

## REMARKABLE OXYGEN INTAKE/RELEASE CAPABILITY OF YBaCo<sub>4</sub>O<sub>7</sub> IN ALKALINE MEDIA BY ELECTROCHEMICAL METHODS

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### Abstract

*The present study proves that YBaCo<sub>4</sub>O<sub>7</sub> perovskite has high performance of oxygen storage capacity in alkaline media by electrochemical oxidation. This perovskite is a promising candidate for applications in which efficient oxide ion conductivity or large oxygen storage capacity is required. The oxygen intake/release propriety of YBaCo<sub>4</sub>O<sub>7</sub> has been studied by cyclic and linear voltammetry. Also, the accumulated oxygen amount in compound was determined by electrochemical oxidation using specific methods: chronoamperometry, chonopotentiometry and chronocoulometry.*

**Keywords:** YBaCo<sub>4</sub>O<sub>7</sub> perovskite, oxygen intake/release capacity, electrochemical methods

### INTRODUCTION

Cobalt perovskite (YBaCo<sub>4</sub>O<sub>7</sub>) is an attractive material from a fundamental scientific and an applied technological point of view (Parkkima O. et al, 2014). YBaCo<sub>4</sub>O<sub>7</sub> is able to intakes/releases rapidly a large amount of oxygen (>3.25 wt %) at moderate temperatures (200 - 400°C) in a perfectly reversible manner (Zhang Y.M. et al, 2012). This uncommon property is typical for the class of layered cobalt perovskites, type 114. It also appeared that YBaCo<sub>4</sub>O<sub>7</sub> exhibits a significant catalytic activity for oxygen evolution, presumably owing to its oxygen-storage ability. A large oxygen-content reversibility makes this studied compound a highly potential candidate for various applications such as oxygen storage, gas separation and oxygen sensor (Hao H. S. et al, 2006).

Nevertheless, thermal instability of YBaCo<sub>4</sub>O<sub>7</sub> can be an obstacle for future applications, since this compound immediately starts to decompose when it is heated at approximately 800°C in air or oxygen atmosphere (Komiya T. et al, 2010).

The oxygen content in YBaCo<sub>4</sub>O<sub>7+δ</sub> perovskite can vary in the range of  $0 \leq \delta \leq 1.5$  (Karppinen M. et al, 2006). In the prepared compound with  $\delta = 0$  the Co<sup>2+</sup>/Co<sup>3+</sup> the ratio is included between 3 ÷ 1, when it adsorb an oxygen atom the Co<sup>2+</sup> ions will change their oxidation state to Co<sup>3+</sup>, the ratio changes to 1:3 in YBaCo<sub>4</sub>O<sub>8</sub> (Hao H. et al, 2009).

In previous studies (Dan M. et al, 2011), the complex oxygen intercalation/de-intercalation process with appearance of several intermediate distorted structures was evidenced, by combination of thermogravimetric analyses, X-ray diffraction, voltammetric methods and scanning electron microscopy.

In the present work, the oxygen intake capacity of  $\text{YBaCo}_4\text{O}_7$  compound in alkaline solution using electrochemical methods was studied.

## MATERIAL AND METHOD

$\text{YBaCo}_4\text{O}_7$  layered perovskite was obtained using solid state reaction, by mixing the precursors  $\text{Y}_2\text{O}_3$  (Aldrich 99,99%),  $\text{BaCO}_3$  (Aldrich 99,999%) and  $\text{CoO}_{4/3}$  (Normapur 99,9%) according to the stoichiometric cations ratio. After decarbonation during 6 h at  $1000^\circ\text{C}$  the powder was reground and fired in air for 48 h at  $1200^\circ\text{C}$ . The mixture was then reground, pressed into discs ( $1\text{ cm}^2$ ) and sintered at  $1100^\circ\text{C}$  for 24 h in air. The structure of obtained perovskite was checked by X-Ray powder diffraction (Philips X-pert Pro).

