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ELECTROCHEMICAL BEHAVIOR OF $CaBaCo_2O_{5\pm\delta}$ IN NEUTRAL AQUEOUS SOLUTION

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ABSTRACT. This paper presents the effect of Y^{3+} substitution with Ca^{2+} ions on the electrochemical behavior of Y-112 perovskite in neutral aqueous solution during oxygen insertion/release. Perovskite electrochemical behavior was studied by cyclic voltammetry and chrono-electrochemical methods. In correlation with these techniques the compound morphology was determined by scanning electron microscopy (SEM). Based on obtained results the electrochemical reactions occurring at interface compound – electrolyte have been identified.

Keywords: *cobalt mixed oxides, $CaBaCo_2O_{5\pm\delta}$, Ca^{2+} ions insertion, cyclic voltammetry, chrono- electrochemical methods.*

INTRODUCTION

Cobalt layered perovskites with 112 type structure attract a great attention in recent years due to a wide magnetic and electrical properties. Compounds from series $LnBaCo_2O_{5+\delta}$ (Ln = Nd-Ho and Y) are promising materials for applications as solid-oxide fuel cell (SOFC) cathodes or as ceramic membranes for oxygen separation [1]. These new technologies provide the enormous economic and environmental advantages.

Electrical charge transfer of those perovskites is achieved by a complex mechanism involving electronic and ionic conductivity, due to the presence of simultaneous deficit of electrons and oxygen holes into the crystalline structure. The oxygen intake/release process in 112 cobaltate perovskites modifies the concentration of electric charges carriers with direct effect on the internal resistance and consequently on the electrical conductivity of these compounds [2,3].

The compounds from 112 series present a tetragonal structure with space group *P4/mmm* or orthorhombic (pseudotetragonal) structure with space group *Pmmm* or *Pmma* [4]. The substitution of Y^{3+} ions with Ca^{2+} is achieved deformation of the perovskite Y-112 initial structure.

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Compound $CaBaCo_2O_{5-\delta}$ was obtained by substitution of Y^{3+} with Ca^{2+} ions. The diminished interest for this perovskite is due to the fact that the valence of Co ions in perovskite structure is +3, which has a negative effect on cobalt 112 perovskites electrical and magnetic properties [5,6].

Oxygen content of Ca 112 mixed oxide is depending on the metallic cation nature included in to the oxide structure, which is determining for the nominal valence of Co ions. Oxygen nonstoichiometry in the perovskite structure is influenced by oxygen content variations which affecting the oxygen permeability and diffusion, and also has a highly importance in order to reveal the perovskite structure. From electrochemical point of view, studied Ca 112 mixed oxide can be attractive due to his oxygen insertion/release capacity.

RESULTS AND DISCUSSION

The purity of obtained Ca-112 compound was checked by X-Ray powder diffraction (Philips X-pert Pro). The result is presented in figure1.

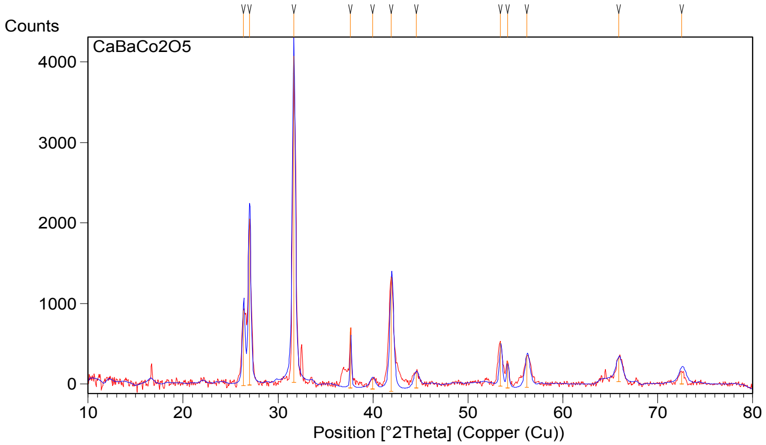
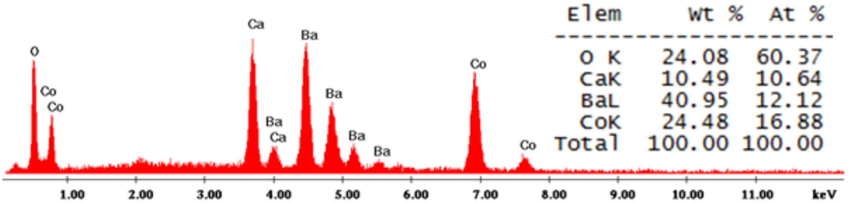


Figure 1. X-ray diffraction pattern for $CaBaCo_2O_5$ obtained by the solid state reaction at 1100°C.

