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Dielectric relaxation analysis for 8 mol% YSZ single crystal

S. KOMINE
Seimi Chemical Co., Ltd., 3-2-10, Chigasaki, Chigasaki-City, Kanagawa 253-8585, Japan
E-mail: sgkkomine@seimichemical.co.jp

F. MUNAKATA
Department of Environmental Engineering, Musashi Institute of Technology, Tamazutsumi, Setagaya-Ku, Tokyo 158-8557, Japan

In order to verify an effectiveness of a dielectric relaxation in the investigation of oxygen ionic conduction mechanism, dielectric and DC, AC measurements have been carried out for single crystalline 8 mol% YSZ. Total activation energies in the dielectric relaxation and the electrical conduction was almost same below T_c. Activation energies change at T_c. Disagreement of both energies above T_c have been improved by the modification of the dielectric relaxation analysis.

1. Introduction

Solid oxide fuel cells (SOFC) are of current interest as energy sources owing to their high thermal efficiency and environmentally friendly nature. However, SOFC systems, which operate at high temperature of about 1000°C due to the low ionic conductivity of electrolyte, include an open question in which inexpensive metal materials are unavailable. Therefore, lower operation temperature is absolutely necessary to make practicable. The most frequently used SOFC system employs cubic zirconia [1, 2] as an electrolyte but such system is operated around 800°C due to low ionic conductivity of electrolyte. Incidentally, Ishihara *et al.* reported that LSGM ($La_{1-x}Sr_xGa_{1-y}Mg_yO_3$) system [3, 4] involves a high potential as an electrolyte because of high ionic conductivity, and SOFC system with LSGM can operate at 200°C—lower temperature than that with cubic zirconia in recent years. This is one of the ideal examples that high ionic conductivity brings about high performance of SOFC system. New electrolyte is very important in development of SOFC system but it is very tough business nevertheless because of the oxygen ionic conduction's mechanism has never been clarified.

Even the simplest activation energy, which estimated with electrical conductivity, provides a lot of important information on the conduction mechanism from the viewpoint of oxygen-ionic diffusion. However, in the case of oxygen-ionic diffusion, which involves various thermal activation processes, since the simplest activation energy does not separate such processes, obtained information is insufficient in order to discuss the ionic conduction mechanism.

Iguchi *et al.* appreciated the activation energies by applying dielectric relaxation with dielectric loss factor and suggested existence of two thermal activation processes for LSG ($La_{0.8}Sr_{0.2}GaO_{3-\delta}$) [5]. This result means that dielectric relaxation is effectiveness for the clarification of the oxygen-ionic conduction mechanism, whereas estimated activation energies are a little larger than expected value from the electrical conductivity. Since, dielectric relaxation analysis is same as a general AC impedance analysis in the experimental method, boundary contribution may affect the measurement in the case of poly crystalline sample. Moreover, there are some unspecified factors for polycrystalline LSG: mixed ionic-electronic conduction, an-isotropic conduction. These make difficult to specify the cause of this slight difference. In this report, we treated single crystalline YSZ without aforesaid unspecified factors, and tried verifying suitability of dielectric relaxation for an analysis of oxygen-ionic conduction mechanism. In addition, the possibility in which the modification of a dielectric relaxation analysis brings about more adequate the activation energies is discussed.

2. Experimental details

Single crystalline 8 mol% YSZ (Dalian Danning Optoelectronics Technology Co., Ltd. in China) was selected as a standard sample of oxygen-ionic conductor. The XRD measurement indicates a phase of cubic, and the direction were also determined. The sample for the dc electrical conductivity measurement was a rectangular parallelepiped with 10 mm × 3 mm × 1 mm, and four-probe method was used with Pt paste as electrode. The direction of an electric field was the longest direction, which is perpendicular to [100] direction. The impedance and dielectric loss factor were obtained as functions of the temperature by the four-terminal pair ac impedance measurement method, using an Agilent 4192A Impedance Analyzer with a frequency of 40 Hz to 10 MHz. The samples were a rectangular with the surface area of 100 mm^2 and the thickness of 1 mm.

Both of the square faces were (100) plane and evaporated with gold for an electrode. These measurements were carried out in a cooling process of 500 to 1100 K.

3. Results and discussion

3.1. Electrical conductivity

An impedance spectrum at 603 K is shown in Fig. 1. Since, there is only one arc and the arc passes the origin on the complex plane, this sample is a single crystal without grain boundary component and this spectrum indicates the bulk resistance. According to an analysis of the impedance spectrum, the electrical conductivity σ_{AC} were obtained [6, 7]. Fig. 2 indicates Arrhenius plots of DC conductivity σ_{DC} and σ_{AC}. Same value in these conductivities also means that this sample is single crystal. DC electrical conductivity is isotropic because of independence of the direction of an electric field.

