Effect of co-dopant addition on properties of gadolinia-doped ceria electrolyte

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Abstract

Various trivalent oxides were added as co-dopants to gadolinia-doped ceria (GDC) electrolyte used for solid oxide fuel cells at up to 5 mol%. An examination was made on how they affect the electrical conductivity of the electrolyte and, eventually, the open-circuit voltage (OCV) of a unit cell. Through a comparison of the thermal expansion coefficients (TEC), it was investigated whether or not the co-doped electrolytes are thermomechanically compatible with other cell components. The addition of co-dopants generally improve the electrical properties of the electrolyte by yielding greater OCV values and not changing the TEC significantly (5% at most), except in the case of Pr. Among the electrolytes examined, the one co-doped with Sm (3 mol%) shows the best improvement in performance. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Recently, ceria-based solid oxides have received increasing attention as electrolyte material for low-temperature solid oxide fuel cells (SOFCs). The low-temperature operation provides an economic benefit through possible replacement of some of the expensive ceramic components of the cell by relatively cheaper metallic alternatives. It can also eliminate problems caused by the reaction of the electrolyte with other cell components.

On the other hand, ceria-based electrolytes easily develop n-type electronic conduction at high temperatures and low oxygen partial pressures [1]. This is one of the constraints for them to be used as the electrolyte material for SOFCs [2–4]. Some efforts have been made to suppress the electronic conductivity and to extend the electrolyte domain of the ceria-based electrolytes. For example, Maricle et al. [5,6] reported that the addition of 3 mol% Pr to gadolinia-doped ceria (GDC) increases the electrolyte domain regime by two orders of oxygen partial pressure.

In this experiment, we selected five trivalent metal (Y, Sm, Nd, Pr and La) oxides as co-dopant materials for 20 mol% GDC and substituted each for gadolinia up to 5 mol%. It will be discussed in this paper how each co-dopant affects the electrical and thermomechanical properties of the GDC electrolyte.

2. Experimental

2.1. Sample preparation

Polymeric precursors for the GDCs, with and without co-dopants, were synthesized using the Pechini process. Cerium nitrate and gadolinium nitrate were used as the starting materials for the synthesis of GDC. For co-doped GDCs, 1, 3 or 5 mol% of each co-dopant metal nitrate was substituted for gadolinium nitrate so that the total amount of dopant was always kept at 20 mol%. In the Pechini process, ethylene glycol and citric acid were used respectively as the solvent and the metal chelating agent. The solution was heated step by step (held over 1 h at each step) to a temperature at which the reaction started, and then held at this temperature until the reaction was completed. The GDC powders, with and without co-dopants,

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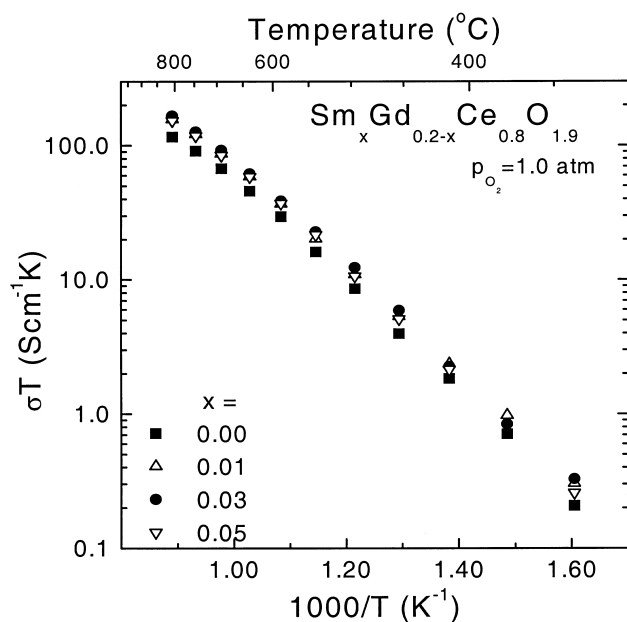
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Temperature ($^\circ$C)

Fig. 1. Arrhenius plot for electrical conductivities of $Sm_xGd_{0.2-x}Ce_{0.8}O_{1.9}$.

were obtained by calcining the corresponding precursors at 450°C for 5 h in an open furnace.

