ORIGINAL PAPER

Solution combustion synthesis of YCoO$_3$ and investigation of its catalytic properties by cyclic voltammetery

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Abstract In this paper, the synthesis of YCoO$_3$ by solution combustion method and investigation of its catalytic activity using cyclic voltammetry is presented. The perovskite phase was obtained by thermal initializing of the solutions of the metal nitrates and the fuel (urea). The obtained solid precursor was further heated yielding the perovskite phase. The obtained perovskite compound has orthorhombic unit cell, within the space group *Pnma*, with unit cell parameters $a=5.4223$Å, $b=7.3657$Å, and $c=5.1385$Å. The catalytic activity of the prepared perovskite was investigated by cyclic voltammetry using YCoO$_3$-modified paraffin impregnated graphite electrode, in several electrolytes. It was found that the YCoO$_3$ perovskite has a distinct catalytic activity towards the oxidation of chloride anions in which Co^{3+} ions being the active centers. Also, this material enhances the oxidation of methanol in KOH.

Keywords Perovskite · YCoO$_3$ · Solution combustion synthesis · X-ray diffraction · Cyclic voltammetry · Catalysis

Introduction

Perovskites are a large family of isotypic crystalline ceramics. This class of compounds is one of the most important and consequently the most investigated in material science.

The general chemical formula of perovskite compounds is ABX$_3$, where A and B are cations of quite different sizes, and X is an anion. The highly versatile ABX$_3$ perovskite crystal structure is composed of three-dimensional network of corner-sharing BX$_6$ octahedra, and the A-site cations fill the 12 coordinated cavities formed by the BX$_6$ network [1]. Although the ideal perovskite structure is cubic, because of the flexibility inherent in the perovskite structure, several lower-symmetry distorted versions are more common in which the coordination numbers of A cations, B cations or both are reduced. This is followed by distortions and tilting of the BO$_6$ octahedra and displacements of the cations from the centers of their coordination polyhedra [2].

The substitution of different cations into the A and B positions is also possible, and these so called complex perovskites may have ordered and disordered variants. The perovskite structure is adopted by many oxides (ABO$_3$), but also some halogenides, nitrides, etc. are known.

Due to huge variety in composition, stoichiometry, and structure perovskite materials exhibit number of interesting properties from both the theoretical and the application point of view. Thus, piezoelectricity, pyroelectricity, ferroelectricity, colossal magnetoresistance, superconductivity, ionic conductivity, and a multitude of dielectric properties, are commonly observed features in perovskite-compounds family [3]. Perovskite compounds exhibit also good catalytic activity in different types of catalytic processes. Namely, these compounds are suitable catalysts for combustion processes, CO oxidation, methane reforming, SO$_2$ reduction, etc. [4, 5]. Perovskites are used as sensors and catalyst electrodes in certain types of fuel cells, and are promising materials as a replacement for platinum in catalytic converts in diesel vehicles. In most of these processes, perovskites have shown

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catalytic activity in heterogeneous oxidation reactions, in which the active centers, in particular, are the B cations.

Among different types of perovskites, rare earth cobaltites have been extensively studied due to their interesting electronic and magnetic properties, which results mainly from the possibility of spin-state changes of Co^{3+} ions [6–8]. Thus, it was found that Co^{3+} ion could undergo temperature driven spin-state changes from low-spin $\left(t_{2g}^6\right)$ to intermediate-spin $\left(t_{2g}^5 e_g^1\right)$ and finally to high-spin state $\left(t_{2g}^4 e_g^2\right)$, or it could exist in mixed intermediate and high-spin state [6]. Triple or substituted cobaltate perovskites are also catalytically active in different processes. Namely, they were investigated as catalysts for oxidation processes, as oxidation of CO, H_2, hydrocarbons, etc. [5, 9–12]. The redox properties and catalytic activity of some perovskites were also investigated by electrotrochemical methods. The investigation of the electrochemical activity of solid compounds, including perovskites, may be performed in different ways [13]. Some La-cobaltates were investigated by preparing electrodes covered by a pervoskite film or perovskite composite films on different solid substrates [14–16]

For all these applications, it is necessary to prepare perovskite powders with defined stoichiometry and structure. The large surface area is expected to show enhanced properties with respect to materials prepared by conventional methods. Therefore, some new synthetic procedures have been developed, one of them being the solution combustion synthesis.

