*Bulgarian Chemical Communications, Volume 50, Special Issue A (pp. 127- 132) 2018*

# One step solid-state synthesis of lanthanum cobalt oxide perovskites as catalysts for oxygen evolution in alkaline media

S. Enache[1*], M. Dragan[1**], A. Soare[1], D. Ion-Ebrasu[1], A. Zaulet[1], M. Varlam[1], K. Petrov[2]

[1] *National Institute for Cyogenics and Isotopic Technologies ICSI-Rm. Valcea, Uzinei Street No. 4, 240050, Romania*
[2] *Acad. Evgeni Budevski Institute of Electrochemistry and Energy Systems, Bulgarian Academy of Sciences, Acad. G. Bonchev Str., Bl.10, 1113 Sofia, Bulgaria*

Received September 27, 2017; Accepted October 05, 2017

Lanthanum cobalt oxide perovskites exhibit good catalytic activity and stability towards oxygen evolution reaction in alkaline media. This makes them especially attractive as electrodes for water electrolysis since they may substitute the more expensive ones used so far, such as iridium and ruthenium oxides. Although various preparation methods are well documented in literature, the fabrication of lanthanum cobalt oxides is often laborious, involving intermediate grinding and annealing steps. Different from that, we show that lanthanum cobalt oxide perovskites can be readily and thoroughly obtained by solid-state synthesis from lanthanum and cobalt oxide precursors, without making use of intermediate processing steps. The resulted powders are essentially within a polycrystalline single phase with well-defined structural and morphological properties. In order to assess the activity towards the oxygen evolution reaction, electrodes obtained from the resulted powders are investigated in a three electrode electrochemical cell in 1N KOH.

**Keywords:** water electrolysis, perovskite, solid-state synthesis

## INTRODUCTION

Although the initial discovery of water electrolysis has been demonstrated in acidic aqueous solutions, nowadays trend towards mass production of hydrogen involves alkaline media, such as potassium hydroxide [1]. When compared to acidic media, the advantage of water electrolysis in alkaline solutions is the increased hydrogen production efficiency and corrosion resilience, together with a prolonged life time performance since the alkaline water electrolysis may be operated at much lower over-potentials and current densities [2]. Apart from that, the possibility to substitute platinum-based catalysts for less expensive materials (e.g., nickel and cobalt oxide) with enhanced catalytic activity and stability towards hydrogen and oxygen evolution reactions makes it especially attractive from an applicative point of view, since the manufacturing of large scale operating hydrogen production stations often demands laborious and expensive processing routes for the catalytic material [3,4].

Among various platinum-free catalysts, the most promising ones are the oxides of the *3d*-band transition metals, with an activity trend towards oxygen evolution reaction varying such as: Ni > Co > Fe > Mn [2-5]. Although mixtures and alloys of these transition metals and their oxides exhibit valuable potency towards oxygen evolution reaction, it is the perovskite-like crystalline structure of these elementals with lanthanum in the form of $LaTMO_3$ (i.e., TM - Ni, Co, Fe and Mn) that has attracted a lot of interest lately, mainly due to their enhanced ionic conductivity and stability in alkaline media [6]. In literature, these systems documented as $ABO_3$ perovskite structures, in which A ions can be rare earth, alkaline earth and alkali that fit into dodecahedral sites of the crystalline lattice, whereas the B ions can be 3-, 4- and 5d-transition metal ions which occupy octahedral sites [3]. The perovskite lattice can accommodate multiple substitutions on both A and B sites, making it possible to fine tune the overall physical properties, such as ionic conductivity and dielectric constant, as well as chemical stability and activity towards oxygen evolution reaction. One special case is $LaCoO_3$, whose microstructure, catalytic activity, electronic and ionic conductivity depend strongly on the synthesis route. To that, oxygen deficiency plays an important role [3,7].

