

Electrochemical Oxygen Uptake/Release Process on Ca Doped Y-114 Electrodes in Aqueous Solutions

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Abstract

In present study, the electrochemical characterization of $Y_{0.5}Ca_{0.5}BaCo_4O_7$ compound in aqueous solution: alkaline (1 molL^{-1} KOH) and neutral (0.5 mol L^{-1} Na_2SO_4) was followed, correlated with the study of oxygen intake/release process. The use of neutral aqueous solutions is an element of originality in electrochemical studies performed on this family of layered cobalt perovskites.

Electrochemical behavior has been studied by cyclic voltammetry and chrono-electrochemical methods: chronoamperometry and chronocoulometry.

Introduction

Extended researches carried out on Y-114 perovskite have revealed his electrical and also magnetic properties, and have shown that there is a correlation between compound structure and his properties, especially due to the average cobalt ion valence. Starting from this emerged the idea to replace half of the Y ions amount (in moles) with Ca ions, leading in this way at changes into the average cobalt valence in $YBaCo_4O_7$ perovskite, in order tu study how is affecting electrical and magnetic properties. When the $Y_{0.5}Ca_{0.5}BaCo_4O_7$ perovskite was firstly synthesized by M. Valldor was defined as semiconductor material [1]. After first preparation, has been deciphered crystalline structure followed by study of electrical and magnetic properties [1-3].

Average cobalt ions valence modification from +2.25 in $YBaCo_4O_7$ at +2.375 in $Y_{0.5}Ca_{0.5}BaCo_4O_7$ explains the electrochemical interest as this compound and justifies the need for future studies. As a consequence of the increase of average cobalt ions valence in studied perovskite it is expected that the maximum oxygen content is decrease from 8.5 in $YBaCo_4O_7$ at 8.25 in $Y_{0.5}Ca_{0.5}BaCo_4O_7$ perovskite. Purposes of carried electrochemical tests were to characterize the compound from electrochemical point of view, and also to study sample oxygen uptake/release capacity.

Experimental

The $Y_{0.5}Ca_{0.5}BaCo_4O_7$ compound was obtained 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 $CoO_{1.38}$ (99,99% Normapur) according to the stoichiometric cation ratio. After decarbonation at $600^{\circ}C$ the powder was reground, and fired in air for 48 h at $1100^{\circ}C$ and then removed rapidly from furnace and set ambient temperature. The mixture was then reground and pressed into discs (1 cm^2) and sintered at $1100^{\circ}C$ for 24 h in air. The structure of obtained $Y_{0.5}Ca_{0.5}BaCo_4O_7$ perovskite was checked by X-Ray powder diffraction (Rigaku Ultima IV).

Electrochemical studies were carried out using a BioLogis SP 150 potentiostat/galvanostat equipped with electrochemical impedance spectroscopy module. Electrochemical cell used during experiments was a three electrode one, formed from two counter electrodes placed symmetrically to the working electrode (a disk with the geometric surface of 0.8 cm^2),

and a reference electrode represented by Ag/AgCl electrode. In electrochemical tests were used KOH 1 mol L⁻¹ and Na₂SO₄ 0.5 mol L⁻¹ solutions.

Results and discussion

Y_{0.5}Ca_{0.5}BaCo₄O_{7+δ} electrochemical behavior was studied using the cyclic voltammetry recorded in a wide potential range in order to identify all the processes occurring in the electrochemical system: oxidation/reduction reactions, oxygen and hydrogen evolution reactions, followed by further cyclic voltammograms focused on processes which are important for practical applications of these perovskites. Based on previous experiments it can say that the voltammograms shape is influenced by the experimental conditions, and one important parameter is represented by polarization speed [4,5].

In figure 1a there are depicted cyclic voltammograms recorded using KOH 1 mol L⁻¹ solution at a polarization speed of 100 mV s⁻¹, starting from open circuit potential, in a potential range of +1.75 V to -2.0 V vs Ag/AgCl electrode. Using such polarization speed, it can observe on the anodic part of curve the appearance of peaks/plateaus associated with: compound oxidation (1), limiting current (2), and oxygen evolution reaction (3). Also, figure 1b shows cyclic voltammograms recorded in neutral solution (1 mol L⁻¹ Na₂SO₄), on which similar processes deployed on electrode surface can be observed.