In aim to study the influence of the synthetic route on crystal structure and redox and catalytic properties of perovskites, in this work the synthesis by soft chemistry methods and electrochemical properties of $YCoO_3$ are presented. Until now, $YCoO_3$ has been synthesized using different methods: solid-state reaction using high oxygen pressure [17–19], solid-state synthesis using different precursors [20, 21], or sol-gel method [22, 23]. Here, it is synthesized by solution combustion method for which there is no literature data. The composition and structure of the obtained $YCoO_3$ perovskite was determined by X-ray powder diffraction (XRD) and electrochemical and catalytic properties were investigated for the first time by utilizing the voltammetry of solid microparticles immobilized on paraffin impregnated graphite electrode (PIGE) [24].

Experimental

$YCoO_3$ was synthesized using solution combustion method. This method consists of heating a mixture of saturated aqueous solutions of metal nitrates and some organic fuel to boiling, when the mixture ignites and a self-propagating, self-sustaining, and fast nonexplosive exothermic reaction occurs, resulting in a dry oxide powder [25]. The combustion reaction of the fuel is exothermic and should provide the heat needed for the synthesis reaction.

The metal ion precursors for this synthesis were $Y(NO_3)_3 \cdot 6H_2O$ and $Co(NO_3)_2 \cdot 6H_2O$ and urea was used as a fuel (F). The theoretical chemical equation for the formation of $YCoO_3$ perovskite may be presented as:

$$2Y(NO_3)_3 + 2Co(NO_3)_2 + 8(NH_2)_2CO \longrightarrow 2YCoO_3$$
$$+ 8CO_2 + 16H_2O + 13N_2$$
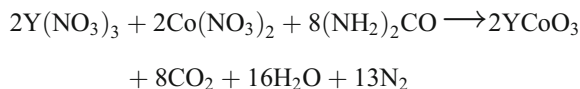
The composition of the initial solution was calculated applying the approach used in the field of propellants and explosives [25]. Namely, oxidizer to fuel ratio was calculated using oxidizing power of metal nitrates (total power for $Co(NO_3)_2 = -10$; total power for $Y(NO_3)_3 = -15$) and reducing power of organic fuel (total valencies +6). The (F/O) ratio was set to one, so the molar ratio of the metal precursors and urea was: 1:1:4.17. However, a small excess of the fuel was used.

For the preparation of the initial solution, the stoichiometric quantities of the metal nitrates ($Y(NO_3)_3 \cdot 6H_2O$ and $Co(NO_3)_2 \cdot 6H_2O$) were dissolved in small quantity of diluted solution of nitric acid (1:1), and the stoichiometric quantity of urea was dissolved in small amount of distilled water. The obtained solutions were thoroughly mixed together, set in furnace and slowly heated up to ~500 °C. After the evaporation of the water, the combustion reaction was initialized and the mixture was burned with releasing gaseous products. As a result, a black voluminous sponge-like powder was obtained. To eliminate the organic residue, the precursor powder was heated in air at 800 °C for 4 h. In order to obtain perovskite powder with better purity, the obtained perovskite was subjected to additional heat treatments. Namely, the powder was heated twice at 900 °C for 6 h and ones at 1,000 °C for 5 h.

XRD patterns of the all samples obtained by consecutive heating were recorded at room temperature on *Bruker D8 Advance* with CuKα radiation and SolX detector. Firstly, three samples were recorded within the range $10° \leq 2\theta \leq 90°$ with scanning rate of 0.04°, and the sample treated at 1,000 °C with scanning rate 0.02°.

The redox and catalytic properties of $YCoO_3$ perovskite were investigated using cyclic voltammetry. The investigations were performed on μAUTOLAB, model III, product of Autolab, the Netherlands. The cyclic voltammograms were recorded on a specially designed PIGE [24]. 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 $YCoO_3$ were deposited on the surface of PIGE by abrasion. The electrochemical activity was investigated at room temperature, in aqueous solutions of different electrolytes: $LiClO_4$, KNO_3, KCl, $(CH_3)_4NCl$, KBr, $NaNO_3$, and

NaCl with concentration 0.5 mol/dm^3, in the potential range from +1.5 mV to −1.0 mV at scanning rate of 5 mV/s. In order to explain the behavior of the modified electrode in the solution of the chloride ions this system was investigated more thoroughly. Namely, we have studied the catalytic activity in solutions with different concentrations of chloride ions (form 0.1 to 1 mol/dm^3), the mechanical stability and the effect of the conditioning. Furthermore, in order to estimate the influence of the substitution (partial and complete) in the position of the B-cation on the catalytic activity of $YCoO_3$, two perovskites with similar composition ($YCrO_3$ and $YCo_{0.5}Cr_{0.5}O_3$) were synthesized using the same methodology.

