Relationship between Oxide-ion Conductivity and Dielectric Relaxation in 20 atom% Nd-Doped CeO$_2$

Hiroshi YAMAMURA, Saori TAKEDA, and Katsuyoshi KAKINUMA

Department of Material and Life Chemistry, Faculty of Engineering, Kanagawa University (2-27-1 Rokkakubashi, Kanagawa-ku, Yokohama 221-8686, Japan)

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The relationship between electrical conductivity and dielectric relaxation was investigated for 20 atom % Nd doped CeO$_2$ (Ce$_{0.8}$Nd$_{0.2}$O$_{2.0}$), which is a typical oxide-ion conductor. Computer simulation clarified that the anomaly large dielectric constant ($\varepsilon_r'$) originated from the superimposition of both Debye-type polarization and interfacial polarization between electrolyte and electrode. Two kinds of the Debye-type relaxation appeared equal and above 773 K, which were ascribed to defect associates, (Nd$_{c^+}^+$-V$_{0^+}^-$) and (Nd$_{c^+}^+$-V$_{0^+}^-$-Nd$_{c^+}^+$). The frequency dependence of ac conductivity ($\sigma_{ac}$) was successfully explained by analyzing the dielectric loss factor ($\varepsilon_r''$). The $\sigma_{ac}$ values in high temperature and high frequency regions agreed with dc conductivity ($\sigma_{dc}$). The activation energy for $\sigma_{dc}$ agreed with that for high frequency Debye-type polarization.

**Key Words**: Oxide-ion Conductivity, Dielectric Constant, Oxygen Vacancy, Defect Associate

1 Introduction

Oxide-ion conductors play an important role in oxygen sensors, oxygen pumps and solid oxide fuel cells (SOFCs) etc. Among many oxide-ion conductors, all-valent cation-doped CeO$_2$ has been widely studied from various viewpoints of such as electrochemistry, crystallography and solid-state chemistry in recent years. Inaba and Tagawa$^{1}$ have summarized many papers concerning the ceria based solid electrolytes. Eguchi et al.$^{2,3}$ reported that the oxide-ion conductivity of Sm- or Gd-doped ceria showed the highest conductivity in the case of 20 atom % rare-earth-doped CeO$_2$ because of the close ionic radii of Sm$^{3+}$ and Gd$^{3+}$ to Ce$^{4+}$.

In order to clarify dynamic characteristics of ion conductors, several researchers have applied ac conductivity measurements to them. It is well known that the ac conductivity ($\sigma_{ac}$) of many cationic conductors obeys a following relation in usual frequency range, $f$ = 1 Hz to 1 MHz:

$$\sigma_{ac} = \sigma(0) + \sigma(\omega)$$ (1)

where $\sigma(0)$ is the extrapolated $\sigma_{ac}$ to zero frequency, which corresponds to the dc conductivity ($\sigma_{dc}$) and $\sigma(\omega)$ is conductivity dispersion ($\omega = 2\pi f$).$^{4}$ This relation is known as Universe Dielectric Response (UDR)$^{5}$ and can be applied to many cationic conductors of crystal and glasses.$^{6-9}$ However, there has been only a few reports concerning the conductivity dispersion of oxide-ion conductors. Henn et al.$^{10}$ reported that $\sigma_{dc}$ and $\sigma(\omega)$ of a single crystal Y-doped ZrO$_2$ obeyed Equation (1). On the other hand, Pimenov et al.$^{11}$ observed a strong dispersion of $\sigma_{ac}$ at relatively high temperatures for the sintered specimens of Y-doped ZrO$_2$ and they have discussed that the dispersion of $\sigma_{ac}$ in intermediate frequency region was ascribed to an effect of grain boundaries. The present authors have investigated the relationship between $\sigma_{dc}$ and $\sigma_{ac}$ for the samples having a pyrochlore-type composition, and found that the $\sigma_{dc}$ value agreed with the $\sigma_{ac}$ one obtained from high frequency plateau because of space charge polarization.$^{12}$ This fact means that the UDR theory could not always be applied to oxide-ion conductors.

