ELECTRICAL AND IONIC CONDUCTIVITY OF Gd-DOPED CERIA

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ABSTRACT

Electrical Conductivity of GdₓCe₁₋ₓO₂₋ₓ₋₄₋₄₋₄ (y=0.1,0.2), as a function of temperature and oxygen partial pressure, was measured with a complex impedance method. It is shown that the increase of electrical conductivity with reducing oxygen partial pressure can be described well by a model that assumes constant mobility of both oxygen vacancy and electron, based on ideal solution model of nonstoichiometry of Gd-doped ceria. Ionic conductivity is calculated and its activation energy is discussed. Electronic conductivity is discussed also.

INTRODUCTION

Moderate temperature SOFCs are widely considered in the process of SOFC's commercialization. Lower operating temperature requires higher ionic conductivity of electrolyte. Lower operating temperature also requires higher reactivities of electrode. Recently, increasing attention has been paid to moderate temperature SOFCs with ceria as electrolyte and La₀.₇₅Sr₀.₂₅CoO₃ as cathode. Both materials are known to have very high oxygen ionic conductivity. Another merit of this combination is that they do not react during sintering process of cell manufacture.

Although it is well known that (Gd or Sm) stabilized ceria has very high ionic conductivity in air, the influence of Po₂ on the ionic conductivity is not yet clear. Because of the difficulty in dividing experimentally the total conductivity, into its ionic contribution and electronic one, some assumptions have been made in literatures. The first assumption was used when electronic conductivity, σₑ, was the main concern (1,2,3): since change of Qj in a reducing atmosphere is expected to be much smaller than that of σₑ, Qj was treated as constant for simplicity. Later, when the ionic conductivity became the main concern, it became clear that ionic radius of doped aliovalent ion affects the conductivity heavily. Another assumption was then proposed (4) that the ionic conductivity of ceria in changing atmospheres can be approximately simulated by measuring the conductivity of La-doped ceria in air. This is because the ionic radius of La³⁺ is very similar to that of Ce³⁺, so the effect of Ce³⁺ should be similar to that of same amount of La³⁺. The ionic conductivity obtained in this way has a maximum value with increasing amount of Ce³⁺(reducing Po₂). That work, however, discussed only high temperature (1273K), and did not give information on model of σᵢ and its activation energy.

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energy.

In the present work, we try another assumption to discuss the ionic and electronic conductivity of CGO10 (γ=0.1) and CGO20 (γ=0.2) at moderate temperature and in the area of small oxygen nonstoichiometry. We assume that mobility of oxygen vacancies and electrons do not change under above conditions. The assumption is based on an ideal solid solution model that was utilized in our previous work (5,6) on the nonstoichiometry of the same materials. The ideal solid solution model suggests less association of defects in doped ceria. It is then reasonable that the mobility of oxygen vacancies and electrons should not change much in reducing P02.

EXPERIMENTAL

Total conductivity was measured by a 2-probe AC impedance method. The sample was molded out from CGO powder supplied by Anann Kasei Co. Limited of Japan. After sintering at 1673K for 7 hours, the sample had a shape of a stick, 15mm in length and 4mm in radius, and had a relative density of over 95%. Pt paste was utilized as electrode. After electrode was pasted and dried, the sample was heated to 1223K and held for 5h. Then the temperature was decreased to 973K to measure the dependence of complex impedance on P02, which was changed from 10^5 Pa (pure O2) to reducing atmospheres with H2/H2O ratio greater than 10. After the measurement at 973K was completed, the sample was heated to higher temperatures (1073K, 1173K) to do new measurement.

THEORETICAL

The method of obtaining conductivity from the complex impedance spectroscopy is well known, so that this section focuses on how the conductivity data is treated in consideration of the properties of doped ceria. Although it is well known that electron conductivity, \( \sigma_e \), makes the total conductivity increase dramatically when ceria is reduced, the change of ionic conductivity, \( \sigma_i \), in reducing atmosphere is not yet clear. Because of the difficulty in dividing total conductivity, \( \sigma_t \), experimentally into \( \sigma_e \) and \( \sigma_i \), the ionic conductivity is discussed theoretically in literature by introducing some assumptions.

