

Effect of Gd (Sm) doping on properties of ceria electrolyte for solid oxide fuel cells

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Abstract

Two systematic electrolytes of $\text{Ce}_{1-x}\text{Gd}_x\text{O}_{2-x}$ (GDC) and $\text{Ce}_{1-x}\text{Sm}_x\text{O}_{2-x}$ (SDC) ($x = 0-0.25$) were synthesized using an oxalate coprecipitation process. Dependence of a , unit cell parameter versus dopant concentration, x , of Gd^{3+} and Sm^{3+} ions show that these solid solutions obey Vegard's rule as $a = 5.4121 + 0.0525x$ for GDC and $a = 5.4117 + 0.1237x$ for SDC, respectively. Electrical conductivity reached maximum at $x = 0.15$ in the temperature range of 400–850 °C for both kinds of doped-ceria electrolyte membranes. A single cell was made for the measurement of open circuit voltage. The results show that the open circuit voltages are greatly influenced by ionic transference number of the electrolyte, gaseous fuel composition and cathode membrane material.

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1. Introduction

Solid oxide fuel cells (SOFCs) have been received much attention in recent years, since they produce electricity directly from a gaseous fuel by electrochemical combination of the fuel with an oxidant in an efficient and environmentally benign way. While some researchers focus on the development of SOFCs for operation at high temperatures of 900–1000 °C, it becomes increasingly important to reduce the operation temperature of the fuel cells down to the range of 600–800 °C in order to substantially increase the life of a SOFC, widen the selection of electrode, interconnect and manifold materials and reduce the cost of the materials processing and cell fabrication.

In order to reduce the operation temperature, two approaches are widely applied to lower the resistance of dense electrolyte membranes, either by decreasing the traditional YSZ (8 mol% Y_2O_3 - ZrO_2) electrolyte thickness or using alternative materials of higher ionic conductivity at lower temperatures [1–3]. In addition, for both strategies adoption of a novel cathode with high performance is also essential.

So far, doped ceria oxides are being extensively studied as a promising candidate solid electrolyte for intermediate-temperature SOFCs [4]. However, reported results of maximum conductivities versus dopant types and concentrations were often inconsistent and sometimes contradictory. On the other hand, little work has been done on measurement of the open circuit voltages of SOFCs based on doped ceria electrolytes under operating conditions.

In this paper, two types of doped ceria electrolyte were prepared. The aim was to clarify how the electrical properties of the electrolyte membranes are influenced by the addition of Gd or Sm. Their influence on the open circuit voltages of corresponding fuel cells was also investigated in detail.

2. Experimental

2.1. Sample preparation

Two systematic ceramic powders of $\text{Ce}_{1-x}\text{Gd}_x\text{O}_{2-x/2}$ (GDC) and $\text{Ce}_{1-x}\text{Sm}_x\text{O}_{2-x/2}$ (SDC) ($x = 0, 0.05, 0.10, 0.15, 0.20$ and 0.25) were synthesized by the oxalate coprecipitation route [5,6] using cerium nitrate and gadolinium or samarium nitrate as starting materials. The appropriate quantities of starting materials were dissolved separately in water, mixed and coprecipitated with dilute oxalic acid

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solution, which was adjusted to neutral pH (6.6–6.9) by using ammonia solution during the reaction. The resulting precipitate was vacuum-filtered, washed five times with water and ethanol, respectively, and dried at 50 °C in an oven. After calcination at 750 °C, the oxide powders were confirmed by X-ray diffraction analysis to be single phase and of fluorite structure.

The resulting GDC and SDC powders were cold pressed into discs and then sintered at 1400 °C for 5 h in air. The relative densities of these sintered pellets were higher than 97% measured by the Archimedes method. These pellets with a thickness of around 1 mm were used for the measurement of electrical conductivity and other electrochemical properties.

