

## ELECTROCHEMICAL OXYGEN INTAKE/RELEASE PROCESS OVER YBaCo<sub>2</sub>Fe<sub>2</sub>O<sub>7.5</sub> ELECTRODES IN AQUEOUS SOLUTIONS

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### Abstract

The present study proves that YBaCo<sub>2</sub>Fe<sub>2</sub>O<sub>7.5</sub> perovskite has high performance for oxygen storage capacity in aqueous solutions by electrochemical oxidation. This perovskite is a promising candidate for applications requiring efficient oxide ion conductivity or large oxygen storage capacity is. The oxygen intake/release propriety of YBaCo<sub>4</sub>O<sub>7</sub> has been studied by cyclic voltammetry and chronoamperometry in alkaline and neutral aqueous electrolytes.

### Introduction

YBaCo<sub>4</sub>O<sub>7</sub> cobalt perovskite, originally discovered by Valldor and Andersson, shows remarkable ability for intake/release oxygen [1-4]. In order to increase YBaCo<sub>4</sub>O<sub>7</sub> stability, the control of chemical composition is one of the most promising methods. Perovskite YBaCo<sub>4</sub>O<sub>7</sub> supports different types of cation substitutions, of which the most important are: Ca and smaller atoms such as rare earth elements (Dy, Ho, Er, Tm, Yb and Lu), able to substitute Y and Fe, Zn, Al and Ga with Co [5]. The substitution of half number of cobalt ions with iron ions was proposed, forming the new compound YBaCo<sub>2</sub>Fe<sub>2</sub>O<sub>7+δ</sub>, where δ=0.5.

Oxygen nonstoichiometry in YBaCo<sub>2</sub>Fe<sub>2</sub>O<sub>7.5</sub> perovskite structure is influenced by the oxygen content variations depending of cobalt or iron ions average number of oxidation which affects the oxygen permeability and diffusion [6]. From electrochemical point of view, YBaCo<sub>4</sub>Fe<sub>2</sub>O<sub>7.5</sub> oxidation/reduction studies in aqueous solutions can be attractive due to his oxygen insertion/release capacity.

In the present work, the oxygen intake/release capacity of YBaCo<sub>2</sub>Fe<sub>2</sub>O<sub>7.5</sub> perovskite in alkaline and neutral solutions using electrochemical methods was studied.

### Experimental

YBaCo<sub>2</sub>Fe<sub>2</sub>O<sub>7.5</sub> layered perovskite was obtained using solid state reaction, mixing the precursors Y<sub>2</sub>O<sub>3</sub>, BaCO<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub> and CoO<sub>4/3</sub> (all, Normapur 99,9%) according to the stoichiometric cations ratio. After decarbonation at 1000°C the powder was reground and fired in air at 1200°C. The obtained mixture was pressed into discs (1 cm<sup>2</sup>) and sintered at 1100°C in air. The structure of obtained perovskite was checked by X-Ray powder diffraction (Philips X-pert Pro). Using this preparation method in air all iron ions from the perovskite structure are found at maximum oxidation number +3.

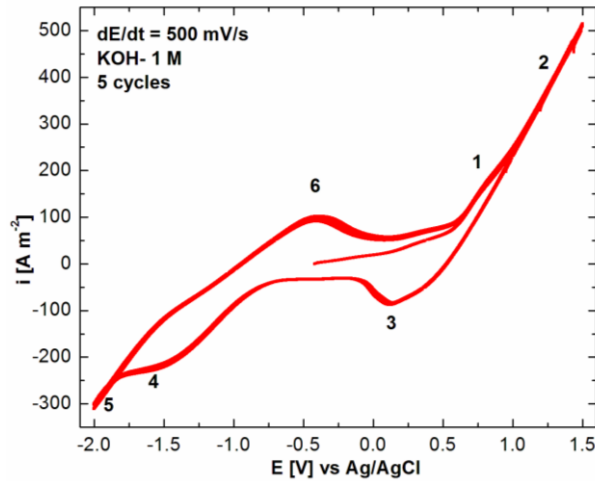
The electrochemical studies were carried out using BioLogic SP150 potentiostat/galvanostat. The electrochemical cell was equipped with two graphite counter electrodes, working electrode (YBaCo<sub>2</sub>Fe<sub>2</sub>O<sub>7.5</sub> disc with 1 cm<sup>2</sup> exposed area) and a saturated Ag/AgCl electrode as reference.