XRD diffraction spectra were recorded for 2θ range between 0 and 80°, after that all peaks from recorded spectra were identified using ICC data base. From that can conclude that the obtained product is the desired $CaBaCo_2O_5$ mixed oxide.

Also, the 112 perovskite composition was confirmed by EDAX analysis performed after sintering stage and the results are presented in figure 2. Although, these analyzes provide approximate information about the compound composition, especially as analyzes are dependent on the compound uniformity and homogeneity, the atomic and mass percentages of the elements from the inserted table confirm the Ca-112 composition.



Elem	Wt %	At %
O K	24.08	60.37
CaK	10.49	10.64
BaL	40.95	12.12
CoK	24.48	16.88
Total	100.00	100.00

Figure 2. EDAX spectrum for compound $CaBaCo_2O_5$.
Inserted the atomic and mass percentages of the components.

Thermal behavior of Ca-112 compound was studied in similar conditions as used in thermal studies of Y-112 compound: nitrogen flow, and temperature range between 30 and 1000 °C. The thermogram obtained is depicted in figure 3.

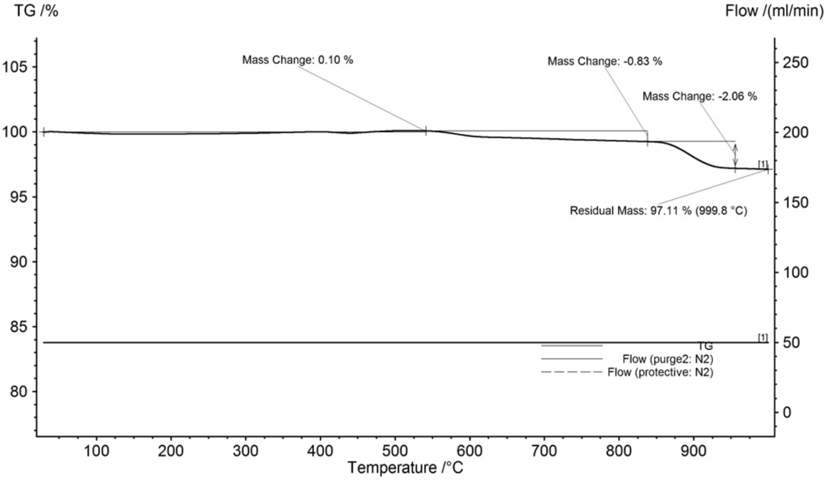


Figure 3. Weight change of $CaBaCo_2O_{5\pm ä}$ with temperature in nitrogen flow.

During thermal study, the compound Ca-112 can intake or release oxygen, which is equivalent with the modification of the average oxidation number of cobalt ions presented in perovskite structure, which may vary between +2 and +4, as indicated the studies performed on Ca-112compound.

In table 1 the weight variations obtained for studied compound and also the oxygen excess/deficiency (δ) versus temperature under a nitrogen flow are presented.

Table 1. Δm values and δ in temperature range 30-1000˚C (gas flow: nitrogen)

Gas flow	Temperature range [˚C]	Δ*m* [%]	*δ* in $CaBaCo_2O_{5\pm\delta}$
Nitrogen	30-550	0.10	+ 0.02
	550-830	-0.83	- 0.17
	830-950	-2.06	- 0.65

Ca-112 thermal behavior under nitrogen flow is specific for cobalt perovskite, especially up to 800°C. The amount of accepted oxygen in studied compound up to 350° C is very low (+ 0.02 ions O^{2-}/mol), probably due to + 3 oxidation number of Co ions in the Ca-112 structure. When the temperature is increasing, Y-112 characteristic perovskite structure is distorted, becoming more compact, and the oxidation of cobalt ions at + 4 is more difficult. In temperature range of 305 -750°C, the amount of oxygen release is much higher than the accepted one which confirms the tendency to released oxygen from this perovskite crystal structure in an inert atmosphere.