As a direct synthesis route, $LaCoO_3$ perovskites can be prepared by solid-state reaction of pure lanthanum and cobalt oxides, carbonates and oxalates at temperatures as high as 1200°C [8]. The procedure often involves intermediate processing steps such as calcination to remove residual solvents and organic contaminants and intermittent grinding to homogenize the mixtures. The resulted powders are inhomogeneous and coarse, with non-uniform particle size distribution. In order to overcome that, wet chemical methods such as sol-gel [9], co-

---

* To whom all correspondence should be sent.
E-mail: stanica.enache@icsi.ro; **mirela.dragan@icsi.ro

precipitation [10] and hydrothermal methods [11] have been employed to synthesise $LaCoO_3$ powders with desired stoichiometry, particle size and even shape. However, several disadvantages have been noted with these techniques such as the evaporation of solvents resulting in phase segregation and the alteration of stoichiometry due to incomplete precipitation, expensive chemicals and time-consuming processes. Alternatively, the combustion of a precursor solution containing metal ions, oxidant and a fuel leads to fine crystalline powders, with homogeneous particle size distribution (i.e., around 10 - 15nm) [12]. Although the combustion method is suitable to obtain catalytic $LaCoO_3$ powders with high specific area (i.e., as high as $80m^2/g$), it turns out that it demands an elaborate preparation procedure, involving corrections for the oxidant-to-fuel ratio and for the pH of solution. Moreover, the inherent contamination with carbon upon the auto-ignition process requires a post-processing annealing step at $1250^0$C, which leads to grain coarsening and sintering, eventually [9, 12].

In this work, we show that $LaCoO_3$ powders can be directly and thoroughly obtained by one step solid state synthesis in air from lanthanum and cobalt oxides upon heat treatment at most 8 hours and temperatures not higher than $1000^0$C, without making use of intermediate processing steps. The resulted powders are essentially within a single crystalline phase (i.e., with hexagonal *R-3c* crystal symmetry) that consists of micro-meter sized grains which may also exhibit a slight difference in oxygen deficiency [12]. This is important since oxygen deficiency is often associated with an increased ionic and electrical conductivity, as well as an enhanced catalytic activity towards oxygen evolution reaction. In order to assess the activity towards the oxygen evolution reaction, electrodes obtained from the resulted powders are investigated in a three electrode electrochemical cell in 1N KOH.

## EXPERIMENTAL

$LaCoO_3$ powders are obtained by conventional solid-state reaction. For that, equimolar quantities of $La_2O_3$ and $Co_3O_4$ (i.e., from Aldrich, with >99.8% purity) were mixed and ground thoroughly in agate mortar using alcohol as lubricant (i.e., isopropanol, with >96% purity from Chimopar SA). The powder was then let to dry out and placed in alumina (i.e., $Al_2O_3$) crucibles, moved to furnace and fired in air at different temperatures between 600°C and 1000°C for 8 h, with a heating / cooling rate of 2°C/min.

Differential scanning calorimetry (DSC) and thermo-gravimetric (TG) measurements are carried out on precursors and their equimolar mixture. For that, we make use of a modular Thermogravimetric Analyzer STA 449 F5 Jupiter® from NETZSCH-Gerätebau GmbH that allows to measure the heat flow and the mass loss simultaneously, upon heat treatment and under specific conditions (i.e. in air). The instrument is equipped with Proteus® software to carry out the measurement and for data evaluation. The DSC/TG curves are recorded up to 1000°C, with a temperature heating rate of 10°C/min. From that, the precursor stability and perovskite formation temperature are determined upon heating, respectively.

Crystalline structure of thermally treated powders is evaluated by X-ray diffraction using a MiniFlex 600 Rigaku with fixed Ni filtered Cu anode and rotating silicon strip detector. $2\theta$ scans are performed between $2\theta = 5°$ and 90°, with a speed of 1°/min and resolution of 0.01°/step. The XRD peaks are indexed by using the Inorganic Crystal Structure Database (ICSD). Lattice constants and quantitative values for the identified phases are obtained from fit to the corresponding XRD spectra by using the PDXL powder diffraction analysis package from Rigaku.