The calcined powder was crushed in a mano mortar, passed through a #120 sieve (125 μm size), and reheated at 950°C for 1 h. It was then put in a jar together with some ethyl alcohol and milled for 20 h using zirconia balls. The slurry was dried in an oven and crushed again in a mortar. This powder was then consolidated into a disc for electrical conductivity measurement or into a rod for thermomechanical measurement and the compact was sintered at 1400°C for 2 h in air.

2.2. Characterization

The ionic conductivity of the electrolyte was measured using an impedance analyzer (HP4192A) at various temperatures in the range of 350–800°C and at an oxygen partial pressure of 1 atm. Oxygen partial pressures were controlled by the flow rate ratio of O_2/CO_2 or CO/CO_2 and monitored through the electric potential shown by the tube-type 8YSZ electrolyte.

A unit cell was made for the measurement of open-circuit voltage (OCV). An anode of Ni(55 wt.%)-GDC cermet and a cathode of $La_{0.5}Sr_{0.5}MnO_3$(50 wt.%)-GDC were formed, using a silk printing technique on each side of a highly dense ($>$97%) electrolyte disc and the whole was sintered at 1400°C for 2 h. A glass ring was used for sealing. A mixture of $H_2/1.5\%H_2O$ and air were used respectively as fuel and oxidant gases. The Pt electrodes necessary for conductivity or OCV measurement were formed by putting some paste on both sides of the disc and firing it at 950°C for 2 h. Pt meshes were welded to the end of a Pt lead wire for low contact resistance.

The thermal expansion coefficient (TEC) of each electrolyte was estimated from the data in the 430–800°C temperature range of the corresponding linear expansion curve obtained using TMA (Rigaku, 881H). A quartz tube was used for TMA as a standard specimen and the heating rate was 10°C/min. X-ray diffraction (Rigaku, DMAX-IIa) was used to identify the phases of the electrolytes and to determine their lattice parameters.

3. Results and discussion

3.1. Electrical conductivity

The Arrhenius plot for the electrical conductivity of GDC co-doped with Sm at 0, 1, 3, or 5 mol% is shown in Fig. 1. The conductivities are the bulk values, i.e., the sum of the grain and the grain boundary contributions. It can be seen that at temperatures higher than 400°C, the conductivity increases with increasing amount of Sm up to 3 mol% and then decreases. It can also be noticed that the Arrhenius curve cannot be fitted by a single straight line. The curve should rather be fitted separately by two straight lines, one for the high-temperature range and the other for the low-temperature range. The changeover point is around 650°C. This implies that the mechanism for electrical conduction changes at this temperature.

Similar Arrhenius plots were produced for GDCs co-doped with Y, Nd, Pr and La, but are not shown here. Instead, two aspects will be summarized. First, as in the case of Sm, the Arrhenius curves for other co-dopants cannot be fitted by a single straight line. Second, the variation of electrical conductivity with the amount of co-dopant appears to be different for different types of co-dopants. This can be seen clearly in Fig. 2 where the conductivity is replotted on a linear scale, rather than a log scale, against the amount of co-dopant at two temperatures, one higher and the other lower than the above-men-
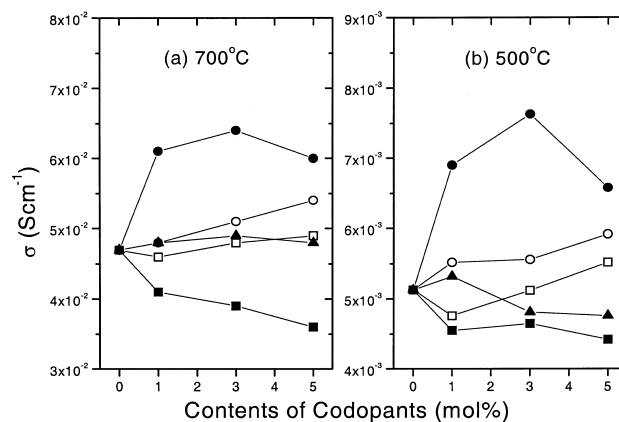