On the other hand, an electrical conductivity is in connection with an Equation 1.

$$\sigma = \frac{A_0}{T} \exp\left(-\frac{E_a}{k_B T}\right) \tag{1}$$

where k_B and T are Boltzman constant and an absolute temperature. A_0 and E_a denote a pre-exponential factor and an activation energy. Activation energies slightly change around $T_c = 910$ K, and E_a' at $T > T_c$ is smaller than E_a'' at $T < T_c$. The activation energies obtained from Equation 1 enumerate in Table I. T_c, E_a' and E_a'' of the single crystalline sample are almost same as previous report which is about bulk component of polycrystalline samples [8–10]. This agreement means that this sample is 8 mol% YSZ in the electrical conductivity, and the activation energy is independence of crystallographic direction for 8 mol% YSZ, because of a crystallographic direction is random in polycrystalline samples.

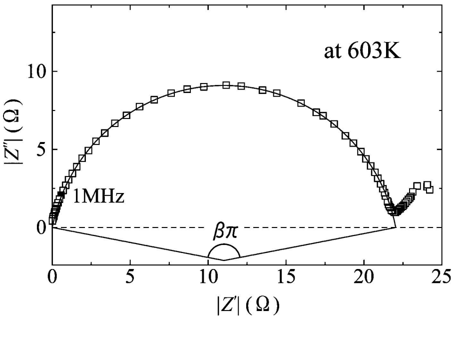

Figure 1 The impedance spectrum for 8 mol% YSZ at 603 K.

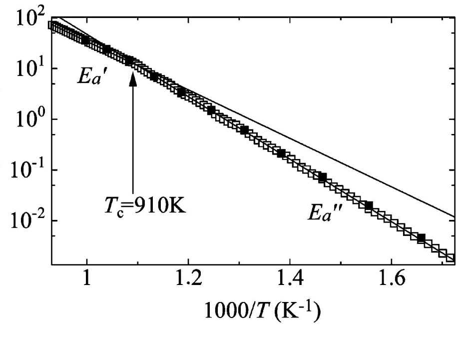

Figure 2 The Arrhenius plots of DC conductivity (null) and AC conductivity (solid) 8 mol% YSZ.

TABLE I Activation energies in an electrical conduction (E_a), a dielectric relaxation (E_M, $E_D^{1)}$) and a modified dielectric relaxation (E_M, $E_D^{2)}$)

	E_a	E_M	$E_D^{1)}$	$E_M + E_D^{1)}$	$E_D^{2)}$	$E_M + E_D^{2)}$
$T < T_c$	1.22 eV	0.94 eV	0.22 eV	1.16 eV	0.22 eV	1.16 eV
$T > T_c$	0.94 eV	0.94 eV	−eV	0.94 eV	∼ 0 eV	0.94 eV

3.2. Dielectric relaxation process and modification of the analysis

Fig. 3 denotes frequency dependencies of a dielectric loss tangent $\tan\delta$ at 603, 803 and 1003 K. A dielectric relaxation occurs and the loss tangent has the maximum $\tan\delta_{\max}$ at the resonance frequency $f_{\tan\delta}$ in measurement temperature range. Activation energy consists of E_D and E_M, where E_D is the dissociation energy of an oxygen vacancy from a cluster and E_M is the migration energy associated with a jump of an oxygen ion, which require ionic displacement around the saddle point in the diffusion path [5, 11]. E_D and E_M are related to $f_{\tan\delta}$ and $\tan\delta_{\max}$ like follow equations approximately [5, 12–14].

$$f_{\tan\delta} \propto \exp\left(-\frac{E_M}{k_B T}\right) \tag{2}$$

$$T \cdot \tan\delta_{\max} \propto \exp\left(-\frac{E_D}{k_B T}\right) \tag{3}$$

Fig. 4 plots $\log(f_{\tan\delta})$ and $\log(T \cdot \tan\delta_{\max})$ vs $1/T$. E_M is independence of temperature and then $E_M = 0.94$eV, but E_D changes at T_c. Below T_c, the relation between $f_{\tan\delta}$ and E_D satisfied with an Equation 3. On the other hand, $\tan\delta_{\max}$ deviates from the relation above T_c. This deviation observed in the case of LSG [5]. However, the