Morphology of as-prepared powders is studied by using a Zeiss Evo 50 XVP scanning electron microscope (SEM) with LaB6 cathode enabling 2 nm resolution. For that, the powder is dispersed in distilled water by using an ultrasonic bath and drop-cast on a conducting double faced carbon tape. Additionally, x-ray dispersive electron spectroscopy (EDS) is used to determine stoichiometry.

The electrochemical assessment of perovskite $LaCoO_3$ catalysts is carried out in a three electrode configuration in 1N KOH aqueous solution at room temperature, with Pt wire as counter electrode and 3M Ag/AgCl electrode as reference (i.e., +0.196 V vs. REH). The working electrode is made out of compacted mixtures of $LaCoO_3$ powders with Teflon on Ni foam used as support. To measure the I-V curve, currents up to 100 mA are applied between the working and counter electrodes, whereas the corresponding potential drop between the working and the reference one is measured by using a multi-meter.

## RESULTS AND DISCUSSIONS

### *Precursor analysis*

The thermal analysis results indicate that $Co_3O_4$ is stable up to 1000°C. The $La_2O_3$ precursor exhibits mass loss upon heating; i.e., up to 1.38 wt.% at temperatures as high as 350°C. This is associated to the decomposition process of $La(OH)_3$ to LaOOH as an intermediate phase. From that, $La_2O_3$ forms readily at about 720°C. These features are in agreement with previous studies [13]. At temperature as high as 750°C, the equimolar mixture of precursors exhibits the onset of perovskite phase formation.

In order to have a clear view on solid-state synthesis process of perovskite $LaCoO_3$ from lanthanum and cobalt oxide, the structural and morphological properties of precursors are investigated by x-ray diffraction (XRD) and scanning electron microscopy (SEM). The results are shown in Fig. 1, together with the corresponding XRD spectrum measured on powder mixture.

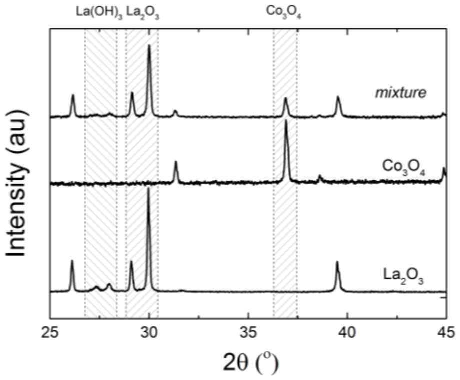

**Fig. 1.** X-ray diffraction characterization of the lanthanum and cobalt oxide precursors and their equimolar mixture. The main Bragg reflections of the $La(OH)_3$, $La_2O_3$ and $Co_3O_4$ phases are indicated.

In Fig. 1, the XRD data measured on $Co_3O_4$ powders indicate that the precursor is single-phase, with cubic crystal symmetry (space group *Fd-3m*) [14]. The lattice constant value obtained from fit to data is $a$ = 0.8083 nm. Different from that, the lanthanum oxide precursor exhibits the features of a mixed phase, which consists of hexagonal $La(OH)_3$ (space group *P63/m*) [15] and tetragonal $La_2O_3$ (space group *P-3m1*) [16]. The corresponding lattice constant values are $a = b$ = 0.6529 nm and $c$ = 0.3859 nm for $La(OH)_3$ and $a = b$ = 0.3937 nm and $c$ = 0.6132 nm for $La_2O_3$.