Fig. 2. Variation of electrical conductivity of $Ln_xGd_{0.2-x}Ce_{0.8}O_{1.9}$ [Ln = Y ($\bigcirc$), Sm ($\bullet$), Nd ($\square$), Pr ($\blacksquare$) and La ($\blacktriangle$)] with co-dopants at (a) 700°C and (b) 500°C.
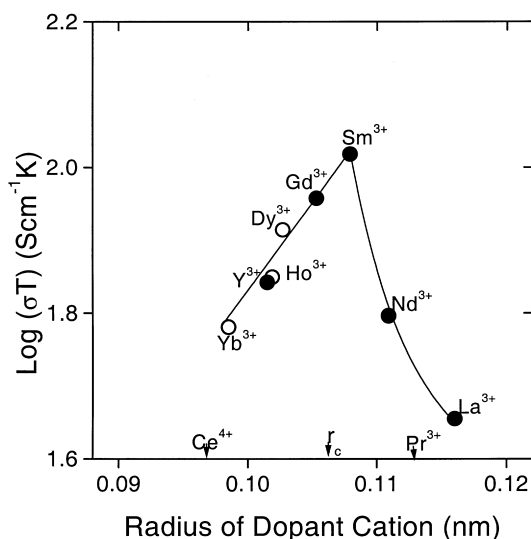
Fig. 3. Ionic conductivity of doped ceria at 800°C against the radius of dopant cation.

Fig. 4. Variation in OCV with operation temperature for a unit cell with a $Sm_xGd_{0.2-x}Ce_{0.8}O_{1.9}$ electrolyte.

tioned changeover point. The variation appears similar at the two temperatures. Only two of the five co-dopants, viz. Sm and Y, increase the electrical conductivity of GDC, but in a different manner. In the case of Sm, the electrical conductivity increases rapidly at 1 mol%, shows a maximum at 3 mol%, and then decreases. On the other hand, Y increases the conductivity little by little in proportion to its amount. Nd and La produce almost no effect on conductivity.

Eguchi et al. [7] compared the electrical conductivities of ceria singly doped with the above-mentioned five metal oxides. As can be seen in Fig. 3 [7], the ones doped with Sm and Y show, respectively, the highest and the second highest conductivities among the five. The authors explained this behavior in terms of the radii of dopant cations. It is interesting to note that, in this study, Sm and Y, though they were not used as a single dopant, increased the electrical conductivity of GDC while the others did not.

3.2. OCV

In Fig. 4, the OCV is plotted against the temperature for a unit cell, which consist of GDC electrolyte co-doped with Sm at 0, 1, 3 and 5 mol%. The data show that, as with the electrical conductivity, the OCV increases rapidly at 1 mol% Sm, passes through a maximum at 3 mol%, and then decreases. This statement, however, has to be changed a little, according to Fig. 5, where the variation in OCV with the amount of co-dopant at 700°C is shown for the five co-dopants, to one in which the OCV increases rapidly at 1 mol% of co-dopant and almost levels off thereafter. The increase in OCV on addition of co-dopants is thought to be due to the movement of the electrolyte domain boundary towards the lower oxygen partial pressure [8].
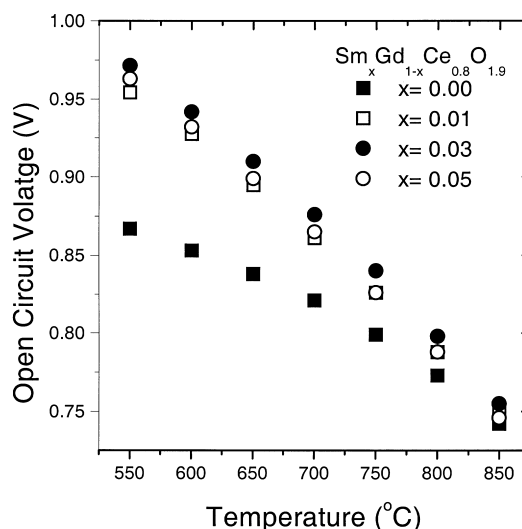
The results given in Fig. 4 also show that the OCV decreases with increasing temperature. This tendency occurs regardless of whether or not Sm is co-doped, but the rate of decrease is faster with co-doping. The decrease in OCV with temperature is due to an increase in electronic conduction. It is known that electronic conduction in the doped ceria occurs by the movement of small polarons via hopping [9,10], and hopping is one of the thermally activated processes.

