Electrode Effects for Dielectric Properties of 8 mol% Y_2O_3 Stabilized ZrO_2

Hiroshi YAMAMURA, Yuhji YAGI, and Katsuyoshi KAKINUMA

Department of Material and Life Chemistry, Faculty of Engineering, Kanagawa University (3-27-1 Rokkakubashi, Kanagawa-ku, Yokohama 221-8686, Japan)

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The frequency dependences of dielectric constant (ϵ_r') for 8 mol% Y_2O_3 stabilized ZrO_2 (8YSZ) with two kinds of electrodes, Pt and $\text{La}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ (LCM), were successfully explained by the superposition of both electrolyte-electrode interfacial polarizations and Debye-type polarizations due to dopant-vacancy associates. The different behaviors in the frequency dependence of ϵ_r' for 8YSZ having the different electrodes were ascribed to the dopant-vacancy associates, ($\text{Y}_{\text{Zr}}'-\text{V}_{\text{O}}''$) and ($\text{Y}_{\text{Zr}}'-\text{V}_{\text{O}}''-\text{Y}_{\text{Zr}}'$), which were very large for 8YSZ with Pt electrode, but almost disappeared for 8YSZ with LCM electrode. The frequency dependences of the ac conductivity (σ_{ac}) were also explained by the relaxation phenomena of the dopant-vacancy associates, suggesting that the dispersion of σ_{ac} can not be ascribed to grain boundary effect of electrolyte.

Key Words : Oxide-Ion Conduction, Dielectric Constant, Oxygen Vacancy, Debye-Type Polarization, Defect Associate

1 Introduction

Y_2O_3 stabilized ZrO_2 , which is well known as an oxide-ion conductor, is a material with high potential applications, for example, as an electrolyte of solid oxide fuel cells (SOFCs). Therefore, many researchers have studied the electrical properties of Y_2O_3 stabilized ZrO_2 systems. The research group belonging the Commission of High Temperature and Solid State Chemistry of I.U.P.A.C. has summarized the electrical conductivities of 8 mol% Y_2O_3 stabilized ZrO_2 (8YSZ), which are measured by impedance spectroscopy in the several laboratories.¹⁾ Furthermore, it has been reported that the power generations in SOFCs are affected by the electrode materials because of the interfacial polarization and/or cathodic overpotential, which strongly depend on dissociation of oxygen molecules to oxide ions at the electrode.²⁾ Steele *et al.*³⁻⁴⁾ have reported that the dissociation activity of oxygen molecules to oxide ions can be expressed by the exchange current density. Takeda *et al.*⁵⁾ who investigated the reactivity at the interface between the electrode of perovskite-type oxides, $\text{La}_{1-x}\text{A}_x\text{MnO}_{3-\delta}$ ($\text{A} = \text{Ca}$ and Sr), and the electrolyte of 8YSZ have found that $\text{La}_{0.3}\text{Ca}_{0.7}\text{MnO}_{3-\delta}$ shows the highest activity for oxygen reduction. Furthermore, many papers concerning the electrode reaction of the stabilized zirconia have been reported in order to clarify the reaction mechanism at the oxide electrode-electrolyte interface in SOFCs.⁶⁻⁹⁾ However, the details of reaction mechanism of oxide ion at the electrode-electrolyte interface have not been clarified.

Recently, the present authors¹⁰⁻¹³⁾ have reported that the frequency dependence of ϵ_r' and ϵ_r'' for Sm-, Nd- or Yb-doped CeO_2 systems which are also typical oxide-ion conductors in air can be explained by the superposition of both electrolyte-electrode interfacial polarizations and

Debye-type polarizations due to dopant-vacancy associates. It has been also confirmed by the measurements of dielectric properties of 9 mol% Y_2O_3 stabilized ZrO_2 (9YSZ) single crystal that the large dispersion of ϵ_r' is not due to the grain boundary effect, but due to the Debye-type and interfacial polarizations.¹⁴⁾

In the present study, we try to apply the numerical analysis of complex dielectric constant to the sintered specimen of 8YSZ in order to clarify the differences in the interfacial phenomena between Pt and perovskite-type oxide $\text{La}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ (LCM) electrodes.

