

ANODIC OXIDATION OF SULPHITE IN ALKALINE SOLUTIONS ON CALCIUM DOPED COBALT LAYERED PEROVSKITE TYPE 114 ELECTRODE

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Abstract

In this paper, anodic oxidation of sulphite ions on a calcium doped cobalt layered perovskite type 114 electrode in aqueous alkaline solution was investigated. The catalytic activity by anodic oxidation becomes a serious issue, mainly for the operation of layered cobalt perovskite electrodes in fuel cells. The research are necessary to understand the oxidation mechanism on the surface of this type of electrodes. Electrochemical behavior has been studied by cyclic voltammetry and linear polarization.

Keywords: $Y_{0.5}Ca_{0.5}BaCo_4O_7$, sulphite ions, anodic oxidation, cyclic voltammetry

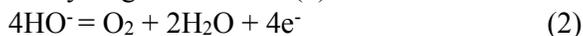
INTRODUCTION

$Y_{0.5}Ca_{0.5}BaCo_4O_7$ layered perovskite, firstly synthesized by M. Valldor, was defined as semiconductor material (Valldor M., 2006). During the last years 114 cobalt perovskites were one of the most investigated transitional metals mixed oxides due to their structural, magnetic and electrochemical properties. Based on these properties mixed cobalt oxides can be used as membranes with high oxygen permeability, oxygen sensors and also fuel cells electrodes. Experimental researches have shown that there is a correlation between compound structure and his properties, especially due to the variable cobalt ions valence. It was found that the original $YBaCo_4O_7$ oxygen adsorption properties can be modified greatly by low valence Ca^{2+} partial substitution with Y^{3+} in perovskite structure (Wang S. et al, 2008, Zhang Y. et al, 2012).

Electrochemical behavior of studied perovskite in alkaline solution can be described by following reaction:

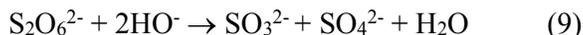
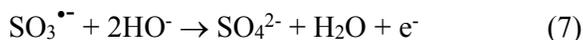
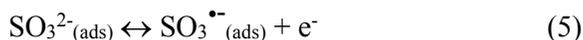


to which are attached two different reactions: anodic oxygen evolution (2) and also cathodic hydrogen evolution (3):



The electrochemical sulphite oxidation in alkaline solution occurs in two steps. In the first one, a radical anion $SO_3^{\bullet-}$ is formed by losing one

electron. Further more oxygen transfer undergoes by losing the second electron. Two sulphite radical can combine and form dithionate, which can then disproportionate into sulphite and sulphate, but the formation of dithionate on the graphite electrode (6) can be neglected in accordance with the literature (J. Lu. et al, 1999, Skavås E. et al, 2006, Skavås E. et al, 2007). Consequently, the anodic oxidation can be described by following equations:



In this paper, the cyclic voltammetry and linear polarization were used in order to describe the anodic sulphite oxidation in alkaline solution on $\text{Y}_{0.5}\text{Ca}_{0.5}\text{BaCo}_4\text{O}_7$ electrode.

MATERIAL AND METHOD

The $\text{Y}_{0.5}\text{Ca}_{0.5}\text{BaCo}_4\text{O}_7$ perovskite was prepared using solid state reaction, by mixing the precursors Y_2O_3 (Aldrich 99,99%), CaCO_3 (Aldrich 99,99%), BaCO_3 (Aldrich 99,99%) and $\text{CoO}_{1.38}$ (99,99% Normapur) according to the stoichiometric cation ratio. After decarbonation at 600°C the powder was reground, and fired in air for 48 h at 1100°C and then removed rapidly from furnace. The mixture was then reground and pressed into discs (1 cm^2) and sintered at 1100°C for 24 h in air. The structure of obtained $\text{Y}_{0.5}\text{Ca}_{0.5}\text{BaCo}_4\text{O}_7$ was checked by X-Ray powder diffraction.