On the other hand, it is well known that when CeO$_2$ was doped with Nd$_{0.3}$, oxygen vacancy could be introduced into the oxygen sublattice sites, as shown in a following defect reaction with Kröger-Vink notation,

$$\text{CeO}_2 \xrightarrow{\text{Nd}_{0.3}} 2\text{Nd}_{c^+}^+ + \text{V}_{0^+}^- + 3\text{O}_0^\ast.$$ (2)

However, the oxygen vacancy introduced by doping of allivalent cation is not necessarily free, but may be bound to the doped cations, producing a defect associate pair (Nd$_{c^+}^+$-V$_{0^+}^-$) due to coulomb interaction. The defect associate can be recognized to behave as an electric dipole, which would contribute on dielectric constant. Sarkar and Nicholson$^{13,14}$ studied the electric field relaxation for the CeO$_2$-Ln$_2$O$_3$ (Ln = Y, La) systems in a relatively low temperature range and reported that two relaxation processes observed in the lightly Ln-doped CeO$_2$ were due to a long range migration of free oxygen vacancies and to an orientation relaxation of the charged associated defects (Ln$_{c^+}^+$-V$_{0^+}^-$). These studies concerning dielectric properties of the oxide-ion conductors have been often carried out using electric modulus $M^\ast (1/c^\ast)$ in order to avoid overlap with low frequency dielectric constant. Wang and Nowick$^{15}$ have also found two relaxation peaks in the study of the dielectric relaxation of Y-doped CeO$_2$ using Thermally Stimulated Depolarization
Current (TSDC) method, which were ascribed to the associated defects (low temperature range) and the long range vacancy migration (high temperature range).

Moreover, most of the studies concerning the relationship between oxide-ion conduction and dielectric properties have been carried out in relatively low temperature range. The dynamic properties of oxide-ion conductors in the fairly high temperature range have not been reported in detail so far in spite of the important characteristics for applications. Recently, the present authors have reported that the frequency dependence of \( \varepsilon_r \) and \( \varepsilon'_r \) in the Sm-doped CeO\(_2\) system could be explained by the superimposition of electrolyte-electrode interfacial polarization and Debye-type polarization due to dopant-vacancy associate. In the present study, 20 atom\% Nd-doped CeO\(_2\) which showed the highest conductivity among the Nd-doped CeO\(_2\) system was investigated from the viewpoints of both dielectric properties and dc- and ac-conduction in the temperature range from 573 to 1073 K.

2 Theoretical Approach for Dielectric Properties

In the present study, it is assumed that the oxide-ion conductor behaves like a capacitor which can be described as parallel circuit model having capacitance (C) and resistance (R). Therefore, dc currents \( I \) can be separated into a charging current \( (j\omega e_r'C/C) \) and a loss current \( (\omega e_r''C/C) \), as shown by a following equation.

\[
I = (j\omega e_r' + \omega e_r'') C/V,
\]

(3)

where \( \omega \), \( e_r' \), \( e_r'' \), and \( C \) denote the angular frequency \( (= 2\pi f) \), the dielectric constant (relative permittivity), the dielectric loss factor, and the capacitance in vacuum, respectively. Using the relation of \( C_r = \varepsilon_r A/d \) \( (\varepsilon_r: \) permittivity in vacuum, \( A: \) area of electrode and \( d: \) distance between electrodes), the current density \( J \) can be related to the complex admittance \( (Y^*) \) as follows.

\[
J = (j\omega e_r' + \omega e_r'') E = (ja\sigma' + \sigma') E = Y^* E.
\]

(4)

Therefore, a following relation can be obtained,

\[
\sigma' = \omega e_r'' \quad \text{and} \quad \sigma'' = \omega e_r',
\]

(5)

where \( \sigma' \) is the loss current conductivity (conductance), which was named as conductivity \( (\sigma_{\text{dc}}) \) hereafter, and \( \sigma'' \) is the conductivity due to charging current (susceptance).

