Review paper

Nano-structure design of doped ceria solid electrolytes for intermediate temperature operation of solid oxide fuel cell

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Doped ceria (CeO_2) compounds are fluorite related oxides which show oxide ionic conductivity higher than yttria-stabilized zirconia in oxidizing atmosphere. As a consequence of this, considerable interest has been shown in application of these materials for 'intermediate temperature (300- 500°C)' operation of solid oxide fuel cells (SOFCs). In this review paper, our experimental data was re-introduced to propose a new design paradigm for development of high quality doped CeO_2 electrolytes. Based on our experimental data, our original idea a control of nano-inhomogeneity of doped CeO_2 electrolytes was proposed. In our work, the nano-sized powders and dense sintered bodies of M doped CeO_2 (M: Sm, Gd, Y, Yb, Dy, Ho, Tb and La) specimens were fabricated using ammonium carbonate co-precipitation method, conventional sintering method and pulsed electric current sintering method. Also nano-structural features of those specimens were carefully observed for conclusion of relationship between electrolytic properties and microstructure in doped CeO_2 . It is essential that the electrolytic properties of doped CeO_2 reflect in changes of microstructure even down to the atomic scale. Accordingly, a combined approach of ultimate analysis, simulation and processing route design is required to develop the superior quality doped CeO_2 electrolytes for the intermediate temperature operation of SOFCs.

Keywords: Doped CeO_2 , Oxide ionic conductivity, Micro-domain, Intermediate temperature operation of SOFCs, Nano-inhomogeneity,

Introduction

Over the past 50 years, the potential of materials with fast oxide ionic conduction has been realized in many applications. Oxide ion conductors are used in a variety of gas sensors,^[1-4] solid oxide electrochemical cells (SOECs),^[5-7] and solid oxide fuel cells (SOFCs).^[8-12] In those applications, SOFCs are being especially developed as a clean and efficient power source for generating electricity from a variety of fuels. For long lifetimes and efficient operation at 'intermediate temperature (300° - 500°C)', high oxide ionic conductivity is required for the development of electrolytes. The 'intermediate temperature' operation of SOFCs means that less expensive materials can be used as interconnects, manifolds and gas transport systems. Yttria stabilized zirconia (YSZ) and scandia stabilized zirconia (SSZ) are common electrolytes used in SOFCs. However, its ionic conductivity is still unsatisfactory for intermediate temperature operation of SOFCs. Accordingly, it is important that a high-quality electrolyte with higher oxide ionic conductivity

than that of YSZ and SSZ be identified.

CeO_2 doped with the oxides of divalent metal oxide such as calcia or rare earth oxide (yttria (Y_2O_3), gadolia (Gd_2O_3), and so on) doped ceria (CeO_2) compounds possess higher oxide ionic conductivity than any reported stabilized zirconia.^[13-17] At high oxygen partial pressures, those doped CeO_2 electrolytes show high oxide ionic conductivity. At low oxygen partial pressures associated with anodic conditions, however, the Ce^{4+} ion can be partially reduced to Ce^{3+} ion in doped CeO_2 . Quasi-free electrons are introduced into a fluorite lattice in such reducing atmospheres. Doped CeO_2 compounds are partially reduced and develop electronic conductivity under anodic conditions in the fuel cell. The stability in both oxidizing and reducing atmosphere is an essential requirement for candidate electrolytes rare earth doped CeO_2 systems. To overcome this problem and improve the conductivity for 'intermediate temperature' operation of SOFCs, a design of nano-structure in doped CeO_2 solid electrolytes is required. In the present short review paper, the authors

re-introduce our works on the basis of a micro-analysis of the doped CeO_2 electrolytes and suggest a new design paradigm for fabrication of nano-structured doped- CeO_2 solid electrolytes for application of 'intermediate temperature' operation of SOFCs. In our new challenge, a control of nano-inhomogeneity in doped CeO_2 is a key for development of our new design paradigm. We expect that combination of a control of processing route of doped CeO_2 ceramics, atom-level observation of the microstructure and simulation of nano-structural feature of the doped CeO_2 solid electrolytes will clarify the best pathway for development of high quality doped CeO_2 solid electrolytes in intermediate temperature operation of SOFCs.