The co-existence of $La(OH)_3$ and $La_2O_3$ phases within the lanthanum oxide precursor is in essence related to a high affinity of the hexagonal $La_2O_3$ phase to partially decompose and form $La(OH)_3$ at the grain boundary interface, upon exposure to air. From TGA data, the residual hydroxide phase is found to be ~1.38 wt.%. However, in order to restore stoichiometry, lanthanum oxide powders are often subjected to a calcination step at temperatures above 600ºC. This also assures that water and organic contaminants are removed so as mixed powders of lanthanum and cobalt oxides with desired stoichiometry can be prepared. In our case, we do not make use of that, since the stoichiometry deficiency may always be compensated by adding the molar equivalent of 1.38 wt% $Co_3O_4$.

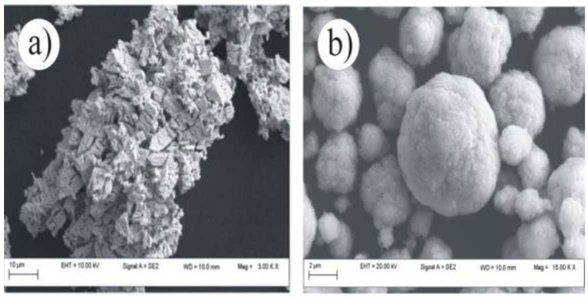

**Fig. 2**. SEM micrographs of lanthanum oxide in a) and cobalt oxide in b) powders used in this work.

In Fig. 2, we show the SEM micrographs of the lanthanum and cobalt oxide powders used in this work. They exhibit different degrees of clustering, owing to their intrinsic morphology. For instance, lanthanum oxide has chalky aspect, which is most probably due to lanthanum hydroxide presence at the grain boundary interface. Different from that, cobalt oxide powders consist of nano-meter sized grains which are self-organized in bulky conglomerates due to their high surface energy.

### *Solid-state synthesis of perovskite $LaCoO_3$*

For the solid-state synthesis, the alumina crucibles containing the equimolar mixture of precursors are heat-treated at temperatures between 600ºC and 1000ºC for 8 h, with a heating rate of 2 ºC/min. After each treatment step, the structural properties are investigated by x-ray diffraction in order to monitor formation and evolution of the perovskite $LaCoO_3$ phase at the expense of precursor consumption. The XRD data indicate that the lanthanum hydroxide phase is vanished upon heat-treatment at 600ºC. This feature indicates that the perovskite $LaCoO_3$ phase forms readily from $La_2O_3$ and $Co_3O_4$.

In Fig. 3, we show the XRD spectra measured on powders thermally treated at the selected temperatures. Together with that, the diffraction peaks corresponding to $La_2O_3$, $Co_3O_4$ and $LaCoO_3$ are indicated. The XRD data show that the perovskite $LaCoO_3$ phase forms upon heat treatment at 750ºC and grows gradually with increasing temperature, up to 1000ºC. This is accompanied by a gradual decrease of the peak intensities of the precursor phases (i.e., $La_2O_3$ and $Co_3O_4$). Upon heat treatment at 1000ºC, the resulted powder is essentially within a single phase, which corresponds to perovskite $LaCoO_3$ with trigonal crystal symmetry space group *R-c3* [17]. The lattice constant values obtained from fit to data are $a = b$ = 5.444 nm and $c$ = 13.102 nm.

As a general rule, XRD spectra measured on mixed powders present *all* Bragg reflections of the constitutive phases. The relative intensity values of their main peaks mediated by their corresponding areas is a quantitative measure of the degree of mixture in these powders. One can use that to de-convolute the XRD spectra in order to obtain valuable information on the amount of each phase present in powder mixtures. For instance, we use that to analyze the XRD spectra in Fig. 3 to determine the amount of $LaCoO_3$ formed upon solid-state synthesis at the given temperatures. The results are shown in Fig. 4. Note that solid-state synthesis of $LaCoO_3$ is a thermally activated process whose kinetics depends strongly on the synthesis temperature. This is essential since the grain coarsening during the synthesis process may be controlled by dwelling at lower temperatures in order to obtain powders with smaller particle size.

