Improvement of the supercapacitor characteristics of perovskite oxides upon impregnation by RuO_2

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Abstract

The supercapacitive charging/discharging (C/DC) response of lanthanum-based perovskite oxides, obtained by ultrasonic spray pyrolysis (USP), was discussed according to galvanostatic and the dynamic ac impedance C/DC data. We have synthesized perovskite type lanthanum strontium cobalt oxide (LSCO, $La_{0.6}Sr_{0.4}CoO_3$) by USP and mixed LSCO/RuO_2 by subsequent hydrothermal impregnation method. The obtained composites were investigated as electrode for electrochemical supercapacitors and their electrochemical performances have been investigated. Microstructures and surface morphologies, observed by scanning electron microscopy, appears crystalline with spherically-shaped nm-sized particles. The aim of our work was study of structural and electrochemical properties of ternary perovskite and LSCO/RuO_2 as a supecapacitive material of improved stability with respect to carbonaceous ones. Potentiostatic ac impedance analysis has indicated lower charge transfer resistance of the LSCO/RuO_2 sample confirming its enhanced electrochemical performances. The measurements indicated that nanocomposite LSCO/RuO_2 is more suitable catalytic material with improved electrochemical performances.

1. Introduction

In development of advanced electrochemical energy storage devices to comprehend both high-power and high-energy densities such as fuel cells, rechargeable batteries and supercapacitors, an electrode material with a specific and stable structure is desirable for the penetration of electrolytes and reactants into the whole electrode matrix [1]. The main direction in the field of renewable energy was the development of higher power and more energy-dense storage devices, such as supercapacitors [2]. Therefore, supercapacitors have attracted considerable attention in recent years as a promising energy storage system [3]. Supercapacitors are devices capable of managing high power rates compared to typical batteries [4]. Although supercapacitors provide up to one thousand times higher power in the same volume, they are not able to store the same amount of charge as rechargeable batteries, which is usually 3-30 times lower [4].

Perovskites oxides have been attracted much attention in past decades because of their stable structure, high-temperature sustainability, catalytic property and crucial role in solid fuel cells, SOFC [5]. Perovskites are compounds that have the general formula ABO_3 originated from $CaTiO_3$, discovered in 1839 by Gustav Rose [5]. In this triple oxide structure A stands for alkali earth elements like lanthanum, with dodecahedral co-ordination, and B is a transition metal having six-fold coordination [6]. The oxidation state of cation and ionic radii of A and B depends on the structure of the perovskite material which enables the tailoring of its properties. The synthesis route and control of morphology of the perovskite materials are very crucial and have strong impact on their properties [6]. Instead of widely used noble metal oxides, the use of perovskite oxides has the potential to enhance the stability of the supercapacitor due to the different charge storage ability. Therefore, the analysis of electrochemical properties and charge storage capacity of different perovskite materials associated with the usage of different electrolyte system has been explored [5].

Among perovskite materials, strontium-substituted lanthanum cobaltite, $La_{1-x}Sr_xCoO_{3-\delta}$ (LSCO), has been studied as a promising candidate for electrode materials for this purpose [7]. LSCO is a perovskite-type oxide with high electronic and ionic conductivity in wide range of temperatures and is considered for use in high temperature ceramic membranes and devices such as electrolysers and SOFC [8]. Additionally, the specific capacitances of the perovskite can be enlarged by doping by La, Co, Cr, Fe, Ru, Ca, Mg and Sr on A and/or B-sites, which changes the LSCO electrochemical behavior considerably [9]. One possible way to improve perovskite properties is the impregnation by ruthenium oxide. Alkaline earth ruthenates with perovskite structure containing ruthenium on the B position have been shown to exhibit pseudocapacitance behavior [10]. These materials show metallic conductivity and are stable in aqueous alkaline electrolytes [10].

Different processes for synthesis of perovskite oxides are presented, such as direct annealing, solid state reaction, impregnation method, hydrothermal treatment and ulrtasonic spray pyrolysis [11,12]. Ultrasonic spray pyrolysis (USP) is a simple method to prepare sub-µm particles of metals and oxides by atomizing the precursors, as well as homogeneous thin films of various oxides and sulphides [13]. The advantages of the method are simple and inexpensive the apparatus (no vacuum system is necessary), and that deposition conditions and film composition are easily controlled. Herein, two different kinds of lanthanum-based perovskite were prepared, $La_{0.6}Sr_{0.4}CoO_3$ (LSCO) and LSCO/RuO_2, through one-step USP synthesis and subsequent hydrothermal deposition.

