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ENGINEERING, ENVIRONMENT
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PROCESSING INDUSTRY

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JAHORINA
11th - 13th March 2019

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**“ENGINEERING, ENVIRONMENT AND MATERIALS IN
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**PROMOTION OF SUPERCAPACITANCE OF NOVEL GENERATION
SUPERCAPACITORS BASED ON LANTHANUM STRONTIUM COBALT OXIDE AND
HYDROTHERMAL RUTHENIUM OXIDE**

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Abstract

In this study we report of considerable promotion of supercapacitive performances of ruthenium oxide hosted by perovskite-like structure of rare earth–CoO₃ composite and vice versa. Spherical, sub- μm -sized, regular spheres of La_{0.6}Sr_{0.4}CoO₃ (LSCO) were synthesized by ultrasonic spray pyrolysis (USP). The sphere surface was subsequently hydrothermally doped by RuO₂. LSCO and LSCO/RuO₂ composites were investigated for their supercapacitive performances in alkaline solution. Microstructure and surface morphology were studied by scanning electron microscopy (SEM) and X-ray diffraction (XRD). It was found that amorphous Ru species decorate the surface of LSCO spheres, and possibly incorporate partially into a B-site of the LSCO lattice. Electrochemical characterization by cyclic voltammetry (CV) clearly revealed that capacitive performances of LSCO are considerably improved by 20 mass% addition of RuO₂. The registered capacitance for LSCO/RuO₂ reaches the values of USP-synthesized pure RuO₂, which reveals the promoting influence of LSCO on RuO₂ pseudocapacitance. This intrinsic interactive promotion introduces the LSCO/RuO₂ composite as a unique supercapacitive material.

Keywords: *perovskite oxide, supercapacitor, cyclic voltammetry, ultrasonic spray pyrolysis*

Introduction

Nowadays, the development of high energy supercapacitors has received considerable attention worldwide. Supercapacitors, as a new promising energy storage device, are electrochemical energy storage devices that play an important role in energy storage and delivery. They have many advantages such as faster charging/discharging rate, long idle life cycle, higher power energy density and green environmental protection compared to other chemical energy storage devices (Arjun, Pan, & Yang, 2017; Cao, Lin, Sun, Yang, & Zhang, 2015a; Zhu et al., 2014). The boundary of energy and power density of supercapacitors existing between high power electric capacitors and high energy fuel cells can be determined in the Ragone plot.

However, the previous supercapacitors suffer from low energy density (Cao et al., 2015a; Cao, Lin, Sun, Yang, & Zhang, 2015b). Hence, in order to meet the development of supercapacitors, their energy density should be substantially enhanced without deteriorating their high power capability and cycle life (Nasri, Ben Hafsia, Tabellout, & Megdiche, 2016). Since the active

materials in electrodes of supercapacitor determine its electrochemical performance and energy storage capacity a lot, numerous new materials have been widely designed and prepared (Bi et al., 2017; Guo et al., 2016). It is well-known that the performance of supercapacitors is strongly determined by the properties and structures of electrode materials (Vellacheri et al., 2014). Thus, many efforts have been made to design and prepare the electrodes of supercapacitors.

Most popular materials today are particle materials, which have high surface areas for charge storage (Cao et al., 2015a; Yadav & Chavan, 2017). Among them, transition metal oxides (TMOs) are considered as ideal electrode materials for supercapacitors as they can provide both a high specific capacitance and a high energy density. A promising candidate for application is strontium substituted lanthanum cobalt oxide $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$, a perovskite-type material with a mixed ionic and electronic conductivity (MIEC) at elevated temperatures (Hayd, Dieterle, Guntow, Gerthsen, & Ivers-Tiffée, 2011). Perovskite oxide (ABO_3) displays both good oxygen ion and electron conductivity which could provide some oxygen vacancies to enhance the transfer of oxygen ion. These characteristics make them become excellent cathode materials of solid oxide fuel cell and the potential substitution of bifunctional catalyst compared with precious metal catalyst in Li-air batteries (Sun, Liu, Yu, Zheng, & Shao, 2014). Perovskites have been paid much attention in past decades because of their stable structure, high-temperature sustainability, catalytic property, and crucial role in solid fuel cells and solar cells (Zhu et al., 2014).