Microanalysis of doped CeO_2 electrolytes

CeO_2 electrolytes doped with tri-valent rare earth cation or di-valent alkaline earth cation have been widely investigated. The additives produce materials with extensive solid solubility in the fluorite CeO_2 lattice. The relationships among physical, chemical, electrochemical properties, dopant size, and dopant content in CeO_2 electrolytes were widely examined before.^[14-16] It has been considered that aforementioned doped CeO_2 electrolytes exhibited high oxide ionic conductivity due to the small association enthalpy between dopant cation and oxygen vacancy in the fluorite lattice. However, these arguments lacked an important viewpoint from careful micro-analysis in doped CeO_2 electrolytes. The prospective improvements in the electrolytic properties (i.e. conductivity, activation energy, oxygen partial pressure dependence of conductivity and so on) of doped CeO_2 would be limited. In light of this limitation, a careful atom-level observation is required for development of doped CeO_2 .

The authors examined the relationship among oxide ionic conductivity, dopant content and microstructural features of Y doped CeO_2 electrolyte.^[18-20] The conductivity showed the maximum at the composition around $x=0.15$ in $\text{Y}_x\text{Ce}_{1-x}\text{O}_{2-x/2}$ ($x=0.1, 0.15, 0.2$ and 0.25) system. Also, the activation energy of Y doped CeO_2 electrolytes was minimized at the same composition (i.e. Y: 15at.%) in CeO_2 doped with Y system. This indicates that the mobility of oxide ion is maximized at the aforementioned composition in the $\text{Y}_x\text{Ce}_{1-x}\text{O}_{2-x/2}$ system. To conclude why the conductivity and activation energy have optimum value in Y doped CeO_2 , the crystal phase and nano-structural features in the sintered bodies were examined.

To fabricate the dense sintered bodies of $\text{Y}_x\text{Ce}_{1-x}\text{O}_{2-x/2}$ ($x=0.1, 0.15, 0.2$, and 0.25), the nano-sized easy sinterable powders were prepared using soft chemical approach (Fig.1(a)). Also dense sintered bodies were fabricated using those calcined powders as shown in Fig.1(a). X-ray diffraction profiles recorded from those sintered

bodies consist of simple fluorite structure (Fig.1(b)), but the selected area electron

Figure 1 (a) Scanning electron microscope (SEM) photographs of calcined powders, sintered bodies of $\text{Y}_x\text{Ce}_{1-x}\text{O}_{2-x/2}$, (b) X-ray diffraction patterns recorded from $\text{Y}_x\text{Ce}_{1-x}\text{O}_{2-x/2}$ calcined powders. Calcination temperature: 700°C .^[19]

diffraction patterns (SAEDPs) recorded from $\text{Y}_x\text{Ce}_{1-x}\text{O}_{2-x/2}$ ($x = 0.1, 0.15, 0.2$ and 0.25) sintered bodies have diffuse scattering in the background of SAEDPs (Fig.2). The intensity of extra reflection and diffuse scattering in SAEDP of $\text{Y}_{0.25}\text{Ce}_{0.75}\text{O}_{1.875}$ is much stronger than that of $\text{Y}_{0.15}\text{Ce}_{0.85}\text{O}_{1.925}$.

Figure 2 Selected area electron diffraction patterns (SAEDPs) recorded from $\text{Y}_x\text{Ce}_{1-x}\text{O}_{2-x/2}$ ($x = 0.1, 0.15, 0.2$ and 0.25) sintered bodies, (a) $x=0.1$, (b) $x=0.15$, (c) $x=0.2$, (d) $x=0.25$, white arrows indicate diffuse scattering in the background of SAEDPs.^[19]

This indicates that all observed specimens have the micro-domains with ordered structure of oxygen vacancies. The micro-domain size in $\text{Y}_{0.25}\text{Ce}_{0.75}\text{O}_{1.875}$ is bigger than that in $\text{Y}_{0.15}\text{Ce}_{0.85}\text{O}_{1.925}$.

