Title:SIMULATION OF OXYGEN DIFFUSION PROCESS ON ELECTRICAL
CONDUCTIVITY RELAXATION

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Abstract

Finite element method (FEM) simulations was carried out for modeling the electrical conductivity relaxation (ECR) process of a mixed ionic electronic conductor upon abrupt change of oxygen partial pressure. Oxygen diffusion pathway was simulated considering enhanced surface exchange rate on the current and voltage terminals formed on the specimen. The results suggested that the vacancy diffusion coefficient, $D_{V, ECR}$, obtained from ECR method appears to be dependent on vacancy concentration, δ , even though the true D_V is constant. The effects of the following parameters were investigated; degree of catalytic effect, surface reaction rate constant and sample dimension. Change in the sample dimension in a realistic range did not effectively suppress the modification of diffusion paths, and the change of apparent chemical diffusion coefficient, $D_{chem, app}$, were inevitable when surface reaction rate constant, k_{chem} , and D_{chem} are in the same range. The results of the FEM simulation were confirmed by ECR experiments with catalytic active (Pt) and inactive (Au) electrodes.

1. Introduction

Mixed ionic electronic conductors (MIECs) are widely studied as a cathode material of intermediate temperature solid oxide fuel cells (IT-SOFCs). To understand the oxide ion diffusivity in MIEC oxides is important especially when it is a rate controlling factor. It is, however, difficult to evaluate oxide ion conductivity directly by conductivity measurement, because electronic hole conductivity is usually dominant in MIEC cathode materials. There are a couple of evaluation techniques for oxide ion diffusivity. Electrical conductivity relaxation (ECR) method is one of the most popular techniques for oxygen nonstoichiometric oxides.

In oxygen substoichiometric oxides, oxide ion diffuses by vacancy mechanism. The oxygen vacancy diffusion coefficient, D_V is theoretically independent of vacancy concentration as far as the concentration is sufficiently low. This phenomenon is widely observed for many oxides including perovskite-type [1-2]. Some researchers [3-5], however, reported the values of D_V of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ (LSCF) decrease with the decrease in oxygen partial pressure, $p(\text{O}_2)$, or the increase in oxygen nonstoichiometry, δ . In these reports [3-5], D_V was estimated from chemical diffusion coefficient, D_{chem} . Yashiro et al. [4] also reported the $p(\text{O}_2)$ -dependence of D_V , which was calculated from reported D_{chem} [6-7] and nonstoichiometry data [8]. In all these reports [3-7], D_{chem} was obtained by analyzing the relaxation process of the electrical conductivity [3-4, 6-7] or the oxygen nonstoichiometry [5] upon stepwise change of $p(\text{O}_2)$. In spite of difficulty in fitting the relaxation process by diffusion equation [9] and dependence of D_V on measurement technique [10], the δ -dependence of D_V cannot be explained.

In contrast, δ -dependence of D_V on $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF6428) measured by oxygen isotope

exchange method in our previous study [11] was much smaller than those estimated from D_{chem} [3-7]. In order to discuss the reason of the apparent δ -dependent D_V obtained by ECR technique, the oxide ion diffusion profile and the resulting electrical current flow in ECR measurements were simulated. Since catalytic effect of dispersed nm-sized platinum particles in porous $\text{La}(\text{Sr})\text{CoO}_3$ cathode was reported [12], a finite element method (FEM) was applied considering the catalytic effect of platinum electrodes in our previous paper [13]. The simulation results suggested that the catalytic effect of the platinum electrodes on the surface reaction is one of the causes of the apparent δ -dependent D_V due to the change of the diffusion path.

In this study, we have investigated the effects of parameters; degree of catalytic effect, surface reaction rate constant and sample dimension, on conductivity relaxation process in FEM simulation. Additionally, ECR experiments were carried out under a certain condition in order to confirm the simulation results.

2. Experimental

2.1. Method of Simulation of Conductivity Relaxation

MSC.Marc / Mentat 2012 software was used as a FEM application to simulate the oxygen diffusion in MIEC specimens during electrical conductivity relaxation process using the d. c. four-probe method. Due to the symmetry of the sample, quarter parts of the cross section surfaces of the models were simulated in two dimensions as shown in Fig. 1. That is, the diffusion from the top and bottom surfaces as well as the side surfaces is taken into account while the diffusion from the front and back surfaces are neglected in this calculation. The distance between two voltage terminals (L) was 5 mm. The width of the electrodes was 1 mm and the current electrodes include the edge faces. The electrical potentials on the vertical center lines were fixed and the constant currents were applied between the current electrodes and the vertical center lines. The local conductivities were determined to be proportional to the local concentrations of oxide ion, then, the entire conductivities were determined by the potentials at the voltage terminals and the constant currents. The number of time steps was chosen for relaxation process to have finished by 500th step. From the calculated conductivities in each step, simulated relaxation curve was obtained. Apparent chemical diffusion coefficient, $D_{\text{chem, app}}$, and apparent surface reaction rate constant, $k_{\text{chem, app}}$, were determined by analyzing the simulated relaxation curve. Simple and realistic value were chosen for the preset parameters of each simulation, the thickness, $2h$, the length, $2l$, of the models, chemical diffusion coefficient, $D_{\text{chem, set}}$, and surface reaction rate constant, $k_{\text{chem, set}}$, according to our previous study [11] and were listed in Table 1.