2.2. Characterization

Phase formation of the calcined oxide powders was determined by X-ray diffraction (XRD) analysis using Cu K α radiation (Kigaqu D/Maz- γ_A) at room temperature. The ac conductivity of sintered pellets was obtained from two-probe impedance spectroscopy. The two electrodes were formed by applying platinum paste to the two ends of the pellet and firing at 850 °C for 15 min. Measurements were made with an impedance analyzer (GenRad 1689 Precision RLC Digibridge) at various temperatures in the range of 450–850 °C in air. The lead resistance, as obtained by measuring the impedance of a blank cell, was subtracted out from all of the impedance measurements.

A single fuel cell was made for the measurement of open circuit voltage (OCV). An anode of Ni (55 wt.%)–Ce_{1.8}Ln_{0.2}O_{1.9} cermet and a cathode of Sm_{0.5}Sr_{0.5}CoO₃ (50 wt.%)–Ce_{1.8}Ln_{0.2}O_{1.9} were formed, using a screen-printing technique on each side of a dense electrolyte membrane and the whole was sintered at 1250 °C for 2 h. Here, Ln in Ce_{1.8}Ln_{0.2}O_{1.9} is used instead of Gd or Sm for the cells based on Gd- or Sm-doped ceria electrolyte membranes, respectively. The effective areas of both electrodes were ca. 0.5 cm². The Pt electrodes necessary for OCV measurement were formed by putting paste on both sides of the pellet and firing it at 850 °C for 30 min. H₂ (99.999%) and O₂ were fed respectively as fuel and oxidant gases. In some cases, a mixture of H₂/3.1% H₂O or 9.5% H₂O, which were obtained by bubbling H₂ through water at 25 or 45 °C, was used as fuel instead of H₂ for OCV comparison under different fuel cell conditions.

3. Results and discussion

3.1. Phase formation

Fig. 1 shows the X-ray diffraction patterns of sample powders, GDC and SDC, respectively. They indicate that all powders crystallize to a single phase of cubic fluoride structure, the same as the original substance of pure ceria,

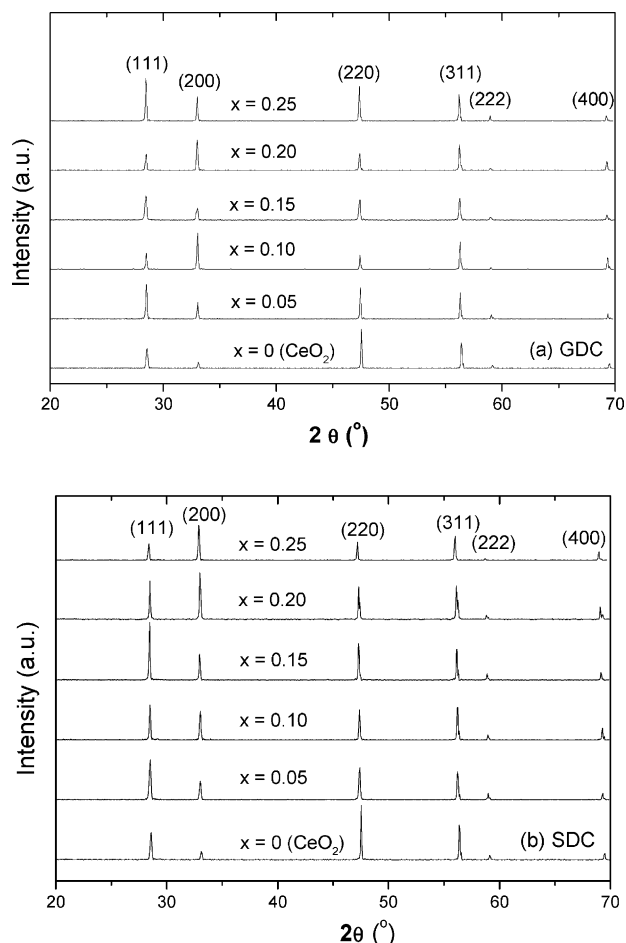


Fig. 1. X-ray diffraction patterns of doped ceria oxides (a) GDC and (b) SDC.