2 Experimental

8YSZ powder samples (Tosoh, Japan) were uniaxially molded at a pressure of 5 MPa and then subjected to rubber pressing at 200 MPa. Compacts thus obtained were sintered to disks for the electrical measurements by firing at 1873 K for 10 h in air. The relative density of the sintered specimen, which was estimated from the dimensions and weight, showed above 95% of the X-ray density. The powdered sample of the sintered specimen was characterized by X-ray diffraction (XRD) analysis (model: Multiflex, Rigaku, Japan) with monochromated Cu $\text{K}\alpha$ radiation. Lattice constant was determined from the XRD peaks by least squares method.

Complex dielectric constant (ϵ_r^*) was measured as a function of frequency by the ac two-probe method in the temperature range from 673 to 973 K in air. The impedance analyzer (4192a LF, Yokogawa-Hewlett-Packard, Japan) was used for the measurements of ϵ_r^* in the frequency range from 5 Hz to 13 MHz.

Two kinds of electrodes, platinum (Pt) and $\text{La}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ (LCM), were used for the dielectric measurements. LCM was prepared by firing the appropriate mixtures of La_2O_3 , CaCO_3 and MnO_2 at 1573 K in air.

These starting materials of 99.99% were purchased from the High Purity Chemicals, Japan. The LCM powders were mixed with paraffin to prepare the pastes for electrode, and then fired at 1473 K after painting the pastes to both sides of the 8YSZ disk. On the other hand, Pt electrodes were also attached to the 8YSZ disk by firing at 1223 K for 30 min in air.

The regression program in Kaleida Graph (Synergy Software) was used for the numerical calculation of the dielectric parameters.

3 Results and Discussion

It was confirmed by XRD experiments that 8YSZ was a single phase of the cubic fluorite-type structure with a lattice parameter, $a = 0.5139$ nm, which agreed well with the value (0.51407 nm) of the cubic YSZ after Toraya.¹⁵⁾ LCM was a single phase of orthorhombic perovskite-type structure with lattice parameters, $a = 0.5449$, $b = 0.7691$, $c = 0.5457$ nm, which agreed with the JCPDS data (46-0513).

It is supposed in the present study that the dielectric constant (ϵ_r') of 8YSZ can be composed of both Debye-

type polarization and electrolyte-electrode interfacial polarization which depends on the inverse of frequency. The detail explanations concerning the theoretical treatment of dielectric properties for oxide-ion conductors are given elsewhere.¹⁰⁻¹³⁾ Therefore, the apparent dielectric constant (ϵ_r') can be given by the following equation, assuming the presence of various Debye-type dipoles with multiple relaxation times:

$$\epsilon_r' = \epsilon_{r\infty} + \sum_i \frac{\epsilon_{roi} - \epsilon_{r\infty}}{1 + (\omega\tau_{oi})^2} + \frac{\epsilon_r(0)}{\omega^s} \quad (1)$$

where ω , ϵ_{roi} and τ_{oi} represent the angular frequency ($= 2\pi f$), the dielectric constant at the low-frequency limit due to the i -th Debye-type polarization and the i -th dipole relaxation time ($= 1/2\pi f_{oi}$), respectively. $\epsilon_{r\infty}$ represents the dielectric constant at the high-frequency limit. $\epsilon_r(0)$ is defined as a dielectric constant due to the interfacial polarization at the low-frequency limit. The exponent of frequency (s) is introduced to generalize the equation a function of frequency. The first two terms of the right side in eq. (1) represent the Debye-type dispersion.

Fig. 1 Frequency dependences of ϵ_r' for 8YSZ with Pt electrode (a) and with LCM (b) at temperatures of 673 (○), 723 (●), 773 (□), 823 (■), 873 (◇), 923 (◆), and 973 (△) K.

Fig. 2 Results of the numerical analysis of ϵ_r' for 8YSZ with Pt electrode (a) and with LCM electrode (b) at 773 K; observed ϵ_r' (○), calculated ϵ_r' (—), ϵ_{roi1} (·····), ϵ_{roi2} (---), ϵ_{roi3} (-·-·-), $\epsilon_r(0)$ (-----), and $\epsilon_{r\infty}$ (—).