The spray-pyrolysis method was applied for synthesis of the starting powders of the cathode ($\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$) and anode (a samaria-doped ceria-NiO composite powder). In this study, different microstructures of the cathode were obtained by varying the sintering temperature from 950 to 1200 °C (Maric et al., 1999).

La-doped SrTiO_3 (LST) powders were prepared by ultrasonic spray pyrolysis using an aqueous solution of a metal nitrate (Genji, Myoujin, Koderu, & Ogihara, 2013). SEM images showed that the as-prepared LST powders had a spherical morphology with a diameter of 1 μm . XRD patterns showed that the crystal phase of the as-prepared powders was amorphous and that the powders crystallized to the perovskite phase by calcination at 900 °C. The sintered LST body had the highest electrical conductivity at a La doping concentration (La_x) of 0.1 under a reducing atmosphere.

The material characterization techniques were implemented to acquire the crystallinity, surface area, and porosity. Consequently, the good electrochemical response was obtained from cyclic voltammetry (CV) studies. The as-prepared samples clearly revealed that the perovskite materials are promising candidate for supercapacitor electrode materials. This work aims to investigate supercapacitive potentials of pure LSCO prepared by single step USP and LSCO doped with RuO_2 . The incorporation of RuO_2 into LSCO was examined upon USP-subsequent hydrothermal synthesis of LSCO/ RuO_2 . Modified supercapacitive properties of LSCO were investigated by standard electrochemical methods.

Experimental Part

Synthesis of $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$ powder by ultrasonic spray pyrolysis

The synthesis of Co-based oxide, namely $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$ (LSCO), was performed with in single-step ultrasonic spray pyrolysis (USP) procedure. Aqueous solutions with 0.10 M concentration of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.9% rare earth oxide), $\text{Sr}(\text{NO}_3)_2$ (99 %) and $\text{Co}(\text{NO}_3)_2$ (98%), all from Alfa Aesar, were prepared and used as precursors for the synthesis of LSCO. The solution for the LSCO synthesis was prepared by mixing starting precursor solutions in stoichiometric La: Sr: Co mole ratio of 3:2:5. The temperature and pressure control was adjusted using a thermostat and a vacuum pump. Atomization of the obtained solution after dissolution of precursor took place in an ultrasonic atomizer with one transducer to create the aerosol. The resonant frequency was selected to be 2.5 MHz. Under spray pyrolysis conditions, synthetic air ($\text{O}_2:\text{N}_2=2:1$) overpassed continuously through the quartz tube (at a flow rate of the 3 dm^3/min). Then atomized droplets

were further transported by carrier gas to the horizontal furnace. The temperature was adjusted to 800°C. After thermal decomposition of transported aerosol in the furnace, the formed nanopowder of $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$ was wet collected in mixture of water and ethanol (50 vol.% of ethanol).

Preparation of ruthenium oxide-impregnated LSCO nanocomposite

LSCO/ RuO_2 (20 mass. % RuO_2 , nominal) composite was synthesized through simple chemical precipitation method. Water suspension of USP-synthesized $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$ powder and ruthenium chloride ($\text{RuCl}_3 \cdot \text{H}_2\text{O}$) were used as starting materials. LSCO powder was ultrasonically suspended for 30 min and the pH value of the magnetically stirred suspension was afterwards adjusted to 10 by 0.10 M KOH. With pH kept constant, 0.10 M water solution of RuCl_3 is added to the LSCO suspension and the stirring is continued for another 1 h to obtain a stable blackish precipitate. The resulting precipitate was washed with distilled water and ethanol several times, and finally dried at 150 °C for 3 h.

Characterization

SEM and EDS analysis of strontium substituted lanthanum cobalt oxide $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$, a perovskite-type material were performed using scanning electron microscope (Zeiss DSM 982 Gemini; Vega TS 5130 MM Tescan). The elemental composition was determined by EDS with a Si(Bi) X-ray detector connected to the SEM and a multi-channel analyzer. The identification of elements was performed *via* the unique set of peaks from reflected X-ray spectrum (Bhujun, Tan, & Shanmugam, 2016).