at a very large dopant concentration range after calcined at 750 °C. After indexing by the Rietveld method, the lattice parameter (a) of the doped ceria can be calculated by the relation:

$$a = d\sqrt{h^2 + k^2 + l^2}$$

Fig. 2 shows the dependence of a , unit cell parameter versus dopant concentration, x , of Gd³⁺ and Sm³⁺ ions. As the Gd and Sm composition increases, the lattice constant increases linearly as

$$a(x) = 5.4121 + 0.0525x$$

and

$$a(x) = 5.4117 + 0.1237x$$

for Ce_{1-x}Gd_xO_{2-x/2} and Ce_{1-x}Sm_xO_{2-x/2} ($x = 0-0.25$), respectively, which indicate these solid solutions obey Vegard's rule very well. As we know, the radii of Ce⁴⁺, Gd³⁺ and Sm³⁺ are 0.096, 0.105 and 0.108 nm, respectively [7]. When doped with larger sized Gd³⁺ and Sm³⁺ ions and higher dopant concentration, the cubic ceria lattice will expand.

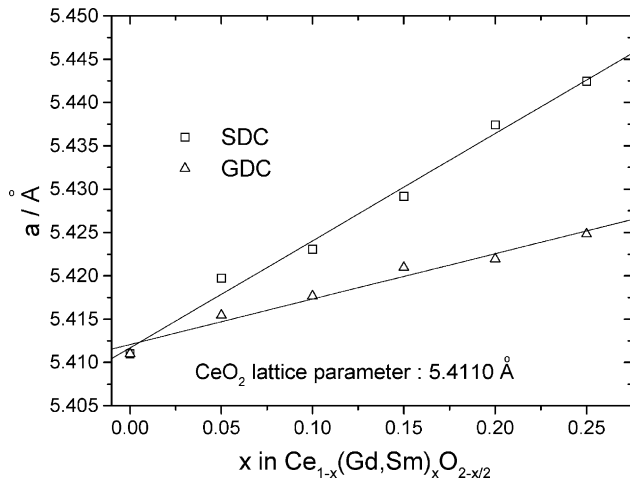


Fig. 2. Dependence of unit cell parameter vs. dopant concentration of Gd^{3+} and Sm^{3+} ions.

3.2. Electrical conductivity

The Arrhenius plot for the electrical conductivity of CeO_2 , GDC and SDC electrolyte membranes is shown in Fig. 3. The conductivities are the bulk values, i.e. the sum of the bulk grain and the grain boundary contributions. For both Gd and Sm doped ceria electrolytes, the maximum electrical conductivity are observed to be at a dopant concentration of $x = 0.15$, i.e. $\text{Ce}_{0.85}\text{Gd}_{0.15}\text{O}_{1.875}$ and $\text{Ce}_{0.85}\text{Sm}_{0.15}\text{O}_{1.875}$ have the maximum values in GDC and SDC solid solution at the whole temperature range of 400–850 °C. This result is somewhat different from those reported values. For example, Kudo and Obayashi [8] found the peak conductivities for Gd doped ceria were at 20 mol% $\text{GdO}_{1.5}$ dopant concentration. Yahiro et al. [9] also observed the optimal dopant concentration was 20 mol% $\text{SmO}_{1.5}$ for Sm doped ceria compounds. The difference between them may be due to the investigated concentration ranges. In this work, the dopant concentration were intensively researched from $x = 0$ –0.25 with interval of 0.05, while in the latter two works, the researched range was from $x = 0$ –0.5 or 0.6 with a larger interval of 0.10. While, in a more recent paper Steele [10] summarized other authors' work and indicated that the total conductivity peaks around 25 mol% $\text{GdO}_{1.5}$ concentration, which is much higher than that in the present work.

