

Ca Doped Y-114 Layered Cobalt Perovskite Electrodes with Catalytic Effect for Methanol Electrooxidation in Alkaline Solutions.

I. Voltammetric studies

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Abstract: This paper investigates anodic oxidation of methanol on a calcium doped cobalt layered perovskite type 114 electrode in aqueous alkaline solution (1M KOH). Electrocatalytic activity formethanol anodic oxidation becomes a serious issue, especially due to the utilization of layered cobalt perovskite electrodes in fuel cells. In order to understand the oxidation mechanism on the surface of these type of electrodes, comprehensive researches were necessary. Electrochemical behavior has been studied by cyclic voltammetry and linear polarization.

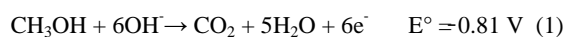
Keywords: $Y_{0.5}Ca_{0.5}BaCo_4O_7$, cobalt layered perovskite, methanolelectrooxidation.

1. Introduction

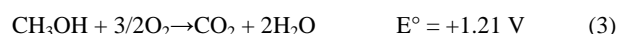
Direct alkaline alcohol fuel cells with methanol or ethanol benefit of height interest over the past 60 years because of their advantageous reaction mechanism and kinetics in alkaline media, higher energy densities achievable and easy handling of the liquid fuels [1, 2]. This cell was initially equipped with Pt and Pt alloys catalysts. Due to high costs, Pt was gradually replaced with others materials, having lower prices and approximately the same catalytic activity: Pd, Au and Ag. Currently, non-precious metal catalysts, lanthanum, strontium oxides and perovskite-type oxides are tested [2]. First studies of alcohol oxidation in fuel cells were conducted by Palve in 1954 who demonstrated the possibility to use methanol as fuel in aqueous electrolytes [3]. In direct alcohol fuel cells, methanol is directly oxidised at the anode in acidic or alkaline support electrolytes. Methanol use was favored because it is the simplest alcohol with only one carbon in its molecule and without C-C bonds [2].

It is known that for alcohols oxidation processes, electrocatalysts perform better in alkaline electrolytes. Justi and Winsel developed in 1955 the first direct methanol fuel cells operating in alkaline media, equipped with porous nickel anode and porous nickel-silver cathode [3].

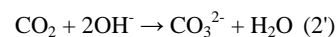
Electrochemical reactions occurring at electrodes are: on the anode surface, methanol is oxidised to carbon dioxide releasing six electrons (1) and simultaneously, on the cathode side, molecular oxygen accepts electrons and it is reduced to hydroxide ions (2). Hydroxide ions migrate from the bulk of the solution to the anode [2].



The characteristic overall reaction of direct methanol fuel cell is (3):



The disadvantage of alkaline media is progressive carbonation with CO_2 when carbonate and dicarbonate are produced in the cathodic compartment (2'); this will affect the cell performance, lowering the concentration of the electrolytes.



The new electrode materials family, oxide-ion conducting perovskites, have appeared in the literature for several years, but only recently compositions with high enough conductivities to be used in fuel cells have been obtained [4]. Perovskite electrocatalysts as $SrPdO_3$, $SrRuO_3$, $La_{0.8}Ce_{0.2}CoO_3$, $La_{0.8}Sr_{0.2}CoO_3$ have demonstrated activity towards direct methanol oxidation during cyclic voltammetry measurements [5].

Lanthanum-based perovskite-type oxides, among which $La_{2-x}Sr_xNiO_4$ ($0 \leq x \leq 1$) known as functional materials with a wide range of applications, have been used as electrocatalysts for alkaline fuel cells and as environmental catalysts: hydrocarbon oxidation, CO oxidation and NO_x reduction [6, 7].

Of late years, a new class of transitional metals mixed oxides, named layered cobalt perovskites type 114, was most investigated due to their structural, magnetic and electrochemical properties. Based on these properties cobalt perovskites can be used as membranes with high oxygen permeability, oxygen sensors and also fuel cells electrodes. Part of this family is $Y_{0.5}Ca_{0.5}BaCo_4O_7$, first synthesized by M. Valldor by partial substitution of Y^{3+} with low valence Ca^{2+} cations in perovskite structure [8]. Experimental researches have shown there is a correlation

between compound structure and his properties, especially due to the variable cobalt ions valence and it was found that oxygen adsorption properties can be modified greatly by Y^{3+} ions substitution in the original structure of $YBaCo_4O_7$ [9, 10].