2.2. Experiment of Conductivity Relaxation

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2 Specimens for ECR measurement were prepared from commercial LSCF6428 powder (DOWA
3 Electronics Materials Co., Ltd.). Purity and crystal structures were analyzed by X-ray diffraction
4 (MAC Science Co., M18X) using Cu K α radiation. The powder was pressed isostatically at 120
5 MPa and sintered at 1523 K for 6 hours. This procedure gave uniform samples with density above
6 97 % of the theoretical value. The samples were cut into rectangular parallelepipeds, and all the
7 surfaces were polished with 1 μ m diamond compounds. Platinum paste (Tanaka precious metals,
8 TR7905) or gold paste (Tanaka precious metals, TR1530) was painted on the sample surface, and
9 then sintered at 1123 K to form current and voltage electrodes. Platinum or gold wires were wound
10 on each electrode as electrical leads. The properties of the samples for ECR measurement are shown
11 in Table 2.

12

13 Electrical conductivity was measured by d.c. four probe method using a current source (Advantest,
14 R6144) and a digital voltmeter (Keithley, 2000). The measurement was conducted in partial oxygen
15 pressure range of 10^{-3} - 10^{-1} bar at 873-1073 K. The conductivity, σ , was calculated by the following
16 equation

$$\sigma = \frac{I L}{V S} (1)$$

17 where I is the current through the specimen; V is the voltage between two voltage terminals; L is the
18 distance between two voltage terminals; S is the cross-section area of the specimen.

3. Results and Discussion

3.1. Simulation of Conductivity Relaxation

Fig. 2 shows distribution of relative oxide ion concentration simulated by FEM, when the MIEC oxide was 50% relaxed during ECR process with preset parameter shown in Table 1. The direction of oxide ion diffusion is normal to contours of oxide ion concentration. Assuming ideal ECR process, oxide ion should diffuse only along thickness (y) direction. Figs. 2 (c) and (e) show the dependence on sample dimension models with homogeneous k_{chem} . As the specimen becomes thicker (Fig. 2(c)), or as distance between current and voltage terminal becomes shorter (Fig. 2(e)), oxide ion diffuses not only along y -direction but along length (x) direction due to edge effect at the current terminal. Since the diffusion pathways through x direction are longer than y direction, the apparent D_{chem} should be smaller especially with short or thick samples like the model No. 2 or 4.

Fig. 2 (a) shows the dependence of diffusion path on catalytic effect. The diffusion paths are longer in the model with stronger catalytic effect. Fig. 2 (b) shows the results with different k/D ratio. The diffusion paths are longer in the case of smaller k/D ratio. Figs. 2 (d) and (f) show the dependence on the dimension with inhomogeneous k_{chem} . The difference of these diffusion paths seems to be a little. Consequently when ECR measurements are performed with catalytically active electrodes, the error of apparent D_{chem} is mainly affected by strength of catalytic effect and k/D ratio. Further quantitative analyses of D_{chem} will discuss in the following section.

3.2. Calculation of apparent D_{chem} and k_{chem} from the simulated profile

The one-dimensional solution of Fick's diffusion equation in a plane sheet with a boundary of constant atmospheric concentration including surface reaction effect given by the reference [14],

$$\frac{\sigma(t) - \sigma(0)}{\sigma(\infty) - \sigma(0)} = \frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{2L^2 \exp(-\beta_n^2 D_{\text{chem}} t / h^2)}{\beta_n^2 (\beta_n^2 + L^2 + L)} \quad (2)$$

where $\sigma(t)$ is electrical conductivity at time t , M_t is total amount of diffusing substance which has entered the sheet at time t , M_∞ is the corresponding quantity after infinite time, h is the height of models, β_n s are the positive roots of

$$\beta \tan \beta = L \quad (3)$$

and L is a dimensionless parameter.

$$L = hk_{\text{chem}} / D_{\text{chem}} \quad (4)$$

From the calculated entire conductivities in each step, the simulated relaxation curves were obtained. Apparent chemical diffusion coefficient, $D_{\text{chem, app}}$, and apparent surface reaction rate constant, $k_{\text{chem, app}}$, were determined by fitting the simulated conductivity relaxation data to Eq. 2 to simulated conductivity relaxation process using nonlinear least-square analysis. Since the relaxation curves with catalytically effected k_{chem} could not be fitted well by Eq. 2, only the data of latter half relaxation were used and starting times were treated as fitting variables.

