

The Effect of Multiple Doping on Electrical Conductivity of Gadolinia-Doped Ceria Electrolyte

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(Received 8 March 2001 • accepted 26 December 2001)

Abstract—Combinations of two or four trivalent oxides were substituted for gadolinia up to 5 mol% in the 20 mol% gadolinia-doped ceria electrolyte as additional dopants. Most of them increased the electrical conductivity of the electrolyte but some did not. Among them $(YLa)_{0.01}Gd_{0.19}Ce_{0.8}O_{1.9}$ and $(YSm)_{0.03}Gd_{0.17}Ce_{0.8}O_{1.9}$ showed the highest electrical conductivities, respectively, at 800 °C and 600 °C. These experimental results were analyzed in terms of activation enthalpy and entropy for ionic conduction. Among the various possible contributions to the activation entropy, only the configurational entropy was taken into account for the explanation.

Key words: SOFC, Ceria Electrolyte, Dopants, Conductivity, Configurational Entropy

INTRODUCTION

State-of-the-art solid oxide fuel cells (SOFC) utilizing doped zirconia as the electrolyte are generally operated at ~1000 °C to achieve useful power outputs. High temperature operation offers various advantages. For example, it eliminates the need for expensive noble metal catalysts, a fuel processing system, etc. and allows high tolerance to impurities in the fuel [Choi et al., 1994]. On the other hand, it limits the range of material selection for cell components to expensive ceramics and metals. It is therefore desirable to lower the cell operating temperature. One method is to use an alternative electrolyte with higher oxygen ion conductivity.

Doped ceria is one of the candidates that can replace doped zirconia as electrolyte and allow lower operating temperature. Generally, rare earth metal oxides are highly soluble in ceria and, therefore, when used as dopants to ceria, enhance the electrical conductivity. The electrical conductivity of the ceria singly doped with a rare earth metal oxide is reported to be related with the dopant cation size and the one doped with gadolinia or samaria shows relatively higher conductivity [Kilner and Steele, 1981; Inaba and Tagawa, 1996; Eguchi et al., 1992]. The doped ceria, however, easily develops electronic conduction at high temperatures and low oxygen partial pressures. Double doping, for example, (GdPr)-doping or (GdSm)-doping, is one solution to this problem sought by Maricle et al. [1991, 1992].

We have studied how the second dopant such as yttria, samaria, neodymia, praseodymia and lanthania affects ionic and electronic conductivities of 20 mol% gadolinia-doped ceria (called GDC below), which is the composition reported to show the highest electrical conductivity among gadolinia-doped ceria electrolytes [Kudo and Obayashi, 1975]. It was found that all the five second dopants did suppress the electronic conduction and, among the five, yttria and samaria apparently increased the electrical conductivity while praseodymia was to the contrary [Kim et al., 2000].

This study is now extended further to triple or quintuple doping. In this experiment various combinations of the above-mentioned oxides except praseodymia were substituted for gadolinia up to 5 mol% in GDC, and the effect of multiple doping on the electrical conductivity was examined.

EXPERIMENTAL

Polymeric precursors for GDCs with and without additional dopants were synthesized by using Pechini process [Lessing, 1989]. All the materials used in the process were in the nitrate form. Details of the process have been described in a previous paper [Kim et al., 2000]. The additional doping was done in such a way that $(Y_{0.5}La_{0.5})_2O_3$, $(Y_{0.5}Sm_{0.5})_2O_3$, $(La_{0.5}Nd_{0.5})_2O_3$ or $(Y_{0.25}Sm_{0.25}Nd_{0.25}La_{0.25})_2O_3$ were substituted for Gd_2O_3 in GDC by 1, 3 or 5 mol% so that the total amount of dopants was kept at 20 mol% in all cases. The GDC powders, with and without additional dopants, were obtained by calcining the corresponding precursors at 450 °C for 5 hours in an open furnace.

The powder was then heated at 950 °C for 1 hour, put in a jar together with some ethyl alcohol, and ball-milled for 24 hours by using zirconia balls. The slurry was dried in an oven and crushed in a mortar. This powder was consolidated into a disc for electrical conductivity measurements and the compact was sintered at 1,400 °C for 2 hours in air.

