Oxygen diffusion in $\text{Sr}_3\text{YCo}_4\text{O}_{10.5}$: An electrical conductivity relaxation and thermogravimetric analysis approach

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Abstract

Chemical oxygen diffusion coefficients and chemical surface exchange rates along with oxygen self-diffusion coefficients in dense samples of $\text{Sr}_3\text{YCo}_4\text{O}_{10.5+\delta}$ were studied by using a combination of electrical conductivity relaxation measurements (ECR) and thermogravimetric analysis data (TGA) in the temperature range of 650 °C – 900 °C. Arrhenius behavior, $A = A_0 \exp(\frac{-E_A}{RT})$, was observed with activation energies of $E_A^{D_{chem}} = 1.16 \pm 0.01$ eV, $E_A^{D_o} = 1.56 \pm 0.01$ eV and $E_A^{k_{chem}} = 0.76 \pm 0.05$ eV for the chemical oxygen diffusion coefficient, the oxygen self-diffusion coefficient, and the chemical surface exchange rate, respectively. The thermodynamic factor changes with temperature from 611 at 650 °C to 177 at 900 °C.

Keywords: Perovskites, Cathode, SOFC, Oxygen Diffusion, Electrical Conductivity Relaxation

1. Introduction

In order to make solid oxide fuel cells (SOFCs) more commercially viable, it is desirable to decrease their operating temperature as much as possible [1]. Lower operating temperature also decreases the reactivity of all SOFC components thereby improving stability and reliability. However, the requirement of high values of electronic and ionic conductivity can become a limitation on the performance at lower temperature. The rate of the oxygen reduction reaction is a particular problem and consequently, it is necessary to determine oxygen diffusion and electrical conductivity in a wide range of temperatures (500 °C – 1000 °C) for all novel and prospective cathode materials for SOFC applications.

Several different techniques have been used to determine oxygen diffusion coefficients in ceramic materials. The most developed method is isotope exchange and depth profiling in combination with secondary ion mass spectrometry (IEDP/SIMS) [2]. This technique allows measurements of oxygen diffusion coefficients in both electron-conducting and dielectric materials [3, 4] over a wide range of temperature, and in case of single crystals, along different crystallographic directions [5]. But, at the same time IEDP/SIMS requires the use of expensive ^{18}O and SIMS damages the sample. Another technique for the determination of oxygen diffusion, namely molecular dynamic simulations (MD), became available with increases in computational power. MD provides detailed information about oxygen diffusion pathways and rates, and requires information only about the crystal structure of the particular compound studied [6]. Due to the assumption of ideal conditions in MD simulations, the results may deviate from IEDP/SIMS experimental measurements [3].

Relaxation techniques are commonly used for studying kinetics. The change in a specific property of the system to a new equilibrium state is observed after the system has experienced a rapid change in its physical or chemical environment. To study oxygen transport, any property that reflects the

oxygen concentration, such as weight, volume, conductivity, optical properties, can be investigated [7]. Given the relationship between oxygen concentration and oxygen partial pressure, relaxation experiments on mixed ionic and electronic compounds (MIECs) can be performed by rapid changing the oxygen partial pressure in the ambient environment at a constant temperature.

Compared with other relaxation techniques, electrical conductivity measurements are much less affected by gas fluctuations or other minor physical changes that occur during the relaxation experiment. Moreover, conductivity is extremely sensitive to the defect concentration [8, 9]. Therefore, the electrical conductivity relaxation (ECR) experiment is the most commonly employed relaxation technique for determining oxygen transport kinetics [9-13].

In present work, we used the ECR technique to determine oxygen diffusion in $\text{Sr}_3\text{YCo}_4\text{O}_{10.5+\delta}$, which was studied previously with both IEDP/SIMS and Molecular Dynamic simulations [3, 6]. The relative oxygen stoichiometry was determined by thermogravimetric analysis at different partial pressures of oxygen (2% - 75%), while absolute values were determined by iodometric titration.

2. Experimental

The perovskite-related compound $\text{Sr}_3\text{YCo}_4\text{O}_{10.5}$ (314-phase) was synthesized by solid-state reaction of stoichiometric amounts of SrCO_3 , Co_3O_4 and Y_2O_3 with intermediate grindings and sinterings in the range of temperatures 900 °C – 1200 °C [14]. The temperature of the final sintering (1160 °C) was adjusted to allow formation of a single phase material but at the same time to prevent densification of the powder. A single-phase compound with small particle size was necessary for densification using a cold isostatic press (CIP) and subsequent sintering.

The crystal structure and phase purity of $\text{Sr}_3\text{YCo}_4\text{O}_{10.5}$ powder were analyzed by X-Ray Powder Diffraction using $\text{Cu-K}\alpha$ radiation.