Results and discussion

The formation of the perovskite was confirmed by XRD of the obtained powders. The XRD patterns of $YCoO_3$ obtained at different temperatures are given in Fig. 1. By comparison of the d values of the diffractograms and the data given in the literature, it could be concluded that this method of synthesis yields compound with perovskite structure. However, the X-ray powder diffraction pattern of the perovskite obtained at 800 °C (Fig. 1a) clearly shows that besides $YCoO_3$ as major phase, Co_3O_4 and Y_2O_3 are also present. In order to improve the purity of the perovskite phase, the powder was additionally heated: two times for 6 h at 900 °C (Fig. 1b, c) and 5 h at 1,000 °C (Fig. 1d). Also, the literature data show that $YCoO_3$ perovskite obtained by different synthetic methods contains up to 3% impurities of Y_2O_3 [18, 20–22]. According to some authors [19] using high pressure/high temperature method of synthesis, $YCoO_3$ perovskite should be obtained
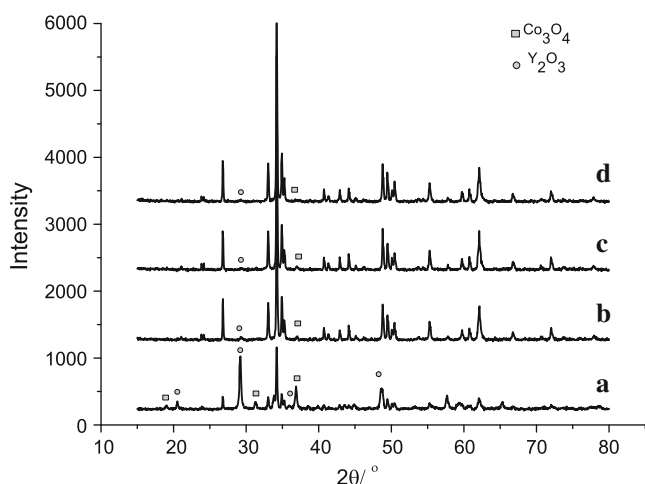
Fig. 1 X-ray diffractograms of $YCoO_3$ heated in consecutive manner at different temperatures for different time: **a** 4 h at 800 °C, **b** 6 h at 900 °C, **c** 6 h at 900 °C, and **d** 5 h at 1,000 °C
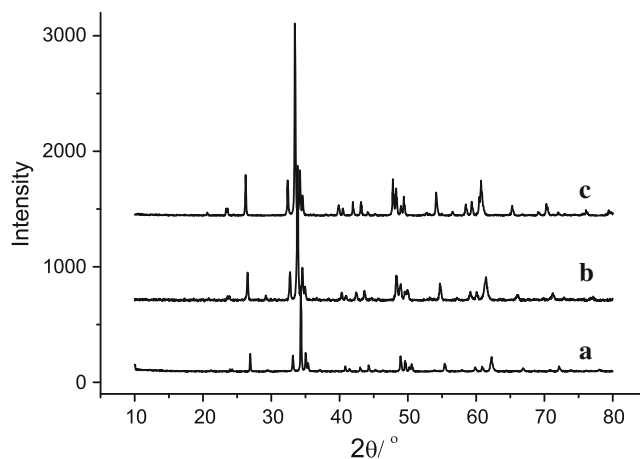
Fig. 2 X-ray diffractograms of **a** $YCoO_3$, **b** $YCo_{0.5}Cr_{0.5}O_3$, and **c** $YCrO_3$

as stoichiometric. The solution combustion method used in this work shows some nonstoichiometry in ytrrium, which is also noticed in the work of other authors [21]. As can be noticed from Fig. 1, the perovskite obtained after the heat treatment at 1,000 °C for 5 h, has best crystallinity and purity. So, the obtained perovskite could be used for X-ray analysis, and the investigation of its electrochemical and catalytic properties.