The electrochemical studies were carried out using BioLogic SP150 potentiostat/galvanostat. The electrochemical cell was equipped with two graphite counter electrodes positioned symmetrically towards the working electrode ( $\text{YBaCo}_4\text{O}_7$  disc with  $1\text{ cm}^2$  exposed area) and a saturated  $\text{Ag}/\text{AgCl}$  electrode as reference. All potentials are given versus the reference electrode. All experimental measurements were carried out in  $1\text{ mol L}^{-1}$   $\text{KOH}$  solution.

Cyclic voltammetry, linear polarization and chrono-electrochemical methods (chronoamperometry, chronopotentiometry and chronocoulometry) were used in order to emphasize the remarkable oxygen intake/release of  $\text{YBaCo}_4\text{O}_7$  in alkaline media.

## RESULTS AND DISCUSSIONS

Open circuit potential (OCP) of  $\text{YBaCo}_4\text{O}_7$  electrode in  $1\text{ mol L}^{-1}$   $\text{KOH}$  solution was determined by chronopotentiometry at  $I = 0\text{ A}$  for 12 hours. The time required to establish equilibrium was chosen so long due to the perovskite electrode morphology, in order to allow penetration of the electrolyte flow in existing microchannels of the electrode structure. The OCP value determined by this method was  $E_{OCP} = -0,195\text{ V}/\text{Ag}/\text{AgCl}$ , being characteristic for the case when oxygen excess ( $\delta$ ) in  $\text{YBaCo}_4\text{O}_{7+\delta}$  is  $\delta = 0$ .

Cyclic voltammetry was used in order to show the peaks associated with the electrochemical processes occurring at the interface  $\text{YBaCo}_4\text{O}_7 - 1\text{ mol L}^{-1}$   $\text{KOH}$ . Cyclic voltammograms recorded between  $-1.1$  and  $+0.7\text{ V}/\text{Ag}/\text{AgCl}$  for  $\text{YBaCo}_4\text{O}_7$  electrode with  $5\text{ mV s}^{-1}$  scan rate, are depicted in

Figure 1, starting from OCP. Peak 2 can be associated with cobalt oxidation reaction ( $\text{Co}^{\text{II}} \rightarrow \text{Co}^{\text{III}} + \text{e}^-$ ) and when the potential becomes more positive, a plateau 3 characteristic for oxygen evolution reaction can be observed.

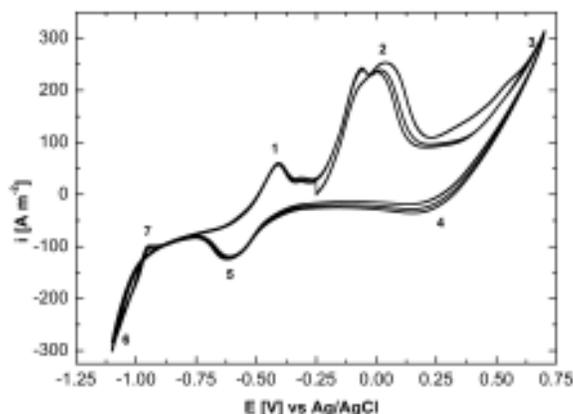


Fig.1 Cyclic voltammograms (3 cycles) on  $\text{YBaCo}_4\text{O}_7$  in  $1 \text{ mol L}^{-1}$  KOH solution at  $5 \text{ mV s}^{-1}$  scan rate.

On the backward scan, a low intensity cathodic current 4 is recorded, and it is correlated with reduction of the remnant oxygen on the electrode surface. When the electrode potential reaches approximately  $-0.5 \text{ V/Ag/AgCl}$ , the cathodic peak 5 correlated with  $\text{Co(III)}$  ions reduction appears. At more negative electrode potentials the current increase, that can be associated with the hydrogen evolution reaction. It is possible that at these potential values the reduction process of  $\text{Co(II)}$  ions to metallic  $\text{Co}$ , occurs consecutively with hydrogen evolution. Continuing the potential scan in the anodic direction up to OCP the appearance of two new oxidation peaks are observed: oxidation of hydrogen adsorbed into the mixed oxide network 7 and metallic  $\text{Co}$  oxidation to  $\text{Co(II)}$  1.

In order to establish optimal parameters for the compound oxidation in alkaline solution, linear voltammetry as one of the most important characterization methods was used, the voltammograms were recorded in anodic domain.