Structural and phase analysis of the LSCO and LSCO/ RuO_2 particles were examined by X-ray diffraction (XRD) measurements on Philips PW 1050 powder diffractometer at room temperature with Ni-filtered $\text{CuK}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$) and scintillation detector within $10\text{--}82^\circ 2\theta$ range in steps of 0.05° , and scanning rate of 5 s per step.

Electrochemical measurements

Electrochemical properties of LSCO and LSCO/ RuO_2 were studied by cyclic voltammetry (CV). The electrochemical measurements were performed in a conventional three-electrode cell. A platinum wire and Hg/HgO/1M KOH electrode were used as counter and reference electrode, respectively. All potentials in the discussion are referred to the Hg/HgO electrode. The working electrode was glassy carbon (GC, Sigradur – Sigri, Elektrographite, GmbH, Germany) with the surface area of 0.39 cm^2 covered by a thin layer of LSCO or LSCO/ RuO_2 according to the following procedure. $39 \mu\text{L}$ of LSCO or LSCO/ RuO_2 water suspension (3 mgmL^{-1}) was added onto GC by micropipette. After two hours of drying in air, the same volume of nafion solution (1:50 vs. water), achieved by dissolving liquid nafion in 1 mL water, was added on top of the layer and left to dry at room temperature. The thin nafion film binds perovskite supported catalyst particles on GC electrode and provides necessary proton transport in the perovskite layer. The cell was purged with N_2 for 30 min prior to and continuously during electrochemical measurements. An electrochemical work station (BioLogic SAS, SP-240, Grenoble, France) of potentiostat/galvanostat provided with corrosion and physical electrochemistry software was employed. The CV responses in 1.0 M KOH were checked at the scan rate of 50 mVs^{-1} . The specific capacitance, the most important indicator for the evaluation of electrode properties for supercapacitors (Gaikar et al., 2017; Lü et al., 2015), was calculated from the CV data according to the following Eq. (1):

$$C_s = \frac{1}{2m\nu(|E_a| + |E_c|)} \int_{E_c}^{E_a} I(E) dE \quad (1)$$

where C_s (F g^{-1}) is the specific capacitance, m (g) is the mass of the active material, $I(E)$ is the current recorded during CV, ν (V s^{-1}) is the scan rate, and E_a and E_c (V) are low and high potential integration limits or the capacitive potential window.

Results and Discussion

SEM and EDS analysis

Morphology plays an important role in the electrochemical behavior of the porous materials since it should to allow maximal availability of active sites (Shafi, Joseph, Thirumurugan, & Bose, 2018; Thiele, Lopez-Camacho Colmenarejo, Grobety, & Züttel, 2009). Morphology of the LSCO powder is presented in Figure 1a by the SEM appearance. LSCO powder was mixed and stirred with 0.10 M KOH in order to determine its stability in alkaline solution. There was no change in alkali immersed LSCO powder morphology compared to as prepared LSCO powder by USP synthesis, which can be seen in Figure 1b. Elemental analyses (EDS) of the LSCO composition of as prepared and immersed LSCO powder are done on three spots and the average value of these elemental compositions are listed in Table 1.