The analysis of the X-ray diffraction data showed that the obtained perovskite, $YCoO_3$, is of orthorhombic structure within the space group *Pnma*. Calculated unit cell parameters for the obtained diffractogram of $YCoO_3$ (Fig. 1d) are: $a=$ 5.4223 (2) Å, $b=7.3657$ (3) Å, and $c=5.1385$ (2) Å, and they are in accordance with literature data [21] where the obtained values are $a=5.4190$Å, $b=7.3657$Å, and $c=5.1387$Å.

As was mentioned in the experimental part, some substituted perovskites ($YCrO_3$ and $YCo_{0.5}Cr_{0.5}O_3$) were synthesized. The obtained XRD patterns are presented in Fig. 2, showing that they are isomorphous with $YCoO_3$. The obtained values for the lattice parameters (Table 1) show very good regularity. Thus, with substitution of Co^{3+} ions with Cr^{3+} ions the lattice parameters are increasing, as it was expected. The lattice parameters of $YCrO_3$ are in agreement with the literature data [26].

Voltammetry of $YCoO_3$ microcrystals

Electrochemistry of $YCoO_3$ was investigated by applying cyclic voltammetry at PIGE modified by $YCoO_3$ micro-crystals. The immobilization of the perovskite was achieved by a simple abrasion, as common for voltammetry of microcrystals [24]. The electrochemical behavior was investigated in contact with several aqueous electrolytes such as $LiClO_4$, KNO_3, KCl, $(CH_3)_4NCl$, KBr, KI, $NaNO_3$, and NaCl. From the large set of recorded voltammograms, it can be concluded that a well-defined Faradaic voltammetric

Table 1 Lattice parameters of $YCoO_3$, $YCo_{0.5}Cr_{0.5}O_3$, and $YCrO_3$ determined from X-ray powder diffraction pattern (space group: *Pnma*)

Lattice parameters	$YCoO_3$	$YCo_{0.5}Cr_{0.5}O_3$	$YCrO_3$
a/Å	5.4223	5.4693	5.5195
b/Å	7.3657	7.4488	7.5311
c/Å	5.1385	5.1896	5.2400

response can be obtained only in a chloride containing electrolyte solutions (Fig. 3). A typical cyclic voltammogram recorded in a chloride solution is attributed with an well-defined reduction pick at a potential of 0.672 V, preceded by intensive oxidation current, manifested as an anodic tail of the voltammogram commencing at about 1.00 V (see curve in Fig. 3). The oxidation current is so intensive that it is out of the measuring range of the instrument. If the anodic switching potential is less positive than 1.00 V, i.e., before the emerging of the oxidation current tail, the reduction peak at 0.672 V vanishes. These results imply that the reducible reactant, giving raise to the reduction peak at 0.672 V, is in situ formed during the intensive oxidation process represented by the anodic tail of the voltammogram.

In order to test the stability of the perovskite-modified electrode and the reliability of the electrochemical data in a chloride containing medium, repetitive cyclic voltammograms were recorded by consecutive potential cycling. The inset of Fig. 3 shows the voltammetric response being particularly stable and reproducible, revealing the electrochemical processes do not prompt dissolution or degradation of attached

microcrystals. Besides, the mechanical stability of the attached microcrystals was checked by interrupting the consecutive recordings and gentle washing of the electrode with redistilled water. This procedure was repeated for three times, while each recording included three repetitive cyclic voltammograms. The washing of the electrode did not produce any significant distortion either diminishing of the voltammetric response, implying an excellent mechanically stability of the attached microcrystals at the PIGE surface.

The effect of the increasing concentration of chloride ions in the aqueous phase to the voltammetric parameters of the cathodic peak is summarized in Table 2. Over the concentration interval from 0.1 to 0.9 mol/dm^3 the cathodic peak permanently increases. The dependence $I_{p,c}$ versus $c(Cl^-)$ has a shape of an isotherm, implying an adsorption complicated electrode process. At the same time, the position of the peak shifts mainly in a positive potential direction. In particular, the dependence $E_{p,c}$ versus $\log(Cl^-)$ is a line with a slope of 59 mV ($R=0.905$) over the concentration interval from 0.1 to 0.5 mol/dm^3. On the other hand, changing the type of the counter cation, i.e., K^+, Na^+, $(CH_3)_4N^+$, while keeping the concentration of chloride ions constant, did not produce any significant variation of the voltammetric response (data not shown), ruling out the role of the solvent cation in the studied electrochemical processes.

