Chemical reactivity and cathode properties of LaCoO$_3$ on lanthanum silicate oxyapatite electrolyte

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Abstract. Chemical reactivity and cathode properties of LaCoO$_3$ were investigated using new oxide ion conductor, lanthanum silicate oxyapatite. The LaCoO$_3$ is found to be good candidate for cathode of the lanthanum silicate oxyapatite solid-electrolyte since no chemical reaction occurred between the LaCoO$_3$ and lanthanum silicate oxyapatite heating at 1273 K for 60 h in air. Based on electrochemical measurements, lower overpotential between the LaCoO$_3$ and lanthanum silicate oxyapatite was confirmed compared to the overpotential at YSZ/LaCoO$_3$ interface. From analysis on the extended interfacial conductivity as function of oxygen activity at the triple phase boundary at fixed temperature, the overpotential evaluated by impedance spectra is the rate limiting process by oxygen diffusion on the LaCoO$_3$ surface. Comparing to the bulk conductivity of LaCoO$_3$, the electrode resistance evaluated by impedance spectra was confirmed to be different from the electrical transport properties of the LaCoO$_3$ bulk.

1. Introduction

Lanthanum cobaltite with provskite structure (LaCoO$_3$) is famous mixed conductor by electron holes and oxide ions and is the candidate for applications to cathode for solid oxide fuel cell (SOFC) and oxygen permeable membrane [1-7]. Although the LaCoO$_3$ shows high performance as SOFC cathode when yttria stabilized zirconia (YSZ) is used as solid electrolyte [1, 2], decrease in the cathode performance with continuous SOFC operation condition. Cause of the decrease in the cathode performance is the formation of insulator phase, La$_2$Zr$_2$O$_7$, by the chemical reaction between the YSZ and LaCoO$_3$ [8-10]. Hence, it is necessary to replace the solid electrolyte from YSZ if one wants to utilize the excellent cathode property of LaCoO$_3$ for SOFC.

Lanthanoid silicate oxyapatites have known as new oxide ion conductors since Nakayama et al. have reported their high oxide ion conductivity from 1995 to 1998 [11-13]. In particular, the lanthanum silicate oxyapatite shows high oxide ion conductivity even in the ceramic electrolyte. In addition, the oxide ion conductivity of the lanthanum silicate oxyapatite is higher than the conductivity of YSZ below about 873 K because of its low activation energy [13, 14]. Hence, the lanthanum silicate oxyapatite is the candidate of the solid electrolyte material for middle temperature operation SOFC [15]. On the other hand, no research has been done to develop specified electrode materials for the lanthanum silicate oxyapatite. We focused on the LaCoO$_3$ which could not apply as cathode material on the YSZ electrolyte even though the LaCoO$_3$ itself has excellent potential.

In this study, the chemical reactivity at the LaCoO$_3$/lanthanum silicate oxyapatite interface and fundamental research on the cathode performance was investigated. For investigation of the cathode properties, we applied new analysis theory by extended interfacial conductivity [16, 17]. Based on this
approach, we discussed about an origin of the overpotential between the LaCoO$_3$/lanthanum silicate oxyapatite interface.

2. Experimental

2.1. Sample Preparation

The LaCoO$_3$ and lanthanum silicate oxyapatite were synthesized by the water-based sol-gel method [18-20]. The raw materials were lanthanum nitrate hexahydrate (La(NO$_3$)$_3$·6H$_2$O, 99.9% purity, Nacalai Tesque, Inc., Japan), cobalt(II) nitrate hexahydrate (Co(NO$_3$)$_2$·6H$_2$O, 99.9% purity, Kojundo Chem. Lab. Co. Ltd., Japan), amorphous silicon dioxide (99.8% purity, Wako Pure Chem. Industry Ltd., Japan), and citric acid (98% purity, Wako Chem. Industry Ltd., Japan).

The lanthanum nitrate hexahydrate and cobalt nitrate hexahydrate were separately dissolved in distilled water and the solutions were stocked in glass bottle. The concentrations of two aqueous solutions were titrated by chelatometric titration method [18-21]. The concentrations of both solutions were about 1 mol/l.