In terms of crystalline structure, intake/release of a small amount of oxygen not produce major changes in the original structure, and most probably a rearrangement of bonds in the Ca-112 structure occurs. At temperatures over 750°C, sudden release of 0.65 ions/mol of oxygen may have a destruction effect on 112 layered structures and consequently, other oxides of constituents are formed [10].

An important factor influencing kinetics of oxidation process is the surface morphology; studied by scanning electron microscopy immediately after the sintering stage and also after the electrochemical studies. SEM images obtained for Ca-112 electrodes involved in this work are presented in figure 3.

It can be observed that perovskite has a compact structure, with few channels existing in excrescences (figure 4a), which facilitate access of the reactants and favor oxygen adsorption/desorption process. Also, in the SEM image recorded after electrochemical oxidation (figure 4b) an advanced compaction of electrode surface is observed. This can be associated with the deployment of electrochemical processes especially at interface electrode/ electrolyte. The oxidation/reduction process in the bulk electrode will be more difficult.

The equilibrium of Ca-112 electrode in 0.5 mol L^{-1} Na_2SO_4 solution is quasi-stationary, equilibrium potential value (OCP) is modified after each determination and it is in a correlation with compound oxygen content variation (*δ*). Versus initial equilibrium potential, it can have negative values in case of oxygen deficiency (5-*δ*) or positive when an excess of oxygen (5 + δ) was observed. OCP determined by chronopotentiometry at zero current in 0.5 mol L^{-1} Na_2SO_4, for 12 hours, was E_{ech} = + 0.255 V, displaced by approximately 200 mV towards more positive values in comparison with the values obtained for Y-112 electrode. At this value of potential we can consider that the studied perovskite has preserved his stoichiometry and the oxygen excess (*δ*) in compound remains 0, which is equivalent with an oxidation number of +3 for cobalt ions.

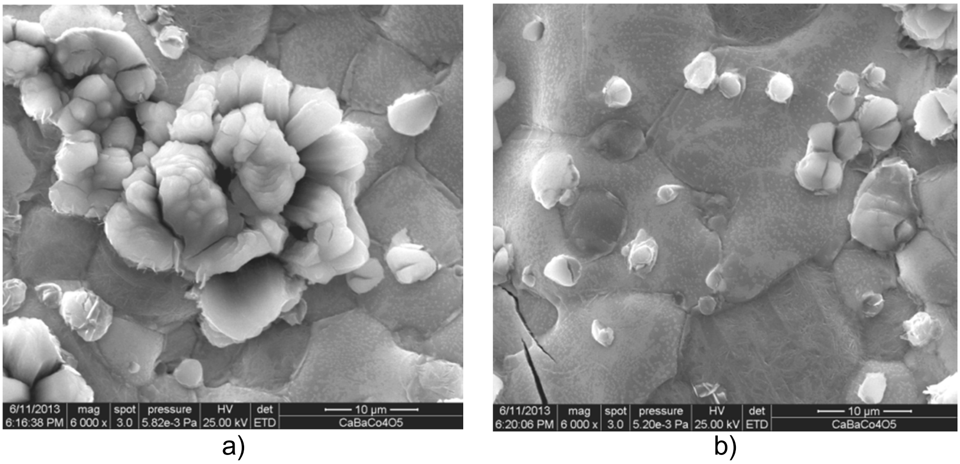
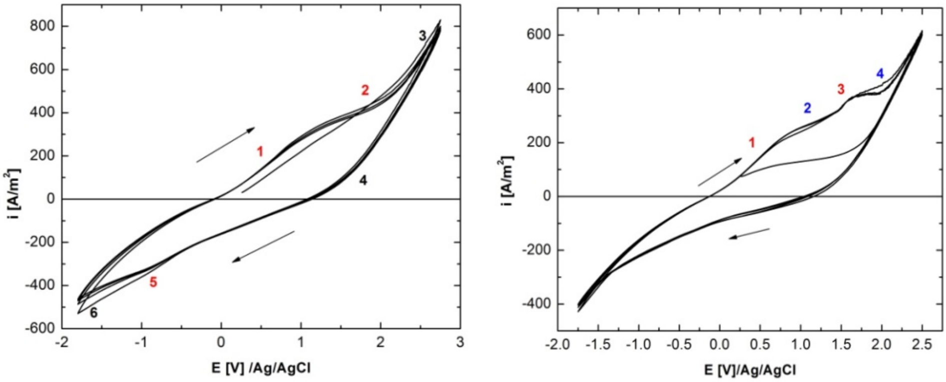


