$Y_{0.5}Ca_{0.5}BaCo_4O_7$ PEROVSKITE ELECTRODES WITH CATALYTIC EFFECT FOR METHANOL AND ETHANOL ELECTROOXIDATION IN ALKALINE MEDIA

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Abstract
In this paper, preliminary data of methanol and ethanol anodic oxidation on $Y_{0.5}Ca_{0.5}BaCo_4O_7$ perovskite electrode in aqueous alkaline solution (1 M KOH) are presented. Electrocatalytic activity of methanol and ethanol anodic oxidation becomes a serious issue, especially due to the utilization of 114 layered cobalt perovskite electrodes in fuel cells. In order to elucidate the mechanism of methanol (MOR) and ethanol oxidation reactions (EOR) which occur at this perovskite electrodes interface, advanced studies are required. Electrochemical behavior has been studied by cyclic voltammetry, chronoamperometry and chronopotentiometry. Obtained results have shown that $Y_{0.5}Ca_{0.5}BaCo_4O_7$ perovskite electrodes are suitable as anodes in fuel cells.

Introduction
Direct alcohol fuel cells (DAFCs) are electrochemical devices that convert the chemical energy of methanol and ethanol electrooxidation in electrical one [1]. DAFCs are promising auxiliary power sources in transportation, portable electronics, and other modern applications [2,3]. They belong to alkaline fuel cells (AFCs) family [4]. Methanol and ethanol electrooxidation efficiency is a continuous challenge from research point of view. Platinum is known for its highest catalytic activity of MOR and EOR compared to other pure metals in alkaline media. An advantage of alkaline fuel cells is the potential use of non-Pt catalysts as electrodes [5]. Noble metal (Au) and non-noble metals (Cd, Pb, Bi, Ti) were investigated as anode for alcohol oxidation in alkaline media [4]. Latterly, electronically conducting mixed oxides were tested as anode materials; oxides of V, Fe, Ni, In, Sn, La and Pb were used [6]. In recent years, studies on various transition metal mixed oxides have shown that perovskite oxides can be used as fuel cell electrodes [6].
In this paper, new aspects of MOR and EOR on $Y_{0.5}Ca_{0.5}BaCo_4O_7$ electrode have been studied using cyclic voltammetry. Also, a mechanism was proposed for both electrochemical oxidation reactions. The results are expected to provide basic information in order to understand the mechanism of MOR and EOR on cobalt layered perovskites type 114 electrodes.

Experimental
$Y_{0.5}Ca_{0.5}BaCo_4O_7$ perovskite was obtained using solid state reaction, mixing Y_2O_3, $CaCO_3$, $BaCO_3$ and $CoO_{1.38}$ precursors (all reagents were Aldrich p.a. min 99,99%) according to the stoichiometric cations ratio. Perovskite powder was prepared in two steps: decarbonation at 600°C, fired in air for 48 h at 1100°C and then quickly removing from furnace and set room temperature. After reground, the mixture was pressed into discs (1 cm^2) and sintered at 1100°C for 24 h in air.
Electrochemical tests were performed at room temperature using a SP-150 potentiostat/galvanostat (Bio-Logic, SAS, France). A 100 mL typical glass cell was equipped with three electrodes: working electrodes consisting of $Y_{0.5}Ca_{0.5}BaCo_4O_7$ perovkites samples,

Ag/AgCl reference electrode (E_{ref} = 0.197 V vs NHE) and two graphite rods counter electrodes. In electrochemical experiments, the exposed surface of working electrode was 0.2 cm^2. All potentials are given versus the reference electrode.
Cyclic voltammograms (CVs) were recorded at different scan rate, between 5 and 500 mV s^{-1}. 1 M KOH solution (prepared using Merck KOH, p.a.) ensured the alkaline media used in all experimental studies, in which 0.06 M methanol and ethanol concentration was added, prepared from Sigma-Aldrich reagent p.a. min 99.8%.