In this work, new aspects of the electrocatalytic oxidation of methanol on $Y_{0.5}Ca_{0.5}BaCo_4O_7$ electrode have been studied using cyclic and linear voltammetry. Also, a mechanism was proposed for the electrochemical reaction. The results are expected to provide basic information in understanding the methanol oxidation reaction (MOR) process on 114 cobalt layered perovskites catalysts.

2. Experimental

$Y_{0.5}Ca_{0.5}BaCo_4O_7$ perovskite was obtained using solid state reaction, mixing the precursors Y_2O_3 (Aldrich 99,99%), $CaCO_3$ (Aldrich 99,99%), $BaCO_3$ (Aldrich 99,99%) and $CoO_{1.38}$ (99,99% Normapur), according to the stoichiometric cation ratio. After decarbonation at $600^\circ C$, the powder was reground, fired in air for 48 h at $1100^\circ C$ and then removed rapidly from furnace and set ambient temperature. The mixture was reground again, pressed into discs (1 cm^2) and sintered at $1100^\circ C$ for 24 h in air [11]. The structure of obtained $Y_{0.5}Ca_{0.5}BaCo_4O_7$ pure compound was checked by X-Ray powder diffraction (Rigaku Ultima IV).

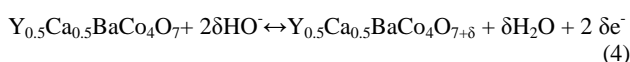
Electrochemical tests were performed at room temperature using a SP-150 potentiostat/galvanostat (Bio-Logic, SAS, France). A 100 mL typical glass cell was equipped with three electrodes: working electrodes consisting of skeletal nickel samples, Ag/AgCl reference electrode and two graphite rods used as counter electrodes. For performed experiments, the exposed surface of working electrode was 0.2 cm^2 . All potentials are given versus the reference electrode ($E_{ref} = 0.197\text{ V}$ vs NHE).

Cyclic voltammograms (CVs) were recorded at different scan rate, between 5 and 500 mVs^{-1} . Linear polarization curves were registered potentiostatically with 1 mVs^{-1} scan rate. 1 mol L^{-1} KOH solution (prepared using Merck KOH, p.a.) ensured the alkaline media used in all experimental studies. Different concentrations of methanol were added: 0.06, 0.12, 0.25, 0.5, 1 and 2 mol L^{-1} , all prepared from Sigma-Aldrich reagent p.a. min 99.8%.

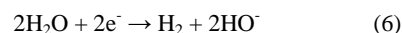
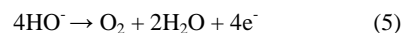
3. Results and Discussion

3.1. Preliminary data

Electrochemical behaviour of studied perovskite in alkaline solution (1M KOH) can be described by the following reaction [11]:



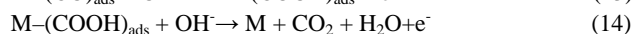
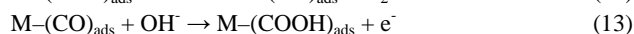
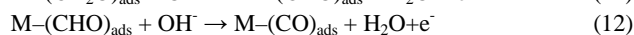
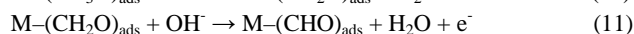
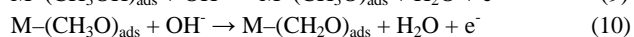
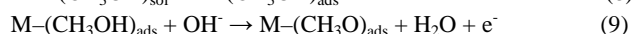
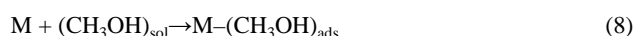
Simultaneously, anodic oxygen evolution (5) and cathodic hydrogen evolution (6) occur:



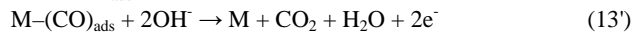
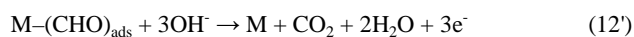
Anodic oxidation process of $Y_{0.5}Ca_{0.5}BaCo_4O_7$ perovskite consists in oxygen insertion in oxide structure, assigned to Co (II) oxidation (7) [11]:



Methanol anodic oxidation is a complex process, involving 6-electron transfer and several intermediate organic species are produced [12]. Oxidation mechanism of methanol in alkaline medium on metallic electrode, like Pt or Pt-alloys, was complete described by S. S. Mahapatra and J. Datta in 2011 and proceeds through the following steps [12]:



Reactions (12) and (13) can proceed directly to CO_2 production [12]:



In Figure 1 linear voltammograms recorded with 1 mV s^{-1} scan rate are presented, in absence and presence of methanol lowest concentrations used in the alkaline electrolyte.