The electrical conductivity of the disc electrolyte was measured with an impedance analyzer (Hewlett Packard, HP4192A) at various temperatures in the range of 500-850 °C. For the measurement, Pt electrodes were formed on both sides of a disc by painting some paste and firing the disc at 950 °C for 2 hours [Tsuchida et al., 1996].

RESULTS AND DISCUSSION

The Arrhenius plots for the electrical conductivities of GDCs additionally doped with (YLa) by 0, 1, 3 and 5 mol% are shown together in Fig. 1 for comparison. The conductivities are the bulk values and only the fitted lines are shown without data points for

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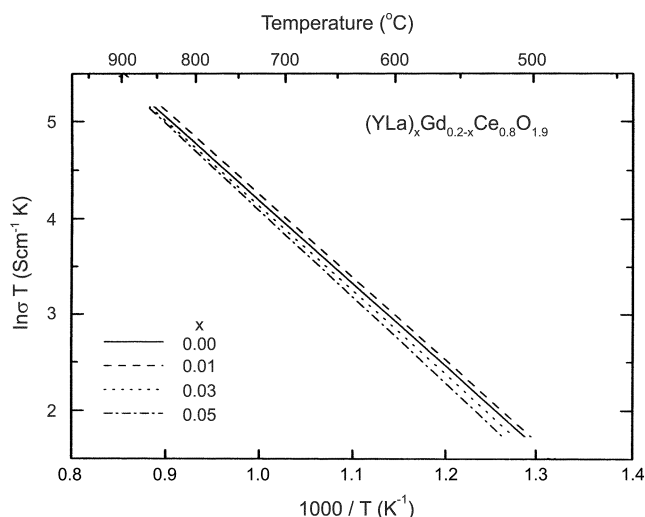


Fig. 1. Arrhenius plots for electrical conductivities of $(\text{YLa})_x \text{Gd}_{0.2-x} \text{Ce}_{0.8} \text{O}_{1.9}$.

simplicity of comparison. Though not shown here, similar plots were also obtained for GDCs additionally doped with (YSm), (NdLa), and (YSmNdLa). According to the figure, the electrical conductivity of (YLa)-doped GDC exceeds that of GDC at 1 mol% of additional dopants, but gets down below at more content of dopants. This tendency, however, can be seen more clearly in the curves of electrical conductivity vs. amount of additional dopants drawn at some specified temperatures.

The electrical conductivities of (YLa)-, (YSm)-, (NdLa)-, and (YSmNdLa)-doped GDCs at a temperature of 800 °C or 600 °C are plotted against the amount of additional dopants in Fig. 2. No particular trend can be noticed in the variation of electrical conductivity with the amount of additional dopants but, as already mentioned above for the case of (YLa)-additional doping, all the GDCs additionally doped by 1 mol% show higher value of electrical conductivity than GDC. Among the doped GDCs tested in this experiment, the highest value of electrical conductivity is shown competitively by 1 mol% (YLa)-doped GDC and 3 mol% (YSm)-doped GDC.

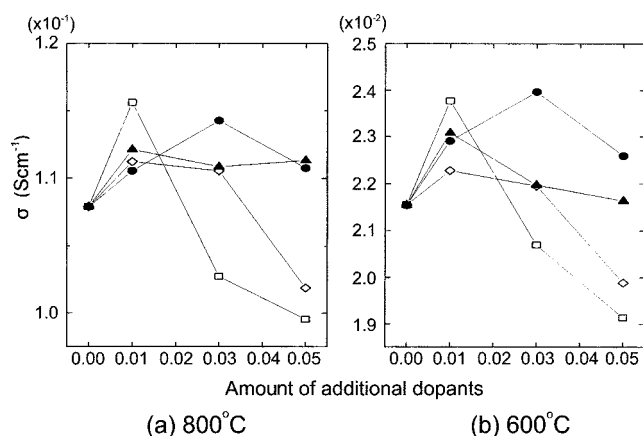


Fig. 2. Variation of electrical conductivity of $\text{Ln}_x \text{Gd}_{0.2-x} \text{Ce}_{0.8} \text{O}_{1.9}$ [$\text{Ln}=(\text{YLa})(\square)$, $(\text{YSm})(\bullet)$, $(\text{NdLa})(\diamond)$ and $(\text{YSmNdLa})(\blacktriangle)$] with amount of additional dopants at (a) 800 °C and (b) 600 °C.