Procedures of the LaCoO$_3$ synthesis was following: Corresponding amount of the lanthanum nitrate and cobalt nitrate aqueous solutions were pipetted into a glass beaker and mixed by magnetic hot stirrer. Then, citric acid with the same mole amount to sum of the lanthanum and cobalt in mixed aqueous solution was dissolved in the mixed aqueous solution. The homogeneous dissolved solution was heated with stirring using magnetic hot stirrer. The aqueous solution was changed into a viscous gel by evaporation of excess water. The viscous gel was dried by further heating on the hot stirrer and then, the dried gel in the beaker was replaced to heating mantle. Ash-like residue was obtained by pyrolisis of the dried gel about 673 K. Precursor powder was obtained from the ash-like residue by crashing into powder using agate mortar and pestle. The LaCoO$_3$ powder was prepared by heating of the precursor powder at 973 K for 3 h in air. The LaCoO$_3$ is denoted as LCO, hereinafter.

The procedures of the synthesis on lanthanum silicate oxyapatite were the same with the previous paper [18-20, 22]. The composition is La$_{9.50}$(SiO$_4$)$_6$O$_{2.25}$ which is denoted as LSO, hereinafter. The LSO precursor was pre-heated at 1273 K for 3 h in air to remove residual carbons. Then, the pre-heated powder was pressed into pellets with 20 mm diameter and about 1.5 mm thickness. Well sintered pellets were obtained by sintering at 1773 K for 6 h in air. After the sintering, the diameter of the pellets was about 16 mm.

2.2. Chemical reactivity

Separately synthesized LCO and LSO powders were mixed in weight ratio of one to one using agate mortar and pestle. Then, the mixed powder was placed in YSZ crucible and heated at 1273 K for 60 h in air. After the heat-treatment, the formed phase was confirmed by powder X-ray diffraction (XRD) analysis using RINT-2500 (Rigaku Co. Ltd., Japan). For comparison of the reactivity of LCO and electrolyte material, formed phase was also confirmed by mixture of LCO and YSZ after the same procedures.

2.3. Preparation of the LCO ink

For fabrication of LCO porous-electrode on the LSO electrolyte, it was necessary to control its particle size and homogeneous dispersion in organic medium. Hence, the LCO powder was homogenized by planetary ball mill using zirconia ball having diameter of 0.8 mm. Ethanol was used as medium. The rotation velocity and milling period were 1000 rpm and 2 h, respectively. After the milling, 1 wt% of polyethyleneimine versus to the weight of LCO powder was added into the LCO dispersed ethanol to avoid the aggregation of the LCO particles. Amount of LCO powder in this ink is about 0.05 g/ml.
2.4. Preparations of the cell

Cathode properties of the LCO on LSO electrolyte were investigated by a half cell configuration. In order to fabricate the LCO electrode, both surfaces of the sintered LSO ceramics were polished using #100 to #2000 waterproof abrasive papers. In addition, thin groove was made using a diamond wheel for binding platinum wire.

Two polyester-mask-seal with hole diameter of 6 mm were attached at the center on both surfaces of the LSO disk. Platinum paste (TR-7907) Tanaka Kikinzoku Kougyo, Ltd., Japan) was attached inside of the hole and then, dried the paste at 373 K for 30 min. Then, 5 ml of the LCO ink was pipetted and pulled into the seal hole. After drying the LCO ink, mask seals on both side of the LSO pellet were removed. Then, both electrodes were attached by heating at 1273 K for 5 h in air.

Before the electrochemical measurements, platinum wire was wound at the side of the pellet and then, small amount of the platinum paste was painted between the LSO pellet and the platinum wire in order to make electrical contact among them.

2.5. Electrochemical Measurements

Electrochemical measurement was performed by three terminal method in one room condition. One platinum wire attached to the side of the LSO pellet was wired to a platinum lead wire. The cell was sandwiched by two platinum meshes fixed on porous alumina plates. Two platinum wires were welded to each mesh to connect a load circuit and sensing circuit of the potentiogalvanostat (R-600, Gamry, USA). Three electrochemical measurement techniques, cyclic voltammetry, electrochemical impedance with- and without d.c. voltage convolution were used for the analysis. The electrochemical measurements were made at the temperature range between 723 K and 1173 under the oxygen partial pressure from 10^{-2} atm to 1 atm. The oxygen partial pressure around the cell was changed using Ar + O_2 gas mixture. The oxygen partial pressure was monitored by zirconia oxygen sensor fixed at the downstream side from the electrochemical cell.

Cyclic voltammetry was measured in air at voltage scan rate of 5 mV/s. Potential difference range among the working electrode (LCO) and reference electrode (Pt) was between -1.0 V and 1.0 V. Electrochemical impedance was measured in frequency range between 1 MHz and 0.01 Hz depending on the temperature. The electrochemical properties were analyzed based on the extended interfacial conductivity theory [18, 19].