Figure 4. SEM images of the Y-112 electrodes surface before (a) and after electrochemical oxidation/reduction (b) at 6000x magnification

Preliminary voltammetric studies show that in neutral medium in a wide range of potential (+ 2.5 and - 2 V), Ca-112 electrode behaves as a support material, being observed only oxygen and hydrogen evolution reaction on the electrode. This behavior can be explained either by surface morphology presented previously or through the fact that, at anodic polarization, Co^{3+} ions from perovskite are oxidized very slowly and only in some conditions at Co^{4+}, while at cathodic polarization the quantity of electricity which passes the interface is not large enough to initiate the reduction process of Co^{3+} to Co^{2+}.

Therefore, preliminary studies demonstrated the need of an initial superficial activation stage by pre-polarizing the electrode at -1.00 V versus Ag/AgCl in order to reduce a part of Co^{3+} ions. After a superficial activation, the peak separation corresponding to the processes occurring at interface $CaBaCo_2O_5$ – electrolyte solution can be observed or recorded voltammograms (scan rate less than 50 mV s^{-1}).

In cyclic voltammograms depicted in fig. 5.a (5 cycles recorded starting from OCP towards positive potentials, scan rate 50 mV s^{-1}) can be observed at the occurrence of an anodic peak (1) associated with the oxidation process ($Co^{2+} \rightarrow Co^{3+} + e^-$), followed by a current limit plateau (2). When, the electrode potential is more positive, oxygen evolution reaction can be observed (3). On the CV backward scan it can be observed a limiting current plateau (4) associated with the oxidation of superficial remanent oxygen. When the electrode potential is shifted to more negative values a cathodic peak (5) associated with Co^{3+} reduction process appear around -0.8 V. At more negative potentials, the current increase can be associated with hydrogen evolution reaction ($2H^+ + 2e^- \leftrightarrow H_2$).



a) b)

Figure 5. Cyclic voltammograms (5 cycles) on Ca-112 working electrode in 0.5 mol L^{-1} Na_2SO_4 solution, pH 6.8 at 50 mV s^{-1}(a) and 10 mV s^{-1} (b) scan rate.

When the CV's were recorded at 10 mV s^{-1} (fig. 5.b) it can be observed the occurrence of a new peak (3) and also of a new plateau (4), which can be associated with interfacial Co^{3+} ions oxidation ($Co^{3+} \rightarrow Co^{4+} + e^-$) or with bulk oxidation of Co^{2+} ($Co^{2+} \rightarrow Co^{3+} + e^-$) ions, because the electrode surface is completely oxidized.

When the CV are recorded using lower scan rate (5 mV s^{-1}) anodic peak 1 was associated with Co^{2+} oxidation, followed by a limiting current plateau 2, alongside hydrogen and oxygen evolution reactions (fig. 6).

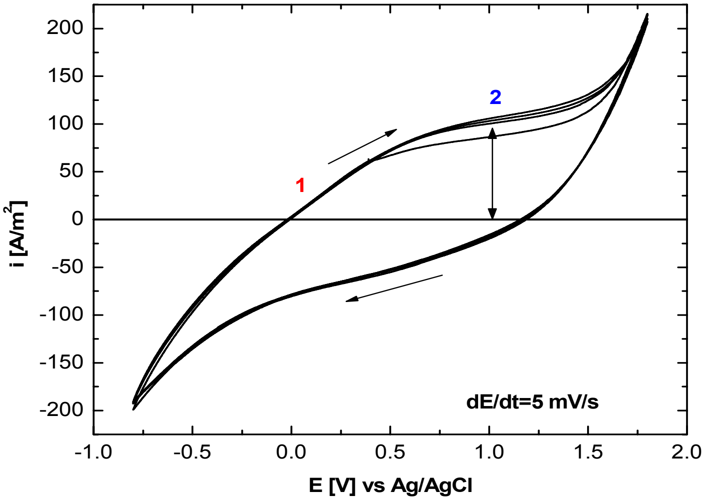


Figure 6. Cyclic voltammograms (5 cycles) on Ca-112 working electrode in 0.5 mol L^{-1} Na_2SO_4 solution at 5 mV s^{-1} scan rate.