3.3. Effect of Various Parameters

To evaluate the effect of the above mentioned parameters on chemical diffusion coefficients, ratio of $D_{\text{chem, app}} / D_{\text{chem, set}}$ was estimated under several conditions, where $D_{\text{chem, set}}$ and $k_{\text{chem, set}}$ are true chemical diffusion coefficient and surface reaction rate constant, respectively, under a certain condition. When $D_{\text{chem, app}} / D_{\text{chem, set}}$ is unity, oxide ion diffuses ideally in a specimen. Table 3

shows $D_{\text{chem, app}}/D_{\text{chem, set}}$ from simulated conductivity relaxation curves. In the case of homogeneous $k_{\text{chem, set}}$, $D_{\text{chem, app}}$ was almost same to the preset values except for the case with higher h/l ratio. On the other hand, for the model with inhomogeneous $k_{\text{chem, set}}$, when $k_{\text{chem, Pt, set}}/k_{\text{chem, set}}$ became larger or $k_{\text{chem, set}}/D_{\text{chem, set}}$ became smaller, calculated $k_{\text{chem, app}}$ became larger; and calculated $D_{\text{chem, app}}$ became smaller. In these models, as Fig. 2 shows, the diffusion paths are longer than those for the ideal case. This leads to smaller diffusion coefficients. Since k decreases with δ , $k_{\text{chem}}/D_{\text{chem}}$ dependence suggested that the analysis of ECR process ignoring catalytic effect on platinum electrodes is one of the causes of $p(\text{O}_2)$ -dependent and δ -dependent D_V . The dimension of a sample was of less relevance to δ -dependence of D_V compared to the catalytic effect. When the ECR experiment is carried out especially with small $k_{\text{chem}}/D_{\text{chem}}$ samples, it is concluded that electrodes having catalytic effect like Pt should not be used for accurate measurement of D_{chem} .

3.4. Experimental Results of Conductivity Relaxation

Fig. 3 (a) shows a typical experimental relaxation curves of electrical conductivity and $p(\text{O}_2)$. The flush time of the reactor could be ignored in these experiments. D_{chem} and k_{chem} were determined by fitting the two-dimensional equation which is made from Eq. 2[14,15] to ECR curves using nonlinear least-square analysis. As is the case with the simulations on the samples with Pt electrodes, only the data of latter half relaxations were used and starting times were treated as fitting variables. Fig. 3(b) shows typical electrical conductivity experimental relaxation curves of the $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ samples with Pt or Au electrodes. Comparing the data of first half relaxations, ones of the sample with Pt electrodes are more distant from the extended fitting curve. D_V were calculated from D_{chem} using following equation[4, 16].

$$D_V = -2D_{\text{chem}} \frac{\partial \ln \delta}{\partial \ln p(\text{O}_2)} [5]$$

1 where $\partial \ln p(\text{O}_2) / \partial \ln \delta$ is a thermodynamic factor [17]. Fig. 4 shows ECR experimental result of σ and D_V
 2 of the samples with Pt and Au electrodes. There is no significant difference between reduction and
 3 oxidation process. D_V of the samples with Pt electrodes were smaller than those of the samples with
 4 Au electrodes. They were smaller when δ is larger, too. These results are corresponding to the
 5 simulation results of $k_{\text{chem, Pt}}/k_{\text{chem}}$ ratio dependence and $k_{\text{chem}}/D_{\text{chem}}$ ratio dependence. In other words,
 6 it is possible that erroneous δ dependence of D_V is measured by ECR technique with the sample
 7 with Pt electrodes.

4. Conclusion

Finite element method (FEM) simulations was carried out, for modeling the electrical conductivity relaxation (ECR) process of a mixed ionic electronic conductor upon abrupt change of oxygen partial pressure. Oxygen diffusion pathway was simulated considering enhanced surface exchange rate on the current and voltage terminals formed on the specimen. The effects of the following parameters were investigated; degree of catalytic effect, surface reaction rate constant and sample dimension. The results suggested that the vacancy diffusion coefficient, $D_{V, ECR}$, obtained from ECR method appears to be dependent on vacancy concentration, δ , even though the true D_V is constant. Even if the sample dimension changed in realistic value, the changes of diffusion paths and the change of apparent chemical diffusion coefficient, $D_{chem, app}$, are inevitable. The results of the FEM simulation were confirmed by ECR experiments with catalytic active (Pt) and inactive (Au) electrodes.

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Figure(1)

Figure(2)

(a)

(b)

(c)

(d)

(e)

(f)

Figure(3)

(a)

(b)

Figure(4)

(a)

(b)