It can be noticed that the Arrhenius curve of doped ceria electrolyte cannot be fitted by a single straight line. The curve exhibits differing slopes in the low- and high-temperature range with the transitional point at around 650 °C. This implies that the mechanism for electrical conduction changes at this temperature. The temperature dependence of the electrical conductivity of doped ceria oxides, which have a large number of oxygen vacancies, can be shown as two regions in general according to Kilner and Walters [11]. At elevated temperatures, the electrical conduction is controlled by the population of charge-carrying defects determined by an aliovalent dopant (Gd or Sm). At low temperatures, the population of charge-carrying defects is

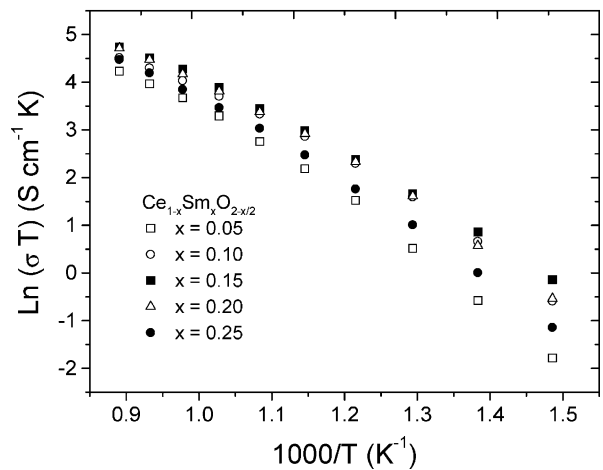
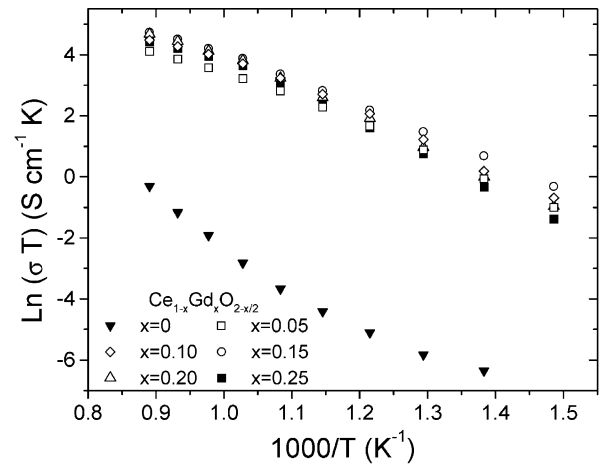


Fig. 3. Arrhenius plots for electrical conductivities of (a) GDC and (b) SDC electrolyte membranes.

determined by the thermodynamic equilibrium between the free defects and the associated pairs. Thus, the line slope becomes sharper due to larger activation energy of electrical conduction. But for the undoped CeO_2 electrolyte, the conductivity is much lower than doped samples and the temperature dependence of the electrical conduction is opposite to the above changing pattern of doped ceria, which was also shown in Fig. 3(a). This is due to a quite different conduction mechanism in CeO_2 . The electrical conduction of undoped ceria results from impurity and intrinsic factors. At low temperatures, its conduction is dominated by the dissociated electron concentration from the energy gap of the impurity, whose activation energy of electrical conduction is much lower than that of the intrinsic conduction. At high temperatures, the conductivity increase is predominantly due to the intrinsic factor, while electrons from the energy gap of the impurity are all dissociated and activated.

The conductivity of GDC and SDC ($x = 0.10$ –0.25) at 700 °C almost equals the value of YSZ at 1000 °C, which indicates that doped ceria is a promising electrolyte candidate for intermediate-temperature SOFCs. However, although the peak conductivities were obtained at

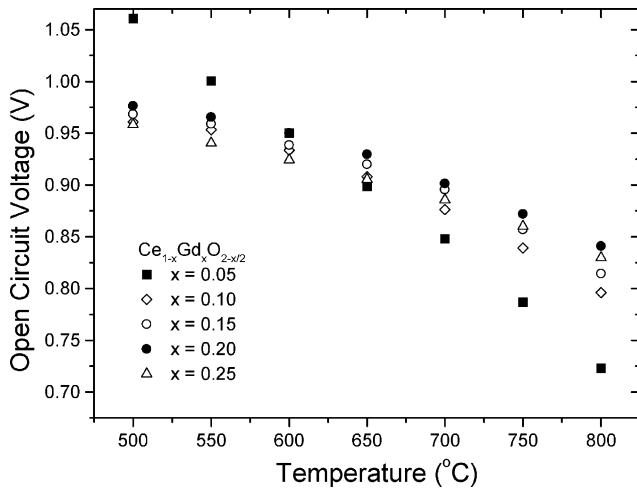


Fig. 4. Variation in OCV with operation temperature for single fuel cells with GDC electrolyte.