Other doped GDCs also show higher electrical conductivities than GDC except the three samples, the one doped with (NdLa) by 5 mol%, and the ones doped with (YLa) by 3 and 5 mol%.

It is interesting to note that the slopes of the fitted lines in Fig. 1 are different for different compositions, and it is not so difficult to imagine the intercepts on $(\ln \sigma T)$ -axis at $1/T=0$ to be so. Since the values of electrical conductivities are determined by these two parameters, that is, the slope and the intercept, it was thought necessary to find a possible explanation for the difference in these parameters.

The Arrhenius plots for electrical conductivity are based on the following empirical equation.

$$\sigma = \frac{\sigma_0}{T} \exp\left(-\frac{E_a}{kT}\right) \quad (1)$$

where σ is the electrical conductivity, σ_0 is the temperature-independent preexponential term, and E_a is the activation energy of ionic conduction. Thus, a straight line is supposed to be produced for a $\ln \sigma T$ versus $1/T$ relation, where the slope is $-E_a/k$ and the intercept on $(\ln \sigma T)$ -axis at $1/T=0$ is $\ln \sigma_0$. The theoretical basis for this empirical equation can be found in diffusion theory combined with Einstein relation between ionic mobility and diffusivity. The theory allows us to derive the expression for electrical conductivity as follows [Kilner, 2000].

$$\sigma = N \frac{q^2 z}{kT} f c (1-c) \alpha^2 v_0 \exp\left(-\frac{\Delta H_m}{kT}\right) \exp\left(\frac{\Delta S_m}{k}\right) \quad (2)$$

where N is the number of equivalent atomic sites per unit volume, q is the charge on the ion, z is the number of equivalent near neighbor sites, f is the correlation factor, c is the occupied fraction of N , α is the distance between equivalent sites, v_0 is a characteristic lattice frequency, and ΔH_m (or ΔS_m) is the enthalpy (or entropy) of migration. Comparing the above two equations, we see that:

$$E_a = \Delta H_m \quad (3)$$

$$\text{and } \sigma_0 = N \frac{q^2 z}{k} f c (1-c) \alpha^2 v_0 \exp\left(\frac{\Delta S_m}{k}\right) \quad (4)$$

It can be realized in Eq. (3) that the slope of the Arrhenius plot is a measure for ΔH_m . In Eq. (4), ΔS_m can be said to be the dominant parameter to determine the value of σ_0 or the intercept of the Arrhenius plot, and the reason is explained as follows. Among the parameters in Eq. (4), N , z , f , and v_0 are not expected to alter substantially for such small compositional variation as made in this experiment and for the same crystal structure. And, since all the metallic dopants have the same valency and the total amount of the dopant is fixed at 20 mol%, the fraction of oxygen vacancy or equivalently c is supposed to be the same for all the GDCs considered. The distance between equivalent sites α , however, may vary with the amount of dopants due to the possible change in lattice parameter. But, according to Fig. 3, the lattice parameters calculated from XRD data for the doped GDCs vary within $\pm 0.2\%$ of the value for GDC and this variation is so small to produce substantial difference in α .

The enthalpy of migration ΔH_m was estimated for each specimen from the slope of the corresponding Arrhenius plot and plotted against the amount of additional dopants in Fig. 4. Two comments have to be made here. First, ΔH_m increases in the order $(\text{YSm}) <$

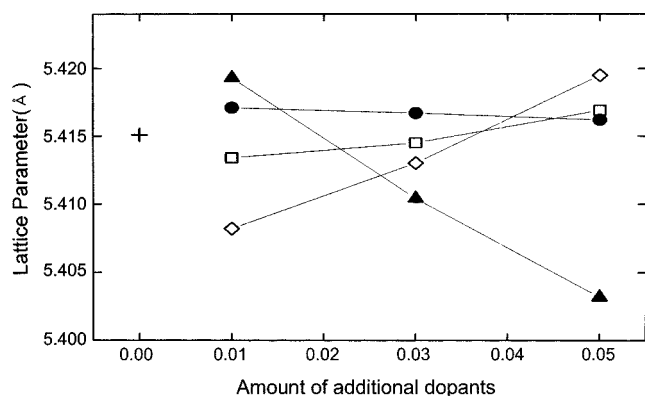


Fig. 3. Lattice parameters of $\text{Ln}_x\text{Gd}_{0.2-x}\text{Ce}_{0.8}\text{O}_{1.9}$ [$\text{Ln}=(\text{YLa})(\square)$, $(\text{YSm})(\bullet)$, $(\text{NdLa})(\diamond)$ and $(\text{YSmNdLa})(\blacktriangle)$] calculated from XRD data and plotted as a function of the amount of additional dopants. + denotes the lattice parameter for GDC.