Electrochemical studies were performed using a BioLogis SP 150 potentiostat/galvanostat. Electrochemical cell used during experiments was equipped with two counter electrodes placed symmetrically to the working electrode and Ag/AgCl reference electrode. In electrochemical tests 1 mol L^{-1} NaOH solutions were used in which was added different concentrations of Na_2SO_3 between 10^{-3} and $10^{-1} \text{ mol L}^{-1}$.

RESULTS AND DISCUSSION

Based on previous experiments it can conclude that $\text{Y}_{0.5}\text{Ca}_{0.5}\text{BaCo}_4\text{O}_7$ electrochemical behavior is influenced by the experimental conditions (Dan M. et al, 2011). A typical cyclic voltammograms recorded on $\text{Y}_{0.5}\text{Ca}_{0.5}\text{BaCo}_4\text{O}_7$ compound in alkaline solution are depicted in figure 1. It

can be observed that at anodic polarization an anodic peak (1) appears, which is associated with Co(II) ions oxidation $\text{Co(II)} \rightarrow \text{Co(III)} + e^-$, followed by a limiting current plateau (2). At more positive potentials the peak (3) associated with oxygen evolution reaction appears.

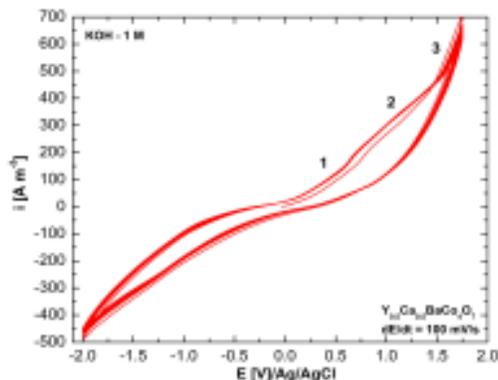


Fig.1. Cyclic voltammograms (10 cycles) recorded on $\text{Y}_{0.5}\text{Ca}_{0.5}\text{BaCo}_4\text{O}_7$ electrodes in 1 mol L^{-1} KOH at 100 mV s^{-1} .

If the perovskite is initially put to an advanced electrochemical oxidation stage using chronoamperometry method at $E = +2.0 \text{ V/Ag/AgCl}$, its surface is compacted, as presented in figure 2.

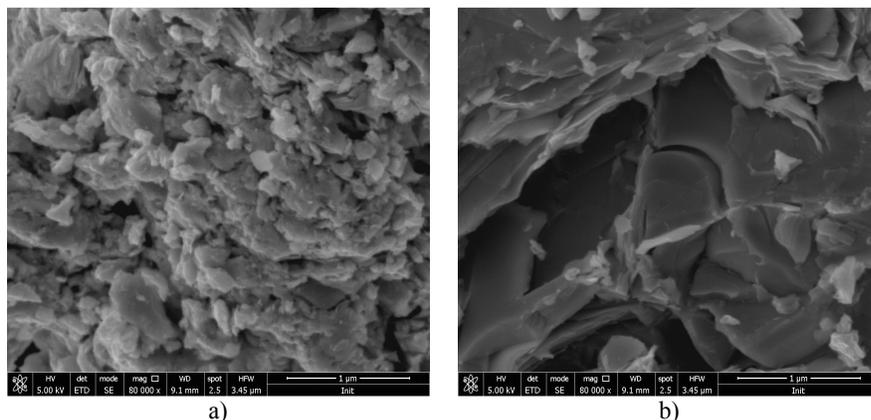


Fig.2 SEM images of $\text{Y}_{0.5}\text{Ca}_{0.5}\text{BaCo}_4\text{O}_7$ electrode's surface before (a) and after chronoamperometric oxidation.

After this step, the voltammetric studies recorded on $\text{Y}_{0.5}\text{Ca}_{0.5}\text{BaCo}_4\text{O}_7$ electrode showed that layered cobalt perovskite acts as support material in alkaline solutions, for a long potential range (between $+2.5$ and -1.5 V/Ag/AgCl), where only the peaks associated with oxygen and respectively hydrogen evolution reactions can be observed. In figure 3

there are presented cyclic voltammograms recorded using 1 mol L⁻¹ NaOH solution with 100 mV s⁻¹ polarization speed, starting from open circuit potential, in different potential range +1.75 V to -2.0 V/Ag/AgCl.