15 mol% for Gd- and Sm-doped ceria, it does not mean that they are the best ones among GDC and SDC electrolytes for a practical SOFC. Other electrochemical and mechanical properties, such as ionic transference number, thermal expansion constant and compatibility with other fuel cell components, should also be taken into account in the selection of appropriate electrolyte materials.

3.3. Open circuit voltage

In Fig. 4, the OCV is plotted against the temperature for a single fuel cell, which has a GDC electrolyte membrane. A similar plot was produced for a SDC electrolyte membrane, but is not shown here. Three common aspects will be summarized. Firstly, the OCV decreases with increasing temperature. This coincided with the theoretical analysis based on thermodynamic equilibrium [12]. Secondly, the OCV reaches the maximum value at $x = 0.20$ for both $Ce_{1-x}Gd_xO_{2-x/2}$ and $Ce_{1-x}Sm_xO_{2-x/2}$ ($x = 0.10-0.25$) based fuel cells in the temperature range of 500–800 °C. This can be ascribed to the fact that the highest ionic transference number occurred at $x = 0.20$ [8,9]. Thirdly, the doped ceria $Ce_{1.95}Gd_{0.05}O_{1.975}$ (i.e. where $x = 0.05$) has an unusual OCV value rather different from the other doped oxides. At the high temperature range of 650–800 °C, the OCV of $Ce_{1.95}Gd_{0.05}O_{1.975}$ is lower than that of $x = 0.10-0.25$. But in the low temperature range of 500–600 °C, the change is reversed. The unique behavior of $Ce_{1.95}Gd_{0.05}O_{1.975}$ shows that the dependence of ionic transference number on temperature is much greater than that of other Gd-doped ceria oxides.

Fig. 5 shows the OCV versus temperature curves obtained for $Ce_{0.8}Gd_{0.2}O_{1.9}$ under various anodic atmospheres. The anodic oxygen partial pressure was higher when H_2 was moistened by H_2O , which should result in a lower OCV value. This rule took effect in the temperature range of 550–800 °C when the anode was fed with dry hydrogen, 3.1% H_2O and 9.5% H_2O-H_2 mixtures. However, it is interesting

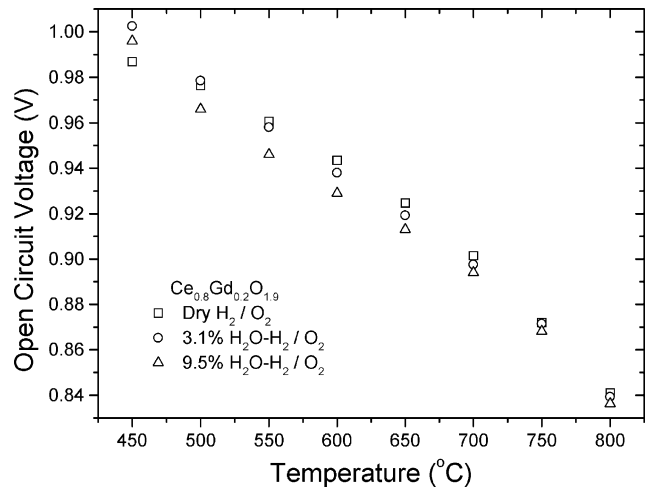


Fig. 5. Variation in OCV with operation temperature for a fuel cell with $Ce_{0.8}Gd_{0.2}O_{1.9}$ electrolyte under various anode atmospheres.