The OCV vs. temperature curves obtained for a co-dopant composition of 3 mol% are shown in Fig. 6 together for direct comparison. The OCV values, though a little lower in the case of Pr, are practically the same in the other cases. When both the electrical conductivity and OCV are taken into account, however, the GDC electrolyte
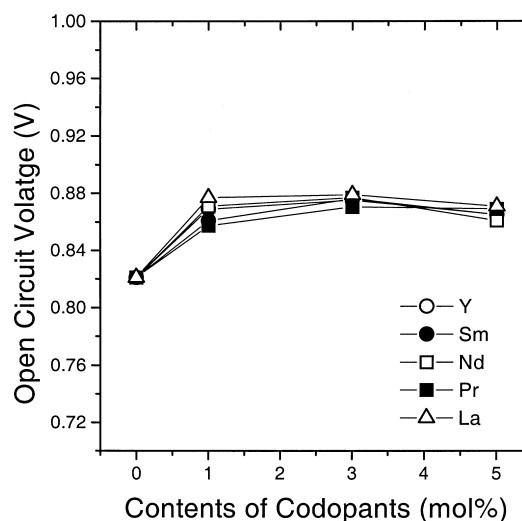

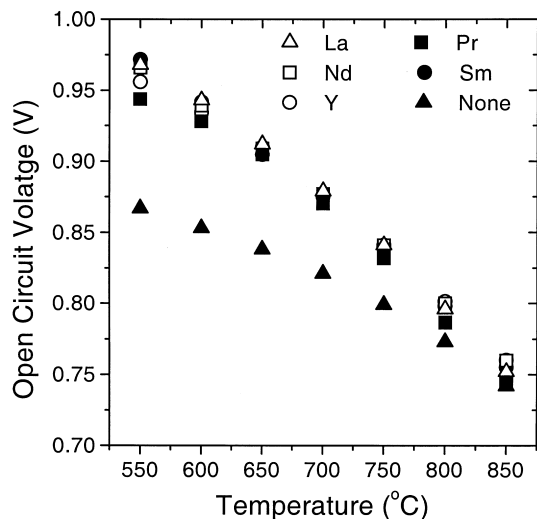Fig. 5. Variation in OCV with amount of co-dopant at 700°C.

Fig. 6. Comparison in OCV of a unit cell with GDC electrolyte containing 3 mol% of Ln (= Y, Sm, Nd, Pr and La) co-dopant.

is considered to show the best electrical property when co-doped with Sm at 3 mol%.