Starting from OCP, the linear polarization curves were recorded at the low-scan rate of  $1 \text{ mV s}^{-1}$  until different potential values, to highlight the specific oxidation processes for  $\text{YBaCo}_4\text{O}_7 - 1 \text{ mol L}^{-1}$  KOH interface. Initially, the anodic polarization limit was chosen the potential value ( $E = +1.0 \text{ V/Ag /AgCl}$ ) specifically for starting of oxygen generation reaction on perovskite surface (Figure 2a). Subsequently, determinations were made up to  $E = +3.0 \text{ V/Ag /AgCl}$  (Figure 2b). In Figure 2a are shown the same processes which occur on the anodic branch of cyclic voltammograms,

which are presented in Figure 1: (1) - (2) - Co(II) oxidation process to Co(III) and (3) oxygen evolution reaction.

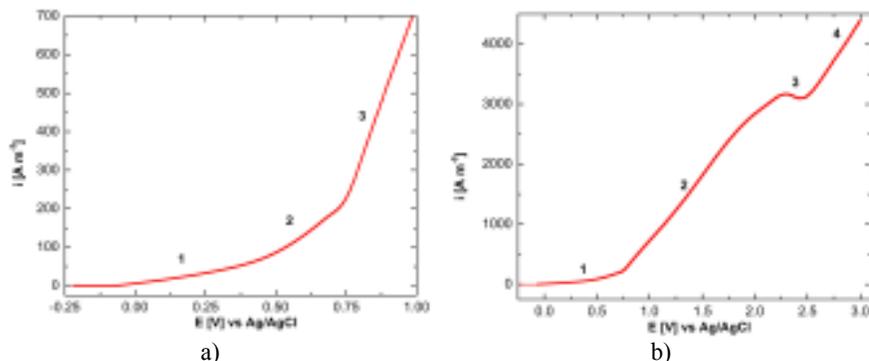


Fig. 2. Linear voltammograms on YBaCo<sub>4</sub>O<sub>7</sub> in 1 mol L<sup>-1</sup> KOH solution at 1 mV s<sup>-1</sup> scan rate recorded up to anodic potential value: (a) 1.00 and (b) 3.00 V/Ag/AgCl

On linear voltammograms from Figure 2b a high intensity limiting anodic current is observed at approximately 2.50 V/Ag/AgCl potential value 3. For cobalt perovskite, reference literature presents the possibility of Co (IV) ions existence in layered crystal structures. In this case, we can say that the plateau 3 characterizes the oxidation of Co (III) ions to Co (IV) ions in YBaCo<sub>4</sub>O<sub>7</sub> structure, indicating that these ions are not stable and will be reduced easily to an oxidation number more stable, such as +3. From visually point of view, the electrode remained intact, without characteristic destruction signs in the system, which were observed when higher cathodic polarization is applied (Raveau B. et al, 2015). We can affirm that using electrochemical oxidation methods, the flexibility of perovskite structure allowing, at least for a short period of time, the incorporation an oxygen quantity in compound crystal structure larger than 1.5 ion/unit cell (the maximum value when all the oxidation number of cobalt ions in the perovskite is +3).

Chronoamperometric and cronopotentiometric studies had as a starting point the linear voltamograms shown in Figure 2. Analyzing these curves three potential values were chosen in order to carry out the chronoamperometric measurements: two values correspond of the compound oxidation plateau: 1 -  $E = + 0.20$  V/Ag /AgCl and 2 -  $E = + 0.50$  V/Ag/AgCl and 3 -  $E = +1.00$  V/Ag /AgCl corresponding to the oxygen release process at YBaCo<sub>4</sub>O<sub>7</sub> electrode surface.

YBaCo<sub>4</sub>O<sub>7</sub> electrochemical oxidation by chronoamperometry was followed by cronopotentiometry at  $I = 0$  A. Chronoamperometric studies were performed for 15, 30, 60 and 90 minutes. In chronopotentiometric measurements a double timeframe was chosen (30, 60, 120 and 180 minutes), compared to the range in which electrode was oxidized. The aim

was to observe rapidly with which the potential value returns closer to initial value of OCP ( $E_{OCP} = -0.195 \text{ V/Ag/AgCl}$ ).

