

Electrochemical Oxygen Uptake/Release Process over Ca-112 Electrodes in Aqueous Solutions

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Abstract

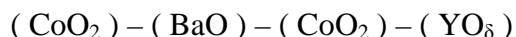
This paper presents the electrochemical study of Y^{3+} substitution with Ca^{2+} ions on intake/release of oxygen. These studies were performed using alkaline solution (1 mol L⁻¹ KOH) and also neutral solution (0.5 mol L⁻¹ Na₂SO₄). All electrochemical behavior presented in this paper has been studied by cyclic voltammetry.

Introduction

YBaCo₂O_{5+δ} ($0 \leq \delta \leq 1$), named Y-11,2 present a 112 phase which is a structure derived from LnBaCo₂O₅ perovskites by ordering the rare element and also the barium cations in layers along *c* crystallographic axis, by removing the oxygen ions from yttrium layer.

It is expected, that oxygen carriage inside of YBaCo₂O_{5+δ} compound takes place really easily due to high electrical conductivity of studied perovskite, and also due the high concentration of oxygen vacancies. Based on these considerations it is expected that the studied perovskite can be used as cathode in solid oxide fuel cells.

Crystalline structure of Y-112 perovskite can be regarded as a layered structure formed by consecutive layers:



Different ways of the oxygen arrangement inside of studied compound lead at superstructure formation in which the oxygen atoms are arranged differently into the YO_δ layer.

In the literature there are presented the substitution and doping possibility of Y-112 perovskites [1]. Until now, in all cases the structural modifications which occurs during Y-112 substitution were studied, and also the influence on the electrical and magnetic properties. Likewise the possibility to replace Y^{3+} ions with Ca^{2+} ones was confirmed, there are a small number of studies involving the Y_{1-x}Ca_xBaCo₂O_{5+δ}, where $0 < \delta \leq 0,5$ [1,2] and only one study for the compound with $x = 1$ (CaBaCo₂O_{5+δ}) [3]. Aurelio et al. demonstrate in 2013 that Ca^{2+} ions replace Y^{3+} ions and not Ba^{2+} ones inside of the perovskite structure [1]

The present paper describes the influence of Y^{3+} substitution with Ca^{2+} ions on to the oxygen intake/release capacity, by studying the compound electrochemical behavior in alkaline and neutral solutions.

Experimental

CaBaCo₂O₅ perovskite (Ca-112) was prepared in a similar way with YBaCo₂O₅ compound by using the solid state synthesis, replacing Y₂O₃ precursor with CaCO₃ and using a similar thermal treatment as the one used for Y-112 preparation [4].

Electrochemical studies were carried out using a BioLogic SP 150 potentiostat/galvanostat equipped with electrochemical impedance spectroscopy module. During experiments a three electrodes electrochemical cell was used, consisting of two counter electrodes placed symmetrically to the working electrode (a disk with a geometric area of 0.8 cm²), and a reference represented by Ag/AgCl electrode. In electrochemical tests

KOH 1 mol L⁻¹ and Na₂SO₄ 0.5 mol L⁻¹ solutions were used.

Results and discussion

In order to demonstrate the oxygen intake/release affinity the prepared Ca-112 perovskite was firstly studied by thermogravimetric methods, showing that during thermal treatments in air it can accept and also release oxygen from his structure, which can be associated with the modification of average oxidation number of cobalt ions.

Preliminarily, voltammetric studies shown that Ca-112 compound is acting in both solutions (alkaline and also neutral one) as support material, for a long potential range (between +2 and -2 V/Ag/AgCl), when it can be observed only the peaks associated with oxygen and respectively hydrogen evolution reactions (figure 1).

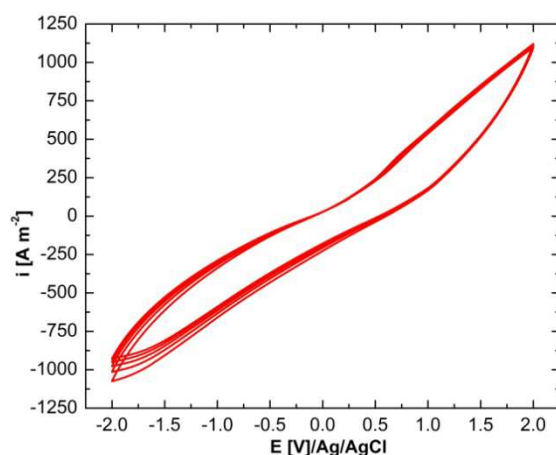


Figure 1. Cyclic voltammograms (5 cycles) on Ca-112 in 0.5 mol L⁻¹ Na₂SO₄ solution at 100 mV s⁻¹ scan rate.