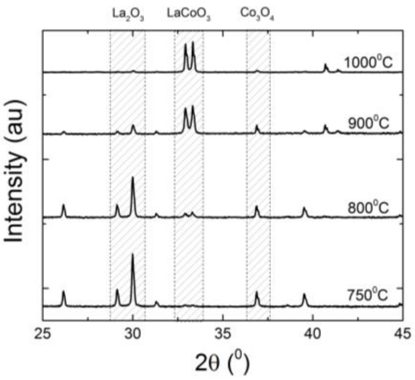

**Fig. 3.** Temperature dependent x-ray diffraction spectra measured on equimolar mixtures calcined at the indicated temperatures. The peaks corresponding to precursors (i.e., $La_2O_3$ and $Co_3O_4$) and reaction product (i.e., $LaCoO_3$) are indicated.

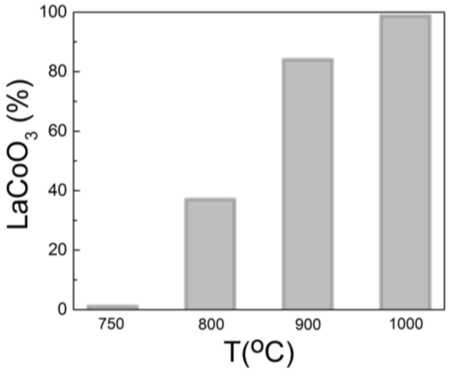

**Fig. 4**. Temperature dependent phase evolution (i.e., in wt.%) of the perovskite $LaCoO_3$ phase upon solid state synthesis, determined from fit to the XRD data in Fig. 3.

In Fig. 5, the perovskite $LaCoO_3$ powders obtained by solid-state synthesis at 1000°C consist of pre-sintered conglomerates of grains with well defined shape and size. From an application point of view, it is, however, essential to obtain well-dispersed powders with high specific surface area and narrow grain size distribution.

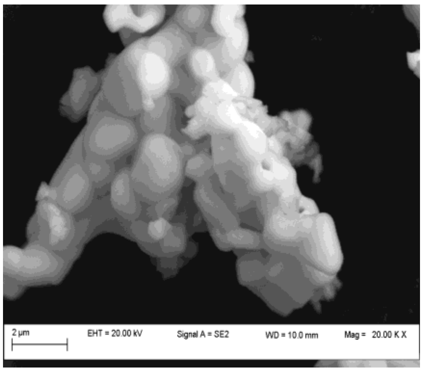

**Fig. 5.** SEM micrograph of $LaCoO_3$ powders obtained by solid-state synthesis at 1000°C

An estimate for the specific surface area (i.e., in $m^2/g$) of spherical particles is $6 / (d \cdot \rho)$, with $d$ the particle size (i.e., in µm) and $\rho$ the density (i.e., 7.27 $g/cm^3$, for perovskite $LaCoO_3$). This leads to a relatively low specific surface area, whose average value is as high as 0.82 $m^2/g$ for 1 µm sized $LaCoO_3$ grains. One should note that, however, the specific surface area may be increased by up to one order of magnitude by optimizing both the solid-state synthesis temperature and the dwell time, in a way that the grain coarsening is hampered by slow reaction kinetics at lower temperatures.

### *I-V characterization*

In order to assess the electrochemical activity of perovskite $LaCoO_3$ powders towards oxygen evolution reaction, hot pressed electrodes are made by using Teflon as binder on nickel foam supports. The compacted electrode is then moved to an electrochemical cell containing 1N KOH aqueous solution. The I-V characteristic is determined by applying constant currents up to 100 mA, whereas the potential is measured with respect to a reference electrode (i.e., Ag/AgCl , +0.196 mV *vs.* RHE). The results are shown in Fig. 6, together with those obtained for $Co_3O_4$ electrodes prepared in a similar way.