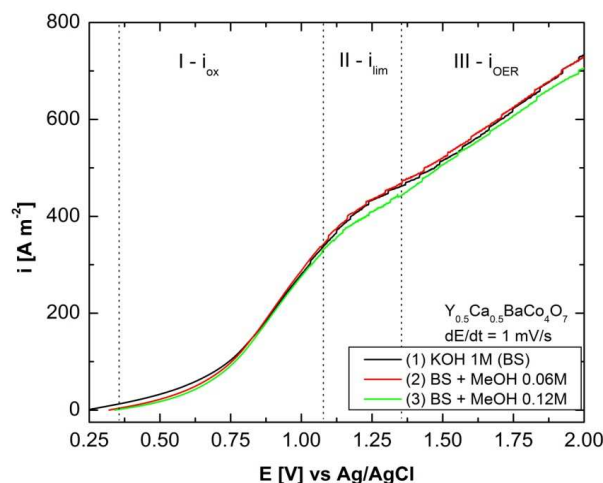


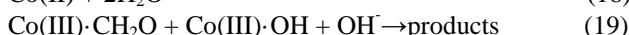
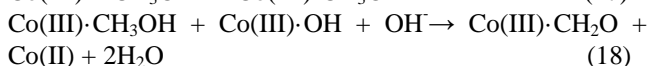
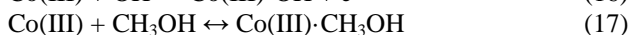
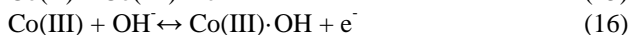
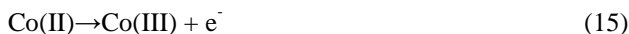
Figure 1. Linear voltammograms recorded on $Y_{0.5}Ca_{0.5}BaCo_4O_7$ electrode in 1M KOH solution, without and with 0.06 M and 0.12M MeOH, at 1 mV s^{-1}

Analyzing voltammograms from Figure 1, it can be observed the potential domain specific for methanol

oxidation, between +0.25 and +1.30 V, includes the electrooxidation potential of Co(II) to Co(III).

This shows the potential region for Co(II) electrooxidation inside of perovskite vis-à-vis of methanol anodic oxidation is the same. This behavior is somehow specific for layered perovskites, being previously shown also for LaSrNiO_4 in alkaline media [7].

Methanol anodic oxidation process on $\text{Y}_{0.5}\text{Ca}_{0.5}\text{BaCo}_4\text{O}_7$ perovskite occurs with similar mechanism as on $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ in KOH solutions and involves the following steps [7]:



Methanol electrocatalytic oxidation seems to be mediated by the Co(III)/Co(II) redox couple from inside of perovskite. Also, methanol dehydrogenation is catalyzed by the same couple. Reactions (15) and (20) take place rapidly [7].

According to the processes at the interface electrode/electrolyte, linear voltammograms from Figure 1 can be divided in three potential domains for both perovskite oxidation and MOR: I - oxidation region, II - limiting current domain and III - domain of oxygen evolution reaction (OER) on electrode surface.

Table 1 presents the values of conductivity for electrolyte solutions used in experimental data.

TABLE 1. Conductivity of different electrolytes used in experimental studies

Electrolyte	Conductivity [S m^{-1}]
Distilled water	$2.25 \cdot 10^{-6}$
MeOH p.a. min 99.8%	$11.22 \cdot 10^{-6}$
KOH 1M (BS)	$168.8 \cdot 10^{-3}$
BS + MeOH 0.06M	$165.1 \cdot 10^{-3}$
BS + MeOH 0.12M	$163.5 \cdot 10^{-3}$
BS + MeOH 0.25M	$157.5 \cdot 10^{-3}$
BS + MeOH 0.5M	$149.7 \cdot 10^{-3}$
BS + MeOH 1M	$140.3 \cdot 10^{-3}$
BS + MeOH 2M	$127.9 \cdot 10^{-3}$

Analysing data from Table 1, it can be noticed the decrease of the conductivity along with the increasing of methanol concentration. In electrochemical measurements, the effect of these values on MOR has been observed.