### Results and discussion

In order to show the peaks associated with the electrochemical processes occurring at YBaCo<sub>2</sub>Fe<sub>2</sub>O<sub>7.5</sub> - aqueous solution interface, cyclic voltammetry was used.

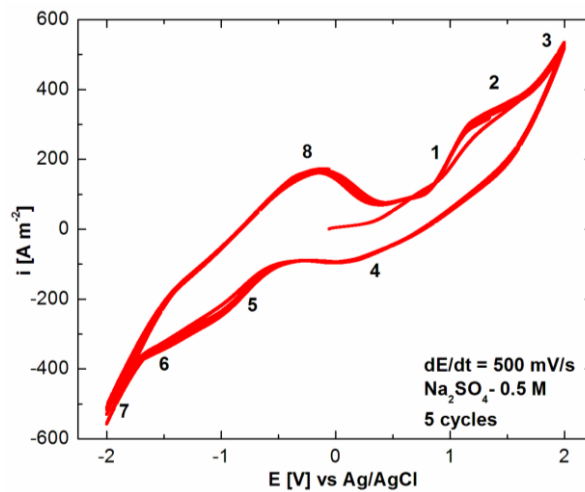
Cyclic voltammograms recorded in 1 mol L<sup>-1</sup> KOH, between -2.0 and +1.5 V/Ag/AgCl with 500 mV s<sup>-1</sup> scan rate, are depicted in Figure 1, starting from OCP. Peak (1) can be associated

with  $\text{Co}^{2+}$  ions oxidation reaction inside of perovskite structures. When the potential becomes more positive, a plateau (2) characteristic for oxygen evolution reaction can be observed. The others peaks correspond to adsorbed oxygen reduction or  $\text{Co}^{3+}$  reduction (3),  $\text{Fe}^{3+}$  or  $\text{Co}^{2+}$  ions reduction (4), hydrogen evolution reaction (5) and  $\text{Fe}^{2+}$  or Co metallic oxidation (6).



**Figure 1.** Cyclic voltammograms plotted on  $\text{YBaCo}_2\text{Fe}_2\text{O}_{7.5}$  in alkaline aqueous solutions.

Similarly, in figure 2 are presented cyclic curves plotted in  $0.5 \text{ mol L}^{-1} \text{Na}_2\text{SO}_4$  at  $500 \text{ mV s}^{-1}$  scan rate. Peaks are (1) and (2) are associated with  $\text{Co}^{2+}$  oxidation.

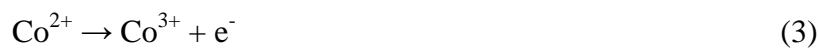


**Figure 2.** Cyclic voltammograms plotted on  $\text{YBaCo}_2\text{Fe}_2\text{O}_{7.5}$  in neutral aqueous solutions.

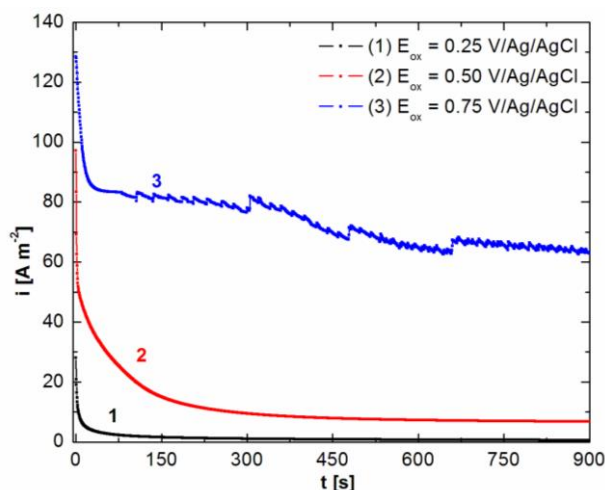
Global reactions at the electrode/electrolyte interface at anodic polarization can be describes by equation (1) in alkaline solution and equation (2) in neutral one:



In both electrolytes, anodic oxidation process of  $\text{YBaCo}_2\text{Fe}_2\text{O}_{7.5}$  perovskite consists in oxygen insertion in oxide structure, assigned to  $\text{Co}^{2+}$  oxidation (3) [3,4]:

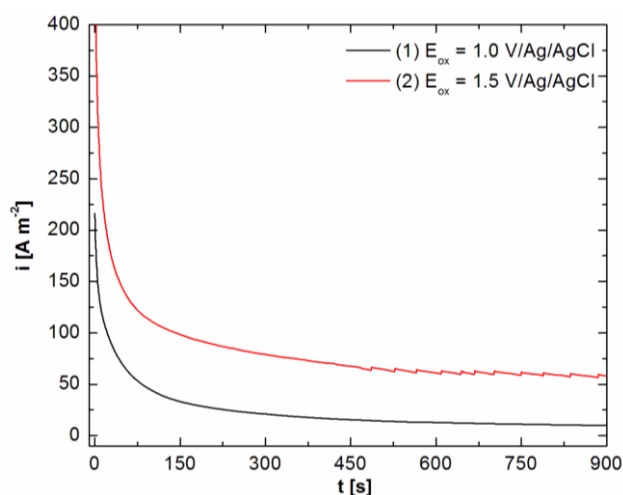


In preliminary studies, chronoamperometric measurements had as a starting point the cyclic voltamograms shown in Figure 1 and 2. Analyzing these curves, three potential values were chosen for the chronoamperometric measurements in alkaline solution: two values correspond with the compound oxidation plateau: (1)  $E = +0.25$  V and (2)  $E = +0.50$  V and (3)  $E = +1.00$  V, corresponding to the oxygen release process on electrode surface. For neutral electrolyte were chosen only two potential values (1)  $E = +1$  V and (2)  $E = +1.50$  V, both corresponding to perovskite oxidation. All potentials values are given versus the reference electrode ( $E_{\text{ref}} = 0.197$  V vs NHE). Chronoamperometric studies were performed for 15 minutes. Graphical results are presented in figure 3 for alkaline solutions and 4 for neutral media.



**Figure 3.** Chronoamperometric studies on  $\text{YBaCo}_2\text{Fe}_2\text{O}_{7.5}$  electrode, in alkaline solutions.

Analyzing graphical data can conclude the following aspects: at +0.25 and +0.50 V potential values, the only process occurring at perovskite interface is oxidation. If chronoamperometric measurements are carried out at +0.75 V, value characteristic for oxygen evolution reaction on perovskite electrode surface, the curve shape (3) indicates that oxygen evolution reaction occurs simultaneously with  $\text{YBaCo}_2\text{Fe}_2\text{O}_{7.5}$  oxidation.



**Figure 4.** Chronoamperometric studies on  $\text{YBaCo}_2\text{Fe}_2\text{O}_{7.5}$  electrode, in alkaline solutions.

### **Conclusion**

Experimental data have proven the oxygen uptake/release capability of  $\text{YBaCo}_2\text{Fe}_2\text{O}_{7.5}$  at lower temperature range using cyclic voltammetry. The results showed the possibility to increase the oxygen content in  $\text{YBaCo}_2\text{Fe}_2\text{O}_{7.5}$  using chronoamperometry.

### **Acknowledgements**

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### **References**

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