The total electrical conductivity of doped ceria is generally accepted as the sum of its electronic conductivity and ionic (oxygen vacancy) conductivity:

\[
\sigma_t = \sigma_e + \sigma_i \tag{1}
\]

Both \( \sigma_e \) and \( \sigma_i \) can be expressed as the product of mobility, carrier concentration and the electrical charge.

\[
\sigma_e = \mu_e e \left[ C_{e^+} \right], \quad \sigma_i = \mu_i 2e \left[ V_{O^-} \right] \tag{2}
\]

In our previous work (5,6), nonstoichiometry of CGO10 and CGO20 was
measured thermogravimetrically. From nonstoichiometry data the concentration of
electron and oxygen vacancy, \( V_{0^-} \), can be calculated easily. If the dependence
of mobility on \( P_{O_2} \) is known, the change of conductivity with \( P_{O_2} \) can be discussed from
equation [2].

Mobility of ion is generally believed to be dependent on the crystal structure, type
of dopant, and association among defects. In many cases, however, it is the change of
carrier concentration that affects the electrical conductivity heavily, especially when one
discusses a sample without remarkable change of structure and lattice constants and
association among defects can be ignored. From the result of nonstoichiometry
measurement, it became clear that performance of oxygen vacancy in CGO can be well
explained by an ideal solid solution model. This means that association among electrons,
oxogen vacancies, and dopant is not strong in this system. Such a performance is
because of the similarity of ionic radius of dopant \( Gd^{3+} \) and host \( Ce^{4+}, Ce^{3+} \). The change
of lattice constant with \( Gd^{4+} \) doping is also not severe. It is then quite reasonable to
assume a constant mobility of oxygen vacancies, at least in the area of small
nonstoichiometry, in discussing the dependence of \( \sigma \) on \( P_{O_2} \).

In the area of high oxygen partial pressure, where electrical conductivity is
believed almost ionic, the concentration of \( V_{0^-} \) is determined by the doped amount of
allovalent ions and is equal to \( y/2 \) for \( Gd_x Ce_{1-y}O_{2-y/2} \). The mobility of \( V_{0^-} \) can be
calculated from the total conductivity in this area.

In the area of small oxygen nonstoichiometry, it is found that oxygen deficiency,
\( x \), is proportional to \(-1/4\) power of \( P_{O_2} \). \([V_{0^-}]\) in equation [2] can be expressed as
following,

\[
[V_{0^-}] = \frac{y}{2} + k P_{O_2}^{1/4}
\]  

Where \( k \) is a temperature depending constant that can be obtained from
nonstoichiometry data.

Substituting equation [3] into [2], we get

\[
\sigma_i = 2\mu_e (y/2 + k P_{O_2}^{1/4})
\]  

As for electronic conductivity, because the concentration of \( Ce^{3+} \) is two times of \( x \), the
oxygen deficiency, and \( x \) is proportional to \( P_{O_2}^{1/4} \), if the mobility of electrons is not
changed by defects association, \( \sigma_e \) should be proportional to \( P_{O_2}^{1/4} \) also. That is,

\[
\sigma_e = 2\mu_e e k P_{O_2}^{1/4}
\]  

In this way, the total conductivity can be expressed as
\[ \sigma_i = a + b P_{O_2}^{1/4} \]  
[6]

where

\[ a = \gamma \mu_i e \]  
[7]

and

\[ b = 2(\mu_i + \mu_e)ek \]  
[8]

By fitting experimental data to determine \( a \), \( b \) and \( k \), it is possible to obtain values of mobility at various temperatures and discuss its activation energy.

**RESULTS AND DISCUSSION**

The cole-cole plots of CGO10 in pure oxygen, normal Ar and \( H_2/H_2O \) mixture are compared in Fig.1. In pure \( O_2 \), two arcs are observed. The left cross section, \( R_1 \) is thought to correspond to the resistance of sample, in which the resistance of both bulk and grain boundary are included. \( R_2 \) corresponds to resistance of electrode reactions. The physical meaning of the second arc is not clear yet. In \( Ar \), although \( R_2 \) becomes very large, \( R_1 \) does not change much. In \( H_2/H_2O \), however, both \( R_1 \) and \( R_2 \) become much smaller. Change in \( R_1 \) is because of the increase of carriers' concentration; change in \( R_2 \) may be due to enhancement of electrode activity by reducing atmosphere, which is beyond the scope of this work.

For CGO20, although the values of resistances changed the shape of cole-cole plot, its variation with atmosphere looks very similar to CGO10.