3.3. Thermal expansion coefficient

The TECs of the electrolytes are plotted as a function of the co-dopant contents in Fig. 7. Only a slight change (within $\pm 5\%$) is produced in the value of TEC by the addition of co-dopants except the case of Pr, in which TEC increases relatively rapidly and almost linearly with Pr content. The change in TEC is thought to be related to the
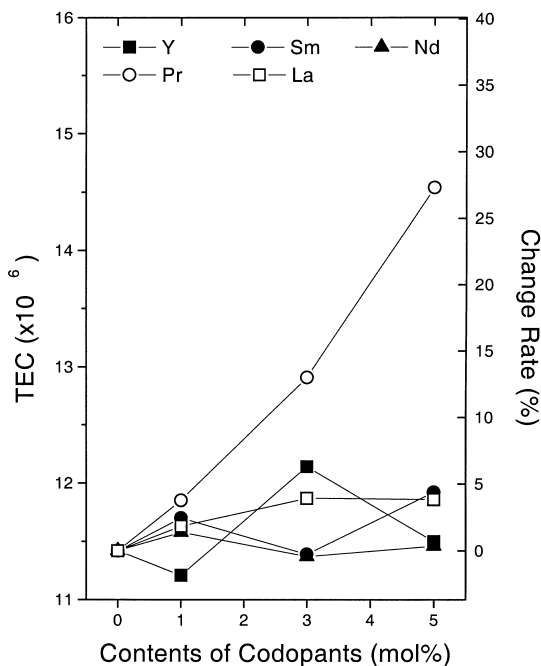

Fig. 7. Variation of thermal expansion coefficient of $Ln_xGd_{0.2-x}Ce_{0.8}O_{1.9}$ electrolytes (Ln = Y, Sm, Nd, Pr and La) with Ln content.
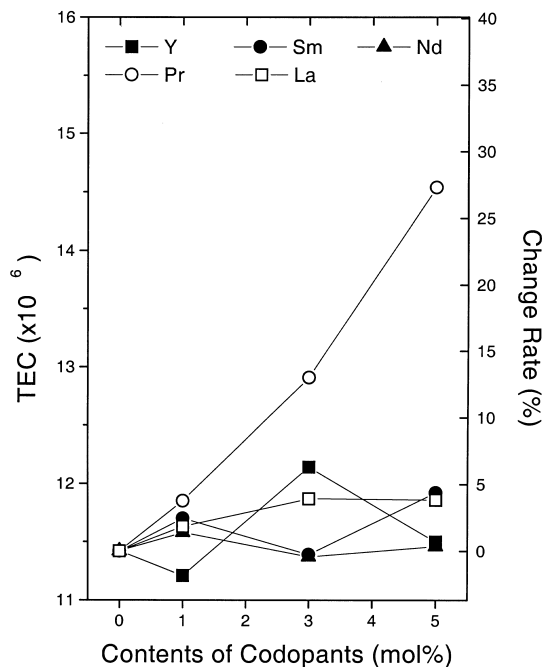

Fig. 8. Variation of lattice parameters of $Ln_xGd_{0.2-x}Ce_{0.8}O_{1.9}$ (Ln = Pr and La) electrolyte with Ln content.

change in lattice parameter produced by the addition of co-dopants.

The variation of lattice parameter of Pr- or La-co-doped GDC with co-dopant content is presented in Fig. 8. According to Shannon [11], the ionic radii increase in the order $Gd^{3+} < Ce^{4+} < Pr^{3+} < La^{3+}$. Therefore, it can be expected that Pr- or La-co-doped GDC has a larger lattice parameter than GDC, and that this effect becomes stronger as the amount of the co-dopant is increased. According to data in Fig. 8, this is found to hold for La, but not for Pr. The effect is opposite to expectation in the case of Pr. Thus, it was thought that the ions in GDC become more closely packed when Pr is co-doped than the other cases and that this might yield the larger TEC in the Pr-co-doped GDC.

4. Conclusions

In this study, five trivalent metal (Y, Sm, Nd, Pr and La) oxides were added separately as a co-dopant to 20 mol% GDC electrolyte up to 5 mol%. Only two of the co-dopants, Sm and Y, increase the electrical conductivity of the electrolyte and the maximum value is observed for Sm at 3 mol%. The OCV, on the other hand, is increased by all the co-dopants, rapidly up to 1 mol%, but remained almost constant thereafter. All the co-dopants except Pr change the TEC only by $\pm 5\%$. Thus, when both electrical properties and thermomechanical properties are taken into account, it is concluded that the GDC shows the best improvement in performance when co-doped with 3 mol% Sm.

Acknowledgements

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