2. **Experimental**

2.1. Material synthesis

$La_{0.6}Sr_{0.4}CoO_3$ was synthesized through a simple one-step ultrasonic spray pyrolysis (USP). Lanthanum nitrate, strontium nitrate and cobalt nitrate were used as precursors. Atomization of the obtained solution after dissolution of precursors in water took place in an ultrasonic atomizer (Gapusol 9001, RBI/France) with a transducer to create the aerosol. The resonant frequency was selected to be 2.5 MHz. Under spray pyrolysis conditions, nitrogen flows continuously through the quartz tube (at a flow rate of the 7 L min^{-1}). Atomized droplets of the solution of La, Sr, and Co nitrates, generated in the ultrasonic atomizer, were further transported by carrier gas to a vertical furnace (Thermostar, Aachen). After thermal decomposition of transported aerosol in the furnace, the formed LSCO powder was collected on an electrostatic precipitator.

Prepared USP LSCO powder was suspended in water and pH was adjusted to 10.0 by NaOH to a stirring dispersion, we added $RuCl_3$ solution with pH kept constant. The stirring was continued for 1 h to obtain stable precipitate. The resulted mixture was centrifuged and washed with water and ethanol followed by drying at 150 °C for 3 h. The black-colored powder is labelled as LSCO/RuO_2.

2.2. Characterization techniques

The morphology of as-prepared LSCO and LSCO/RuO_2 (20 wt.% RuO_2) was investigated by scanning electron microscopy (SEM) by a microscope VEGA TS 5130MM, Tescan, Czech Republic. The electrochemical behavior of the powders was studied with electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) and galvanostatic charge/discharge (G-C/DC) tests. All electrochemical measurements were performed in a three electrode arrangement connected with an electrochemical work station BioLogic, SP-240, France. A platinum foil and Hg/HgO/1M KOH electrode (E^0 = 0.098 V vs NHE at 25°C) were used as counter and reference electrode, respectively. The working electrode was prepared by dispersing LSCO and LSCO/RuO_2 powders in water. Then, the mixture was uniformly spread on GC electrode. The working electrode geometric area exposed to electrolyte was 0.39 cm^2. The cell was filled with 0.1 M KOH electrolyte and purged with N_2 for 30 min prior to and continuously during all electrochemical measurements.

3. Results and discussion

Morphology plays an important role in the electrochemical studies of material since it is supposed to allow maximum availability of active sites [6,14]. SEM images of LSCO and LSCO/RuO_2 are shown in Figure 1. It was found that as-prepared LSCO powder had a spherical morphology with a sphere diameter in the range of 0.5 - 3 μm. Figure 1b represents the LSCO/RuO_2 powder with the same spherical shape with slightly different surfaces. It can be seen that fabricated RuO_2 is placed onto the LSCO surface. The particle size of RuO_2 on the surface of LSCO particle is around 2-3 nm. The enlarged view in Figure 1c shows that RuO_2 is uniformly arranged on whole surface of powder.

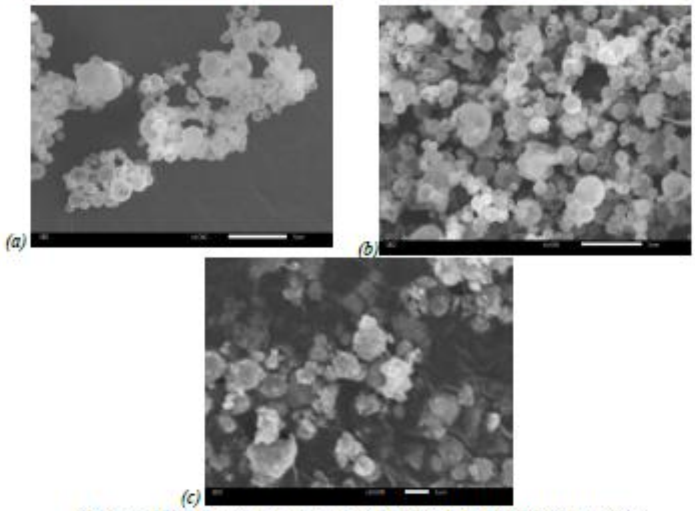

Figure 1. SEM microphotographs of (a) LSCO and (b) LSCO/RuO_2 powders.

A capacitive performance of the samples, with and without ruthenium oxide, was systematically investigated by employing EIS (Figure 2) and G-C/DC (Figure 3) measurements. The Nyquist plots consisted of two regions; one is a well-defined semicircle in the high frequency region and second is a straight sloping line in the low frequency range. The diameter of the semicircle corresponds to the interfacial faradic charge transfer resistance (R_{ct}) of the redox reactions, which usually represents the resistance of the electrochemical reactions at the electrode surface [15].

The best equivalent circuit mode that fits these plots is shown in inset of Figure 2, it consists of R_{ct} and CPE_p are in parallel and in series with CPE_{dl}, while all are in series with R_s. The equivalent circuits consist of the electrolyte resistance, R_s, the charge transfer resistance, R_{ct}, and constant phase elements, CPE_{dl} and CPE_p, which represent all the frequency-dependent electrochemical phenomena, such as the of double layer capacitance, C_{dl}, and pore capacitance, C_p. The fitting results are listed in Table 1. In the high frequency region, the semicircle of LSCO/RuO_2 is smaller compared to LSCO powder. There is a contact resistance for LSCO of 1.34 kΩ, while the supercapacitor exhibits a small resistance of 0.36 kΩ. This indicates the low charge transfer resistance (intrinsic resistance) and excellent electronic conductivity which come from the RuO_2 in nanocomposite powder.

