EFFECT OF CODOPANT ADDITION ON ELECTRICAL PROPERTIES OF GADOLINIA-DOPED CERIA ELECTROLYTE

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ABSTRACT

Various trivalent oxides of up to 5 mol% were added as codopants to the gadolinia-doped ceria (GDC) electrolyte used for solid oxide fuel cells (SOFC), and their effect on the electrical conductivity of the electrolyte and eventually the open circuit voltage (OCV) of a unit cell was examined. The addition of codopants generally improved the electrical properties of the electrolyte, thus yielding greater values of OCV compared to the cases without codopants. When both the electrical conductivity and OCV were taken into accounts, the GDC electrolyte showed the best electrical property when codoped with Sm by 3 mol%.

INTRODUCTION

Recently ceria-based solid oxides have received increasing attention as the electrolyte material for low-temperature SOFC's. 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 ones. It can also eliminate problems caused by the reaction of the electrolyte with other cell components.

On the other hand, the ceria-based electrolytes easily develop n-type electronic conduction at high temperatures and low oxygen partial pressures. This is one of the constraints for them to be used as the electrolyte material for SOFC's[1-4]. 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. reported that the addition of 3 mol% Pr to gadolinia-doped ceria increases the electrolyte domain regime by two orders of oxygen partial pressure[5,6].

In this experiment we selected five trivalent metal (Y, Sm, Nd, Pr and La) oxides and added each as a codopant to 20 mol% gadolinia-doped ceria (GDC) up to 5 mol%. In this paper, the effects of codopant will be discussed on the electrical properties of the GDC electrolyte.
EXPERIMENTAL

Powder Preparation

Polymeric precursors for the GDC's with and without codopants were synthesized using Pechini process. Cerium nitrate and gadolinium nitrate were used as the starting materials for GDC. For the GDC's with codopants 1, 3, or 5 mol% of yttrium nitrate, samarium nitrate, neodymium nitrate, praseodymium nitrate, or lanthanum nitrate was substituted for gadolinium nitrate so that the total amount of dopant was always 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 hour at each step) to a temperature at which the reaction started and held at this temperature until the reaction was completed. The GDC powders with and without codopants were obtained by calcining the corresponding precursors at 450°C for 5 hours in an open furnace.

Milling, Consolidation and Sintering

The calcined powders were crushed in a mano mortar, passed through a #120 sieve (below 125 μm) and reheated at 950°C for 1 hour. They were then put in a jar together with some ethyl alcohol and milled for 20 hours using zirconia balls. The slurry was dried in an oven and crushed again in a mortar. This powder was then compacted into a form of a disc and sintered at 1400°C for 2 hours in air.

Electroding

Pt paste was put on both sides of a disc by silk printing and fired at 950°C for 2 hours to form electrodes necessary for the measurement of ionic conductivity. For the measurement of OCV, a unit cell was made by forming an anode of 55 wt.% Ni-GDC cermet and a cathode of 50 wt.% La0.5Sr0.5MnO3-GDC on each side of a highly dense (>97%) electrolyte disc and sintering the whole at 1200°C for 2 hours.

Characterization

The ionic conductivity of the electrolyte was measured using impedance analyzer (HP4192A) at various temperatures in the range of 350~800°C and an oxygen partial pressure of 1 atm. Oxygen partial pressures were controlled by the flow rate ratio of O2/CO2 or CO/CO2 and monitored through the electric potential shown by the tube-type YSZ electrolyte. A unit cell was located on a housing made of SUS 303 stainless steel for the measurement of OCV. A glass ring was used for sealing. Mixed gas of H2/1.5%H2O and air were used respectively as fuel and oxidant. Pt meshes were welded to the end of Pt lead wire for low contact resistance.
RESULTS AND DISCUSSION

Electrical conductivity

The Arrhenius plot for the electrical conductivity of GDC codoped with Sm by 0, 1, 3, or 5 mol% is shown in Figure 1. The conductivities are the bulk values (sum of grain and grain boundary conductivities). It can be seen in the figure 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 in the figure 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 higher temperature range and the other for the lower range. The turning point is around 650°C. This implies that the mechanism for electrical conduction changes at this temperature.