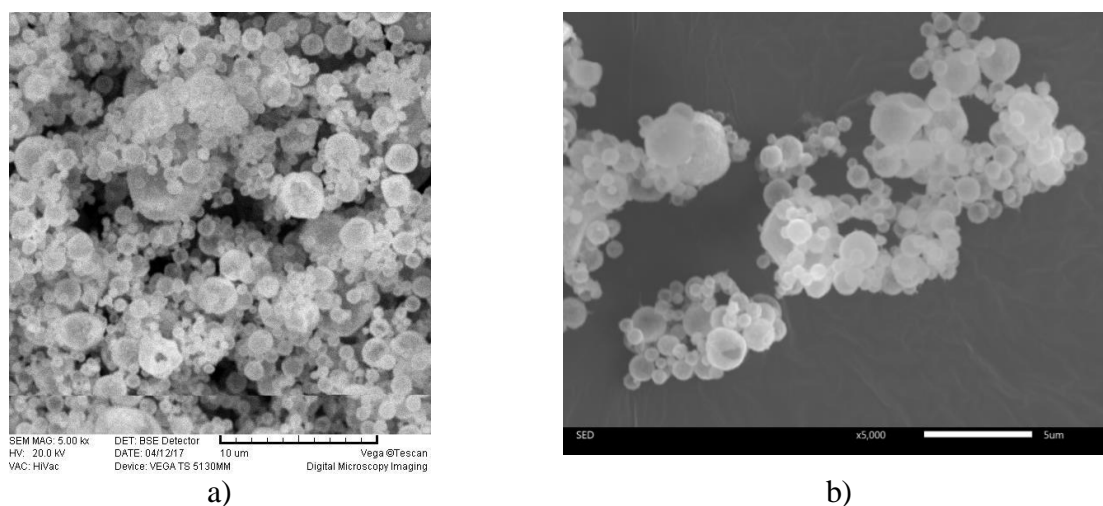


Figure 1. SEM microphotograph of a) $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$ powder synthesized by ultrasonic spray pyrolysis and b) LSCO powder after immersion in 0.10 M KOH.

Table 1. Quantitative EDS analysis of as prepared LSCO powder and LSCO powder after immersion in alkaline solution (at.%).

Element	at. %	KOH
O	63.86	63.55
Sr	8.66	8.65
La	10.56	11.18
Co	16.92	16.62

It was found that as-prepared LSCO powder is consisted of almost ideal spherical grains, with a sphere diameter in the range of 0.5–3 μm . It can be observed by comparing EDS values from Table 1 that there is no dissolution of any component in KOH. Therefore, the LSCO powder is chemically stable and of preserved morphology in alkaline solution

The morphology of novel LSCO/RuO₂ material was also characterized by SEM and the images are shown in Figure 2. Spherical structure of initial LSCO powder is maintained. Although LSCO/RuO₂ powder has the same spherical shape some changes of particle edges are noticed. Also, it can be seen that some new very small particles are placed onto the LSCO surface. We presume that these particles RuO₂ on the surface of LSCO particle with size around 2-3 nm. The enlarged view in Figure 2b shows that supposed RuO₂ is uniformly arranged on whole surface of powder.

The apparent elemental composition of the grains was analyzed by EDS, confirming the Ru presence in the nanocomposite LSCO/RuO₂ powder.

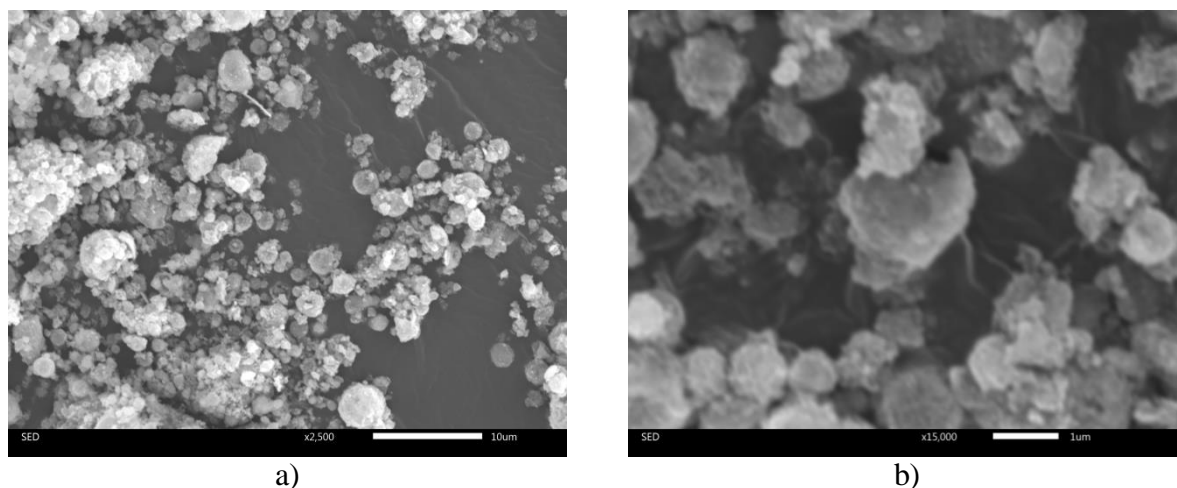


Figure 2. SEM microphotographs of LSCO/RuO₂ powder: (a) general view and (b) magnified view.

Table 2. Elemental analysis of LSCO/RuO₂ nanocomposite from EDS measurements.