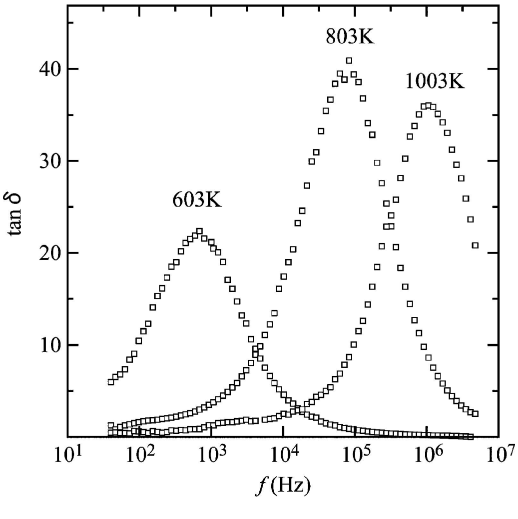

Figure 3 Dielectric loss tangent $\tan\delta$ vs applied frequency for 8 mol% YSZ at 603, 803 and 1003 K.

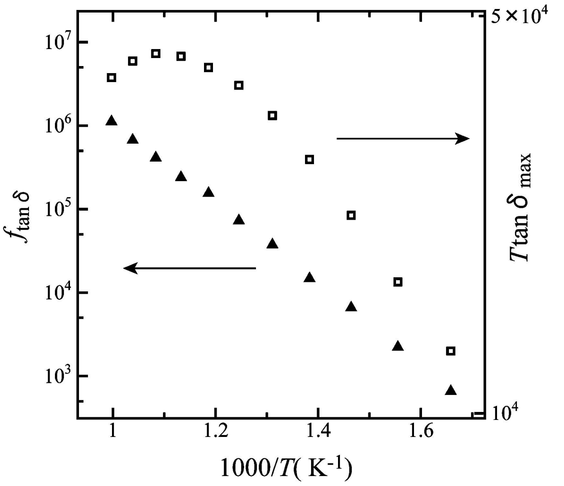

Figure 4 The Arrhenius relation between $\log(f_{\tan\delta})$ and $1/T$ on left axis, and $\log(T\cdot\tan\delta_{\max})$ and $1/T$ on right axis for 8 mol% YSZ.

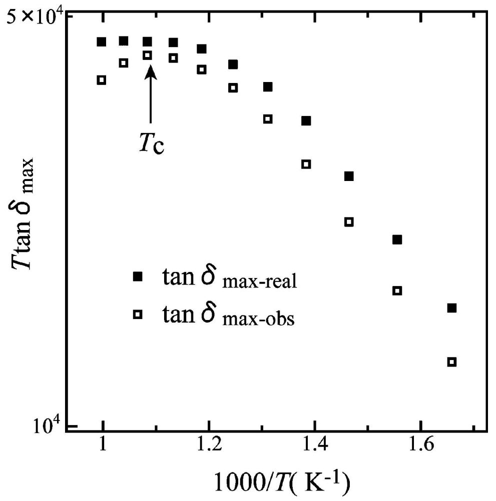

Figure 5 The Arrhenius relation between $\log(T\cdot\tan\delta_{\max-\text{real}})$ and $1/T$ as solid symbol, and $\log(T\cdot\tan\delta_{\max-\text{obs}})$ and $1/T$ as null symbol for 8 mol% YSZ.

sum of E_M and E_D is same as the activation energy E''_a, which is obtained from electrical conductivity, below T_c. This fact indicates that thermal activation process involves two processes, and E_M and E_D correspond to migration energy and dissociation energy; therefore, dielectric relaxation process reflects thermal activation process at low temperature region below T_c for 8 mol% YSZ.

3.3. Modification of the dielectric relaxation analysis

The impedance spectra at 603 K indicated in Fig. 1 is not perfect semi circle, that is, *Cole-Cole*'s circular arc not *Debye*'s one. In this case, the center of circular is in the region $|Z''| < 0$, and then β is less than 1. Here, the center of a circular makes $\beta\pi$ with the circular. β is evidently 0.87 at 603 K. β means a distribution of a relaxation time in the dielectric relaxation theory and the distribution become broad with reduction in β. It should be recognized that the distribution observed in an impedance spectrum also appears in the dielectric relaxation. On the other hand, a relative dielectric loss factor ϵ'' has the maximum as same as $\tan\delta$, and then the maximum $\epsilon''_{\max}$ is indicated as the follow equation.