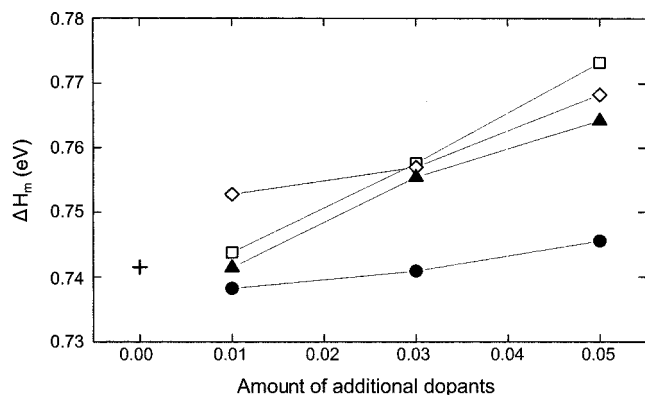


Fig. 4. Variation of activation enthalpy of $\text{Ln}_x\text{Gd}_{0.2-x}\text{Ce}_{0.8}\text{O}_{1.9}$ [$\text{Ln}=(\text{YLa})(\square)$, $(\text{YSm})(\bullet)$, $(\text{NdLa})(\diamond)$ and $(\text{YSmNdLa})(\blacktriangle)$] with amount of additional dopants. + denotes the activation enthalpy for GDC.

$(\text{YSmNdLa}) < (\text{YLa}) < (\text{NdLa})$ at 1 mol% of additional dopants. It is even lower than or almost equal to the value of GDC for the case of (YSm) or (YSmNdLa), respectively. Second, for the specimens of the same combination of dopants, ΔH_m generally increases with increasing amount of additional dopants. But the rate of increase is very slow for (YSm), a little faster for (NdLa), and much faster for (YLa) or (YSmNdLa).

The same results at 3 or 5 mol% of additional dopants are obtained. All these differences in ΔH_m are, partially, due to the difference in average radius of dopant cations. In Fig. 5 the values of ΔH_m for all the specimens tested in this experiment are shown as a function of the average radius of dopant cations and approximate proportionality exists between the two quantities.

The intercepts of the Arrhenius plots $\ln \sigma_0$ are shown in Fig. 6 as a function of the amount of additional dopants. As stated earlier, $\ln \sigma_0$ is a measure for ΔS_m . Here the feature of the general trend looks very similar to that in Fig. 4, but a very interesting phenomenon appears. The rate of increase is similar for the three cases of double additional doping and the magnitude of $\ln \sigma_0$ (or naturally ΔS_m) increases in the order $(\text{YSm}) < (\text{YLa}) < (\text{NdLa})$. The rate is much faster

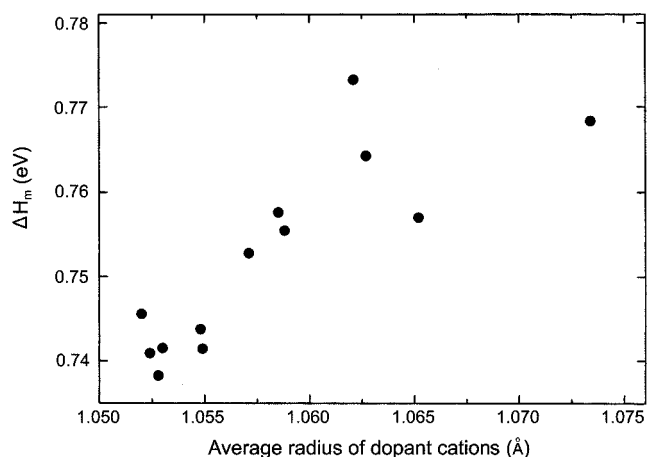


Fig. 5. Activation enthalpy of $\text{Ln}_x\text{Gd}_{0.2-x}\text{Ce}_{0.8}\text{O}_{1.9}$ as a function of average radius of dopant cations.