Element	at. %
O	80.22
Sr	-
La	5.61
Co	12.40
Ru	1.77

From Table 2 it can be observed that average value of 2 at. % of ruthenium was detected in this powder. Spectrum show very small Sr content and it is below detection limit, therefore it is not measured by EDS. The mass % value of ruthenium oxide was calculated from at. % of ruthenium. Around 13 mass. % of ruthenium oxide is incorporated into the LSCO. Obviously, ruthenium oxide nanoparticles supported on LSCO surface was obtained by USP method.

X-ray diffraction analysis

XRD patterns for two powders ultrasonically synthesized e.g. lanthanum strontium cobalt oxide (La_{0.6}Sr_{0.4}CoO₃) and LSC doped with 20 wt. % RuO₂ are represented in Figure 3.

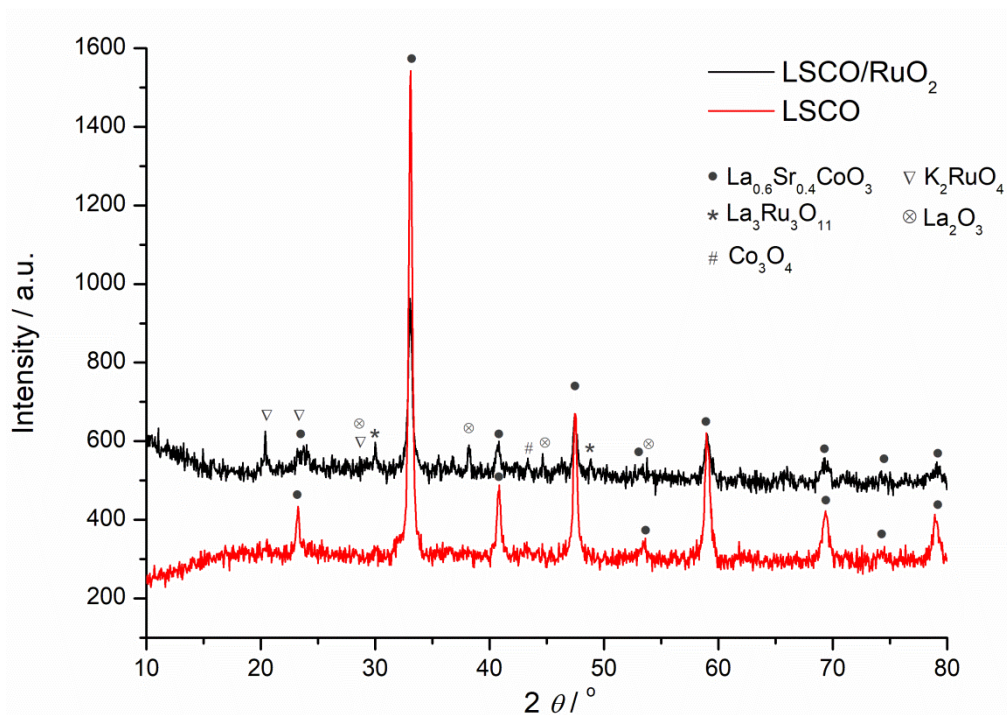


Figure 3. XRD patterns of LSCO and LSCO/RuO₂ powders.

Figure 3 shows the XRD patterns of the as-fabricated sample and powder doped with ruthenium oxide. By comparing the results with XRD pattern (JCPDS PDFNo. 01-89-2528) of the standard La_{0.6}Sr_{0.4}CoO₃ sample, it can be seen that all of the XRD peaks of each sample in the 2θ range of 10–80° could be well indexed, as shown in Figure 3. In other words, the LSCO powder was of single-phase with rhombohedral crystal structure. For perovskite, as well as other crystalline materials, the variation in the crystal structure may lead to distinct electrocatalytic activities. It was found that LSCO has identical rhombohedral lattice which can be indexed according to R-3c space group symmetry (#161). This fact rules out the significant effect that crystal structure may have on the activities. However, new diffraction peaks can be distinguished after doping with 20 wt. % of RuO₂ due to the presence of new Co₃O₄, La₂O₃, La₃Ru₃O₁₁ and K₂RuO₄ phases, indicating that the new nanoparticle (NP) compounds were highly dispersed on the LSC surface. An unknown weak peak at around 2θ=38° was attributed to lanthanum oxide, La₂O₃, according to the JCPDS PDFNo. 00-40-1279 XRD database, which was considered to be the result of a partial decomposition of the LSC. In addition, the diffraction signals assignable to the La₃Ru₃O₁₁ and K₂RuO₄ (JCPDS PDF No.01-070-1086 and 01-051-1751, respectively) phase became apparently detected in doped samples, indicating the formation of small amount of ruthenium compound with lanthanum and potassium. Figure 4 also shows the typical XRD peak of the obtained Co₃O₄ in which all the diffraction could be indexed as the cubic Co₃O₄ spinel phase (JCPDS PDF No. 01-078-1969).