3. Results and discussion

3.1. Chemical reactivity

By comparison of the XRD patterns of the initial mixed powder and the heated powder at 1273 K for 60 h, the LCO and LSO seemed to be equilibrated as two phase coexisting state because the patterns were found to be almost the same and new phase formation was not observed except for a sharpening of the LCO peaks around 2θ = 33 to 35 as shown in Fig. 1. Peak width of the XRD is known to be related to the crystallinity and grain size. Therefore, the main reason for variation of the XRD peaks by heating at 1273 K for 60 h is improvement of the crystallinity and grain growth of the LCO powder.

On the other hand, XRD pattern of initial mixed powder by LCO and YSZ changed into different one by heating at 1273 K for 60 h by showing in Fig. 2(a) and (b). New phase showing strong intensity peaks were indexed by the peaks of La_2Zr_2O_7 [24] as shown in Fig. 2(a). In addition to the peaks by YSZ and La_2Zr_2O_7, weak peaks by Co_3O_4 and LCO were confirmed (Fig. 2(b)). It can be concluded that the LCO is very reactive to YSZ and easily decomposed at 1273 K. Hence, it is difficult to use the LCO as cathode of YSZ electrolyte.

In contrast to the case of the LCO/YSZ interface, the LCO is stable even though the LCO is attached to the LSO electrolyte at 1273 K and therefore the LCO is found to be unique candidate as cathode material of LSO electrolyte.
Fig. 2. XRD peaks of LCO and YSZ powder mixture. Whole patterns are shown in (a). Expanded pattern is shown in (b) in order to clearly showing the small peaks. The peaks (I) is the sample as mixture powder and (II) is the sample after heated at 1273 K for 60 h in air. The reported XRD peaks of LCO [23] and LSO [18] are shown for comparison.

3.2. Electrochemical impedance under open cell circuit condition

Typical impedance spectra corrected at 1023 K were shown in Fig. 3 as function of oxygen partial pressure. All of the spectra were found to be constructed by two decompressed arcs at high frequency and low frequency region. With respect to the high frequency region arc, it seemed to be distorted signal by the instrument because similar distorted spectrum was measured when the circuit was connected to a test cell constructed by resistors and condenser. Therefore, only the spectra shown in low frequency region were analyzed by the equivalent circuit. The equivalent circuit used in this study is shown in Fig. 4 to fit the obtained spectra. The $R_b$ is the bulk resistance of the electrolyte, $R_2$ and $R_3$ are the resistance of the electrode response, respectively. The $CPE_2$ and $CPE_3$ are the constant phase element of the electrode response, which are the empirical element to give the Cole-Cole type relaxation [27]. Reason for the separation with two elemental parts by $R_2$ and $CPE_2$, and $R_3$ and $CPE_3$ is to fit the distorted spectra. It is necessary to emphasize that no clear physicochemical meaning of $R_2$, $R_3$, $CPE_2$, and $CPE_3$, and is reasonable to consider that sum of these elemental parts should be treated
as electrode impedance \(Z_{\text{electrode}}\) as shown in Fig. 4. Therefore, sum of the \(R_2\) and \(R_3\) are treated as electrode resistance \(R_E\), hereafter.

Based on the interfacial conductivity proposed by Mizusaki et al. [28, 29], the interfacial conductivity \(\sigma_E\) is defined by

\[
\sigma_E = 1/(A\cdot R_E),
\]

where \(A\) is the electrode area. The relationships between the \(\sigma_E\) and oxygen partial pressure show that the \(\sigma_E\) is almost independent of oxygen partial pressure (Fig. 5). It is necessary to emphasize that the \(\sigma_E\) is not an electrical conductivity but a chemical one [16, 17, 28, 29]. Although it is difficult to conclude the rate determining step by the \(p(O_2)\) dependences of \(\sigma_E\) because the measured \(p(O_2)\) range is narrow, the \(p(O_2)\) dependences on the \(\sigma_E\) becomes weak if about a half of the adsorption site on the metallic electrode surface is fulfilled by the adsorbed oxygen [28, 29]. On the other hand, if the \(\sigma_E\) corresponds to the oxygen permeation by mixed conductive properties in LaCoO₃, the \(\sigma_E\) should be proportional to 1/4 power of \(p(O_2)\) by considering into the \(p(O_2)\) dependence of the partial conductivity of oxide ions in LaCoO₃ [30].
3.3. Cyclic voltammetry