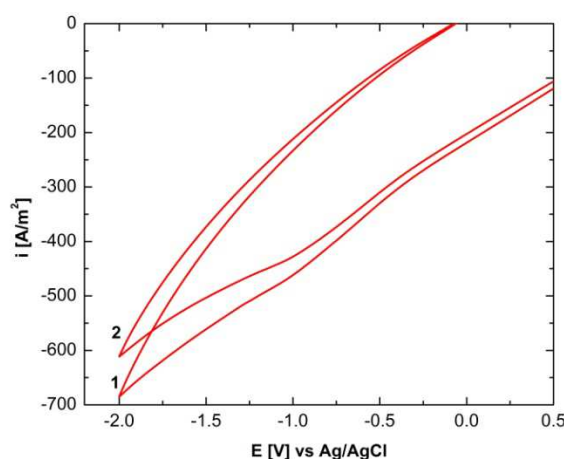


Figure 2. Cathodic domain of cyclic voltammograms (2 cycles) on Ca-112 in 0.5 mol L⁻¹ Na₂SO₄ solution at 100 mV s⁻¹ scan rate.

Because the Ca-112 compound is not participant in electrode reactions, it is necessary to activate the electrode surface (figure 2) by cathodic pre-polarization at -1.00 V/Ag/AgCl, when a part of Co³⁺ ions are reduced.

After the surface activation at polarization speed of 100 mV s⁻¹ the separation of peaks corresponding to the electrochemical processes taking place at Ca-112 interface can be observed. On cyclic voltammograms depicted in figure 3a (1 mol L⁻¹ KOH) and 3b (0.5 mol L⁻¹ Na₂SO₄), recorded for OCP, it can observe that at anodic polarization appear first anodic peak (1) associated with Co(II) ions oxidation $\text{Co}^{\text{II}} \rightarrow \text{Co}^{\text{III}} + e^-$ (Co(II) ions are produced in

activation period, followed by a limit current plateau (2), and at more positive potentials the peak (3) associated with oxygen evolution reaction appears.

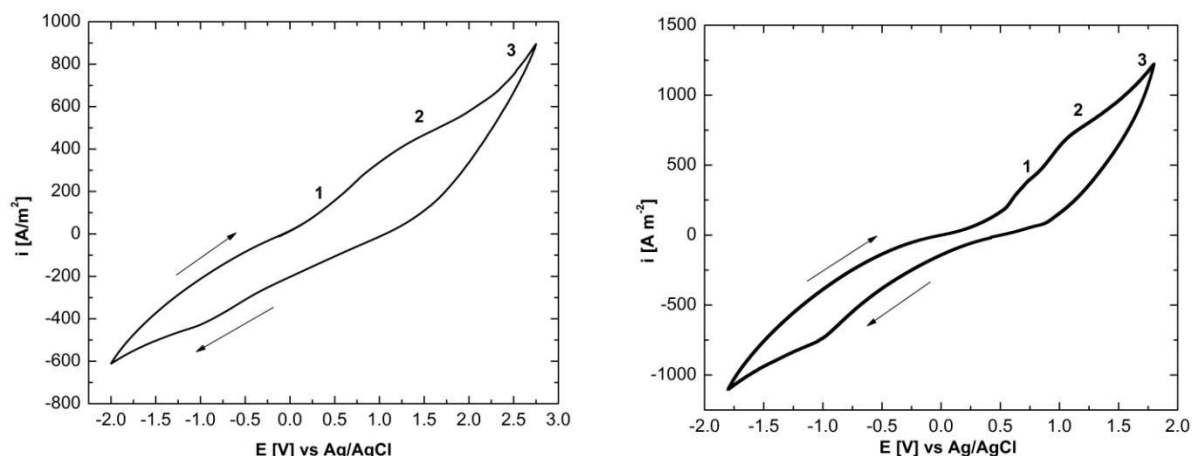


Figure 3. Cyclic voltammograms recorder on Ca-112 at 100 mV s^{-1} :
a) $1 \text{ mol L}^{-1} \text{ KOH}$, b) $0.5 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$

As effect, the oxidation of Co(II) ions at Co(III) ions supplementary oxygen is inserted into the Ca-112 crystalline structure. Intake/release oxygen ability is a consequence of structural flexibility of 112 stratified perovskites, which allows small distortions without destroying the crystalline structure.

Conclusion

Based on voltammetric studies it can say that Ca-112 perovskite presents the oxygen intake/release property. Electrochemical oxidation occurs at lowered speed in case of Ca-112 perovskites in comparison with Y-112 one. Ca-112 electrodes require a surface activation stage, which allow the studied compound to be used in all areas where the 112 layered perovskites can be used.

References

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