The frequency dependences of ϵ_r' of 8YSZ with Pt- and LCM-electrode in the temperature range from 673 to 973 K are shown in Figs. 1, respectively. In the present study, we named Pt-8YSZ and LCM-8YSZ for the 8YSZ electrolytes with Pt- and LCM-electrodes, respectively. As seen in Figs. 1, the frequency dependence of ϵ_r' for two kinds of samples having the different electrodes showed noticeably different behaviors in both frequency and temperature dependences. The $\log \epsilon_r'$ values for Pt-8YSZ decreased stepwise with increasing frequency, while the values for LCM-8YSZ decreased almost linearly. The solid lines in Figs. 1 represent the estimated ϵ_r' values according to eq. (1), which agreed well with the observed ones with the correlation factors (R) of around 0.998. The frequency dependences of ϵ_r' for Pt-8YSZ were very similar with those for the single crystal of 9YSZ with Pt electrode, as shown in our previous study.¹⁴⁾ According to the case of the 9YSZ single crystal, three kinds of Debye-type dipoles observed for Pt-8YSZ were named Dipoles 1, 2 and 3 in order of increasing frequency, and their dielectric constants were denoted as ϵ_{r01} , ϵ_{r02} and ϵ_{r03} , respectively. Furthermore, Dipoles 1, 2 and 3 have been assigned to the polarizations of trimer associate ($Y_{Zr}'-V_O''-Y_{Zr}'$), dimer associate ($Y_{Zr}'-V_O''$) and long range migration of oxide ion, respectively.

Figures 2 represent typical examples of the curve fittings of ϵ_r' for Pt- and LCM-8YSZ at 773 K. The relaxation frequencies of Dipoles 1, 2 and 3 for Pt-8YSZ at 773 K were estimated to be $f_{01} = 49$, $f_{02} = 420$ and $f_{03} = 9.4 \times 10^5$ Hz, respectively. Above 773 K, only two types of dielectric constants, ϵ_{r01} and ϵ_{r02} , were observed and ϵ_{r03} disappeared. On the other hand, for LCM-8YSZ (Fig. 2 (b)), only two kinds of Debye-type dipoles were observed in the low- and high- frequency regions at 873 K and below. The Debye-type polarizations in the low- and high-frequency regions can be assigned to Dipoles 1 and 3 by comparing with the relaxation frequencies of ϵ_{r0} for Pt-8YSZ, respectively. Above 873 K, only Dipole 1 remained in LCM-8YSZ. The typical dielectric parameters estimated for Pt- and LCM-8YSZ are summarized in Tables 1 and 2, respectively. It should be noticed that although the magnitude of ϵ_{r03} was comparable between both samples, the small ϵ_{r01} value and the disappearance in ϵ_{r02} were observed in the case of LCM-8YSZ and that the $\epsilon_r(0)$ values of LCM-8YSZ were conversely larger than those of Pt-8YSZ in the fairly high- temperature region. The decrease in ϵ_{r01} of Dipole 1 and the disappearance of ϵ_{r02} of Dipole 2 in LCM-8YSZ may be ascribed to the decrease and disappearance in the dopant-vacancy associates, ($Y_{Zr}'-V_O''$) and ($Y_{Zr}'-V_O''-Y_{Zr}'$), due to the oxide-ion migration into the oxygen vacant sites of the associates of 8YSZ from the oxide-electrode, respectively.

It has been reported that the oxygen vacancy in the Y_2O_3 stabilized ZrO_2 coordinates preferentially to the Zr^{4+} site and that Y^{3+} can be rather stabilized by the octahedral oxygen-coordination.¹⁶⁻¹⁸⁾ As the ($Zr_{Zr}^{\times}-V_O''$) does not show the Debye-type dipole-moment because of the electrical neutrality of $Zr_{Zr}^{\times}$, the polarization observed in the present study must be assigned to the

Fig. 3 Arrhenius plots of $\log f_{01}$ (○), $\log f_{02}$ (□), and $\log f_{03}$ (●) for 8YSZ with Pt electrode (a) and with LCM electrode (b).

Debye-type ($Y_{Zr}'-V_O''$). Therefore, the smaller Debye-type dipoles in the 8YSZ systems than those in the Sm- or Nd-doped CeO_2 systems may originate from the preferential coordination of oxygen vacancy to the Zr^{4+} site.