Figure 4 shows the effect of conditioning of the system at the anodic limiting potential of 1.50 V. More specifically, the voltammograms were recorded starting from the potential of −1.00 V in a positive potential direction, holding the potential at the positive limit of 1.5 V for different periods of time ($t_{con}=10$ s, 20 s and 30 s), and continuing with the

Fig. 3 Typical cyclic voltamograms of $YCoO_3$ microparticles modified paraffin impregnated graphite electrode recorded in contact with 0.5 M $LiClO_4$ (*1*), KNO_3 (*2*), and KCl (*3*) at a sweep rate of 20 mV/s. The *inset* shows repetitive cyclic voltammograms of the same electrode recorded in contact with 0.5 M KCl. The plot shows 1st, 3rd, and 6th potential cycle
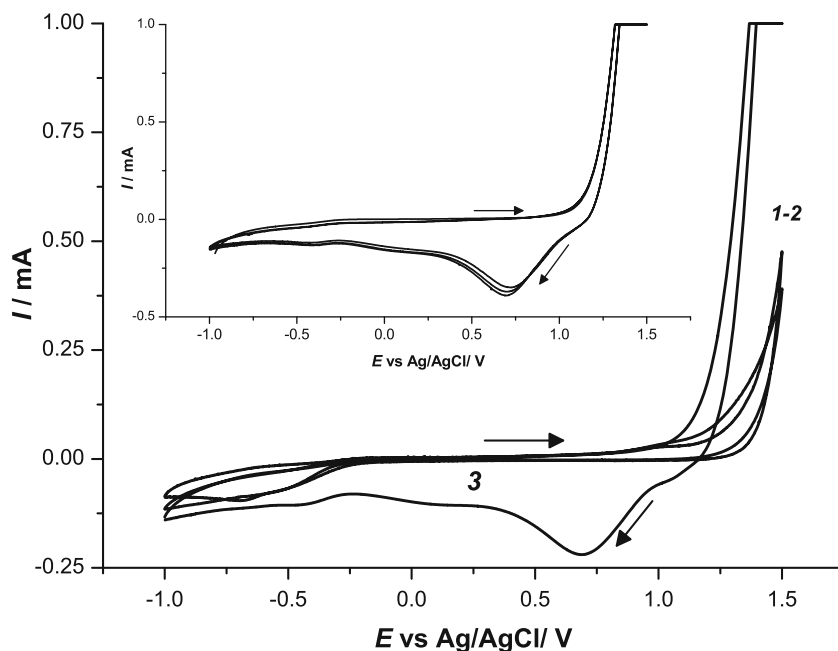
Table 2 Variation of the peak currents for the reductive peak under increasing concentration of the chloride ions in the aqueous phase recorded by cyclic voltammetry at PIGE modified with YCoO$_3$ microcrystals

c(KCl)/mol dm^{-3}	I$_p$/mA
0.1	−0.007963
0.2	−0.08980
0.3	−0.1431
0.4	−0.2206
0.5	−0.2250
0.6	−0.2750
0.7	−0.2610
0.8	−0.2797
0.9	−0.2761

reverse cathodic potential sweep back to –1.00 V. As can be seen from the figure, the conditioning of the system at such positive potential, where the oxidation process proceeds at significant rate, causes strong enhancement of the reductive peak, while the peak potential is insignificantly affected. For instance, the peak current increases from 0.19 to 0.43 mA for the conditioning of 0 and 10 s, respectively, while the peak potential changes for only 2 mV. The overall dependence $I_{p,c}$ versus t_{con} resembles again the shape of an isotherm. These results are in accordance with the data presented in Fig. 3, confirming that the reducible reactant is in situ formed during the anodic process commencing at about 1.00 V.

All the foregoing results strongly imply that the electrochemical activity of perovskite-modified PIGE in a chloride containing medium are related with catalytic redox transformation of chloride ions, rather than the genuine redox transformation of perovskite microcrystals itself. The strong oxidation current tail is assigned to the catalytic oxidation of chloride ions to chlorine, catalyzed by perovskite microcrystals. The electrochemical process is confined predominantly along the three-phase electrode|perovskite|water junction line, where the electrode serves as a source or a sink for electrons, the perovskite crystals provides catalytic sites, and the aqueous phase supplies the electroactive material. The oxidation process of chlorides yields, most probably, atomic chlorine or some other chlorine containing species that adsorbs on the modified electrode, giving raise to the reductive voltammetric peak in the corresponding cathodic potential sweep. This electrochemical scenario provides explanation why the voltammetric response is observed only in a chloride containing medium (cf. Fig. 3), as well as rationalizes the effect of the conditioning time (cf. Fig. 4)