![Arrhenius plot for electrical conductivities of Sm$_x$Gd$_{0.2-x}$Ce$_{0.8}$O$_{1.9}$](image)

**Figure 1.** Arrhenius plot for electrical conductivities of Sm$_x$Gd$_{0.2-x}$Ce$_{0.8}$O$_{1.9}$.

Similar Arrhenius plots were produced for the GDC's codoped with Y, Nd, Pr and La, but are not shown here. Instead, two things will be summarized on them. Firstly, for all types of codopants, the Arrhenius curve can not be fitted by a single straight line. Secondly, the tendency of variation of electrical conductivity with the amount of codopant appears to be different for different types of codopants. This can be seen clearly in Figure 2 where the conductivity is replotted on a linear scale rather than a log scale against the amount of codopant at two temperatures, one higher and the other lower than the above-mentioned
turning point. The tendency of variation looks similar at the two temperatures. Only two of the five codopants, Sm and Y, increase the electrical conductivity of GDC, but in different manners. 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 of its amount. Nd and La produce almost no effect on conductivity.

![Graph showing variation of electrical conductivity](image)

**Figure 2.** Variation of electrical conductivity of Ln₀.₃Gd₀.₇Ce₀.₄O₁₉ [Ln=Y(□), Sm (■), Nd(□), Pr(■) and La(▲)] with contents of codopants at (a) 700°C and (b) 500°C.

Yahiro et al.[7,8] compared the electrical conductivities of ceria singly doped with the above-mentioned five metal oxides. As can be seen in Figure 3[7], the ones doped with Sm and Y show respectively the highest and the second highest conductivities among the five, and they tried to explain it 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 others did not.

**Open circuit voltages**

In Figure 4 the OCV is plotted against the temperature for a unit cell consisting of the GDC electrolyte codoped with Sm by 0, 1, 3, and 5 mol%. This figure shows that, similar to the electrical conductivity, the OCV increases...
rapidly at 1 mol% of Sm, passes through a maximum at 3 mol%, and then decreases. This statement, however, has to be changed a little, according to Figure 5 where the variation of OCV with the amount of codopant at 700 °C is shown for the cases of five codopants, into the one that the OCV increases rapidly at 1 mol% of codopant and almost levels off thereafter. The increase of OCV by the addition of codopants is thought to be due to the movement of electrolyte domain boundary toward the lower oxygen partial pressure[9].

Figure 3. Ionic conductivity of doped ceria at 800 °C against the radius of dopant cation[7].

Figure 4 also shows that the OCV decreases with increasing temperature. This tendency appears regardless of whether or not Sm is codoped but the rate of decrease is faster for the codoped. The decrease of OCV with temperature is due to the increase of electronic conduction. It is known that the electronic conduction in the doped ceria occurs by the movement of small polaron via hopping[10,11], and hopping is one of the thermally activated processes.

In Figure 6, all of OCV vs. temperature curves obtained for codopant composition of 3 mol% are shown together for direct comparison. According to the figure, OCV values, though a little lower in the case of Pr, are practically the same in the other cases. But when both the electrical conductivity and OCV are taken into account, the GDC electrolyte is considered to show the best electrical property when codoped with Sm by 3 mol%.
Figure 4. Variation of open circuit voltages with operation temperature for a unit cell using Sm$_{x}$Gd$_{1-x}$Ce$_{0.8}$O$_{1.9}$ electrolyte.

Figure 5. Variation of open circuit voltages with the amount of codopant at 700°C.
CONCLUSIONS

In this study, we selected five trivalent metal (Y, Sm, Nd, Pr and La) oxides and added each as a codopant to 20 mol% gadolinia-doped ceria (GDC) up to 5 mol%. Only two of the five codopants, Sm and Y, increased the electrical conductivity of GDC. The GDC showed the highest value of electrical conductivity when codoped with Sm by 3 mol%. On the other hand, all the five codopants increased the OCV. The OCV increased rapidly at 1 mol% of codopant and almost leveled off thereafter. It was concluded that, when both the electrical conductivity and OCV were taken into accounts, the GDC showed the best electrical property when codoped with 3 mol% of Sm.

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