Relationship between current and potential difference between the working electrode and reference electrode measured by cyclic voltammetry are shown in Fig. 6. In case of solid-state electrochemical system constructed by oxygen ion conductor and electrode, terminal voltage difference between the working electrode and reference electrode \( E_{w-r} \) is theoretically given when the following two situations are established; (I) steady-state is achieved, and (II) local equilibrium is established [16, 28],

\[
E_{w-r} - E_{op} = i(O^2^-) R_b + \eta, \tag{2}
\]

where \( E_{op} \), \( i(O^2^-) \), and \( \eta \) are the terminal voltage at open cell circuit condition, oxygen ionic current, and overpotential, respectively. Furthermore, the \( \eta \) is presented by,

\[
\eta = \frac{RT}{2F^2} \ln \left\{ \frac{a_o(w)}{p(O_2, w)^{1/2}} \right\} = \frac{RT}{4F^2} \ln \left\{ \frac{p(O_2)}{p(O_2, w)} \right\}.
\]

\( R \), \( T \), and \( F \) are the gas constant, absolute temperature, and Faraday constant, respectively. The \( a_o(w) \) is the oxygen activity under the oxygen ionic current flow at the triple phase boundary among the working electrode, solid electrolyte, and gas phase. The \( p(O_2) \) is the oxygen partial pressure at the triple phase boundary under ionic current flow condition. The \( p(O_2, w) \) is the oxygen partial pressure at the working electrode side with no current flow condition. In case of this study, \( p(O_2, w) \) is equal to 0.21. From the impedance analysis described above, the \( R_b \) value was already evaluated, and therefore, we could convert the relationship between the \( E_{w-r} \) and \( i(O^2^-) \) as shown in Fig. 6 into the relationship between the \( \eta \) and \( i(O^2^-) \) (Fig. 7). Results on the case at LCO/YSZ cell were also plotted for comparison. For the case of LCO/LSO cell, almost no hysteresis was observed by the scan rate at 5 mV/s. On the other hand, clear hysteresis was found in the case of LCO/YSZ cell.

Cathode properties at the LCO/LSO interface is found to be better than the properties at the LCO/YSZ interface by comparison of the \( \eta - i(O^2^-) \) relationships at the same \( \eta \) and temperature condition. One reason is that no insulator phase is formed at the LCO/LSO interface as discussed in section 3.1.
3.4. Electrochemical impedance with applying d.c. bias

In order to discuss the triple phase boundary situation under steady-state oxygen ionic current flow, impedance spectra were corrected under fixed d.c. bias applied condition. Typical impedance spectra are shown in Fig. 8. The shapes of the spectra are similar to the spectra measured under open cell circuit condition in Fig. 3. Hence, the spectra were analyzed by the same equivalent circuit shown in Fig. 4. The $R_E$ value measured under d.c. bias applied condition is indexed as $R_{Ex}$. Similarly, the interfacial conductivity under d.c. bias applied condition is named as extended interfacial conductivity ($\sigma_{Ex}$) which is presented by [16];

$$\sigma_{Ex} = 1/\left(A \cdot R_{Ex}\right).$$  \hspace{1cm} (4)

Taking into consideration of the electrochemical impedance model based on the interfacial conductivity theory, the $\sigma_{Ex}$ is a function of $p(O_2)$ at steady-state current flow condition [16]. If the electrode resistance is determined by the neutral oxygen diffusion on the LCO surface obeying the law of classical irreversible thermodynamics, $\sigma_{Ex}$ and $\sigma_E$ values measured by different experiments become the same with each other at the same $\alpha_o(w)$ and temperature. From the plots of $\sigma_{Ex}$ and $\sigma_E$ versus $p(O_2)$ (Fig. 5), $\sigma_{Ex}$ and $\sigma_E$ show almost the same values. These results indicate that the electrode resistance is not the electric resistance but a kind of chemical resistance by neutral oxygen diffusion by the chemical potential gradient yielding to the classical irreversible thermodynamic process [16]. In order to check an adequacy of this result, we confirmed the total conductivity ($\sigma_t$) of the LCO bulk as functions of oxygen partial pressure and temperature (Fig. 9). The $p(O_2)$ dependence on the $\sigma_t$ shows similar tendency to the previous report [30, 31]. Although the oxygen partial pressure dependence of the $\sigma_t$ of LCO is similar to the $p(O_2)$ dependence of the $\sigma_E$ and $\sigma_{Ex}$, the temperature dependence of the $\sigma_t$ is opposite to the dependences of the $\sigma_E$ and $\sigma_{Ex}$. These facts are also supported that the $\sigma_E$ and $\sigma_{Ex}$ are not governed by the electric properties in the LCO bulk.