On the other hand, it was supposed that \( e_r' \) of oxide-ion conductors was composed of both Debye-type polarization and electrolyte-electrode interfacial polarization which depends on the inverse of frequency. Therefore, the apparent dielectric constant \( (\varepsilon_r') \) can be given as a following equation, assuming the presence of various dipoles with multiple relaxation times.

\[
\varepsilon_r' = \varepsilon_r'' + \sum \frac{\varepsilon_{\text{dc}}}{1 + (\omega\tau)^2} + \frac{\varepsilon(0)}{\omega^2},
\]

(6)

where \( \varepsilon_{\text{dc}} \) and \( \tau \) represent the dielectric constant at low frequency limit due to the \( i \)-th Debye-type polarization and the \( i \)-th dipole relaxation time, respectively. \( \varepsilon(0) \) represents the dielectric constant at high frequency limit. \( \varepsilon(0) \) is defined as the dielectric constant due to the interfacial polarization at low frequency limit, which corresponds to the susceptibility \( (\varepsilon'' = \varepsilon'/\omega) \) in Eq. (5). Frequency exponent \( (\nu) \) was introduced to generalize a function of frequency. The first two terms of the right side in Eq. (6) represent the Debye-type dispersion, where \( \varepsilon_{\text{dc}} \) in the second term was used in place of \( \varepsilon(\omega) \) in the usual Debye's equation, because \( \varepsilon_{\text{dc}} > \varepsilon(\omega) \) in the present study. Although the physical meaning of \( \nu \) has not been clarified, it may have a close relation to the charging mechanism of oxide ion into electrode.

According to the assumption for \( \varepsilon_r'' \), it was supposed that \( \varepsilon_r'' \) was composed of a contribution of the conduction term \( (\sigma/\omega\varepsilon_r) \) in addition to the Debye-type dipole. Therefore, the apparent \( \varepsilon_r'' \) can be given by a following equation,

\[
\varepsilon_r'' = \sum \frac{\varepsilon_{\text{dc}}}{1 + (\omega\tau)^2} + \frac{\sigma}{\omega\varepsilon_r},
\]

where the first term of the right side means the multiple Debye-type peaks and \( \sigma \) represents the loss current conductivity at low frequency limit. Equation (7) also suggests that the subtraction of \( \sigma/\omega\varepsilon_r \) from \( \varepsilon_r'' \) value will give Debye-type relaxation peaks. The dielectric parameters in Eq. (6) and (7) were estimated by numerical analysis for curve fitting using computer.

3 Experimental

Powder samples of 20 atom\% Nd-doped CeO\(_2\) (Ce\(_{0.80}\)Nd\(_{0.20}\)O\(_2\)) were synthesized by a solid-state reaction, using CeO\(_2\) (99.9\%, High Purity Chemicals Co.), Nd\(_2\)O\(_3\) (99.9\%, Furushichi Chemicals Co.) as starting materials. The weighed starting reagents were wet ball-milled for 16 h, using a milling pot made of synthetic resin and resin-coated balls, and ethanol as the dispersion reagent. The dried powder mixtures were calcined at 1273 K for 5 h in air. After sieving under 53 \( \mu \)m in mesh size, the powder samples were molded uniaxially under the pressure of 5 MPA and then subjected to rubber press under the pressure of 200 MPA. The powder compacts thus obtained were sintered at 1873 K for 10 h in air. Relative densities of the sintered specimens, which were estimated from the geometrical dimensions and weight, were 92.4\%, of which value may be enough to investigate the electrical and dielectric properties.

Powdered samples were characterized by means of X-ray diffraction (XRD) (Multi Flex, Rigaku Co.) with monochromated CuK\( \alpha \) radiation. The lattice constant was determined from the XRD peaks by a least square method, using Si powder as an external standard. Microstructures of the sintered specimens were observed by SEM (JSM-5200), after thermal etching at 1873 K for 1 hr in air.

