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Dedicated to prof. dr. I. C. Popescu
on the occasion of his 70th anniversary

ON THE ELECTROCATALYTIC PROPERTIES OF $YCo_{1-x}Fe_xO_3$ (x = 0, 0.5 and 1) PEROVSKITE SERIES

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ABSTRACT. The results on the investigation of the electrocatalytic activity of $YCo_{1-x}Fe_xO_3$ (x = 0, 0.5 and 1) perovskites towards several redox reactions, are presented. The perovskites were synthesized by solution combustion method using citric acid as a fuel. They are isomorphous with orthorhombic perovskite structure, within the space group *Pnma.* The electrocatalytic properties of these perovskites were studied by cyclic voltammetry using paraffin impregnated graphite electrode (PIGE) modified with microcrystals of the investigated perovskites. Such modified electrodes were used to study their catalytic properties towards: oxidation of OH^- ions, oxidation of H_2O_2 in phosphate buffer and oxidation of CH_3OH in alkaline solution. It was found that, in general, the catalytic activity is strongly dependent on the cobalt content.

Keywords: *perovskites, cyclic voltammetry, electrocatalytic properties*

INTRODUCTION

Perovskites (ABO_3) are well-known class of ceramic materials with specific chemical and physical properties based on the huge flexibility in composition and structure but still keeping the basic perovskite-type structural pattern. The ideal perovskite-type structure is cubic ($Pm\bar{3}m$) consisting of BO_6 corner-sharing octahedra with A-cations in the cubooctahedral cavities [1]. The

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partial substitution in A or/and B positions in so-called complex perovskites, leads to different types of structural distortions such as tilting of the octahedra, displacement of the cations from the centers of coordination polyhedra, and Jahn-Teller distortion of the octahedra [1]. These compositional and structural variations are responsible for exhibition of important and unique properties determining their application.

The rare-earth perovskites containing Mn, Fe, Co, Ni in B-position, and particularly those with partial substitution in A or/and B position, are considered as catalysts in numerous catalytic processes [2], such as CO oxidation [2, 3], hydrocarbon oxidation [2], nitrogen oxides decomposition [2] etc. The electrical properties of simple and complex perovskites are also very important. According to the literature data perovskites show insulating, semiconducting and metal-conducting properties, depending on the constituents, structure and metal-to-insulator transitions with variation of the temperature [4, 5]. Some perovskites exhibits appropriate performances as cathode materials in solid-oxides fuel cells (SOFCs) [2, 6, 7], and some are used as electrochemical gas sensors [8].

In recent years the electrocatalytic properties of perovskite-type materials have been also extensively studied. Thus, some complex perovskites containing Ni in B-position were used in preparation of carbon paste electrodes as glucose sensors [9, 10], as well as, some other complex perovskites [11]. Manganese containing complex perovskites were also used for preparing carbon paste modified electrodes for amperometric determination of hydrogen peroxide [12]. Also, manganites partially substituted with Sr in A position show electrocatalytic activity towards hydrogen peroxide in alkaline solutions [13]. Xu et al. [14] have developed a nonenzymatic biosensor for hydrogen peroxide based on a glassy carbon electrode loaded with layered nano-structured perovskite-type oxide. Most recently [15] Liotta et al. fabricated and tested $La_xSr_{1-x}FeO_{3-d}$ and $La_xSr_{1-x}Co_yFe_{1-y}O_{3-d}$ modified carbon screen printed electrodes for H_2O_2 and glucose electrochemical sensors. The electrodes were electrochemically characterized in alkaline medium by cyclic voltammetry and chrono-amperometric methods. It was found that the key factor for sensing characteristics is the mixed valence states stabilized in the perovskite structure, in particular to the presence of Co^{3+}/Co^{2+} and Fe^{3+}/Fe^{2+} couples accountable for charge transfers.