Global reaction which occurs at interface electrode/electrolyte is:

$$Ca_2BaCo_2O_5 + \delta H_2O \rightarrow Ca_2BaCo_2O_{5+\delta} + 2\delta H^+ + 2\delta e^-$$

Similar with chronoamperometric and chronocoulometric studies performed in case of Y-112 compound, in order to calculate the amount of oxygen introduced in Ca-112 crystalline structure by electrochemical methods, were chosen two potential values significant for the electrochemical oxidation of studied perovskite in neutral aqueous solution: one corresponding for oxidation peak (+ 0.50V/Ag/AgCl) and the second for the current limit plateau (+1.00V/Ag/AgCl). These tests were performed in order to study the oxygen intake capacity for different times intervals. Based on cronocoulometry data was estimated the amount of oxygen (δ) introduced into the crystalline structure for different oxidation times (table 2). Should be noted that before each chorno-coulometric study, electrodes suffer a cathodic polarization in order to sufficiently reduce the Co^{3+} ions quantity, such that during oxidation stage the amount of oxygen introduced in perosvkite structure not exceed compound initial stoichiometry.

Table 2. *δ* variation in the electrochemical oxidation of Ca-112

Electrolyte	**Time [min]**	***δ* in $YBaCo_2O_{5+\delta}$**	
		E = 0,50 V/Ag/AgCl	*E* = 1,00 V/Ag/AgCl
Na_2SO_4 0,5 mol L^{-1}	15	0,48 x 10^{-3}	1,02 x 10^{-3}
	30	0,79 x 10^{-3}	1,36 x 10^{-3}
	60	1,11 x 10^{-3}	1,88 x 10^{-3}
	120	1,34 x 10^{-3}	2,25 x 10^{-3}

From data presented in table 2 can be observed that the studied compound present all the characteristic specific to layered cobalt perovskite – the oxygen intake / release capacity. Also, due to smaller amount of oxygen accepted in Ca-112 perovskite structure, in same time interval, oxygen intake / release process occurs with smaller speed, in comparison with the speed observed in case of Y-112 perovskites.

CONCLUSIONS

The results obtained in this first electrochemical study performed in neutral sollution studies showed that the Ca-112 mixed oxide is sensitive at anodic or cathodic polarization, oxidation process consists in oxygen insertion in crystal structure. Consequently, during oxidation the Ca-112 crystalline network becomes denser, so that the oxygen diffusion rate is lowered. The compaction of Ca-112 during oxidation imposes a partial irreversible character of the oxidation process. Although, the *δ* obtained for Ca-112 oxidation are lower than ones obtained for Y-112.

EXPERIMENTAL SECTION

Ca-112 mixed oxide was obtained using a solid state reaction, by mixing the precursors: $CaCO_3$ (Aldrich 99.99%), $BaCO_3$ (Aldrich 99.99%) and $CoO_{4/3}$ (Normapur 99.9%), according to the stoichiometric cation ratio. Preparation method of selected perovskite was similar with that used for the preparation of Y-112 cobalt perovskite [7-9]. After decarbonization at 900°C for 6 hours, the powder was pressed into pellets with geometrical active surface of 1 cm^2, later fired in air for 48 h at 1100°C and then removed quickly from oven and set to ambient temperature [7-9]. Compound purity was checked by X-Ray powder diffraction (Philips X-pert Pro). Surface morphology of Ca-112 electrodes has been characterized by scanning electron microscopy (SEM) using a FEI INSPECT S microscope.

Electrochemical studies were carried out using a BioLogics SP150 potentiostat/galvanostat. The electrochemical cell was equipped with two graphite counter electrodes positioned symmetrically against the working electrode (Ca-112 electrode) and an Ag/AgCl reference electrode. All potentials used in this work are given versus the Ag/AgCl reference electrode. All electrochemical measurements were performed in 0.5 mol L^{-1} Na_2SO_4 electrolyte solution.

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