3.2. Cyclic voltammetry studies

On CVs recorded at 100 mVs^{-1} in alkaline solutions, in the absence and presence of methanol, in a wide range of the potential (+1.75 and -1.75 V), depicted in Figure 2, there is observed a pronounced anodic peak associated with all methanol oxidation steps described by reactions (15) – (20) and with Co(II) to Co(III) oxidation for blank solution.

When the electrode potential is over +1.00V, OER on electrode surface can be noticed. On the backward scan, a low intensity reduction peak associated with adsorbed oxygen reduction was recorded. When the electrode potential becomes more negative than -0.75V, hydrogen evolution reaction (HER) occurs.

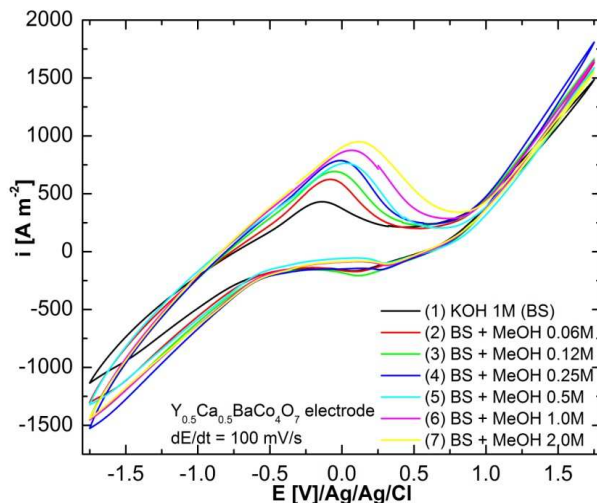


Figure 2. Cyclic voltammograms recorded on $\text{Y}_{0.5}\text{Ca}_{0.5}\text{BaCo}_4\text{O}_7$ electrode in 1M KOH solution, without and with different concentration of MeOH, at 100 mVs^{-1}

CVs recorded with low scan rate (10 mV s^{-1}) in the potential range from 0 to -1.50 V show a separation of the reduction peaks (Figure 3). Starting from open circuit potential (OCP) towards anodic polarization (+1.60 V), characteristic peaks which may be attributed to methanol oxidation reaction products are not distinguished.

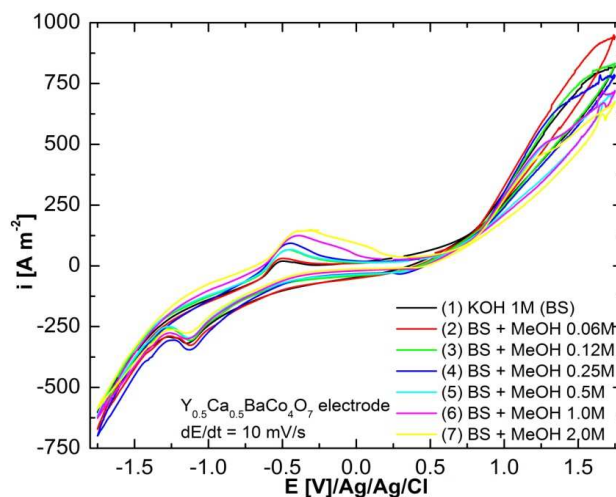


Figure 3. Cyclic voltammograms recorded on $\text{Y}_{0.5}\text{Ca}_{0.5}\text{BaCo}_4\text{O}_7$ electrode in 1M KOH solution, without and with different concentration of MeOH, at 10 mVs^{-1}

The oxidation-reduction peaks in the potential range from +0.50 to -1.30 V are detailed in Figure 4. These are associated with formaldehyde/formate redox couple in alkaline medium.

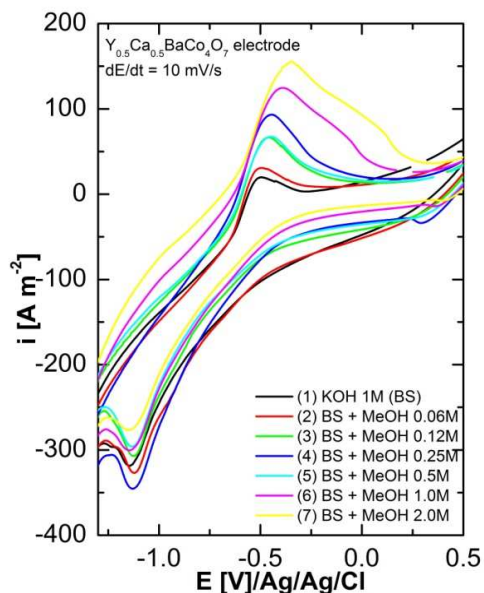


Figure 4. Oxidation-reduction peaks for HCHO/HCOO⁻ redox couple from cyclic voltammograms