Perovskites with partial substitution of Co^{3+} were subject of our previous investigations regarding the synthesis and electrical properties [16-19]. However, we were also interested in their electrocatalytic activities. Thus, we have reported [20] on the catalytic properties on $YCoO_3$ and $YCo_{0.5}Cr_{0.5}O_3$ towards oxidation of chloride anions and oxidation of methanol in alkaline solutions, studied by cyclic voltammetry. We have also started the investigation of $YCo_{1-x}Fe_xO_3$ (x = 0, 0.33, 05. 0.67 and 1) perovskite series. The publication of the results on their crystal structure and crystallochemical characteristics is in progress [21], and the results on the influence of Y-ion substitution on structural and electrochemical properties of $YCo_{0.5}Fe_{0.5}O_3$ have been published most recently [22]. Continuing our work on this perovskite series, here we present the electrocatalytic properties of $YCo_{1-x}Fe_xO_3$ (x = 0, 0.5 and 1) perovskite series towards oxidation of OH^- ions, oxidation of methanol in basic solutions and oxidation of H_2O_2, in phosphate buffer.

RESULTS AND DISCUSSION

The perovskite series $YCo_{1-x}Fe_xO_3$ (x = 0, 0.5 and 1) was synthesized by solution combustion method with citric acid as a fuel. The compounds were identified and characterized by powder XRD. They are isomorphous and crystallize in *Pnma* space group with Z = 4 (Fig. 1).

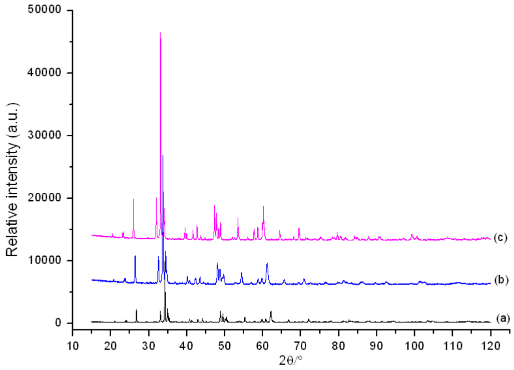

Fig.1. The powder XRD patterns of: (a) $YCoO_3$, (b) $YCo_{0.5}Fe_{0.5}O_3$ and (c) $YFeO_3$.

The lattice cell parameters calculated by Rietveld refinement are given in Table 1.

Table 1. The lattice cell parameters of $YCo_{1-x}Fe_xO_3$ (x = 0, 0.5 and 1)

	$YCoO_3$	$YCo_{0.5}Fe_{0.5}O_3$	$YFeO_3$
a/Å	5.42156(12)	5.5087(2)	5.59245(7)
b/Å	7.36536(16)	7.4807(3)	7.60387(10)
c/Å	5.13809(11)	5.2133(2)	5.28056(7)

The electrochemical behaviour of these perovskites was investigated by cyclic voltammetry by means of a specially designed paraffin impregnated graphite electrode (PIGE) [23]. The electrode was modified by deposition of the microcrystals of the investigated perovskites on its surface by abrasion.

Firstly, the electrochemical behaviour of such modified electrode was investigated in 0.1 M KOH solutions (Fig. 2).

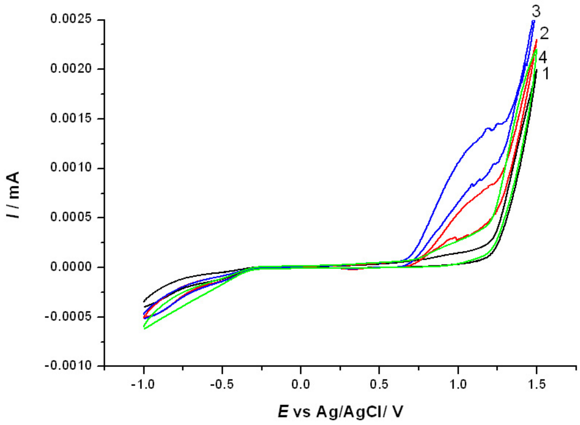

Fig. 2. The voltammograms of modified electrodes in contact with 0.1 M solution of KOH. 1- blanc electrode; 2 - $YFeO_3$; 3 - $YFe_{0.5}Co_{0.5}O_3$ and 4 - $YCoO_3$.