Electrochemical analysis

The cyclic voltammograms of LSCO, LSCO/RuO₂ and pristine RuO₂ on GC substrate were recorded at the scan rate of 50 mV s⁻¹ in the potential region from –200 mV to 500 mV in 0.10 M KOH, at room temperature. A representative CV curves are shown in Figure 4. Upon exposure of LSCO, LSCO/RuO₂ and RuO₂ thin layers to potentiodynamic conditions, a stable capacitive CV response was registered in a potential window as wide as 0.7 V.

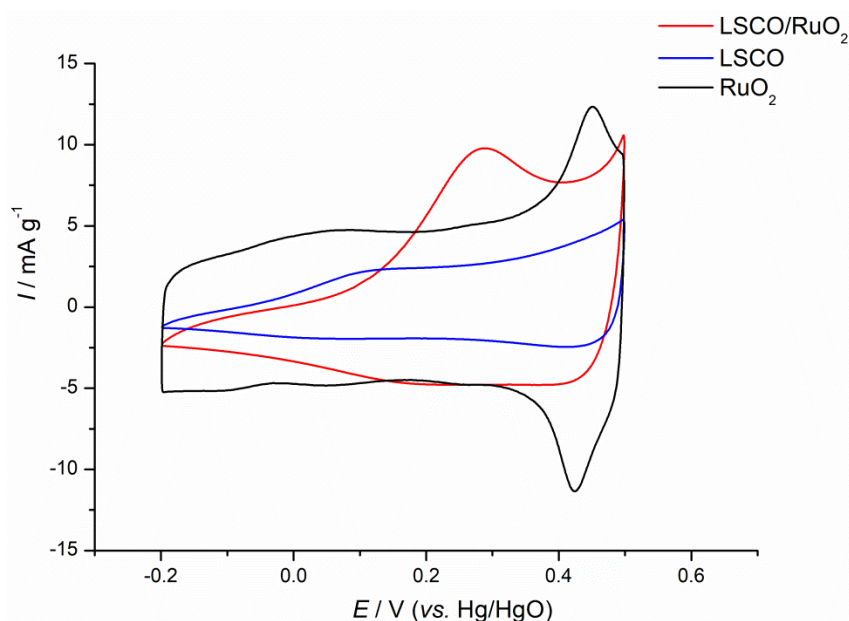


Figure 4. Cyclic voltammograms at a scan rate of 50 mVs^{-1} for LSCO, LSCO/RuO₂ and RuO₂ in 0.10 M KOH, recorded at room temperature.

The specific capacitance is affected by two contributions, such as electrical double layer capacitance (EDL) and pseudocapacitance (Zhang et al., 2010). Unique capacitive features in considerable portions come from pseudocapacitance due to reversible Ru(III)/Ru(IV), Ru(IV)/Ru(VI) and Ru(VI)/Ru(VIII) redox transitions (Chalupczok, Kurzweil, Hartmann, & Schell, 2018). The cyclic voltammogram of pure RuO₂ (Figure 4, black line) clearly shows the pair of distinguished anodic and cathodic peaks at 450 and 420 mV that are assigned to highly reversible Ru(VI)/Ru(VII) redox reaction - adsorption and desorption of OH groups (Chalupczok et al., 2018).