Dc electrical conductivity \( (\sigma_{\text{dc}}) \) of the sintered specimens was measured by a dc four-probe method in the
temperature range of 873 to 1273 K in air. The geometrical dimensions of the sintered bar for the dc conductivity measurements were $4 \times 4$ and $\sim 30$ mm length.

Dielectric parameters were obtained as a function of frequency by an ac two-probe method in the temperature range from 573 to 1073 K in air. An impedance analyzer (4192A LF, Yokogawa-Hewlett-Packard Ltd., Japan) was used for these measurements in the frequency range of 5 Hz to 13 MHz. The dimension of the sintered disk for the ac conductivity measurements was 10 mm in diameter and 2 mm in thickness. For the all measurements, platinum electrode was attached to both sides of the specimen by firing at 1223 K for 30 min in air.

4 Results and Discussion

It was confirmed by XRD experiments that Ce$_{0.8}$Nd$_{0.2}$O$_2$ was a single phase of cubic fluorite-type structure with lattice parameter, $a = (0.5445 \pm 0.0003)$ nm, which was larger than that ($a = 0.5411$ nm)$^{10}$ of CeO$_2$ because of the larger ionic radius of Nd$^{3+}$ (0.1109 nm) than that of Ce$^{4+}$ (0.097 nm). The grain size of sintered specimens having relative density of 92.4% was estimated to be $4 \sim 5$ $\mu$m by SEM observation.

Figure 1 shows frequency dependence of $\varepsilon_r'$ for various temperatures, where the data of non-doped CeO$_2$ at 973 K were also shown as reference. The $\varepsilon_r'$ values, which showed a step-like frequency dependence in intermediate frequency region, reached anomalously large values specially in low frequency range, e.g. the $\varepsilon_r'$ value at 100 Hz reached to $10^3 \sim 10^4$ above 873 K. Pimenov et al.$^{11}$ have also reported such a large $\varepsilon_r'$ in the ZrO$_2$-Y$_2$O$_3$ system. Sarkar and Nicholson$^{10}$ suggested that the large $\varepsilon_r'$ values at lower frequencies were due to an electrolyte-electrode interfacial polarization process. On the other hand, the frequency dependence of log scale $\varepsilon_r'$ for the non-doped CeO$_2$ decreased linearly with increasing frequency.

The present authors$^{17-20}$ have successfully explained the frequency dependence of $\varepsilon_r'$ in the Sm-doped CeO$_2$ system, supposing that $\varepsilon_r'$ was composed of both the interfacial polarization and the Debye-type polarization due to dopant-vacancy associates. As shown in Fig. 1, the frequency dependence of $\varepsilon_r'$ for the Nd-doped CeO$_2$ seems also to be similar with that for the Sm-doped systems. Therefore, it was tried to estimate the dielectric parameters by the numerical calculation on the basis of the assumption which was applied to the Sm-doped system.

Figure 2 typically shows the result of computer simulation for the observed value of $\varepsilon_r'$ at 873 K, where two relaxation frequencies were observed, while only one relaxation frequency was observed below 673 K. The solid line in Fig. 2a represents the calculated values, which agreed well with the observed ones. As seen in Fig. 2b, the dotted and broken lines represent two components of the dielectric constant due to the Debye-type polarization having different relaxation-times, which were named as “Debye peak 1” for the lower relaxation frequency and “Debye peak 2” for the higher one. The one-dotted line represents the $\varepsilon_r(0)/f^\alpha$ component. Therefore, the step-like frequency dependence of $\varepsilon_r'$

![Fig. 1](image1.png)

**Fig. 1** $\varepsilon_r'$ of Ce$_{0.8}$Nd$_{0.2}$O$_2$ at various temperatures and CeO$_2$ at 973 K as a function of frequency.

![Fig. 2](image2.png)

**Fig. 2** The result of computer simulation of the frequency dependence of $\varepsilon_r'$ at 873 K.  
a) Observed (○) and estimated (----) $\varepsilon_r'$, b) Components of the dielectric parameters, $\varepsilon_r(0)/f^\alpha$ (-----), Debye peak 1 (----), and Debye peak 2 (-----).
could be ascribed to the Debye-type polarizations. The various parameters for the various temperatures obtained by the computer simulation are summarized in Table 1. 