It is postulated that the catalytic activity of the studied perovskite is due to presence of cobalt cation in B position. This assumption is supported by the comparative analysis of the voltammograms of YCoO$_3$ and YCo$_{0.5}$Cr$_{0.5}$O$_3$, i.e., a perovskite with a partially substituted cobalt ion with chromium. The voltammograms in Fig. 5 shows that the reductive peak with YCo$_{0.5}$Cr$_{0.5}$O$_3$-modified PIGE is shifted in a negative direction as a result of a weaker catalytic activity of YCo$_{0.5}$Cr$_{0.5}$O$_3$, caused by diminishing of the catalytic active sites by substitution of Co^{3+} with Cr^{3+}. The corresponding peak potentials for YCo$_{0.5}$Cr$_{0.5}$O$_3$ and YCoO$_3$ are 0.632 and 0.693 V, respectively. If cobalt was completely substituted with chromium, i.e., YCrO$_3$ perovskite, the voltammetric response together with the catalytic activity vanishes entirely (see curve 1 in Fig. 5).

Our results are in accordance with other findings referring to the catalytic activity of a variety of cobalt containing perovskites [27]. Nevertheless, to the best of our knowledge, this is the first example for the perovskite catalysis to the chlorine redox transformation. Moreover,

Fig. 4 The effect of the conditioning time at the potential of 1.5 V on the cyclic voltammograms of YCoO$_3$ microparticles modified PIGE recorded in 0.5 M KCl. The time of conditioning was 0 (*1*), 10 (*2*), and 30 s (*3*). All other conditions were the same as for Fig. 3
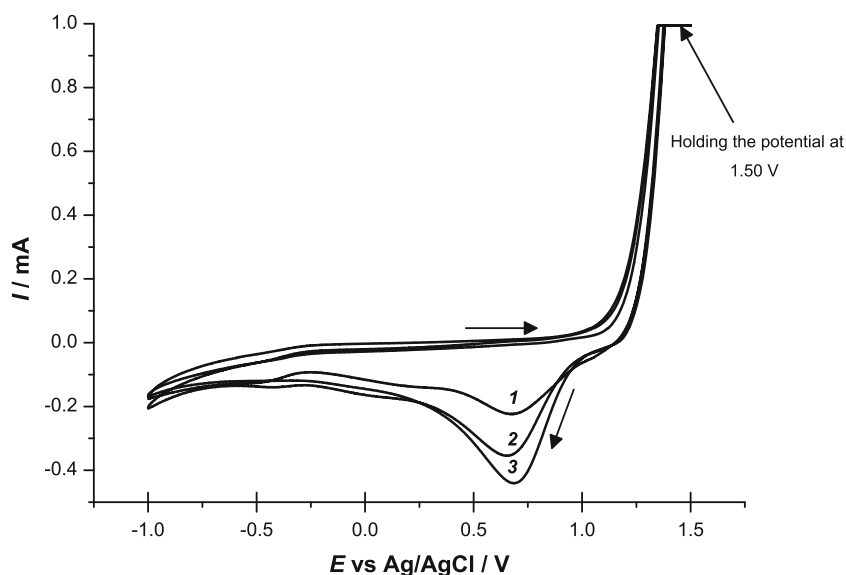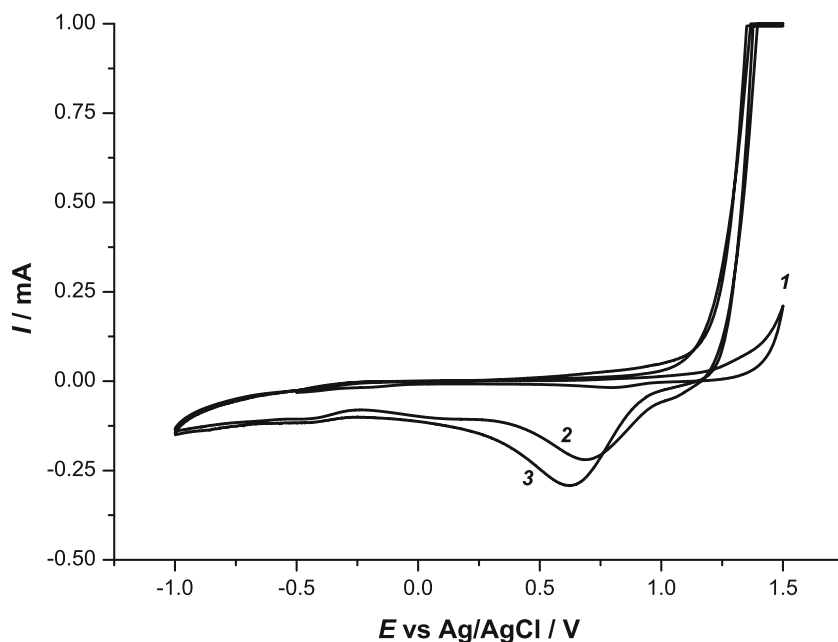
the catalysis is specific for chloride ions, discrimination briomides and iodides. Finally, keeping in mind the importance of perovskites for production of fuel-cell electrodes, it was interesting to test the catalytic activity toward electrochemical methanol oxidation. For that purpose the YCoO$_3$ modified electrode was studied immersed in a solution containing 1 mol/dm^3 KOH+1 mol/dm^3 CH$_3$OH. The comparison of the cyclic voltammogram (Fig. 6) of the bare and the perovskite-modified electrode shows clear electrocatalytic effect. Namely, the limiting anodic potential is shifted for about 120 mV toward less positive potentials for the perovskite-modified electrode compared with the bare