Results and discussion
Figures 1 and 2 presents CVs recorded at different scan rates, between 500 and 5 mV s^{-1}, in alkaline solutions, in a wide range of the potential (+1.75 and -1.75 V), in the presence of methanol (Figure 1) and ethanol (Figure 2). It can be observed a significant anodic peak between -0.50 and +0.25 V and a cathodic current plateau in -1.25 – -1.70 V potential range. These are associated to formadehyde/formate redox couple in alkaline medium for methanol solution, acetaldehyde/acetate redox couple for ethanol solution and Co(II) to Co reduction/oxidation for KOH solution. MOR and EOR characteristic peaks are distinguished only if scan rare is less than 10 mV s^{-1}.

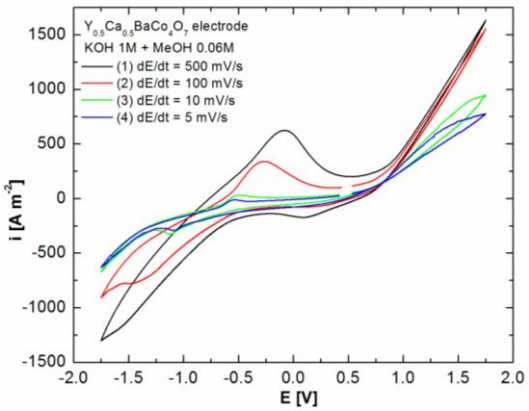

Figure 1. CVs recorded on $Y_{0.5}Ca_{0.5}BaCo_4O_7$ electrode in 1 M KOH with 0.06 M methanol at different scan rates.

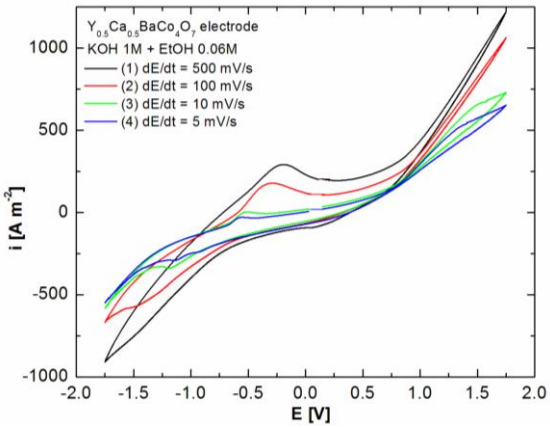

Figure 2. CVs recorded on $Y_{0.5}Ca_{0.5}BaCo_4O_7$ electrode in 1 M KOH with 0.06 M ethanol at different scan rate.

Cyclic voltammetric studies have shown that it is possible to separate the peaks associated with the all electrochemical processes occurring at the interface perovskite electrode-alkaline electrolyte only if the potential scan rate is around 5 mV s^{-1}, as shown in Figure 3.

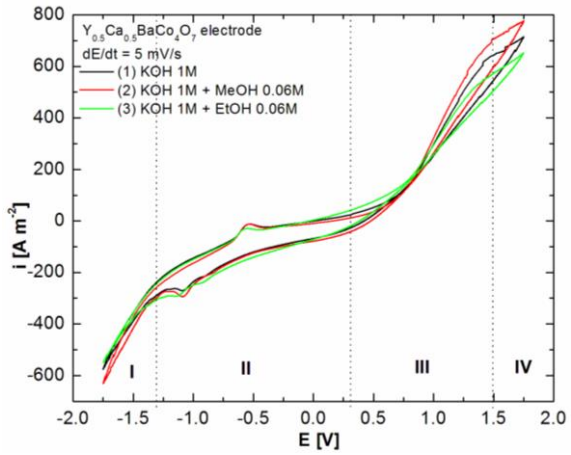

Figure 3. CVs recorded on $Y_{0.5}Ca_{0.5}BaCo_4O_7$ electrode in 1 M KOH in the absence (1) and in the presence of 0.06 M methanol (2) and ethanol (3), at 5 mVs^{-1} scan rate.