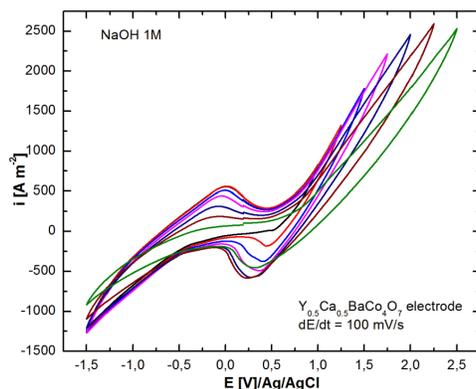


Fig.3. Cyclic voltammograms (5 cycles) recorded on Y_{0.5}Ca_{0.5}BaCo₄O₇ electrodes in 1 mol L⁻¹ NaOH at 100 mV s⁻¹

Cyclic voltammograms plotted with high scan rate (500 mV s⁻¹) on Y_{0.5}Ca_{0.5}BaCo₄O₇ electrode in the alkaline electrolyte in which was added sodium sulphite in different concentrations are shown in figure 4. From the analysis of cyclic curves it is observed a separation of characteristic peaks for Co(II) ions oxidation from the perovskite structure (especially inside of the electrode) as well as SO₃²⁻ to SO₄²⁻ oxidation does not occurs. In electrolyte solutions containing sodium sulphite, the potential of anodic oxygen evolution on the surface of the working electrode is shifted to more positive values, respectively the potential of cathodic hydrogen evolution is shifted to more negative ones.

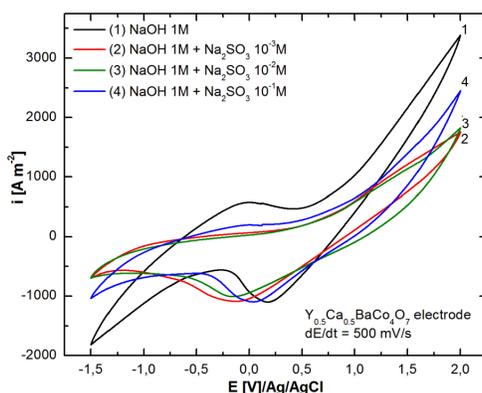


Fig.4. Cyclic voltammograms recorded on Y_{0.5}Ca_{0.5}BaCo₄O₇ electrodes in 1 mol L⁻¹ NaOH without/with different concentration of Na₂SO₃ at 500 mV s⁻¹.

In figure 5 there are shown comparative cyclic voltammograms plotted on $Y_{0.5}Ca_{0.5}BaCo_4O_7$ electrode at a scan rate of 100 mV s^{-1} (figure 5a), respectively 10 mV s^{-1} (figure 5b) in 1 mol L^{-1} NaOH solutions in absence and presence of $10^{-1} \text{ mol L}^{-1}$ Na_2SO_3 . On cyclic curves plotted at 100 mV s^{-1} (a), major changes there are not compared to the voltammograms shown in figure 4.