Formaldehyde (HCHO) to formate (HCOO⁻) oxidation depends on the methanol concentration in the electrolyte solution, increasing the peak intensity along with the increasing of the concentration. As well, from the curve shape it can be seen that oxidation is a multistage process.

It should be emphasized that oxidation-reduction peaks corresponding to HCHO/HCOO⁻ couple are recorded in the same potential range as for Co(II)/Co(III) couple when electrolyte solution without methanol addition have been used, thus confirming the preliminary results.

Cyclic voltammetric studies have shown that it is possible to separate the peaks associated with the electrochemical processes occurring at the interface Y_{0.5}Ca_{0.5}BaCo₄O₇ – 1M KOH + methanol only if the potential scan rate is around 5 mV s⁻¹. The CVs recorded for 1M and 2M methanol added in alkaline electrolyte are depicted in Figure 5.

Starting from OCP towards anodic polarization, methanol oxidation domain (1) is revealed, followed by limiting current plateau (2) characteristic for this reaction. At higher potentials, over +1.25 V, the current increase (3) was associated with the OER.

On the backward scan of the CVs, when the electrode potential shifts towards more negative values, a pronounced cathodic peak (4), associated with formate ions reduction to formaldehyde appears around -1.00 V. At more negative electrode potentials, the current increase (5) is assigned to HER. When the potential is scanned in anodic direction, up to OCP, an oxidation peak (6) is observed at approximately -0.50 V due to the formaldehyde oxidation to formate ions or other products.

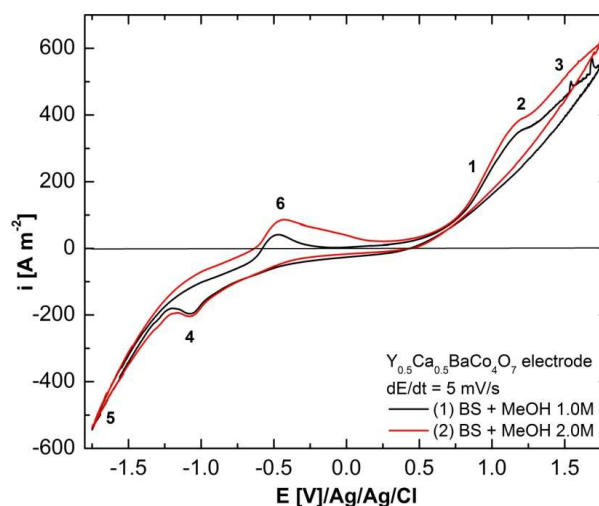


Figure 5. Cyclic voltammograms recorded on Y_{0.5}Ca_{0.5}BaCo₄O₇ electrode in 1M KOH solution with 1M and 2M MeOH, at 5 mV s⁻¹

Comparing voltammograms drawn in the same potential range, an increase of current density related to above processes is ascertained for electrolyte solution containing higher concentration of methanol, as well as a shift of OER to more negative potentials.

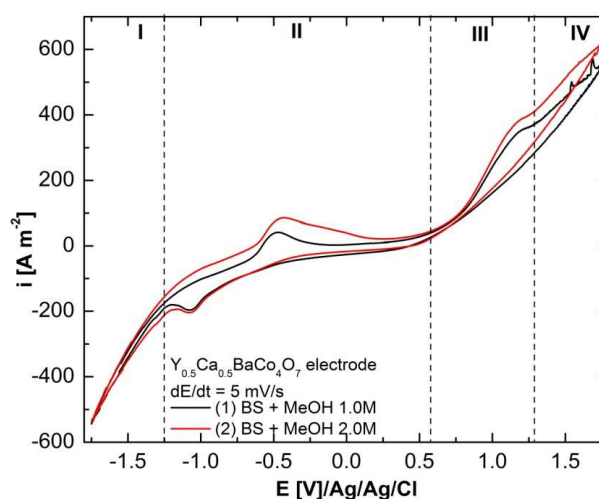


Figure 6. Cyclic voltammograms recorded on Y_{0.5}Ca_{0.5}BaCo₄O₇ electrode in 1M KOH solution with 1M and 2M MeOH, at 5 mV s⁻¹

Oxidation and reduction processes at the interface make possible the voltammograms partition in four potential domains (Figure 6), characteristic for MOR on Y_{0.5}Ca_{0.5}BaCo₄O₇ in alkaline media: I - HER domain, II - formaldehyde/formate ions redox couple domain, III - MOR on 114 layered cobalt perovskite surface domain and IV - OER domain.