The total conductivity is calculated by Ohm's law from \( R_1 \), length and cross section area of the sample. The results in air are shown in Fig.2. Our results are in good agreement with those of other authors. CGO20 has higher conductivity than CGO10.

Dependence of total conductivity, \( \sigma_t \), on oxygen partial pressure is shown in Fig. 3. The experimental data agree well with fitted curves in reducing atmosphere. For clarity, fitted curves are shown for CGO20 only. The effect of reducing \( P_{O_2} \) on \( \sigma_t \) is different for CGO10 and CGO20. At 1073K and 1173K, the total conductivity of CGO20 is higher in the area of high \( P_{O_2} \), but in reducing atmosphere that of CGO10 is higher. This means that electronic conductivity is further reduced by increasing dopant content from 0.1 to 0.2.

Using the data in high \( P_{O_2} \) area, the ionic mobility is calculated and listed in Table 1. It is found that the ionic mobility of CGO10 is a bit higher than that of CGO20, so the higher conductivity of CGO20 is due to its larger concentration of oxygen vacancy.

Assuming constant mobility, and combining the nonstoichiometry data, the dependence of \( \sigma_i \) on \( P_{O_2} \) is obtained as shown in Fig. 4. Because the deficiency of oxygen content heavily depends on temperature, performance of \( \sigma_i \) looks quite different at 1073k and 973K. Above 1073K, obvious increase of \( \sigma_i \) is shown. At 973k, however, it increases only in very low \( P_{O_2} \). Increase of \( \sigma_i \) for CGO20 is not as large as for CGO10, this is because of less nonstoichiometry and slower ionic mobility of CGO20.

Subtracting \( \sigma_i \) from \( \sigma_t \), the electronic conductivity can be obtained. It is...
proportional to \( -1/4 \) power of \( \text{PO}_2 \) because both \( \sigma \) and \( \sigma_i \) can be well fitted by the \( P_{O_2}^{1/4} \) law as discussed in the theoretical section. By evaluating parameters \( a \), \( b \) and \( k \) following equation [5], the mobility of electron is obtained and is shown in Table 1, together with the ionic one. \( \mu_e \) is one order of magnitude larger than \( \mu_i \).

The temperature dependence of mobility is plotted in Fig. 5. Almost linear relationship is obtained. The activation energy of electronic and ionic mobility is obtained from the slope of Fig. 5. For CGO10, the activation energy of electronic mobility is 0.74eV, just a bit smaller than that of ionic mobility, 0.83eV. In comparison to that of pure ceria (7), the activation energy of electronic conduction increases by doping of \( \text{Gd}^{3+} \). However, because the temperature dependence of \( \mu_e \) is very similar to that of \( \mu_i \), the mechanism of electron transportation is the same as for pure ceria, which is well known as small polaron mechanism (7,8).

For CGO20, the electronic activation energy is 0.52eV, and that of ionic mobility is 0.71eV. They are both smaller than for CGO10. The reason for this difference is not yet clear; it may partly be due to the difference of partial molar enthalpy of oxygen in the crystal, which contributes to the forming energy of defects.

We noticed that values of mobility are different in Table 1 for CGO10 and CGO20. Curve fitting also has a discrepancy at 1173K and very low \( \text{PO}_2 \). This means that adjustment is needed when one discusses a large change of dopant concentration and nonstoichiometry.

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Fig. 1 Cole-Cole plot in various atmospheres
(1 atm = 101325 Pa)

| Temperature (K) | CGO10 Mobility/cm²V⁻¹s⁻¹ | CGO20 Mobility/cm²V⁻¹s⁻¹ |
|-----------------|--------------------------|--------------------------|
|                 | $\mu_i$                  | $\mu_e$                  | $\mu_i$                  | $\mu_e$                  |
| 973             | 7.75E-05                  | 7.14E-04                  | 5.11E-05                  | 9.05E-04                  |
| 1073            | 2.05E-04                  | 1.41E-03                  | 1.02E-04                  | 1.34E-03                  |
| 1173            | 3.42E-04                  | 2.70E-03                  | 1.79E-04                  | 2.18E-03                  |

Table 1 Mobility of ionic and electronic conducting species in CGO
Fig. 2  Total conductivity in air

Fig. 3  Total conductivity as a function of PO₂
(1 atm = 101325 Pa)
Fig. 4 Calculated ionic conductivity from nonstoichiometry and mobility in air (1 atm = 101325 Pa)

Fig. 5 Dependence of mobility on temperature