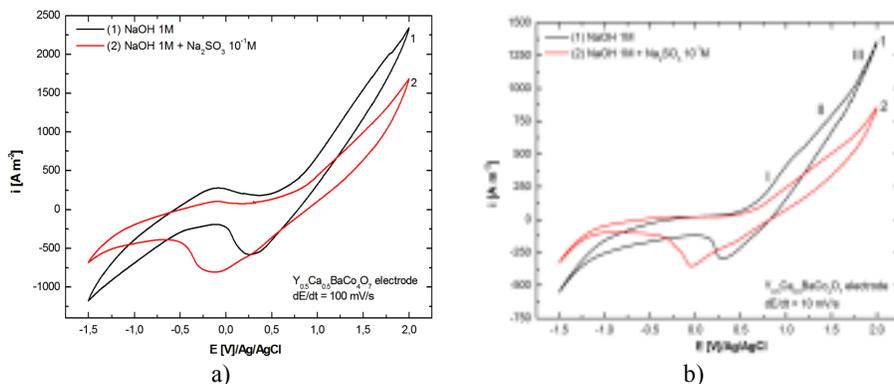


Fig.5. Cyclic voltammograms recorded on $Y_{0.5}Ca_{0.5}BaCo_4O_7$ electrodes in 1 mol L^{-1} NaOH without/with $10^{-1} \text{ mol L}^{-1}$ Na_2SO_3 at: a) 100 mV s^{-1} and b) 10 mV s^{-1} .

Decreasing the scan rate up to 10 mV s^{-1} provides the opportunity to make a first identification of the processes occurring at the interface perovskite electrode / electrolyte. Thus, it can be seen that in alkaline electrolyte without sulphite (curve 1) an oxidation process is observed, up to a value of approximately $+1.0 \text{ V / Ag / AgCl}$ followed by oxygen release on the working electrode surface. Although, initially the electrode acted as a support for electrochemical processes that occur in the system (anodic oxygen evolution and cathodic hydrogen evolution), without effective contribution in electrode reactions, due to oxidation - reduction cycles that have undergone, its surface is activated. The oxidation process that takes place in the potential range of $0.5\text{-}1.0 \text{ V / Ag / AgCl}$ is the oxidation of Co (II) to Co (III) in the perovskite structure, which confirms existing data in the literature (Dan M. et al, 2011). Introducing $10^{-1} \text{ mol L}^{-1}$ sodium sulphite in the electrolyte solution (curve 2), the shape of cyclic voltammograms in the anodic domain is modified without the possibility to identify the processes occurring in the potential range between $+0.5$ and $+1.75 \text{ V / Ag / AgCl}$. Although, in this area of the potential both the Co (II) and SO_3^{2-} oxidation ions occurs, the amount of electricity which crosses the interface electrode/electrolyte is not sufficient to oxidize in the first step Co (II) ions existing at oxide-solution interface and subsequently SO_3^{2-} ions arrived at

interface by diffusion, the effect is the existence of a single common oxidation plateau recorded on voltammograms.

In order to identify specific potential plateaux of both oxidation processes studied in the system electrode ($Y_{0.5}Ca_{0.5}BaCo_4O_7$) / electrolyte (1 mol L⁻¹ NaOH + 10⁻¹ mol L⁻¹ Na₂SO₃) cyclic voltammograms were plotted up to different values of anodic polarization, between +1.0 and +2.5 V / Ag / AgCl, as shown in figure 6. From their analysis we can distinguish three regions: 1 - between +0.5 and +1.0 V / Ag / AgCl characteristic for oxidation of Co (II); 2 - between +1.0 and +1.75 V / Ag / AgCl specific for the oxidation of SO₃²⁻ ions; 3 - at potential values higher than +1.75 V / Ag / AgCl oxygen evolution starts on the electrode.

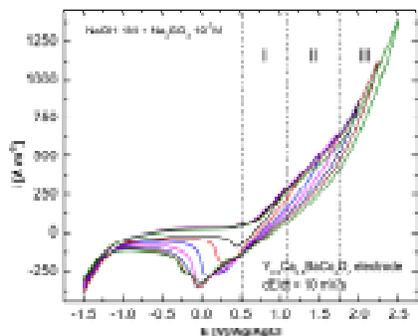


Fig.6. Cyclic voltammograms recorded on $Y_{0.5}Ca_{0.5}BaCo_4O_7$ electrodes in 1 mol L⁻¹ NaOH with 10⁻¹ mol L⁻¹ Na₂SO₃.

Experimental technique by which have been confirmed the results presented above was linear voltammetry at very low scan rate (1 mV s⁻¹), the curves obtained being shown in figure 7.