The powder was ball milled in ethanol for 48 h and dried in a vented oven for another 48 h. Dense pellets of the $\text{Sr}_3\text{YCo}_4\text{O}_{10.5}$ were prepared by isostatically pressing at 30,000 psi with subsequent sintering at 1180 °C for 4 h with heating and cooling rates 1 °C/min. The density of the pellets was measured by the Archimedes technique and was greater than the 95% that is required to prevent oxygen transport through the pores. Due to the fact that during an ECR experiment one dimension of the sample is reserved for the conductivity measurement, the geometry of the sample has special requirements. In theory, the length of the sample in the conductivity measurement direction should be infinite, but good results can be achieved on samples where one dimension is order of magnitude larger than another two [15]. For ECR measurements a bar with dimensions $t = 1.43$ mm, $w = 1.09$ mm and $l = 19.72$ mm was cut and polished to decrease the effect of surface morphology on oxygen diffusion (Fig. 1).

To equilibrate the sample in the apparatus and improve the contacts with the gold wires, the bar was heated from room temperature to 900 °C and then cooled back to ambient temperature before ECR measurements. The electrical conductivity was measured during the heating and cooling cycle.

The oxygen atom transport in a dense mixed ionic electronic conducting (MIEC) oxide can be generally described by two processes namely surface exchange and bulk diffusion. The mathematical solutions of the mass transport equations under various conditions are well established using a linear surface exchange model [16].

The change in oxygen partial pressure in the surroundings of the MIEC sample leads to the oxygen adsorption or rejection and as a result, to a change in electron-hole concentration and change of

electrical conductivity (Eqn. 1), which is measured during an electrical conductivity relaxation experiments (ECR).

$$V_{\ddot{O}} + \frac{1}{2}O_2(g) \leftrightarrow O_O^x + 2h \quad (\text{Eqn. 1})$$

For a rod sample with a $2l_1$ by $2l_2$ cross-section, if its length is much greater than the sides, according to the Wagner's theory and the mass conservative law (Eqns. 2, 3) and boundary conditions (Eqns. 4, 5, 6) it is possible to describe relative electrical conductivity as a function of time, chemical surface exchange and chemical oxygen diffusion (Eqns. 7, 8).

$$j_{O^{2-}}(x, t) = -D_{chem} \frac{\partial c_{O^{2-}}(x, t)}{\partial x} \quad (\text{Eqn. 2}),$$

$$\frac{\partial c_{O^{2-}}(x, t)}{\partial t} = -\frac{\partial j_{O^{2-}}(x, t)}{\partial x} \quad (\text{Eqn. 3}),$$

$$c_{O^{2-}}(x, 0) = c_{O^{2-}}^{(1)} \quad (\text{Eqn. 4}),$$

$$\left. \frac{\partial c_{O^{2-}}}{\partial x} \right|_{x=0} = 0 \quad (\text{Eqn. 5}),$$

$$k_{chem} \left(c_{O^{2-}} - c_{O^{2-}}^{(2)} \right) = -D_{chem} \left. \frac{\partial c_{O^{2-}}}{\partial x} \right|_{x=\pm l} \quad (\text{Eqn. 6}),$$

where D_{chem} and k_{chem} are chemical oxygen diffusion and chemical surface exchange coefficients, $c_{O^{2-}}^{(1)}$ and $c_{O^{2-}}^{(2)}$ are oxygen ion concentrations in the solid at equilibrium with the initial and final oxygen partial pressures, $pO_2^{(1)}$ and $pO_2^{(2)}$, respectively.

$$\frac{M_t}{M_{\infty}} = 1 - \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} \frac{2C_1^2 \exp(-\alpha_{1m}^2 \tilde{D}_O t / l_1^2)}{\alpha_{1m}^2 (\alpha_{1m}^2 + C_1^2 + C_1)} \times \frac{2C_2^2 \exp(-\alpha_{2n}^2 \tilde{D}_O t / l_2^2)}{\alpha_{2n}^2 (\alpha_{2n}^2 + C_2^2 + C_2)} \quad (\text{Eqn. 7}),$$

$$\frac{M_t}{M_{\infty}} = \frac{c_{O^{2-}}(t) - c_{O^{2-}}^{(1)}}{c_{O^{2-}}^{(2)} - c_{O^{2-}}^{(1)}} = \frac{\sigma(t) - \sigma^{(1)}}{\sigma^{(2)} - \sigma^{(1)}} = g(t) \quad (\text{Eqn. 8}),$$

where $g(t)$ is the relative conductivity; M_t/M_∞ is the fractional change of the total mass of oxygen; C is a measure of the importance of the contribution of the surface exchange reaction, and is defined as the ratio of the half thickness to the characteristic length of the sample, l_d (Eqn. 9); α_{1m} and α_{2n} are the positive roots of the transcendental equations (Eqn. 10),

$$C_1 = \frac{l_1}{l_d}, C_2 = \frac{l_2}{l_d}, l_d = \frac{D_{chem}}{k_{chem}} \quad (\text{Eqn. 9}),$$

$$\alpha_{1m} \tan \alpha_{1m} = C_1, \alpha_{2n} \tan \alpha_{2n} = C_2 \quad (\text{Eqn. 10}).$$