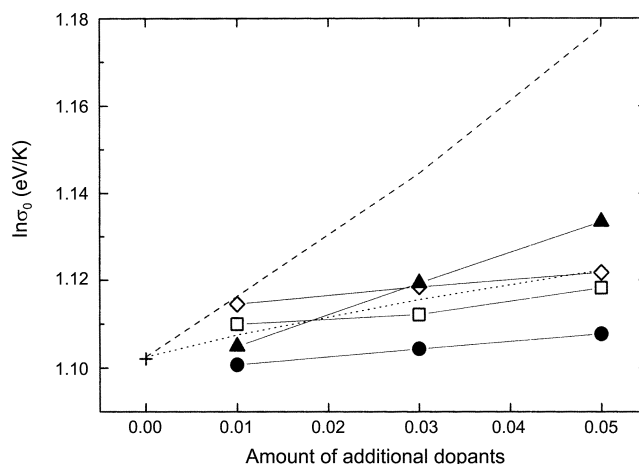


Fig. 6. Variations of $\ln \sigma_0$ of $\text{Ln}_x\text{Gd}_{0.2-x}\text{Ce}_{0.8}\text{O}_{1.9}$ [$\text{Ln}=(\text{YLa})(\square)$, $(\text{YSm})(\bullet)$, $(\text{NdLa})(\diamond)$ and $(\text{YSmNdLa})(\blacktriangle)$] with amount of additional dopants. + denotes $\ln \sigma_0$ for GDC and calculated configurational entropy of triple (dotted line) and quintuple (dashed line)-doped ceria.

in the case of quadruple additional doping. Therefore, at 5 mol% of additional dopants, the value of $\ln \sigma_0$ for (YSmNdLa) is far higher than those for double additional doping though it is relatively lower at 1 mol%. This entropy is associated with the concept of randomness and there may be various contributions to the entropy of migration, such as vibrational entropy, configurational entropy and so forth. Among them the configurational entropy is expected to be different for GDCs of different compositions, but others are not so. According to statistical thermodynamics, the configurational entropy, ΔS_{conf} , is related with the number of ways of arranging atoms (or ions) and can be expressed as follows for a system of 1 mol.

$$\Delta S_{conf} = -R \sum_i X_i \ln X_i \quad (5)$$

where R is the gas constant and X_i is the mole fraction of component i in the alloy system.

The values of ΔS_{conf} were calculated by using Eq. (5) for triply (dotted line) or quintuply (dashed line) doped ceria and are pre-

sented in Fig. 6 together with the experimental data of $\ln\sigma_0$. The rate of increase of configurational entropy with increasing amount of additional dopants is much faster for the quintuple doping than for the triple doping. So the rapid increase of $\ln\sigma_0$ in the case of quintuple doping is possibly caused by the configurational entropy.

CONCLUSIONS

Oxides of (YLa), (YSm), (NdLa), or (YSmNdLa) were substituted for gadolinia up to 5 mol% in 20 mol% gadolinia-doped ceria (GDC) electrolyte as additional dopants. The electrical conductivities of these multiply doped cerias were investigated and the following conclusions were made.

1. Most of the additional dopants increased the electrical conductivity of the GDC electrolyte.
2. $(\text{YLa})_{0.01}\text{Gd}_{0.19}\text{Ce}_{0.8}\text{O}_{1.9}$ and $(\text{YSm})_{0.03}\text{Gd}_{0.17}\text{Ce}_{0.8}\text{O}_{1.9}$ showed the highest values of electrical conductivities, respectively, at 800 °C and 600 °C.
3. The activation enthalpy rose in proportion to the average radius of dopant cations.
4. The variation of activation entropy seemed to be due mainly to the configurational entropy. The rate of increase of configurational entropy with increasing amount of additional dopants is much faster for the quintuple doping than for the triple doping.

ACKNOWLEDGEMENTS

Financial support from Korean Ministry of Education Research Fund for Advanced Material '96 (the third year) is gratefully ac-

knowledgeed.

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