Transport Properties of Composite Cathode Materials $La_{0.8}Sr_{0.2}Fe_{0.7}Ni_{0.3}O_{3-\delta}/Ce_{0.9}Gd_{0.1}O_{1.95}$

YU. S. OKHLUPIN and N. F. UVAROV

Institute of Solid State Chemistry and Mechanochemistry, Siberian Branch of the Russian Academy of Sciences, Ul. Kutateladze 18, Novosibirsk 630128 (Russia)

E-mail: ohlupin@mail.ru

Abstract

Full conductivity, diffusion and oxygen exchange properties in the composites $(100 - x)$ $La_{0.8}Sr_{0.2}Fe_{0.7}Ni_{0.3}O_{3-\delta}/xCe_{0.9}Gd_{0.1}O_{1.95}$ (LSFN/CGO, x is volume fraction, $0 < x < 71.1\%$) were studied by means of the relaxation of electrical conduction at 700 °C for partial oxygen pressure within the range $(0.2-3) \cdot 10^{-3}$ atm. It was demonstrated that the electric conduction of the composites decreases monotonously with an increase in the concentration of CGO, while the coefficient of the chemical diffusion of oxygen (D_{chem}) increases. The constant of oxygen exchange (k_{chem}) is higher for composites than for individual phases LSFN and CGO. The dependence of k_{chem} value on the composition of the composite may be due to the effect of interphase boundaries on oxygen exchange processes. The total efficiency of oxygen transport in LSFN/CGO composites at a temperature of 700 °C is maximal for the composites with the volume fraction of CGO close to 70 %.

Key words: relaxation of electrical conduction, composites $La_{0.8}Sr_{0.2}Fe_{0.7}Ni_{0.3}O_{3-\delta}/Ce_{0.9}Gd_{0.1}O_{1.95}$, oxygen diffusion, oxygen exchange, cathode materials

INTRODUCTION

Oxides with perovskite structure with the composition $La_{1-x}Sr_xM_{1-y}M'_yO_{3-\delta}$ (M, M' = Fe, Co, Ni) with high mixed electronic/oxygen conductivity are promising for using as cathode materials for solid oxide fuel cells (SOFC) [1–3], membranes for selective separating oxygen from gas mixtures and partial methane oxidation into synthesis gas [4, 5]. Usually, in order to form an extended three-phase boundary, to provide mechanical compatibility of phases on the contact and gas-transmission properties of the cathode material the mentioned perovskite-type oxides are mixed with the material of a solid electrolyte being in contact with the cathode. In this case a chemical interaction is possible resulting in the degradation of the cathode material. However, composite cathode materials could be obtained using other oxides, too instead of electrolyte material, those allow one to vary the chemical, mechanical and transport properties of cathodes within a wide range [2].

This work is devoted to the investigation of transport properties (electrical conductivity, diffusion and exchange of oxygen) inherent in composites $La_{0.8}Sr_{0.2}Fe_{0.7}Ni_{0.3}O_{3-\delta}/Ce_{0.9}Gd_{0.1}O_{1.95}$ (LSFN/CGO) by means of electrical conductivity relaxation.

MATERIALS AND METHODS

The LSFN and CGO oxides were synthesized from organometallic precursors by means of Pequini technique using metal nitrates, citric acid, ethylene glycol and ethylene diamine [6, 7]. For the preparation of the composite powders, corresponding mixtures were dispersed in isopropyl alcohol with the addition of polyvinyl butyral under ultrasonic treatment. Then the

mixture was dried, calcined, pressed into pellets and sintered in air at 1330 °C for 5 h. The X-ray diffraction analysis demonstrated that there are no impurity phases present. The relative density of the samples determined by the Archimedes method exceeded 90 %.

Chemical diffusion and oxygen exchange processes in the composites were studied by means of electrical conductivity relaxation technique after sudden changing the pressure of oxygen within the value of $2 \leq (P_1/P_2) \leq 3$ (P_1 and P_2 are the initial and final partial pressure of oxygen, respectively). The values of specific electrical conductivity were measured using disc-shaped samples 0.2–0.4 mm thick by means of van der Poe four-electrode technique [8, 9] in the galvanostatic mode with a current strength ranging within 75–80 mA [10, 11].