As can be seen from the figure, in the voltammograms of the studied perovskites in solutions of 0.1 M KOH, a significant enlargement of the anodic current commencing at potential of about 0.7 V can be noticed. The catalytic effect of the deposited perovskite microcrystals on the electrode is manifested as a shift of the anodic tail in the voltammograms towards less positive potentials. The most pronounced catalytic activity towards oxidation of OH^- ions exhibits $YFe_{0.5}Co_{0.5}O_3$. In the cathodic part of the cyclic voltammograms, within the potential region from – 0.3 to –1.0 V, a voltammetric pattern typical for two-step reduction process appears, the intensity of which increases in proportion to the catalytic effect of the studied perovskites.

The overall voltammetric response can be assigned as a catalytic oxygen evolution reaction (OER) (anodic part of the voltammograms), accompanied with a two-step reduction (cathodic part of the voltammograms) of electrochemically formed oxygen. However, the voltammograms consist of several peaks indicating a complex electrochemical process which takes place in several steps. One of the proposed mechanisms of oxygen evolution reaction on perovskite surface was proposed by Bockris and Otagawa [24]. It is based on interaction of the transition metal in the perovskite structure with the OH^- ions resulting with hydrogen peroxide formation, which is physisorbed on the perovskite surface.

The physisorbed H_2O_2 undergoes further catalytic decomposition with O_2 evolution. The overall process can be represented [24] with the electrode reactions (1-2), followed by the chemical reactions (3-4):

$$M^z + OH^- \longrightarrow M^z\text{—}OH + e^- \tag{1}$$

$$M^z\text{—}OH + OH^- \longrightarrow M^z\cdots H_2O_2 + e^- \tag{2}$$

$$(H_2O_2)_{phys} + OH^- \longrightarrow (HO_2^-) + H_2O \tag{3}$$

$$(H_2O_2)_{phys} + (HO_2^-)_{phys} \longrightarrow H_2O + OH^- + O_2\uparrow \tag{4}$$

Interestingly, similar voltammetric pattern, considering both anodic and cathodic parts of the cyclic voltammograms, was observed with perovskites modified PIGE in contact with phosphate buffer (pH = 7.35) (Fig. 3.). Though the concentration of hydroxide ions is very low in the phosphate buffer, the catalytic effect of perovskites is clearly visible in the anodic part of the voltammograms. Accordingly, the onset of the anodic current is associated with potentials close to 1.0 V, being significantly more positive compared to voltammograms recorded in 0.1 M KOH (cf. Fig. 2.), reflecting both concentration and activation overpotential required for proceeding of the electrode reaction. In accordance with the results presented in Fig. 3, the most pronounced catalytic activity was observed for $YCoO_3$, implying similar mechanism of the catalytic activity. Though, one can speculate that in phosphate buffer solution the initiate reactant of the oxidation process is water itself producing in the first step OH^- ions which further react according to reaction scheme (1-4).

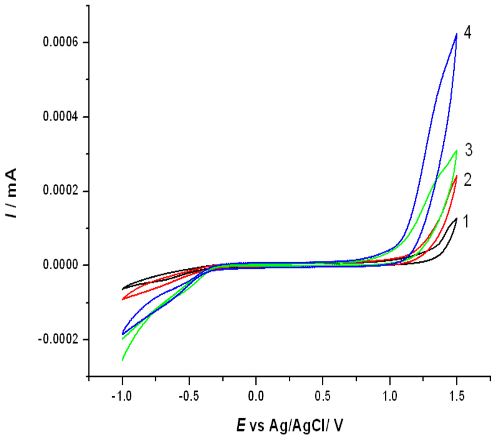

Fig. 3. The voltammograms of modified electrodes in contact with phosphate buffer solution. 1-blank electrode; 2-$YFeO_3$; 3-$YCo_{0.5}Fe_{0.5}O_3$ and 4-$YCoO_3$.