Analysing CVs depicted in Figure 3, there is possible to partition the voltammograms in four potential domains:

I - HER domain;

II - Co^{2+}/Co redox couple domain in alkaline solution from inside of perovskite (1), formaldehyde/formate (2) and acetaldehyde/acetate (3) ions redox couple domain;

III – Co^{2+} oxidation to Co^{3+} in $Y_{0.5}Ca_{0.5}BaCo_4O_7$ electrode (1), MOR (2) and EOR (3) on 114 layered cobalt perovskite surface domain;

IV - OER domain.

Variation of open circuit potential (OCP) after cyclic voltametric experiments for $Y_{0.5}Ca_{0.5}BaCo_4O_7$ electrode in alkaline solution without and with methanol and ethanol are presented in Figure 4. Chronopotentiometric measurements were performed for 60 minutes.

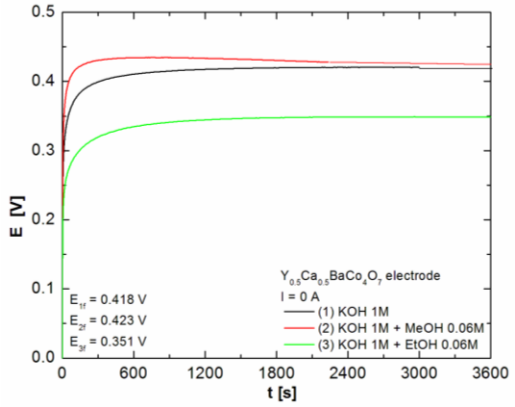

Figure 4. OCP for $Y_{0.5}Ca_{0.5}BaCo_4O_7$ electrode in 1 M KOH (1) without and with 0.06 M methanol (2) and ethanol (3).

Chronoamperometric studies had as starting point the CVs shown in Figure 3. Analysing these curves, +0.75 V potential value, corresponding to the MOR, OER and perovskite oxidation in alkaline solution (domain III from Figure 3) was chosen to carry out the chronoamperometric measurements. The results are presented in Figure 5 for 60 minutes oxidation time.

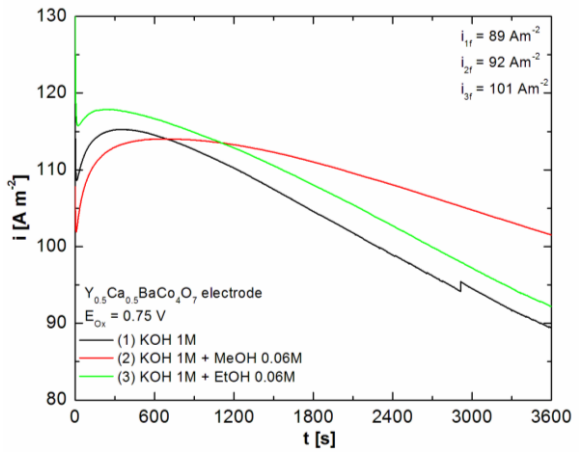

Figure 5. Chronoamperometric measurement at E = + 0.75 V for $Y_{0.5}Ca_{0.5}BaCo_4O_7$ oxidation (1), MOR (2) and EOR (3).

Conclusion

Preliminary data presented in this paper confirmed the possibility to oxidize methanol and ethanol in alkaline media on an $Y_{0.5}Ca_{0.5}BaCo_4O_7$electrode. The potential domain for MOR, EOR and $Y_{0.5}Ca_{0.5}BaCo_4O_7$perovskite oxidation in alkaline electrolyte is the same.

From the perspective of using this electrode type as anode material in alkaline direct alcohol fuel cells with methanol or ethanol electrolyte, the possibility to oxidize alcohols directly on their surface offer a good reason to continue experimental studies in this domain.

Acknowledgements

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