The results are presented in Figures 3a and b for the sample oxidized for 60 minutes at the 3 values of the chosen potential.

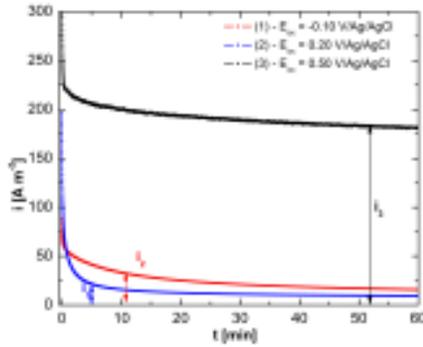


Fig. 3a. Chronoamperometric studies on YBaCo<sub>4</sub>O<sub>7</sub> electrode.

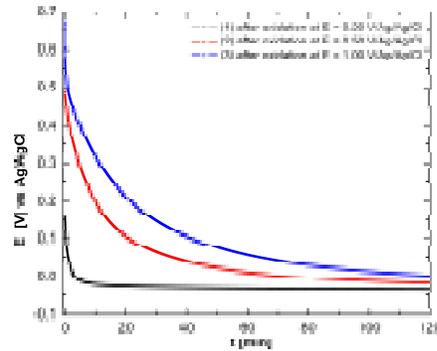


Fig. 3b. Chronopotentiometric studies at  $I = 0 \text{ A}$  on YBaCo<sub>4</sub>O<sub>7</sub> electrode.

Also, the measurements values obtained at four oxidation time-frames, are shown in Table 1.

Table 1

Chronoamperometric and chronopotentiometric measurements on YBaCo<sub>4</sub>O<sub>7</sub> electrode in  $1 \text{ mol L}^{-1} \text{ KOH}$  solution

Chronoamperometric measurements						
$E$ [V]/Ag/AgCl		$i_{\text{final}}$ [ $\text{A m}^{-2}$ ]				
		$t$ [min]				
		15	30	45	60	90
0.20		13.68	12.71	10.01	9.37	7.91
0.50		86.16	40.74	21.82	15.75	10.76
1.00		197.32	188.38	184.38	181.22	179.04
Chronopotentiometric measurements after oxidation						
$I$ [A]	$E_{\text{ox}}$ [V]	$E_{\text{final}}$ [V]/Ag/AgCl				
		$t$ [min]				
		30	60	90	120	180
0	0.20	-0.036	-0.032	-0.031	-0.030	-0.030
	0.50	0.064	0.013	-0.006	-0.016	-0.014
	1.00	0.145	0.056	0.022	0.033	0.005

Analyzing graphical data can conclude the following aspects: at +0.20 and +0.50 V/Ag/AgCl potential values the only process that occurs in the system is perovskite oxidation; if chronoamperometric measurements are carried out at +1.00 V/Ag/AgCl, value characteristic for oxygen evolution reaction on surface perovskite electrode, the curve shape 3 (Figure 3a) indicates that gas evolution reaction occurs simultaneously with the YBaCo<sub>4</sub>O<sub>7</sub> compound oxidation and consequently current density increases

to about  $175 \text{ A m}^{-2}$ . This phenomenon is confirmed by cronopotentiometric data, observing that after perovskite oxidation at  $E = +1.00 \text{ V/Ag/AgCl}$  the electrode potential has more positive potential as compared to its value after the oxidation at  $E = +0.50 \text{ V/Ag/AgCl}$  which indicates a high oxidation degree and hence a greater oxygen amount adsorbed in compound.

Simultaneously with chronoamperometric measurements chronocoulometric data were recorded in  $\text{YBaCo}_4\text{O}_{7+\delta}/1 \text{ mol L}^{-1} \text{ KOH}$  system, measuring accurately the consumed electricity amount in perovskite electrode oxidation at  $+0.20 \text{ V}$  and  $+0.50 \text{ V/Ag/AgCl}$  potential values, when the only process occurring in system is  $\text{Co (II)}$  ions oxidation.