In aim to support the electrocatalytic mechanism proceeding via H_2O_2 formation, H_2O_2 was gradually added to the phosphate buffer solution over the concentration interval from 10^{-3} to 10^{-1} M. Cyclic voltammograms for each of the perovskite modified PIGE electrodes were recorded in the potential range from -1 V to 1.5 V (Fig. 4). The voltammograms recorded at low concentration of H_2O_2 almost overlap the volammogram of the blank electrode. But, obviously, by increasing the H_2O_2 concentration, the current increases and the oxidation e.g. the evolution of oxygen starts at less positive potentials for each of the perovskite modified PIGE electrode (Fig.4.). The onset of the anodic current recorded in H_2O_2 solutions is drastically shifted towards less positive potentials compared with potentials recorded in phosphate buffer (Fig. 3) and are very close to those recorded in 0.1 M KOH (Fig. 2). This could be considered as indirect support of the proposed mechanisms for oxidation of OH^- proceeding in steps (1-4).

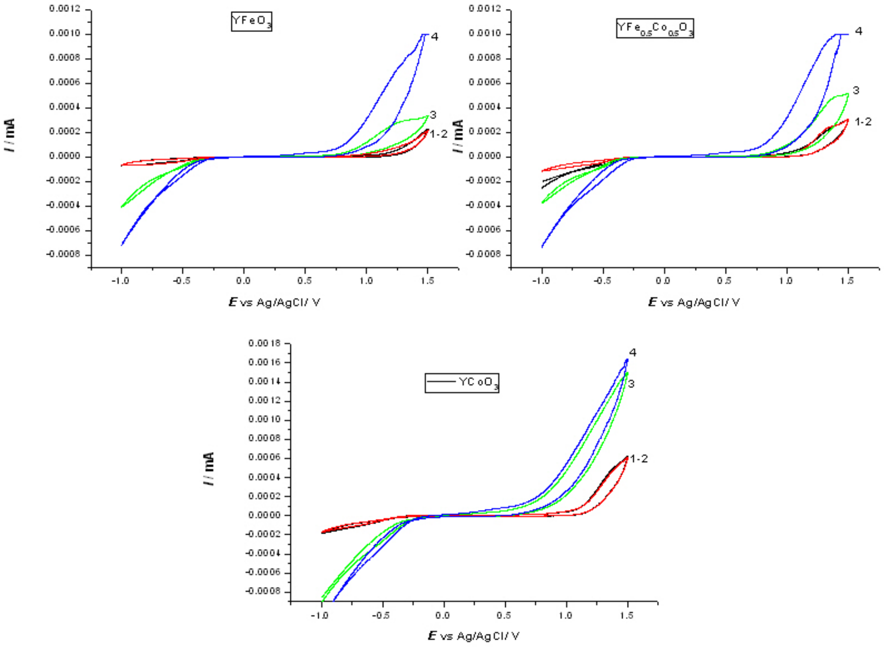

Fig. 4. The investigated compounds in: 1-phosphate buffer solution; 2-phosphate buffer + 10^{-3} M H_2O_2; 3-phosphate buffer + 10^{-2} M H_2O_2; 4-phosphate buffer + 10^{-1} M H_2O_2.

In the last part of our investigation, the electrocatalytic properties of the investigated perovskites were also analysed alkaline solution in the potential range of 0.0 to 0.8 V (Fig. 4.). The oxidation of methanol in alkaline solutions is of special interest since it takes place in so-called direct methanol fuel cells. Therefore, as electrolyte in our investigation 1M CH_3OH in 1 M KOH solution was used. The recorded voltammograms of the blank (1) and of the $YFeO_3$ modified PIGE (2) are of the same shape indicating that $YFeO_3$ do not show any catalytic properties towards methanol oxidation. However, the voltamograms of PIGE modified with Co-containing perovskites clearly shows electrocatalytic effect. In these cases the onset anodic potential of the oxidation of methanol is shifted towards less positive potentials in comparison when it is performed with blank electrode and also the current is extensively increased. The best catalytic activity shows $YCoO_3$ indicating that the electrocatalyitic activity of $YCo_{1-x}Fe_xO_3$ (x = 0, 0.5 and 1) perovskites towards oxidation of methanol in alkaline solutions increases with increasing of the cobalt content in perovskite structure.