one in the presence of the same concentration of methanol in the aqueous electrolyte.

Conclusions

YCoO$_3$ perovskite was synthesized by solution combustion method using urea as a fuel. The compound was characterized by XRD and the unit cell parameters were calculated within the space group *Pnma*. The catalytic activity was investigated using YCoO$_3$-modified PIGE electrode. Well-defined voltammetric response was obtained only in the

Fig. 6 Electrocatalytic effect of YCoO$_3$ toward oxidation of methanol. Typical cyclic volta-mograms of 1 M CH$_3$OH recorded in 1 M KOH at a bare (*1*) and YCoO$_3$ microparticles modified PIGE (*2*) at a seep rate of 20 mV/s
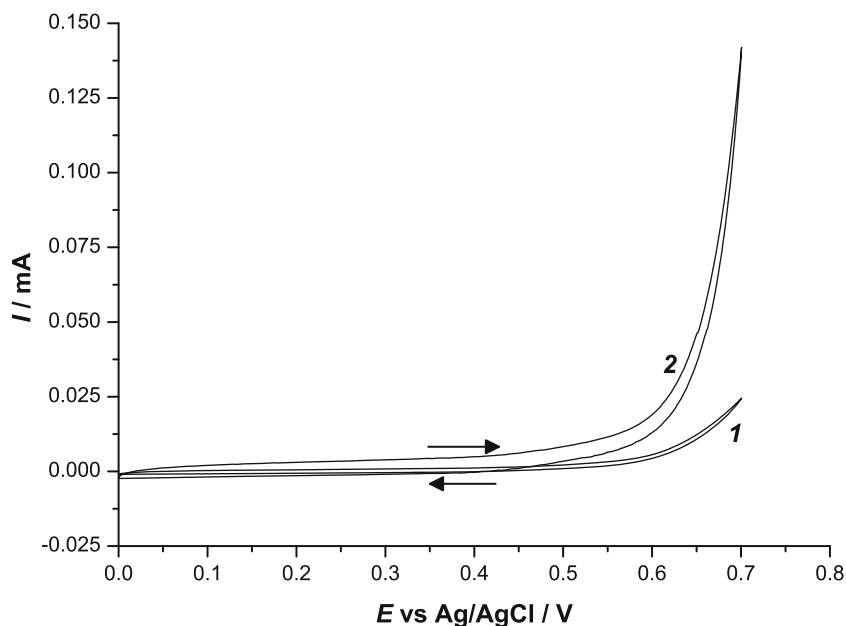
solution of chloride ions regardless of the solvent cation. Taking into consideration the obtained results, several conclusions may be deduced: (1) The obtained modified electrode shows very good mechanical stability. (2) $YCoO_3$ shows a catalytic activity towards oxidation of chloride ions. (3) The catalytic activity decreases with substitution of Co^{3+} cations in the perovskite structure clearly showing that Co^{3+} ions being the active centers in $YCoO_3$ catalyst. (4) In addition, $YCoO_3$-modified PIGE electrode shows an electrocatalytic effect towards oxidation of methanol in basic solution.

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