In Fig. 6, the I-V curves exhibit very similar features, in the sense that they fall on top of each other, although the potential values for the $LaCoO_3$ electrode are lower than those for the $Co_3O_4$ one, at *all* applied currents. The onset potential values for the oxygen evolution reaction at 1 mA applied current are 1.348V vs. RHE for $LaCoO_3$ and 1.355V vs. RHE for $Co_3O_4$.

These features indicate that $LaCoO_3$ has a higher catalytic activity towards oxygen evolution reaction in alkaline media. At currents above 20 mA, the potential dependence on the applied current is linear, corresponding to the ohmic regime.

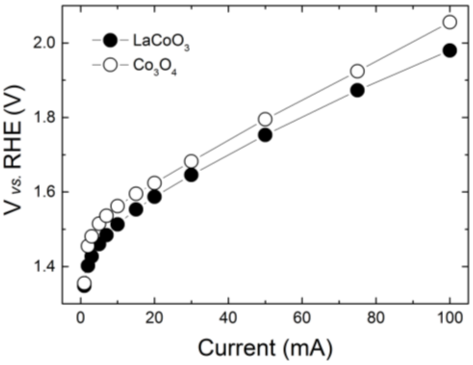

**Fig. 6**. I-V characteristic of $LaCoO_3$ electrodes in 1N KOH aqueous solution. For comparison, the I-V characteristic measured on $Co_3O_4$ in similar conditions is shown.

For $Co_3O_4$, the equivalent resistance value is 5.3Ω, whereas the corresponding value for $LaCoO_3$ is 4.7Ω. These high resistance values are due to the relatively poor intrinsic conductivity of the oxides, mediated by high inter-grain resistances due to presence of insulating Teflon, which acts as binder. In order to minimize that, one may either reduce the binder amount without compromising electrode integrity or add metallic species, to provide a low resistive path for electron conduction and exchange at the catalytic material grain boundary.

## CONCLUSIONS

In this work, we show that perovskite $LaCoO_3$ powders can be readily obtained from lanthanum and cobalt oxide precursors by solid-state synthesis in air, without making use of intermediate steps. In the synthesis process, the $LaCoO_3$ phase nucleates at 750°C and grows gradually with increasing temperature, at the expense of reactants consumption. At $1000^0$C, the reaction is essentially complete. Although the resulted powders are within a single crystalline phase, the constitutive grains have wide particle-size distribution whose average value corresponds to a specific surface area of 0.82 $m^2$/g. In order to prevent grain coarsening, powders with smaller and narrower particle size distribution may be obtained at dwelling at lower synthesis temperatures.

Teflonized $LaCoO_3$ electrodes exhibit catalytic activity towards the oxygen evolution reaction in alkaline media. The onset of oxygen evolution is as high as 1.348V vs. RHE in 1N KON aqueous solution, when a constant current of 1mA is applied. At higher currents (i.e., above 20 mA), the I-V characteristic is linear and corresponds to a ohmic regime, whose equivalent resistance value of 4.5 Ω is high. This is related to a poor intrinsic conductivity of the perovskite, mediated by a high inter-grain resistance due to Teflon presence, which acts as binder. One may, however, enhance that either by reducing binder load or by adding metallic species in order to provide high conductivity paths for electron transfer at the grain boundary of the catalytic material.

***Acknowledgment:*** *This work was supported by the Romanian Ministry of Education and Research, project "RESTORE" - 117/16.09.2016 ID / Cod My SMIS: P_37_595 / 104958.*