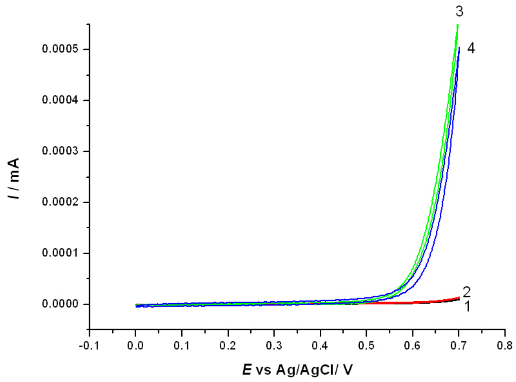

Fig. 4. The voltammograms of PIGE modified electrodes in contact with 1 M KOH + 1 M CH_3OH. 1-blank electrode; 2-$YFeO_3$; 3-$YCo_{0.5}Fe_{0.5}O_3$ and 4-$YCoO_3$.

CONCLUSIONS

$YCo_{1-x}Fe_xO_3$ (x = 0, 0.5 and 1) perovskites were synthesized by solution combustion method using citric acid as a fuel. The identification and characterization was performed by powder XRD. The compounds are isomorphous and crystallize in orthorhombic *Pnma* unit cell with $Z = 4$.

The electrocatalytic properties of the obtained perovskites were studied by cyclic voltammetry by means of perovskite modified PIGE electrode. It was found that these perovskites catalyze the oxidation of OH^- ions. It was supposed that the oxygen evolution process proceeds through H_2O_2 formation. The indirect support for this assumption was obtained from the voltammograms recorded when perovskite modified PIGE was in contact with phosphate buffer in which H_2O_2 was gradually added to the solution over the concentration interval from 10^{-3} to 10^{-1} M. The shift of the oxidation current towards less positive potentials with increasing of the H_2O_2 concentration confirms this assumption.

The perovskites modified PIGE electrodes were also investigated for their catalytic properties towards oxidation of methanol in alkaline solutions. A prominent electrocatalytic activity for this reaction was found for the Co-containg perovskites. The catalytic activity increases with increasing of the cobalt content.

EXPERIMENTAL SECTION

The perovskite series $YCo_{1-x}Fe_xO_3$ ($x = 1$, 0.5 and 1) was synthesized by solution combustion method using citric acid as a fuel. The quantity of the fuel was calculated using the oxidizer/fuel ratio which was set to 1. The citric acid was dissolved in small quantity of water and was slowly added to the solution containing the constituent metal nitrates. The pH of the reaction mixture was adjusted to 7 with addition of NH_4OH. The as-prepared solutions were heated on magnetic stirrer at temperature of 80 °C and after evaporation of the water almost to dryness the beakers were transferred on a hot plate preheated at ~350 °C. The vigorous reaction took place evolving large amount of gases and resulting in formation of black spongy-like powder precursors. The precursors were additionally heated 4 hours at 800 °C, yielding perovskites. However, since all synthesized complex perovskites using citric acid contained small amount of Y_2O_3, they were washed with diluted HCl (c = 1 M). After washing and filtration, the samples were dried and additionally heated for 6 h at 950 °C.

The identification of the obtained perovskites was performed by powder X-ray diffraction. The XRD patterns were recorded at room temperature on *Bruker D8 Advance* with CuKα radiation and SolX detector within the range 10–120 ° 2θ with step-scanning of 0.02°.

The electrocatalytic properties of $YCo_{1-x}Fe_xO_3$ perovskites were investigated by cyclic voltammetry on µAUTOLAB, model III instrument. The electrochemical cell consisted of three electrodes: PIGE as a working electrode, Ag/AgCl (sat. KCl) as reference electrode, and a platinum wire as auxiliary electrode. The microcrystals of the investigated perovskites were deposited on the surface of PIGE. The electrochemical activity was investigated at room temperature, in 0.1 M of KOH; 1M CH_3OH + 1 M KOH; phosphate buffer (pH = 7.35) and buffer in which H_2O_2 (10^{-1} – 10^{-3} M) was added.

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