\( \varepsilon(0) \) increased with increasing temperature in the low temperature region, and then became almost constant above 873 K (Table 1). In the numerical calculations, the correlation coefficients (R) were around 0.99 for the all runs. As \( \varepsilon(0) \) reflects a degree of oxide-ion accumulation at electrolyte-electrode interface, the saturation of \( \varepsilon(0) \) in the high temperature region may be ascribed to consumption of oxide ion due to an electrode reaction. The \( \varepsilon_{\text{rel}} \) and \( \varepsilon_{\text{rot}} \) values which can be ascribed to the Debye-type polarization kept almost constant or slightly increased until given temperatures, and then decreased with increasing temperature. The \( \varepsilon_\infty \) values also kept constant until 773 K and then increased with increasing temperature. The frequency exponent (s) was around unity in the whole temperature ranges.

Figure 3 shows log \( \sigma_{\text{ac}} \) as a function of \( f \) for the various temperatures. The \( \log \sigma_{\text{ac}} \) values increased with increasing frequency, and then two plateaus appeared at given high and low frequency regions. In order to understand the frequency dependence of \( \sigma_{\text{ac}} \), the numerical simulation was tried by using a following equation obtained by combination of Eq. (5) with Eq. (7),

\[
\sigma_{\text{ac}} = \sigma_0 \omega^{s'} = \omega \left[ \frac{\sum \varepsilon_{\text{rot}}(s) \tau_{\text{rel}}}{(\omega \tau_{\text{rel}})^2} + \frac{\sigma_{\text{dc}}}{\omega \tau_{\text{rot}}} \right].
\]

The results of the simulation for the frequency dependence of \( \sigma_{\text{ac}} \) were also shown in Fig. 3. The dielectric parameters of \( \varepsilon_\infty^{s'} \) were first estimated by the computer simulation using Eq. (7), and then \( \sigma_{\text{dc}} \) was calculated by the use of Eq. (8). As seen in Fig. 3, the calculated \( \sigma_{\text{ac}} \) values agreed with the observed values. Therefore, it can be clearly seen that the large dispersion of \( \sigma_{\text{ac}} \) in the intermediate frequency originated from the relaxation of the Debye-type dipoles. The \( \sigma_{\text{ac}} \) values showed plateaus at high frequency region, where it agreed with the \( \sigma_{\text{dc}} \) values. The large dispersion of \( \sigma_{\text{ac}} \) in the relatively low temperatures can be ascribed to the large \( \varepsilon_{\text{rel}} \) and \( \varepsilon_{\text{rot}} \) which decreased above 873 K, as seen in Table 1. On the other hand, it has been frequently reported that the decrease in \( \sigma_{\text{ac}} \) of oxide-ion conductors in the low frequency range was due to grain-boundary contribution on the basis of impedance spectra without any experimental evidence.\(^{13-14}\) However, this explanation would not be necessarily appropriate as the present study showed.

Figure 4 also shows Arrhenius plots of two kinds of relaxation frequencies named as \( f_{\text{rel}} \) (\( \varepsilon_\infty^{s'} \)) and \( f_{\text{rot}} \) (\( \varepsilon_\infty^{s'} \)).

![](image1.png) **Fig. 3** Frequency dependence of the observed (mark) and calculated (solid line) \( \sigma_{\text{ac}} \).

![](image2.png) **Fig. 4** Arrhenius plots of \( \sigma_{\text{ac}}, f_{\text{rel}}, \) and \( f_{\text{rot}} \). Numbers in the figure represent the activation energies.
where \( f_1 = 1/2\tau_0 \). The estimated activation energy of \( f_1 (\varepsilon'_s) \) for the lower frequency region was 85 kJ mol\(^{-1}\), and that of \( f_2 (\varepsilon'_s) \) for the higher one was 63 kJ mol\(^{-1}\). Furthermore, Arrhenius plots of the dc electrical conductivity (\( \sigma_{\text{dc}} \)) is also shown in Fig. 4. The activation energy for \( \sigma_{\text{dc}} \) was estimated to be 69 kJ mol\(^{-1}\), resulting in agreement with the value estimated from \( f_2 (\varepsilon'_s) \), suggesting their thermal activation processes are similar with each other.