$$\epsilon''_{\max} = \frac{1}{2}(\epsilon_{r0} - \epsilon_{r\infty})\tan\frac{\beta\pi}{4} \tag{4}$$

where ϵ_{r0} and $\epsilon_{r\infty}$ are the static and high-frequency dielectric constants. Furthermore, according to the approximation as $\tan\delta \propto \epsilon''_{\max}$, $\tan\delta_{\max}$ can be denoted as the follow equation.

$$\tan\delta_{\max} \propto \frac{1}{2}(\epsilon_{r0} - \epsilon_{r\infty})\tan\frac{\beta\pi}{4} \tag{5}$$

These equations mean that the maximum value of dielectric loss factors reduces when β increases. If β is independence of temperature, the real maximum value of dielectric loss tangent is defined as

$$\tan\delta_{\max-\text{real}} = \tan\delta_{\max-\text{obs}}/\tan\frac{\beta\pi}{4} \tag{6}$$

Here, $\tan\delta_{\max-\text{obs}}$ is observed $\tan\delta_{\max}$ and corresponds to the maximum of $\tan\delta$ when β is 1, e.g. Equation 5. β estimated by an impedance analysis and $\tan\delta_{\max-\text{obs}}$ obtained from dielectric relaxation lead to $\tan\delta_{\max-\text{real}}$. The temperature dependencies of $T\cdot\tan\delta_{\max-\text{real}}$ and $T\cdot\tan\delta_{\max-\text{obs}}$ obeyed Equation 3 is shown in Fig. 5. Both of them is almost same in the tendency below T_c, meanwhile the temperature dependency is large different above T_c. $T\cdot\tan\delta_{\max-\text{obs}}$ decreases but $T\cdot\tan\delta_{\max-\text{real}}$ does not change with an increase in temperature above T_c, altogether.

In generally, it is thought that association pairs of cation-oxygen vacancy [15–17] vanish above T_c in 8 mol% YSZ. Since, $T\cdot\tan\delta_{\max-\text{real}}$ corresponds to carrier concentration, $T\cdot\tan\delta_{\max-\text{real}}$ that is constant means saturation of carrier concentration. In contrast, $T\cdot\tan\delta_{\max-\text{obs}}$ that is decreasing with an increase in temperature shows a reduction in carrier concentration. In these two scenarios, which are carrier concentration not change and decrease, the former is more reasonable than the latter. Moreover, a thermal activation process above T_c is dominated by the migration of oxygen vacancy when $\tan\delta_{\max-\text{real}}$ is adopted, and then total activation energy of an electrical conduction is defined E_M. The relation between total activation energies obtained by a dielectric relaxation and an electrical conductivity is $E_M = E'_a = 0.94$ eV above T_c as shown in Table I. This result also suggests that a dielectric relaxation and this modification is adequate. However, the effect of β may be not so much for this sample. This is considered because oxygen ion transference number of almost 1 and the carrier is only one kind for YSZ. Contrary to YSZ, mixed conductor LSG include more two kinds of carrier. Difference carriers have quite difference relaxation time but difference carriers may affect each other in the point of the distribution of relaxation time. As a result of this effect, there is a possibility that the relaxation time scattering becomes large, and then the gap between total activation energy obtained from dielectric relaxation, and electrical conductivity might be estimated as a little large value.

4. Conclusion

Dielectric relaxation analysis was carried out for single crystalline 8 mol% YSZ in order to verify the suitability of the analysis, because, dielectric relaxation method is a very important technique for an elucidation of the oxygen ionic conduction mechanism of SOFC electrolytes. According to our experimental result of XRD measurement, DC conductivity and AC conductivity, a grain boundary effect and anisotropy was regarded due to single crystalline 8 mol% YSZ sample. In this dielectric relaxation analysis, it becomes clear that the oxygen ionic conduction is consists of two processes for 8 mol% YSZ as same as LSG in experiment, and it was confirmed that a dielectric relaxation is a very effective technique for an elucidation of an oxygen ionic conduction mechanism. Furthermore, the total activation energy $E_M + E_D$ obtained by a dielectric relaxation was good agreement with E''_a obtained from an electrical conductivity below T_c. For E_D, the estimation was insufficient in the usual analysis but this modified analysis suggested an appropriate interpretation, which carrier concentration saturates at T_c and then it is fixed above T_c. Total activation energy is E_M due to insignificant E_D. There is no example; a separation of thermal activation processes in entire temperature range for YSZ in experimentally, as we know. Moreover, this separation must make a large help in the clarification of ionic conduction mechanism in SOFC electrolyte.

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