Figures 3 represents Arrhenius plots of the relaxation frequencies which are estimated from the numerical analysis of ϵ_r' . Activation energies for the relaxation frequencies, f_{01} , f_{02} and f_{03} , for Dipoles 1, 2 and 3 in LCM-Pt were estimated to be 77, 78 and 118 kJ mol⁻¹, while f_{01} and f_{03} of LCM-8YSZ were estimated to be 71 and 90 kJ mol⁻¹, respectively. The activation energies for f_{03} agreed with the reported values for bulk conductivity of 8YSZ with Pt electrode, *i.e.*, 99 kJ mol⁻¹ after Abelard *et al.*¹⁾ and 108 kJ mol⁻¹ after Stafford *et al.*,¹⁹⁾ which correspond the long range migration of oxide ion. On the other hand, the activation energies for the relaxation frequencies of Dipoles 1 and 2 were lower by 30 kJ mol⁻¹ than that of the oxide-ion conduction (Dipole 3). This difference in the activation energy is close to the association enthalpy (35 kJ mol⁻¹) of ($Y_{Zr}'-V_O''$).²⁰⁻²¹⁾ The larger activation energy for oxide-ion migration than that for the dopant-vacancy associate means that the activation energy for oxide-ion migration includes the dissociation enthalpy of the asso-

Table 1 Dielectric parameters of Pt-8YSZ.

$T(K)$	673	723	773	823	873	923	973
$\epsilon_r(0)$	2.15×10^8	2.66×10^8	4.74×10^8	5.46×10^8	3.16×10^8	3.49×10^8	3.75×10^8
$\epsilon_{r\infty}$	165	151	149	170	235	450	920
s	1.61	1.40	1.28	1.16	1.08	1.04	1.02
ϵ_{r01}	–	1.95×10^7	2.49×10^7	3.40×10^7	2.88×10^7	2.09×10^7	1.32×10^7
ϵ_{r02}	7.03×10^5	4.75×10^5	1.13×10^6	3.69×10^6	3.50×10^6	4.99×10^6	6.01×10^6
ϵ_{r03}	165	121	69.1	–	–	–	–
$f_{01}(Hz)$	–	20.3	48.8	79.2	209	348	520
$f_{02}(Hz)$	28.4	142	421	643	1.68×10^3	2.66×10^3	4.14×10^3
$f_{03}(Hz)$	5.99×10^4	2.12×10^5	9.37×10^5	–	–	–	–
R	0.993	0.999	0.998	0.993	0.994	0.995	0.996

Table 2 Dielectric parameters in L CM-8YSZ.

$T(K)$	673	723	773	823	873	923	973
$\epsilon_r(0)$	2.92×10^6	1.29×10^8	5.07×10^8	1.43×10^9	3.30×10^9	5.79×10^9	1.10×10^{10}
$\epsilon_{r\infty}$	120	126	131	138	186	191	299
s	1.01	1.35	1.34	1.34	1.36	1.37	1.39
ϵ_{r01}	1.25×10^6	6.23×10^5	1.18×10^6	1.13×10^6	9.25×10^5	1.20×10^6	1.30×10^6
ϵ_{r03}	179	331	232	154	80.0	–	–
$f_{01}(Hz)$	13.3	41.2	54.3	130	305	393	611
$f_{03}(Hz)$	4.70×10^4	1.18×10^5	3.65×10^5	9.73×10^5	1.56×10^6	–	–
R	0.992	0.991	0.999	0.999	0.998	0.990	0.990

ciate in addition to the migration potential.

According to the assumption for ϵ_r' , it can be also supposed that the dielectric loss factor (ϵ_r'') contains a conduction term (σ/ω) in addition to the Debye-type dipole. Therefore, the apparent ϵ_r'' can be given by the following equation:

$$\epsilon_r'' = \sum \frac{(\epsilon_{roi} - \epsilon_{r\infty})\omega\tau_{oi}}{1 + (\omega\tau_{oi})^2} + \frac{\sigma_{ac}(0)}{\omega} \quad (2)$$