that the OCV value for H_2 was lower than that of the 3.1% H_2O-H_2 mixture at 500 °C. The OCV value for H_2 was lower than in the 9.5% H_2O-H_2 mixture when the temperature was reduced to 450 °C. This can be explained by the electrode reaction mechanism. In Jiang's [13,14] study of the hydrogen oxidation reaction on the cermet anode of SOFC, two limiting reaction steps were identified; hydrogen dissociation adsorption and diffusion on the Ni surface and charge transfer at the three phase boundaries. The first limiting step is pre-dominantly influenced by the existence of water vapor. At elevated temperature, this dissociative adsorption and diffusion process is fast enough that the existence of water vapor has little effect on it. But at lower temperature such as below 500 °C, this process will be promoted by the presence of water vapor. Therefore, when applying moistened H_2 , the anode becomes more activated and the fuel cell will have a higher OCV value.

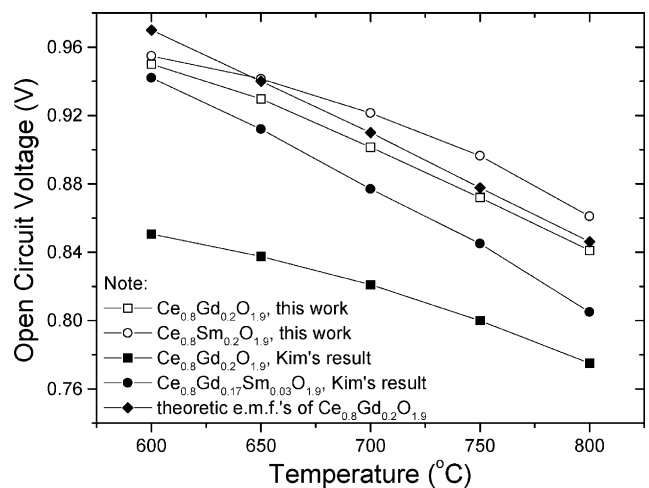


Fig. 6. Comparison of OCV measured from reference and this work. Cathode materials: $La_{0.5}Sr_{0.5}MnO_3$; Kim's work; $Sm_{0.5}Sr_{0.5}CoO_3$; this work.

The cathode membrane material also has a great influence on the electrochemical properties of a fuel cell. Fig. 6 shows some results of Kim's [15] and this work. The theoretic electromotive force (e.m.f.) is also drawn on this figure for comparison. In Kim's work the cathode material was $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ in contrast to $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ cathode material used in this work. It can be seen that the measured OCV of $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ - and $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ -based fuel cells in this work is about 0.1 V higher than that of Kim's work on $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$, and also higher than his best result of $\text{Ce}_{0.8}\text{Gd}_{0.17}\text{Sm}_{0.03}\text{O}_{1.9}$ in 600–800 °C. Moreover, the OCV of a $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ -based fuel cell is fairly near the ideal e.m.f. value [12]. It seems that $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ is an excellent cathode membrane material when used in intermediate-temperature SOFCs.

4. Conclusions

The oxalate coprecipitation process was used to synthesize two kinds of electrolytes, $\text{Ce}_{1-x}\text{Gd}_x\text{O}_{2-x}$ and $\text{Ce}_{1-x}\text{Sm}_x\text{O}_{2-x}$ ($x = 0-0.25$). Their phase formation and electrochemical properties were investigated, and some results obtained were as follows:

1. when doped with larger Gd^{3+} and Sm^{3+} ions, the fluorite lattice of CeO_2 will expand. Dependence of the lattice parameter versus dopant concentration shows that these solid solutions obey Vegard's rule, as $a = 5.4121 + 0.0525x$ for GDC and $a = 5.4117 + 0.1237x$ for SDC, respectively;
2. the total conductivity peaks at $x = 0.15$ in the temperature range of 400–850 °C for both Gd- and Sm-doped ceria electrolyte membranes;
3. the open circuit voltages of the fuel cells are greatly influenced by the ionic transference number of the

doped ceria electrolyte, the gaseous fuel compositions and the cathode membrane material.

However, other electrochemical and mechanical properties, such as the ionic transference number, the thermal expansion constant and compatibility with other fuel cell components, should be also taken into account in the selection of proper electrolyte materials for a solid oxide fuel cell.

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