The computer simulation of the frequency dependence of \( \varepsilon'_s \) revealed the presence of two kinds of Debye-type relaxation process, one of which may occur due to the dipole moment of defect associates such as (Nd\(_{\text{Ce}}\)\(^{3+}\)-V\(_{\text{O}}\))\(^{-} \) in the high frequency range. The another relaxation process observed in the low frequency range above 673 K may be ascribed to such an associate type as a neutral trimer of (Nd\(_{\text{Ce}}\)\(^{3+}\)-V\(_{\text{O}}\)\(^{-}\)-Nd\(_{\text{Ce}}\))\(^{-} \), on the basis of an assumption that the relaxation of the trimer associate will appear in the lower frequency region than that of the dimer. The neutral trimer accompanying the large \( \varepsilon'_s \) values is not a linear, but a bended associate, because the linear trimer will not show any effective dipole moment. Figure 5 shows schematic drawing of the dimer and the trimer in the fluorite-type structure. As seen in Fig. 4, the large activation energy of the trimer associate (85 kJ mol\(^{-1}\)) may be ascribed to the larger migration energy than that of the dimer. This speculation agreed with the discussion after Gong et al.,\(^{29}\) who have reported in the study of \( \text{Y}_2\text{O}_3\)-doped \( \text{ZrO}_2 \) that the activation energy of the trimer defect associate was larger than that of the dimer.

Therefore, when temperature increased, the dielectric constant decreased and the conductivity increased at the same time. The lowering of conductivity in the lower temperature and the lower frequency may be ascribed to occurrence of the mobile dimer associates, which do not contribute to the oxide-ion conductivity, but do to the dipole moment. It should be noted that the frequency region showing the conduction dispersion almost agreed with the Debye-type relaxation frequencies. On the other hand, in the fairly high temperatures, most of (Nd\(_{\text{Ce}}\)\(^{3+}\)-V\(_{\text{O}}\))\(^{-} \) will dissociate to free vacancy (V\(_{\text{O}}\))\(^{-} \) which contributes the oxide-ion conduction, resulting in the agreement of \( \sigma_{\text{ac}} \) and \( \sigma_{\text{dc}} \).

The \( \sigma_{\text{dc}} \) of 20 atom \% Nd-doped \( \text{CeO}_2 \) was slightly lower than that of 20 atom \% Sm-doped \( \text{CeO}_2 \). It was found in the present dielectric analyses that the Debye-type polarizations of the Nd-doped \( \text{CeO}_2 \) were smaller than those of Sm-doped \( \text{CeO}_2 \), while the \( \varepsilon'_s \) values were larger than those of the Sm-doped one.

5 Conclusion

The relationship between electrical conductivity and dielectric relaxation was investigated for 20 atom \% Nd doped \( \text{CeO}_2 \), which is a typical oxide-ion conductor. It was found that the dielectric constant (\( \varepsilon'_s \)) which showed anomalously large values of \( 10^7 \sim 10^8 \) at low frequencies and high temperatures was composed from two kinds of Debye-type polarization and interfacial polarization due to accumulation of oxide ion between electrolyte and electrode. The frequency dependence of ac conductivity (\( \sigma_{\text{ac}} \)) was successfully explained by analyzing the dielectric loss factor (\( \varepsilon''_s \)). The \( \sigma_{\text{ac}} \) values at high temperature and high frequency agreed with the \( \sigma_{\text{dc}} \) values. The activation energy for \( \sigma_{\text{ac}} \) agreed with that for the high frequency Debye-type polarization, suggesting their thermal activation processes are similar with each other.

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