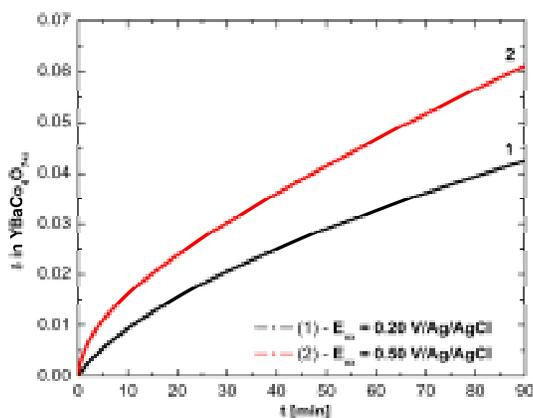


Fig. 4 Oxygen content variation ( $\delta$ ) in  $\text{YBaCo}_4\text{O}_{7+\delta}$  during electrochemical oxidation in  $1 \text{ mol L}^{-1} \text{ KOH}$ .

Based on these results, using Faraday's laws, it has been possible to evaluate the oxygen quantity ( $\delta$ ) inserted in the  $\text{YBaCo}_4\text{O}_{7+\delta}$  crystalline structure as a function of time. In Figure 4 and Table 2 the oxygen excess values ( $\delta$ ) at various intervals of time obtained in oxidation process are given.

Table 2  
Oxygen content variation ( $\delta$ ) in  $\text{YBaCo}_4\text{O}_{7+\delta}$  during electrochemical oxidation

$E$ [V/Ag/AgCl]	$\delta$			
	$t$ [min]			
	15	30	60	90
0.20	0.013	0.020	0.033	0.042
0.50	0.020	0.030	0.047	0.061

From the obtained data in chronoamperometric and cronocoulometric measurements, the perovskite complete oxidation required time by electrochemical methods can be calculated, knowing that the maximum oxygen amount inserted in the  $\text{YBaCo}_4\text{O}_{7+\delta}$  structure can be  $\delta = 1.5$  oxygen

ions/perovskite mol, using polynomial fitting with Origin software and/or curves extrapolation method.

The time duration required for  $\text{YBaCo}_4\text{O}_{7+\delta}$  oxidation at several potential values up to  $\delta_{max}$  in alkaline solution are shown in Table 3.

Table 3

The time duration required for  $\text{YBaCo}_4\text{O}_{7+\delta}$  compound oxidation in alkaline solution:

Electrochemical oxidation	$t$ [h] $\delta=0,25$	$t$ [h] $\delta=0,50$	$t$ [h] $\delta=0,75$	$t$ [h] $\delta=1,00$	$t$ [h] $\delta=1,25$	$t$ [h] $\delta_{max}=1,50$
$E_{ox} = 0,25 \text{ V}$	12.9	26.5	40.5	54	67.5	82
$E_{ox} = 0,65 \text{ V}$	8.2	17.2	26.1	35.1	44.5	53
Cobalt ions average oxidation number	2.375	2.5	2.625	2.75	2.875	3
Stoichiometric formula	$\text{YBaCo}_4\text{O}_{7,25}$	$\text{YBaCo}_4\text{O}_{7,5}$	$\text{YBaCo}_4\text{O}_{7,75}$	$\text{YBaCo}_4\text{O}_8$	$\text{YBaCo}_4\text{O}_{8,25}$	$\text{YBaCo}_4\text{O}_{8,5}$

## CONCLUSIONS

Based on the experimental data we can conclude that the electrochemical oxidation of Co(II) ions from  $\text{YBaCo}_4\text{O}_7$  consists in oxygen insertion into the mixed oxide structure.

The results showed the possibility to increase the oxygen content in  $\text{YBaCo}_4\text{O}_7$  using chrono-electrochemical methods. Experimental data have proven the oxygen storage capability of  $\text{YBaCo}_4\text{O}_7$  at lower temperature range using electrochemical method. Also, the time duration required for  $\text{YBaCo}_4\text{O}_{7+\delta}$  oxidation at several potential values up to  $\delta_{max}$  in alkaline solution has been calculated.

Consequently, the  $\text{YBaCo}_4\text{O}_7$  compound can be an excellent oxygen storage material due to its low cost and has a high oxygen intake/release capability.

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