## REFERENCES

1. V. Maruthapandian, M. Mathankumar, V. Saraswathy, B. Subramanian, S. Muralidharan, *ACS Appl. Mater. Interfaces*, **9**,13132 (2017):.
2. McCrory C.C.L., Jung S., Peters J.C., Jaramillo T.F., *Journal of the American Chemical Society*, **135**, 16977 (2013).
3. E. Fabbri, A. Habereder, K. Waltar, R. Kötz, T.J. Schmidt, *Catal. Sci. Technol.*, **4**, 3800 (2014).
4. D. E. Hall, *J. Electrochem. Soc.*, **128**,740 (1981).
5. A.C.C. Tseung, S. Jasem, *Electrochim. Acta*, **22,** 31, (1977) .
6. X. Wang, H. Luo, H. Yang, P.J. Sebastian, S.A. Gamboa, *Int. J. Hydrogen Energy*, **29** 967 (2004) .
7. T. Ishihara, editor. Perovskite oxide for solid oxide fuel cells (fuel cells and hydrogen energy). New York: Springer Science and Business Media, 2009.
8. P. Ravindranathan, S. Komarneni, R. Roy, *J. Mater. Sci. Lett.*, **12**, 369 (1993).
9. C. Vazquez-Vazquez, P. Kogerler, M.A. Lopez-Quintela, R.D. Sanchez, *J. Mater. Res.*, **13**, 451 (1988).
10. G. Shabbir, A.H. Qureshi, K. Saeed, *Mater. Lett.*, **60,** 3706 (2006).
11. W. J. Zheng, R.H. Liu, D.K. Peng, G.Y. *Meng, Mater. Lett.*, **43,** 19 (2000).
12. S. V. Bangale, D.R. Patil, S. R. Bamane, *Arch. Appl. Sci. Res.*, **3**, 506 (2011).
13. D. Walter, *Z. Anorg. Allg. Chem.*, **632**, 2165 (2006).
14. W.L. Roth, *J. Phys. Chem. Solids* **25**, 1 (1964).
15. I. Djerdj, G. Garnweitner, Su Dangsheng, M.J. Niederberger, *Solid State Chem*. **180**, 2154 (2007).
16. P. Aldebert, J.P. Traverse, *Mater. Res. Bull.*, **14**, 303 (1979).
17. O. Haas, R.P.W.J. Struis, J.M. J. McBreen, *Solid State Chem.*, **177,** 1000 (2004).

# ЕДНОСТЪПКОВ СИНТЕЗ НА ПЕРОВСКИТ- $LaCoO_3$ В ТВЪРДО СЪСТОЯНИЕ КАТО КАТАЛИЗАТОР ЗА ОТДЕЛЯНЕ НА КИСЛОРОД В АЛКАЛНА СРЕДА

С. Енаке[1*], М. Драган[1**], А. Соаре[1], Д. Йон-Ебрасу[1], А. Заулет[1], М. Варлам[1], К. Петров[2]

*[1] Национален институт за криогенни и изотопни технологии, ICSI-Римнику Вълча, 240050, Румъния*
*[2] Институт по електрохимия и енергийни системи „Акад. Евгени Будевски“, Българска академия на науките, ул. Акад. Г. Бончев, бл.10, 1113 София, България*

Постъпила на 27 октомври, 2017г.; приета на 5 октомври 2017г.

(Резюме)

Перовскитите от лантанов кобалтов оксид имат добра каталитична активност и стабилност при реакция на отделяне на кислород в алкална среда. Това ги прави особено атрактивни като електроди за електролиза на вода, тъй като могат да заменят по-скъпите електроди, използвани досега, като иридий и оксиди на рутений. Въпреки, че различните методи за синтез са добре описани в литературата, производството на лантано-кобалтови оксиди често е трудно, включващо междинни етапи на смилане и отгряване. За разлика от този способ, ние показваме, че первоскити от лантанов кобалтов оксид могат лесно да се получат чрез синтез в твърдо състояние от прекурсори на лантанов и кобалтов оксид, без междинни етапи на обработка. По същество, получените прахове са в единична поликристална фаза с добре дефинирани структурни и морфологични свойства. За да се оцени активността по отношение на реакцията на отделяне на кислород, електродите синтезирани от получените прахове, се изследват в три електродна електрохимична клетка в 1 N KOH.

**Ключови думи:** водна електролиза, перовскит, синтез в твърдо състояние