Furthermore, the ac electrical conductivity (σ_{ac}) can be defined by using eq. (2) as follows:

$$\sigma_{ac} = \omega\epsilon_0\epsilon_r'' = \omega\epsilon_0 \left[\sum \frac{(\epsilon_{roi} - \epsilon_{r\infty})\omega\tau_{oi}}{1 + (\omega\tau_{oi})^2} + \frac{\sigma_{ac}(0)}{\omega} \right] \quad (3)$$

where ϵ_0 and $\sigma_{ac}(0)$ represent the permittivity of free space and the loss current conductivity at the low-frequency limit, respectively. Figures 4 (a) and (b) represent the frequency dependences of $\log \sigma_{ac}$ in the temperature range from 673 to 973 K for Pt- and LCM-8YSZ, respectively. The large dispersions in $\log \sigma_{ac}$ of Pt-8YSZ were observed, while the $\log \sigma_{ac}$ dispersions of LCM-8YSZ became small. The solid lines in Figs. 4 represent the values estimated according to eq. (3), using the dielectric parameters obtained from eq. (2). The agreement of the observed values with the estimated ones suggests that the $\log \sigma_{ac}$ dispersion originates from the Debye-type dipoles. Pimenov *et al.*²²⁾ have reported

that the σ_{ac} dispersions for 4 mol% Y_2O_3 stabilized ZrO_2 are attributed to the grain-boundary relaxations. In the present study, however, the large difference in the σ_{ac} dispersions was observed between the 8YSZ samples having the different electrodes. Therefore, it can be suggested that the large dispersion observed for $\log \sigma_{ac}$ of Pt-8YSZ must originate from the Debye-type polarizations, not from the grain-boundary polarizations of the electrolyte.

Figures 5 represent schematic illustrations which show the electrode-electrolyte interface in Pt- and LCM-8YSZ. In the case of Pt electrode, the oxygen ionization-process for the Pt- ZrO_2 interface is limited to the portion around the physical triple-phase boundaries (TPB).²³⁾ Therefore, this process may produce the cathodic overpotential at the electrode-electrolyte interface, which may correspond to the large Debye-type polarization. On the other hand, the oxide ion of LCM electrode can occupy directly the oxygen-vacancy sites of the electrolyte, resulting in the decrease in the dopant-vacancy associate. Therefore, the Debye-type dipoles due to the dopant-vacancy associate of LCM-8YSZ may become to very smaller value than those of Pt-8YSZ. As a result, the cathodic overpotential of LCM-8YSZ decreased. This speculation may not be contradictory to the discussion that TPB is the main active site for oxygen reduction.⁸⁻⁹⁾ Ishihara *et al.*²⁴⁾ have also reported that the oxide cathode-material having high oxide-ion conductivity shows a superior cathodic performance in the SOFC. Their discussion may support our speculations.

Fig. 4 Frequency dependence of $\log \sigma_{ac}$ for 8YSZ with Pt electrode (a) and with LCM electrode (b) at temperatures of 673 (○), 723 (●), 773 (□), 823 (■), 873 (◇), 923 (◆), and 973 (△) K.

Fig. 5 Schematic illustrations of oxygen reaction at cathode/8YSZ interface; Pt-8YSZ (a) and LCM-8YSZ (b).

We can emphasize that the numerical analyses of frequency dependence of the dielectric constants could give important and useful information concerning the electrolyte-electrode interface of oxide-ion conductors.

4 Conclusions

Electrode effects for the frequency dependences of dielectric constants of 8 mol% Y_2O_3 stabilized ZrO_2 (8YSZ) were investigated. The conclusions can be summarized as follows:

(1) The frequency dependences of dielectric constant (ϵ_r') for Pt- and LCM-8YSZ were successfully explained by the superposition of both electrolyte-electrode interfacial polarizations and Debye-type ones.

(2) The two kinds of dopant-vacancy associates in Pt-8YSZ, dimer ($Y_{Zr}'-V_{O}''$) or trimer ($Y_{Zr}'-V_{O}''-Y_{Zr}'$), disappeared or decreased in LCM-8YSZ by incorporating oxide ion into oxygen vacant sites of the electrolyte from the oxide electrode, respectively.

(3) The activation energy for oxide-ion conduction was estimated to be about 110 J mole⁻¹, which were nearly equal to the reference data, while that for the associates was estimated to be about 80 kJ mole⁻¹.

(4) It was clarified that the dispersion of σ_{ac} was also ascribed to the dopant-vacancy associates.

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