The calculation of the chemical diffusion coefficient (D_{chem}) and exchange constant (k_{chem}) was performed basing on the model of infinite thin plate (thickness 2l) [12], wherein the normalized conductivity (σ_{norm}) varies with time according to the equation

$$\sigma_{norm} = \frac{\sigma - \sigma_0}{\sigma_\infty - \sigma_0} = 1 - \sum_{n=0}^{\infty} \frac{2L^2}{\beta_n^2 (\beta_n^2 + L^2 + L)}$$

$$\times \exp(-\beta_n^2 D_{chem} t / l^2) \qquad (1)$$

where t is the relaxation time; σ_0, σ and σ_∞ are the conductivity at the moments of time corresponding 0, t and ∞, respectively; $L = lk_{chem}/D_{chem}$; β_n is a factor equal to the n-th root of the equation $\beta_n \mathrm{tg}\,(\beta_n) = L$; n being the number of roots.

RESULTS AND DISCUSSION

It has been found that the total conductivity of the investigated composites is determined by the p-type conductivity of the LSFN phase, which is several orders of magnitude greater than the n-type ionic conductivity. This is consistent with published data obtained previously for the systems based on lanthanum-strontium ferrite [13]. The efficient activation energy of the p-type conductivity determined from the temperature dependence of the electrical conductivity of the samples with a volume fraction CGO $0 \leq x \leq 71.1$ % (Fig. 1) decreases with
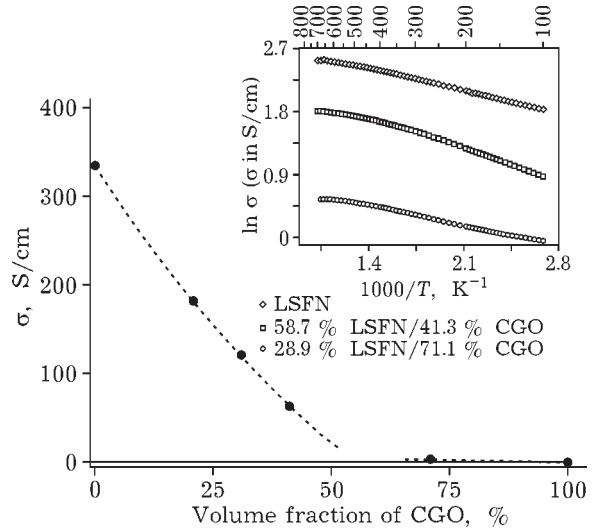

Fig. 1. Total conductivity of composites $(100 - x)$LSFN/xCGO depending on the volume fraction of the phase CGO (x) at 700 °C and $P_{O_2} = 0.2$ atm. The inset demonstrates electrical conductivity depending on the temperature of the composites at $x = 0$, 41.3 and 71.1 %.

increasing the temperature from 5.2±0.6 (within the temperature range of 100–300 °C) to (5.1±0.3) kJ/mol (within the temperature range of 300–700 °C) and does not depend on the concentration of CGO. Activation character of the dependence could be explained by the presence of quasi-free holes, whereas the decreasing the activation energy at high temperature values could be explained by the delocalization of holes and the decrease in their concentration due to changing the oxygen stoichiometry [14, 15]. The electrical conductivity of CGO at $P_{O_2} > 10^{-3}$ atm is ionic [16] to be several orders of magnitude less than the total conductivity of composites. The value of the electrical conductivity of the composites decreases with increasing the content of CGO (see Fig. 1) to be accurately described within in the framework of the percolation model with the percolation transition at $x \approx (60\pm5)$ %.