In Figure 7 CVs (5 cycles) plotted on Y_{0.5}Ca_{0.5}BaCo₄O₇ in alkaline solutions with addition of 0.5 M, respectively 2.0 M methanol are presented.

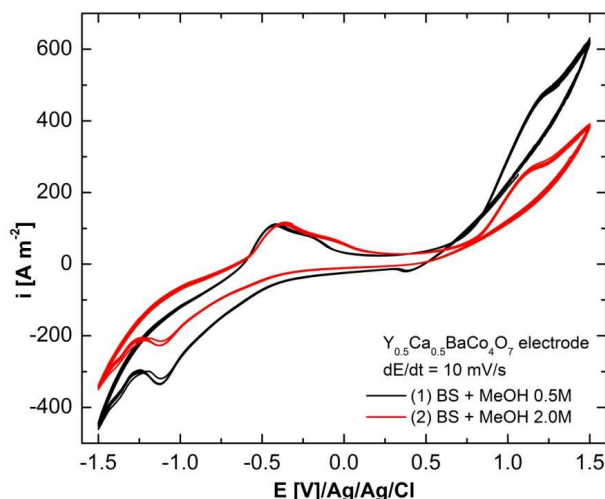


Figure 7. Cyclic voltammograms (5 cycles) recorded on $Y_{0.5}Ca_{0.5}BaCo_4O_7$ electrode in 1M KOH with 0.5M and 2M MeOH, at 10 mV s^{-1}

Analysing the above CVs, it can be stated the peak intensity increases with number of plotted cycles due to the increasing amounts of methanol oxidation products formed, which then participate in electrode surface reactions.

When a low concentration of methanol (0.5 M) is used, on cathodic domain the low intensity peak corresponding to the reduction of adsorbed oxygen on electrode surface and from inside its pores is registered at about $+0.40 \text{ V}$. When a higher concentration of methanol is used (over 1 M), this peak disappears because the entire quantity of cathodic reduced oxygen is immediately consumed for the oxidation of methanol and/or its intermediate products formed in the anodic process, available in high concentration near the electrode surface.

Widening the polarization range in both anodic and cathodic domains significantly influences the electrode

process efficiency, noticeably more when 1 M methanol is used in alkaline media, as can be seen in Figure 8 a and b.

Thereby, using 1M methanol addition in electrolyte solution, in $+1.50 \text{ V}$ up to -1.50 V potential range (Figure 8b), the limiting current density value (i_{lim}) is approximately 325 A m^{-2} , and the current density of formaldehyde/formate oxidation-reduction couple have values: $i_{ox} = 90 \text{ A m}^{-2}$, respectively $|i_{red}| = 225 \text{ A m}^{-2}$. When the potential was scanned between $+1.75$ and -1.75 V , the current density values change to: $i_{lim} = 575 \text{ A m}^{-2}$, $i_{ox} = 110 \text{ A m}^{-2}$ and $|i_{red}| = 325 \text{ A m}^{-2}$, as can be observed.

If methanol concentration in electrolyte solution is lower than 1 M, 0.125 M for instance (Figure 8 a), the changes of corresponding formaldehyde/formate couple are insignificant, only methanol oxidation current density increase from 575 to 700 A m^{-2} being observed

In the same time, a slight catalytic effect on OER and HER is observed by enlarging the potential scan range, regardless of methanol concentration.

3.3. Linear voltammetry studies

Linear voltammograms (LVs) plotted at low scan rate (1 mV s^{-1}) confirms the above presented results. The curves obtained in alkaline media with different concentrations of methanol are shown in Figure 9.

Analysis of linear voltammograms shape indicates only one oxidation process on perovskite electrode surface which validates the mechanism reaction described by (15) – (20) equations.

Methanol oxidation limiting current density decrease along with the increasing of methanol concentration in KOH electrolyte solutions, the same principle being observed for conductivity values presented in Table 1.