The shape of the CV curve of the LSCO powder is different with respect to that registered for the LSCO/RuO₂. One can see that the CV response of LSCO is plain with no peaks correspond to the reaction of material in KOH and the response is considerably lower, which means that active surface area is lower than LSCO/RuO₂. Mixed LSCO/RuO₂ powder exhibits a considerable increase in the voltammetric capacitance, due to the presence of Ru species. The Figure 4 (red line) shows that voltammograms of the LSCO/RuO₂ exhibited a pair of redox peaks, one well-resolved anodic Ru(IV)/Ru(VI) peak ($E_{Pa} = 290 \text{ mV}$) and a corresponding very weak and broad cathodic peak (E_{Pc} in the range from 210 to 150 mV), that are ascribed to combination of these two materials. Although it seems that voltammogram of LSCO/RuO₂ looks irreversible and does not have a clearly defined counterpart but it is most similar to the real capacitor.

The specific capacitance, C_s , of the samples was calculated by integrating the area delimited by CV curve according to the Eq. (1). The C_s calculated for LSCO/RuO₂ is found to be 75.8 Fg^{-1} compare to undoped LSCO (37.8 Fg^{-1}). While the obtained specific capacitance for pure RuO₂ is 90.7 Fg^{-1} , which is in good agreement with the data reported in the literature (Audichon et al., 2017). The capacitance of LSCO was considerably lower. The capacitive current is also very low value because it is directly proportional to capacitance and it induces poor conductivity of material. LSCO/RuO₂ exhibits a considerable increase in the voltammetric capacitance, due to pronounced ruthenium injection into crystal structure of LSCO. Therefore, the Ru substitution can lead to improved electrode/electrolyte contact areas and high rates of electrode reaction, resulting in an enhanced electrochemical performance (Wilde, Guther, Oesten, & Garche, 1999). Since the presence of two peaks (cathodic and anodic) are observed on pure RuO₂ voltammogram which correspond to adsorption/desorption of OH⁻ ions and since we are interested in pure capacitive response of the materials we have calculated C_s values in the range from 0 to 350 mV. In this way calculated specific capacitance values are 43.8, 93.1 and 95.8 Fg^{-1} for LSCO, LSCO/RuO₂ and RuO₂, respectively.

The high C_s values for pseudocapacitors, is attributed to the appropriate porous metal oxide structure with high specific surface area of the electrode active material, which enables the Faradaic reactions (Bhujun et al., 2016; Rakhi, Chen, Cha, & Alshareef, 2012). In our LSCO/RuO₂ sample the addition of ruthenium changes morphology causing to evolve specific surface area that has as a consequence higher C_s value than undoped sample. In general, high specific surface area can be achieved by nanosized particles and mesoporosity in material structure, which enables easy and efficient transportation of both electrons and ions necessary to allow a fast redox reaction at high scan rates (Bhujun et al., 2016; Liu, Dinh, Tade, & Shao, 2016; Rakhi et al., 2012). Therefore, nanoparticles of RuO₂ are responsible for better storage efficiency of novel LSCO/RuO₂ oxide material.

Conclusions

Lanthanum strontium cobalt oxide, La_{0.6}Sr_{0.4}CoO₃ (LSCO), have been successfully synthesized via ultrasonic spray pyrolysis (USP) approach and impregnated in a powdered state by RuO₂ within a simple precipitation procedure. The effect of RuO₂ incorporation into LSCO on the structure, morphology and electrochemical properties of an LSCO/RuO₂ composite was studied. USP-prepared LSCO powder had a homogenous morphology consisted of regular spheres with the diameters in the range of 0.5-3 μm . Upon impregnation by RuO₂, spherical structure of initial LSCO powder was maintained, with RuO₂ nanoparticles deposited onto the LSCO sphere surface. RuO₂ particle size appears to be 2-3 nm. Also, new diffraction peaks, such as Co₃O₄, La₂O₃, La₃Ru₃O₁₁ and K₂RuO₄, distinguished in the pattern of LSCO/RuO₂ can be considered as consequence of presence and slight RuO₂ impregnation.

The voltammetric capacitance of LSCO was considerably improved by incorporating RuO₂ and C_s value was calculated to be 95.8 Fg⁻¹ for LSCO/RuO₂. Excellent conductivity of LSCO powder doped with ruthenium oxide was found in the potential region cathodic to 350 mV. The LSCO/RuO₂ electrode is of enhanced pseudo-capacitive properties with good rate capability and better performance with respect to LSCO, which was found to be a suitable for the carrier of pseudocapacitively active materials.

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