
	1.00	3.78	4.01	0.47	112	3.15	0.63	183	5.70	4.63
0.5	-0.25	3.10	11.32	0.37	104	1.63	0.55	1250	4.48	1.48
	0.00	3.52	10.91	0.38	107	1.99	0.56	817	4.69	2.15
	0.25	3.48	10.38	0.41	113	2.24	0.58	582	5.14	4.97
	0.50	3.91	8.63	0.43	117	3.28	0.59	243	5.55	2.80
	0.75	3.58	6.53	0.47	120	3.24	0.62	181	5.85	3.61
	1.00	3.79	5.99	0.50	124	3.28	0.65	140	6.20	2.81
1	-0.25	3.64	11.63	0.40	107	1.78	0.56	1085	4.86	0.49
	0.00	3.82	11.16	0.42	111	2.08	0.57	747	5.17	0.22
	0.25	4.22	10.26	0.44	114	2.34	0.59	521	5.41	0.43
	0.50	3.88	9.64	0.47	117	3.26	0.61	200	5.85	2.78
	0.75	4.28	7.51	0.51	122	3.72	0.64	115	6.14	1.94
	1.00	4.16	7.05	0.54	130	3.21	0.69	89	6.52	0.45

4. Conclusions

Experimental data presented in this paper have confirmed the possibility to oxidize SO_3^{2-} to SO_4^{2-} on an electrode made of cobalt layer perovskite type 114.

The electrocatalytic effect of this type of electrode has been studied for sulphite oxidation in neutral solution applying cyclic and linear voltammetry, chronoamperometry and electrochemical impedance spectroscopy.

The characteristic range of the optimal potential has been identified and current densities specific for sulphite oxidation and transformation degrees depending on the electrolysis time have been determined by electrochemical methods for each sulphite concentration in the neutral electrolyte solution. The obtained kinetic parameters (α and i_o) show that the overall process is controlled by the charge transfer step. This fact was confirmed by EIS studies, based on which charge transfer resistance (R_{ct}) and double-layer capacity (C_{dl}) were determined for different potential of the chosen range and for each sulphite concentration added in the test solution. The significant value of exchange current density i_o (3.30 A m^{-2}) emphasizes an important catalytic effect of the working electrode for the studied process.

The electrochemical behavior of sulphite ions on $Y_{0.5}Ca_{0.5}BaCo_4O_7$ electrode, especially their facile oxidability in neutral media, suggests that this type of electrode could be used in a Na_2SO_3 (aq) / O_2 fuel cell.

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