During the ECR experiment, the sample was located in a tube furnace at a certain temperature in a flow of gas with a certain oxygen partial pressure (O_2/N_2 mixtures with different concentrations of oxygen) [17]. A rapid switch, less than 2.5 s for the gas switching delay [18], from one oxygen partial pressure to another led to the change of electrical conductivity of the sample, and was measured by AC 4-probe method with SR830 DSP Lock-In Amplifier at a single frequency of 13333 Hz. As a result, conductivity relaxation profiles (conductivity vs. time) were obtained. Oxygen diffusion kinetics were investigated with ECR in the temperature range 650 °C – 900 °C by following switches of oxygen partial pressure: 2% $\leftrightarrow$ 5%, 10% $\leftrightarrow$ 20%, 10% $\leftrightarrow$ 75%.

The results of ECR experiments represent chemical oxygen diffusion and chemical surface exchange and are different from those obtained during the isotope exchange depth profiling experiments (IEDP). The switch of the oxygen partial pressure is an external driving force, while during the IEDP the oxygen partial pressure is fixed. To compare results of IEDP and ECR it is necessary to know the thermodynamic factor (γ), which represents the variation of the oxygen concentration in the sample (c_o) with temperature and oxygen partial pressure, pO_2 , in the surroundings (Equation 11). We used thermogravimetric analysis (TGA) to study this dependence.

$$\gamma = \frac{1}{2} \cdot \frac{\partial \ln(pO_2)}{\partial \ln(c_O)} \quad (\text{Eqn. 11}).$$

TGA was performed at different oxygen partial pressures in the temperature range 25 °C – 900 °C. At each pO₂, three TGA experiments were made to be sure that the heating and cooling profiles were identical. The final measurements at 2%, 20% and 75% of pO₂ were normalized to the initial weight and converted to oxygen content (*c_O*) vs. temperature. Absolute oxygen contents were determined by iodometric titration [19]. Oxygen self-diffusion coefficients were calculated in the temperature range 650-900°C using Eqn. 12.

$$D_O = D_{chem}/\gamma \quad (\text{Eqn. 12}),$$

where D_O is oxygen self-diffusion coefficient.

3. Results and Discussion

The lattice parameters of the synthesized compound were refined by the Rietveld method [20] using the structural model provided by Istomin *et al.* [14]. The unit cell parameters were in good agreement with the ones previously reported in the literature [14], *a* = 7.62389(1) Å and *c* = 15.32701(5) Å and the sample was confirmed to be a single phase.

The measured values for electrical conductivity are in good agreement with literature data [21] with the maximum value of 550 S/cm (Fig. 2). The increase in conductivity at lower temperature corresponds to thermal activation, while the decrease above 600 °C can be explained by formation of oxygen vacancies and the resulting decrease in the electron-hole concentration.

Electrical conductivity relaxation profiles were normalized and fitted to Equation 7. Typical normalized relative conductivity vs. time profiles are presented in Fig. 3. Good agreement between

the experimental data and the fits was observed at all temperatures and all oxygen partial pressure switches. Comparison of the profiles obtained during switches of oxygen partial pressure from 10% to 75% at different temperatures showed as expected significantly faster relaxation with increase of temperature (Fig. 4).

Values of the chemical oxygen diffusion and chemical surface exchange coefficients were obtained after the fitting of all profiles (Figure 5). Activation energies for D_{chem} and k_{chem} are 1.16 ± 0.01 eV and 0.76 ± 0.05 eV, respectively.

The values of chemical oxygen diffusion coefficient do not depend on the initial and final oxygen partial pressures and depend only on the temperature, in good agreement with the model of oxygen diffusion in the bulk material. Comparison of the pO_2 switches $20\% \rightarrow 10\%$ and $75\% \rightarrow 10\%$ shows that chemical surface exchange rates also do not depend on the initial oxygen partial pressure, but do depend on the final oxygen partial pressure (Fig. 5). The dependence of the chemical surface exchange rate on final oxygen partial pressure at different temperatures is presented in the Fig. 6 and follows a power law, $k_{chem} \propto [pO_2^{(2)}]^n$, where n was determined from the slopes of $\log(k_{chem})$ vs. $\log(pO_2^{(2)})$ and is in the range $0.56 - 0.62$.