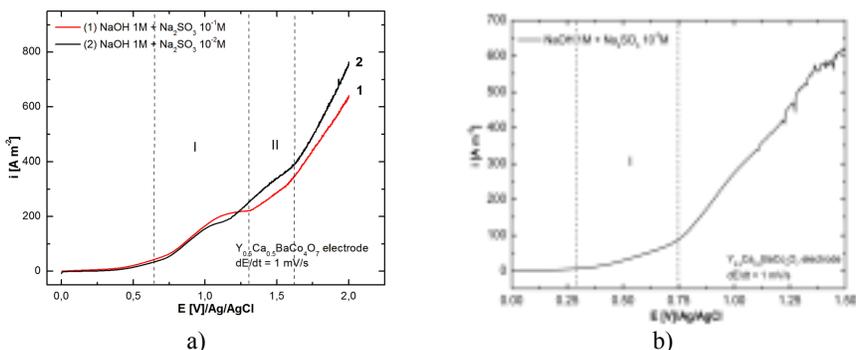


Fig.7. Linear voltammograms recorded on $Y_{0.5}Ca_{0.5}BaCo_4O_7$ electrodes in 1 mol L⁻¹ NaOH with: a) 10⁻¹ mol L⁻¹ (1) and 10⁻² mol L⁻¹ Na₂SO₃ (2); b) 10⁻¹ mol L⁻³.

From the analysis of linear voltammograms, specific potential ranges of both oxidation processes that occur at the interface electrode / electrolyte were identified only for 10^{-1} or 10^{-2} mol L⁻¹ sodium sulphite in electrolyte solution (curve 7). On linear voltammograms plotted in case when into the electrolyte solution was added 10^{-3} mol L⁻¹ Na₂SO₃ it could be identify only the first range of potential to a value about +0.75 V / Ag / AgCl. At more positive potential a separation between the range at which the oxidation of SO₃²⁻ ions occurs and the potential value at which oxygen release begins can not be achieved.

Based on linear voltammograms kinetic parameters (transfer coefficient - α and exchange current - i_0) for electrochemical oxidation of sulphite to sulphate in alkaline solution on Y_{0.5}Ca_{0.5}BaCo₄O₇ electrode have been calculated for each electrolyte solution using Tafel method. Also, the same parameters for Co(II) to Co(III) oxidation was determined. The results obtained are presented in table 1.

Table 1

The kinetic parameters for sulphite oxidation in alkaline solution

Na ₂ SO ₃ concentration [mol L ⁻¹]	Domain	b [V/dec]	α	i_0 [A m ⁻²]
10 ⁻¹	I	0.62	0.094	21.2
	II	1.59	0.037	22.3
10 ⁻²	I	0.50	0.106	21.1
	II	1.12	0.052	18.9
10 ⁻³	I	0.53	0.110	21.3
	II	—	—	—

Correlating voltammetric data relating to Y_{0.5}Ca_{0.5}BaCo₄O₇ perovskite oxidation in alkaline medium with kinetic data presented in table 1, we can conclude that in the domain I Co (II) to Co (III) oxidation process in perovskite structure occurs. The domain II is characteristic for SO₃²⁻ to SO₄²⁻ oxidation on the electrode surface. It should also be specified the fact that these data refer only to the electrochemical oxidation of SO₃²⁻ ions and if the quantitative calculations will be made for a complete description of sulphite oxidation process to sulphate on the electrode, it is necessary to determine the amount of SO₃²⁻ ions chemically oxidized in solution due to the large amounts of oxygen available in the electrolyte solution.

CONCLUSIONS

Experimental data presented have confirmed the possibility to oxidize SO₃²⁻ to SO₄²⁻ on an electrode made of cobalt layer perovskite type 114.

From the perspective of using cobalt layered perovskite as potential electrode materials in fuel cells operating at intermediate temperatures (IT-

SOFC), the possibility to oxidize sulphite ions directly on their surface, provides a good reason for continuing studies presented in this article. A deepening of the research is necessary both for complete characterization of processes occurring at the interface, and to determine characteristic optimum parameters, of which the most important is the efficiency of the oxidation process.

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