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**Fig. 8.** Impedance spectra corrected under d.c. bias applied conditions using the LCO/LCO cell. The $E_{w-e}$ indicate that the d.c. bias between the working electrode (LCO) and reference electrode (Pt).

**Fig. 9.** Relationship between total conductivity ($\sigma_t$) of the LCO bulk ceramic and oxygen partial pressure.
4. Summary

Lanthanum cobaltite (LaCoO$_3$) is found to show low chemical reactivity to the lanthanum silicate oxyapatite solid-electrolyte at 1273 K. From solid-state electrochemical measurements, high cathode performance was confirmed at the LaCoO$_3$/lanthanum silicate oxyapatite interface by comparison to the interface at LaCoO$_3$/YSZ. Based on the analysis on the interfacial conductivity theory, the interfacial conductivity evaluated by the impedance spectra measured under open cell circuit condition are found to be the same with the extended interfacial conductivity measured by the d.c. bias applying condition. This result indicates that electrochemical kinetics at the LCO/LSO interface is governed by the LCO surface properties, namely surface diffusion of neutral oxygen and as a result, the relationship between the current and overpotential can be explained based on the interfacial conductivity theory.

References

[1] O. Yamamoto, Y. Takeda, R. Kanno, M. Noda, Perovskite-type oxides as oxygen electrodes for high temperature oxide fuel cells, Solid State Ionics 22 (1986) 241-246.
[2] Y. Takeda, R. Kanno, M. Noda, Y. Tomida, O. Yamamoto, Cathodic polarization phenomena of perovskite oxide electrodes with stabilized zirconia, J. Electrochem. Soc. 134 (1987) 2656-2661.
[3] Y. Teraoka, T. Nobunaga, K. Okamoto, N. Miura, N. Yamazoe, Influence of constituent metal cations in substituted LaCoO$_3$ on mixed conductivity and oxygen permeability, Solid State Ionics 48 (1991) 207-212.
[4] C.H. Chen, H. Kruidhof, H.J.M. Bouwmeester, A. J. Burgraaf, Ionic conductivity of perovskite LaCoO$_3$ measured by oxygen permeation technique, J. Appl. Electrochem. 27 (1997) 71-75.
[5] B.C.H. Steel, Materials for IT-SOFC stacks. 35 years R&D: the inevitability of gradualness?, Solid State Ionics. 134 (2000) 3-20.
[6] O. Yamamoto, Solid Oxide Fuel Cells: fundamental aspect and prospects. Electrochim. Acta. 45 (2000) 2423-2435.
[7] H.J.M. Bouwmeester, Dense ceramic membrane for methane conversion, Catal. Today. 82 (2003) 141-150.
[8] H. Yokokawa, N. Sakai, T. Kawada, M. Dokiya, Thermodynamic analysis of reaction profile between LaMnO$_3$ (M = Ni, Co, Mn) and ZrO$_2$, J. Electrochem. Soc. 138 (1991) 2719-2727.
[9] J.A. Labrincha, J.R. Frade, F.B.B. Marques, La$_2$Zr$_2$O$_7$ formed at ceramic electrode/YSZ contacts, J. Mater. Sci. 28 (1993) 3809-3815.
[10] F.M. Figueiredo, J.A. Labrincha, J.R. Frade, F.M.B. Marques, Reactions between a zirconia-based electrolyte and LaCoO$_3$-based electrode materials, Solid State Ionics 101-103 (1997) 343-349.
[11] S. Nakayama, H. Aono, Y. Sadaoka, Ionic conductivity of Ln$_{10}$(SiO$_4$)$_6$O$_3$ (Ln=La, Nd, Sm, Gd, and Dy), Chem. Lett. 24 (1995) 431-432.
[12] S. Nakayama, T. Kageyama, H. Aono, Y. Sadaoka, Ionic conductivity of lanthanoid silicates, Ln$_{10}$(SiO$_4$)$_6$O$_3$ (Ln=La, Nd, Sm, Gd, Dy, Y, Ho, Er and Yb), J. Mater. Chem. 5 (1995) 1801-1805.
[13] S. Nakayama, M. Sakamoto, Electrical properties of new type high oxide ionic conductor RE$_{10}$Si$_6$O$_{27}$ (RE = La, Pr, Nd, Sm, Gd, Dy), J. Eur. Ceram. Soc. 18 (1998) 1413-1418.
[14] H. Yoshioka, High oxide ion conductivity in Mg-doped La$_{10}$Si$_6$O$_{27}$ with apatite-type structure. Chem. Lett. 33 (2004) 392-393.
[15] A. Orera, P.R. Slater, New chemical synthesis for solid oxide fuel cells, Chem. Mater. 22 (2010) 675-690.