The dependence of oxygen content (c_o) on temperature and oxygen partial pressure in the surroundings obtained by thermogravimetric analysis is presented in Fig. 7 at $pO_2 = 0.02$ atm, 0.20 atm and 0.75 atm. The profiles are in good agreement with the literature data [14] and show rapid decrease in weight with increasing temperature. Values of the thermodynamic factor calculated with Eqn. 11 at different temperatures change from 611 at 650°C to 177 at 900°C and are listed in Table 1, along with the values of oxygen self-diffusion calculated with Eqn. 12. The significant difference

in the thermodynamic factors measured at different oxygen partial pressures is a consequence of the non-linear oxygen atom release from the structure with increasing temperature.

Comparison of the oxygen self-diffusion in $\text{Sr}_3\text{YCo}_4\text{O}_{10.5}$ obtained by ECR/TGA with our previous results obtained by IEDP/SIMS and MD is presented in Fig. 8 [3, 6]. Very good agreement is observed between oxygen diffusion coefficients obtained in dense samples by ECR/TGA and IEDP/SIMS methods, while slightly higher values result from molecular dynamic simulations which can be explained by ideal conditions and some assumptions made in the simulation experiments [6].

The ECR/TGA approach of oxygen diffusion study provides the same values of oxygen self-diffusion as IEDP/SIMS experiments, but at the same provides additional information about chemical oxygen diffusion and chemical surface exchange along with dependence of oxygen content in the structure on temperature and oxygen partial pressure in the surroundings.

4. Conclusions

Values of chemical surface exchange and chemical oxygen diffusion coefficients in $\text{Sr}_3\text{YCo}_4\text{O}_{10.5}$ were obtained with electrical conductivity relaxation technique in the temperature range 650 °C – 900 °C. The thermodynamic factor calculated from the oxygen stoichiometry measure by thermogravimetric analysis, was used to determine values of oxygen self-diffusion coefficient. Results are in excellent agreement with the oxygen-tracer diffusion coefficients determined previously by isotope exchange depth profiling and molecular dynamic simulations. Activation energies for chemical oxygen diffusion and oxygen self-diffusion are 1.16 ± 0.01 eV and 1.56 ± 0.01 eV, respectively.

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Fig. 1. The sample of $\text{Sr}_3\text{YCo}_4\text{O}_{10.5}$ for ECR measurements with dimensions $t = 1.43$ mm, $w = 1.09$ mm and $l = 19.72$ mm.

Fig. 2. Electrical conductivity of $\text{Sr}_3\text{YCo}_4\text{O}_{10.5}$ in air.

Fig. 3. Relative electrical conductivity vs. time profile obtained during an ECR experiment at 850 °C with an oxygen partial pressure switch from 10% to 75% and the corresponding fit.

Fig. 4. Comparison of profiles of relative conductivity, $g(t)$, of $\text{Sr}_3\text{YCo}_4\text{O}_{10.5}$ vs. time obtained during ECR experiments at different temperatures and for switches of oxygen partial pressure from 10% to 75%.

Fig. 5. Arrhenius plot of the chemical oxygen diffusion and chemical surface exchange coefficients obtained for $\text{Sr}_3\text{YCo}_4\text{O}_{10.5}$ by ECR experiment.

Fig. 6. Dependence of chemical surface exchange rate for $\text{Sr}_3\text{YCo}_4\text{O}_{10.5}$ on final oxygen partial pressure during ECR switches.

Fig. 7. Oxygen content in $\text{Sr}_3\text{YCo}_4\text{O}_{10.5}$ dependence on oxygen partial pressure in the surroundings and temperature determined by TGA.

Fig. 8. Comparison of oxygen self-diffusion coefficients in $\text{Sr}_3\text{YCo}_4\text{O}_{10.5}$ determined by ECR (this work), IEDP/SIMS [3] and Molecular dynamics [6].

	650 °C	700 °C	750 °C	800 °C	850 °C	900 °C
γ	611 (± 34)	483 (± 31)	370 (± 30)	290 (± 22)	230 (± 23)	176 (± 18)
$\log(D_{chem})$	-6.54	-6.22	-5.92	-5.63	-5.35	-5.12
$\log(D_O)$	-9.32 (± 0.03)	-8.90 (± 0.03)	-8.48 (± 0.04)	-8.09 (± 0.04)	-7.72 (± 0.05)	-7.37 (± 0.05)

Table 1. Thermodynamic factor for $\text{Sr}_3\text{YCo}_4\text{O}_{10.5}$ determined from TGA profiles, and chemical oxygen diffusion and oxygen self-diffusion coefficients in the temperature range 650 °C – 900 °C.