Based on LVs discussed above, it can be stated the optimum concentration domain of methanol in alkaline media for maximum efficiency electrooxidation ranges from 0.006 to 0.125 M.

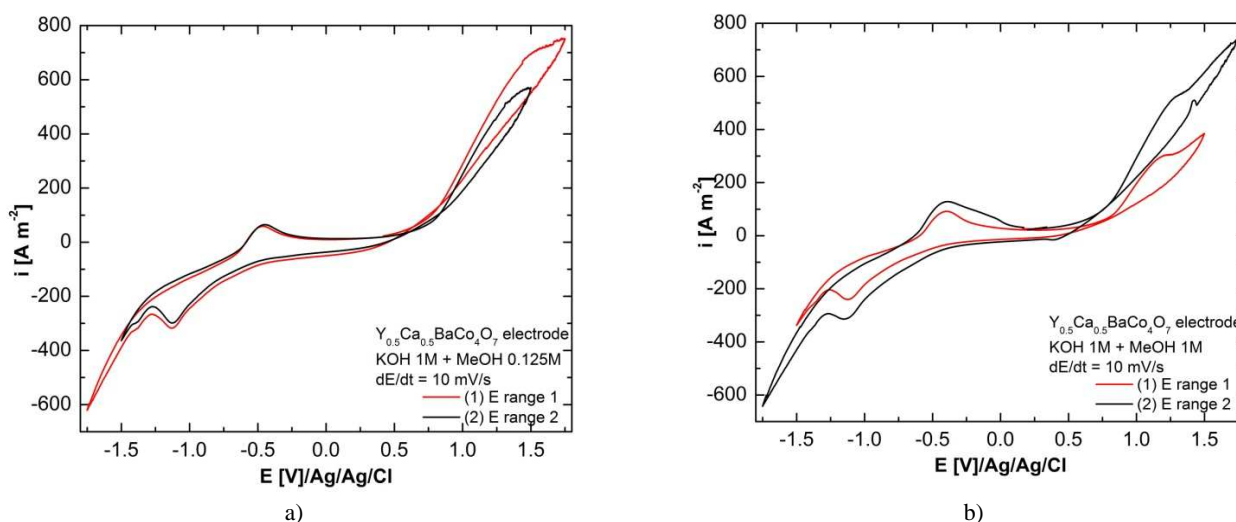


Figure 8. Cyclic voltammograms recorded on $Y_{0.5}Ca_{0.5}BaCo_4O_7$ electrode in 1M KOH with 0.125M (a) and 1M (b) MeOH, at 10 mV s^{-1} , in different potential ranges

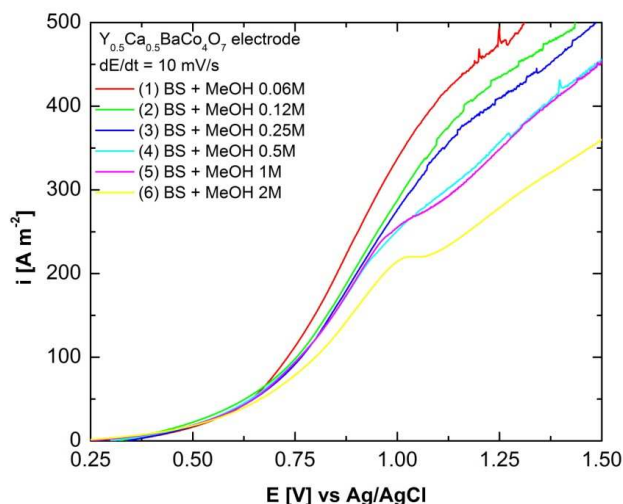


Figure 9. Linear voltammograms recorded on $Y_{0.5}Ca_{0.5}BaCo_4O_7$ electrode in 1M KOH solution with different MeOH concentration, at 1 mV s^{-1}

4. Conclusions

Experimental data presented have confirmed the possibility to oxidize methanol in alkaline media on an electrode made of cobalt layer perovskite type 114.

From the perspective of using cobalt layered perovskite as potential electrode materials in alkaline direct methanol fuel cells, the possibility to oxidize methanol directly on their surface provides a good reason for continuing studies presented in this paper. A deepening of the research is necessary both for complete characterization of processes occurring at the interface by electrochemical impedance spectroscopy, and in order to

determine optimum characteristic parameters, from which the most important is the efficiency of the oxidation process.

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