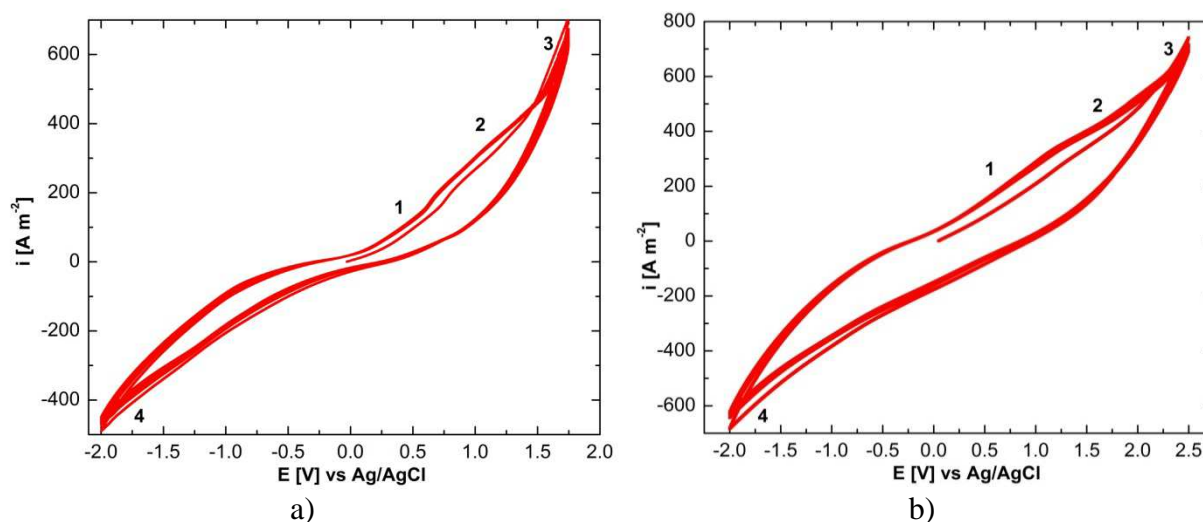


Figure 1. Cyclic voltammograms recorded on Y_{0.5}Ca_{0.5}BaCo₄O₇ electrodes at 100 mV s⁻¹:
a) 1 mol L⁻¹ KOH, b) 0.5 mol L⁻¹ Na₂SO₄

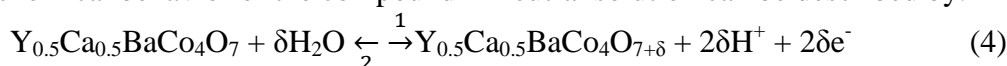
Electrochemical behavior of studied perovskite in alkaline solution can be described by following reaction:



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



Electrochemical behavior of the compound in neutral solution can be described by:



which describes the oxidation process in the sense 1, and also the cathodic reduction in the sense 2. Similarly, to this global equation the reaction describing the oxygen (5) and hydrogen evolution reactions (6) can be associated:



Chronoamperometric study was the starting point the cyclic voltammograms recorded on perovskite compound in alkaline and neutral solutions. From data depicted in figure 1a, 3 potential values for chronoamperometric studies were chosen: 1 - $E = 0.25$ V vs Ag/AgCl on the compound oxidation plateau, 2 - $E = 0.65$ V vs Ag/AgCl on the limiting current plateau, and 3 - $E = 1.0$ V vs Ag/AgCl for the oxygen evolution reaction plateau (figure 2).

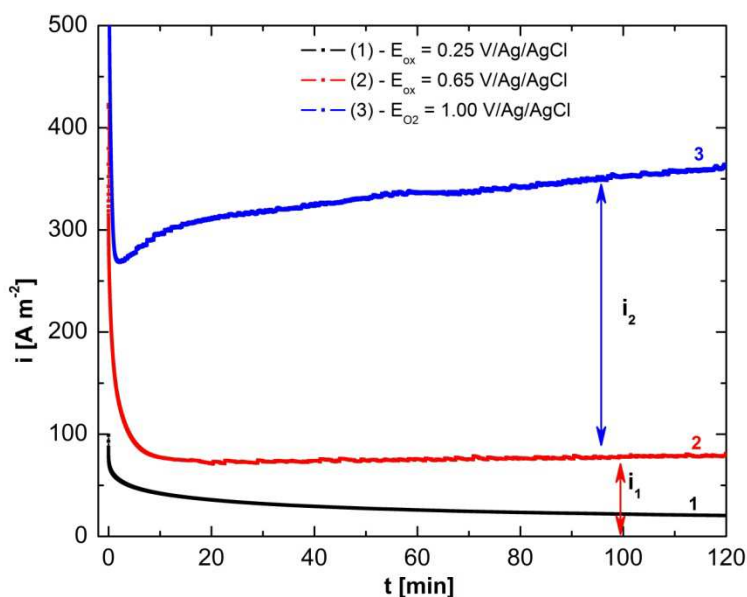


Figure 2. Chronoamperometric study on $\text{Y}_{0.5}\text{Ca}_{0.5}\text{BaCo}_4\text{O}_7$ electrodes in 1 mol L^{-1} KOH.

Simultaneously the chronoamperometric curves were recorded in neutral solutions at: 1 - 0.75 V vs Ag/AgCl for the perovskite oxidation, 1.25 V/Ag/AgCl for limiting current plateau and at 1.75 V/Ag/AgCl for oxygen evolution reaction.

In same time, chronocoulometric data were recorded in alkaline and also neutral solutions, when the quantity of electricity used for perovskite oxidation at working potentials was measured. Based on that, using the electrolysis laws, considering that only Co(II) ions oxidation is taking place, it was possible to evaluate the oxygen quantity (δ) inserted in the compound structure as time a function of time. The δ values obtained in alkaline and neutral solutions are presented in tables 1 and 2.

Table 1. Oxygen content variation (δ) in $\text{Y}_{0.5}\text{Ca}_{0.5}\text{BaCo}_4\text{O}_{7+\delta}$ during electrochemical oxidation in KOH 1 mol L^{-1} :

E [V/Ag/AgCl]	δ			
	t [min]			
	15	30	60	120
0,25	0,022	0,039	0,063	0,097
0,65	0,047	0,080	0,136	0,266

Tabelul 2. Oxygen content variation (δ) in $Y_{0.5}Ca_{0.5}BaCo_4O_{7+\delta}$ during electrochemical oxidation in Na_2SO_4 0.5 mol L⁻¹:

<i>E</i> [V/Ag/Ag/Cl]	δ			
	<i>t</i> [min]			
	15	30	60	120
0,75	0,028	0,048	0,064	0,076
1,25	0,028	0,090	0,127	0,175

Conclusion

Electrochemical oxidation of Co(II) ions at Co(III) ions consists in oxygen atoms insertion into the crystalline network of studied perovskite. Although, in the δ values in the case of electrochemical oxidation, in neutral solution are smaller in comparison with the values obtained for alkaline oxidation. Consiquently can conclude the usage of neutral solution represent a viable alternative for $Y_{0.5}Ca_{0.5}BaCo_4O_{7+\delta}$ oxidation.

References

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