[16] K. Kobayashi, Y. Sakka, Theoretical modeling of electrode impedance for an oxygen ion conductor and metallic electrode system based on the interfacial conductivity theory, Solid State Ionics 232 (2013) 49-57.

[17] K. Kobayashi, K. Terabe, T. Sukigara, Y. Sakka, Theoretical modeling of electrode impedance for an oxygen ion conductor and metallic electrode system based on the interfacial conductivity theory. Part II: Case of the limiting process by non-steady-state surface diffusion, Solid State Ionics 249-250 (2013) 78-85.

[18] K. Kobayashi, Y. Matsushita, N. Igawa, F. Izumi, C. Nishimura, S. Miyoshi, Y. Oyama, S. Yamaguchi, Water-based sol-gel synthesis and crystal structure refinement of lanthanum silicate apatite. Solid State Ionics 179 (2008) 2209-2215.

[19] K. Kobayashi, T.S. Suzuki, T. Uchikoshi, Y. Sakka, Low-temperature formation of Ln silicate oxyapatite (Ln = La and Nd) by the water-based sol-gel method, Solid State Ionics 204-205 (2011) 91-96.

[20] K. Kobayashi, Y. Sakka, Phase relationships in the quasi-ternary LaO$_{1.5}$-SiO$_2$-MgO system at 1773 K, Sci. Tech. Adv. Mater. 13 (2012) 045006 (12pp).

[21] J. Kinnunen, B. Wennerstrand, Some further applications of xylenol orange as an indicator in the EDTA titration, Chemist-Analyst. 46 (1957) 92-93.

[22] K. Kobayashi, C. Nishimura, Electrical transport and electric power generation properties of lanthanum-silicate oxyapatite ceramics prepared by asol-gel method, ECS Trans. 25 (2009) 1785-1790.

[23] O. Haas, R.P.W. J. Struis, J.M. McBreen, Syncrotron X-ray absorption of LaCoO$_3$ perovskite, J. Solid State Chem. 177 (2004) 1000-1010.

[24] E.J. Harvey, K.R. Whittle, G.R. Lumpkin, R.I. Smith, S.A.T. Redfern, Solid Solubility of (La, Nd)$_2$(Zr, Ti)$_2$O$_7$ phases deduced by neutron diffraction, J. Solid State Chem. 178 (2005) 800-810.

[25] M. Walter, C. Nästren, J. Somers, R. Jardin, M.A. Denecke, B. Brendebach, Local atomic structure of a zirconia-based americium transmutati on fuel, J. Solid State Chem. 180 (2007) 3130-3135. YSZ crystal structure

[26] M. Casas-Cabanas, G. Binotto, D. Larcher, A. Lecup, V. Giordani, J.-M. Tarascon, Defect chemistry and catalytic activity of nanosized Co$_3$O$_4$, Chem. Mater. 21 (2009) 1939-1947.

[27] J.R. Macdonald, Note on the parameterization of the constant-phse admittance element, Solid State Ionics 13 (1984) 147-149.

[28] J. Mizusaki, K. Amano, S. Yamauchi, K. Fueki, Electrode reaction at Pt, O$_2$(g)/stabilized zirconia interfaces. Part I: Theoretical consideration of reaction model, Solid State Ionics 22 (1987) 313-322.

[29] J. Mizusaki, K. Amano, S. Yamauchi, K. Fueki, Electrode reaction at Pt, O$_2$(g)/stabilized zirconia interfaces. Part II: Electrochemical measurements and analysis, Solid State Ionics 22 (1987) 323-330.

[30] A.N. Petrov, A.Y. Zuev, A.I. Vylkov, D.S. Tsvetkov, Equilibrium of point defects and charge transfer in lanthanum cobaltite, Russ. J. Phys. Chem. 80 (2006) S128-S133.

[31] A.N. Petrov, V.A. Cherepanov, A.Y. Zuev, Thermodynamics, defect structure, and charge transfer in doped lanthanum cobaltites: an overview. J. Solid State Electrochem. 10 (2006) 517-537.