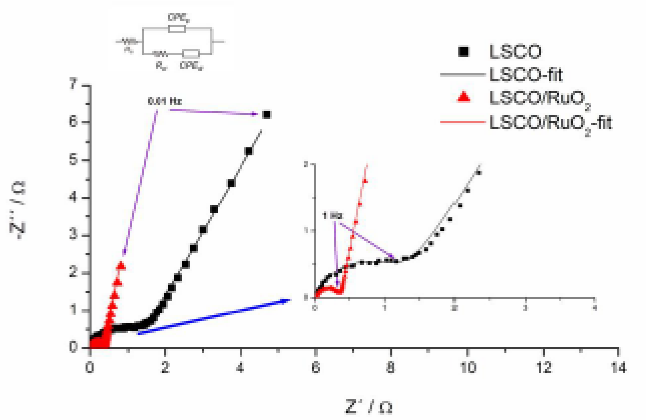

Figure 2. Nyquist plots of LSCO and LSCO/RuO_2 at room temperature. The inset shows a magnification of the high-frequency region and an equivalent electrical circuit. Experimental (symbols) and fitting (lines) results of impedance spectrum with adopted EEC.

Table 1. Fitting values of electrical circuit parameters

Sample	R_s (Ω cm^2)	CPE_p (μFcm^{-2})	n_p	CPE_{dl} (μFcm^{-2})	n_{dl}	R_{ct} (kΩ cm^2)
LSCO	12.7±0.28	45.7±0.31	0.82±0.5	920±0.97	0.66±0.5	1.34±0.002
LSCO/RuO_2	7.6±0.29	83.4±1.74	0.84±0.5	5309±14.5	0.88±0.5	369±0.95

In order to better understand applicability of LSCO and LSCO/RuO_2 as potential supercapacitor electrode material, G-C/DC cycles were measured in 0.1M KOH electrolyte at different C/DC currents of 50 and 500 μA as shown in Figure 3. The shape of the G-C/DC curves show deviation from linearity due to typical pseudocapacitive properties [16,17]. The calculated specific capacitance (C, F g^{-1}) using G-C/DC curves for LSCO for 50 and 500 μA are 60 and 30 F g^{-1}, respectively. On the other hand specific capacitance for LSCO/RuO_2 at different currents trend 50 and 500 μA are 104 and 99 F g^{-1}, respectively.

Charge-discharge curves for LSCO and LSCO/RuO_2, presented in Figure 3a, showed a triangular shape with charge half-cycles and linear discharge for LSCO, and linear charge-discharge for LSCO with ruthenium, which is a typical supercapacitor behavior. From these figures, it can be seen that the LSCO/RuO_2 has steep slope curves indicating better capacitive behavior with losing stability. The minor charge discharge in the charging and the discharging potential window indicate Faradaic redox reactions.

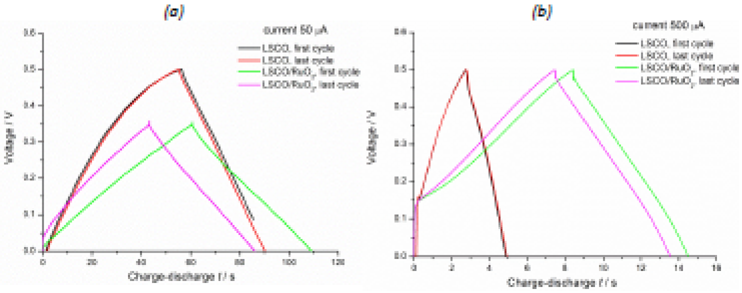

Figure 3. *Galvanostatic charge-discharge curves at different current densities: (a) 50 and 500 μA of LSCO and LSCO/RuO_2 in 0.1 M KOH.*

4. Conclusion

As considering all previous investigation from the microstructure (SEM, EDS and XRD) and electrochemical performances (CV, EIS and GCD) the LSCO/RuO_2 shows superior capacitive characteristics than pure LSCO. Therefore, LSCO with 20 wt. % of RuO_2 was designed as a novel electrode material to modify the traditional perovskite oxides for the supercapacitors. It has a distinct pseudo-capacitance effect and excellent electrical properties which are helpful to improve the electrochemical performance of the composite electrodes. The LSCO/RuO_2 electrode exhibits an improved specific capacitance of 104 F g^{-1} and enhanced pseudo-capacitive properties with good rate capability and better performance. The present results demonstrate this material as a promising electrode material for higher specific capacitance.

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