In the course of mathematical treatment of the relaxation curves we obtained the parameters D_{chem} and k_{chem} depending on the volume fraction of CGO (Fig. 2). The evaluation via the literature data [17] demonstrates that for the compound $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$ at 700 °C and $P_{O_2} = 0.05$ atm the value of D_{chem} is equal to $1.7 \cdot 10^{-6}$ cm/s. The D_{chem} values LSFN/CGO inherent in composites increase monotonically with increasing the content of CGO phase,
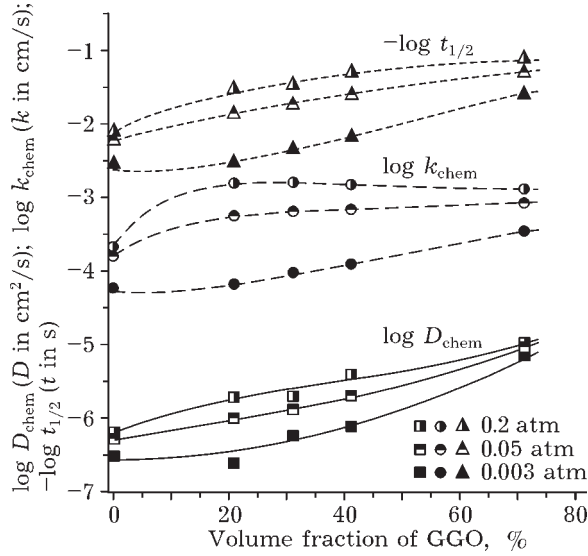
Fig. 2. Parameters D_{chem}, k_{chem} and the half-time $t_{l/2}$ of the relaxation of electrical conductivity depending on the volume fraction of CGO phase in the composites $(100 - x) \times$ LSFN/xCGO at 700 °C and at different values of P_{O_2}. Parameter $t_{l/2}$ was calculated for plate-shaped samples with the thickness of 0.32 mm.

which occurs, to all appearance, due to high D_{chem} values for CGO phase $(5 \cdot 10^{-5} - 5 \cdot 10^{-4} \text{ cm}^2/\text{s})$ [18].

The experimental values of k_{chem} for LSFN at 700 °C and $0.003 \leq P_{\text{O}_2} \leq 0.2$ atm range within $6 \cdot 10^{-5} - 2 \cdot 10^{-4}$ cm/s, which is consistent with data published for related systems La$_{0.5}$Sr$_{0.5}$CoO$_{3-\delta}$, La$_{0.6}$Sr$_{0.4}$Fe$_{0.8}$Co$_{0.2}$O$_{3-\delta}$ [19, 20]. It is known [21] that the CGO exhibits the exchange constant k_{ex} determined from isotopic exchange data at the pressure values $P_{\text{O}_2} > 10^{-3}$ atm at 700 °C to vary within the range of $10^{-8} - 10^{-7}$ cm/s. For the systems those contain only oxygen vacancies and holes as carriers, the parameters k_{chem} and k_{ex} being connected by the expression [22]:

$$k_{\text{chem}} = k_{\text{ex}}(\Gamma_V + 1) \qquad (2)$$

where Γ_v is thermodynamic factor. Thus, taking into account that $\Gamma_V \approx 27$ [18], the k_{chem} for CGO could be estimated as $10^{-7} - 10^{-6}$ cm/s. Therefore, we could expect that the value of k_{chem} would decrease with the introduction of the CGO oxide phase in the composite. However, the results of our studies (see Fig. 2) indicate that the values of k_{chem} increase rather than decrease with increasing x to reach maximum values t intermediate CGO concentrations.

The observed increase of k_{chem} values in the composites as compared to the individual phases could be connected with the influence of LSFN/CGO interfaces, whereon, as we assume, the oxygen exchange could be much more intense.

As a criterion for comparing the transport properties of the composites one could use a half-time value $t_{1/2}$, whereby the normalized conductivity (l) reaches the value of 0.5. Figure 2 demonstrates comparing the $t_{1/2}$ parameters calculated for plate-shaped samples with the thickness of $2l = 0.32$ mm obtained for the composites at 700 °C. The minimum values of $t_{1/2}$ correspond to the most efficient transport of oxygen in the materials under investigation. The maximum value of $-\log t_{1/2}$ approximately corresponds to the CGO volume fraction $x \approx 71\,\%$, but the exact position of the maximum could to a significant extent depend on the microstructure of the composites, on the temperature and other factors, whose effect will be studied in the future.

CONCLUSION

The electrical conductivity of dense composites LSFN/CGO with a uniform distribution of the two phases is reduced with increasing the CGO fraction, whereas its qualitative description within the framework of the percolation model indicates a percolation transition to occur at $x \approx (60\pm5)\,\%$. By means of the conductivity relaxation it has been demonstrated that the composites with increasing the content of CGO exhibit increasing the oxygen chemical diffusion coefficient (D_{chem}), whereas the values of the exchange constant k_{chem} pass through a maximum. High values of k_{chem} for composites as compared to those for the individual LSFN and CGO phases could be attributed to the influence of three-phase interfaces. The highest efficiency of oxygen transfer in the materials under investigation at 700 °C corresponds to the composites, whose composition is close to those with CGO volume fraction equal to 70 %.

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