Figure 3 Relationship between conductivity and microstructural features of Y doped CeO_2 solid electrolytes. (a): microstructure at atomic scale of $\text{Y}_{0.15}\text{Ce}_{0.85}\text{O}_{1.925}$ sintered body with high conductivity, (b): microstructure at atomic scale of $\text{Y}_{0.25}\text{Ce}_{0.75}\text{O}_{1.875}$ sintered body with low conductivity, white arrows and white dashed line indicate the micro-domains and (c): Arrhenius plots of conductivity. [21]

To conclude the relationship between micro-domain structure and conducting properties of doped CeO_2 solid electrolytes in detail, microstructural features and temperature dependence of conductivity of Y doped CeO_2 system were examined as shown in Fig.3. Our high resolution - transmission electron microscopy (HR-TEM) shows us that $\text{Y}_{0.25}\text{Ce}_{0.75}\text{O}_{1.875}$ sintered body with low conductivity includes lots of big messy region so called micro-domain in the microstructure, and a size of the micro-domains in $\text{Y}_{0.15}\text{Ce}_{0.85}\text{O}_{1.925}$ sintered body with high conductivity was much smaller than that of $\text{Y}_{0.25}\text{Ce}_{0.75}\text{O}_{1.875}$. Those indicate that the conductivity in doped CeO_2 solid electrolytes is influenced by the micro-domain size. Also HR-TEM images of aforementioned specimens agree with the conclusion in Fig.2. The dopant cations would aggregate together and precipitate from the matrix. The oxygen vacancies would be deeply trapped by those micro-domains and be arranged with short-ranged orders in the matrix of CeO_2 . Therefore, the authors concluded that the micro-domain size and micro-domain content impacted on the conducting properties in doped CeO_2 . The big micro-domain would lower the conducting properties in Y doped CeO_2 solid electrolytes.

In the previous work about relationship between dopant concentration and conducting properties of doped CeO_2 , the ionic radius mismatch between dopant and host cation Ce was discussed. According to this concept, $\text{Gd}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ can show the highest conductivity

and lowest activation energy in all doped CeO_2 series. It is because ionic radius mismatch between Gd and Ce reaches the minimum and the binding energy of oxygen vacancy and cation becomes a minimum as well.²²⁻²⁴ This concept well explained why the maximum conductivity was changed by the variety of dopant cation in CeO_2 doped with 20% dopant cation. Also the similar tendency was observed in other fluorite systems.²⁵ In the ZrO_2 based system, a part of tetravalent Zr cation site has to be substituted by another cation such as Ca^{2+} , Sc^{3+} , and Y^{3+} . In this system, the ionic radius ratio between Zr^{4+} and aforementioned dopant cation plays a major role to increase the oxide ionic conductivity. The oxide ionic conductivity increases when the ionic radius becomes close to Zr^{4+} (ionic radius of Zr^{4+} for oxygen eight hold coordination: $0.84\text{\AA}$). The best ionic radius of dopant is reached for Sc^{3+} (ionic radius of Sc^{3+} for oxygen eight hold coordination: $0.87\text{\AA}$) with a conductivity equal to 10^{-1} S/cm at 800°C for 10% Sc_2O_3 doped ZrO_2 . This conductivity of Sc_2O_3 doped ZrO_2 is much higher than 10% Y_2O_3 doped ZrO_2 ($3 \times 10^{-2}\text{ S/cm}$) at the same measurement temperature. Also Bi_2O_3 based oxides show the similar tendency. In the case of Bi_2O_3 based system, δ -fcc forms are high oxide ionic conductors. The polymorphism of Bi_2O_3 based materials depends on ionic radius of dopant cation. When the ionic radius ratio between dopant cation and Bi becomes 0.9 to 0.95, δ cubic phase is appeared.

Figure 4 (a) grain size dependence of conductivity of Y doped CeO_2 . [26]

Those results suggest that microstructure at atomic scale can be linked to conducting properties in fluorite type oxide ionic conductors. In the concept of ionic radius mismatch, however, it is not so easy to explain why the lowering of conductivity from $\text{Gd}_{0.15}\text{Ce}_{0.85}\text{O}_{1.925}$ to $\text{Gd}_{0.25}\text{Ce}_{0.75}\text{O}_{1.875}$ is much bigger than that of $\text{Y}_{0.15}\text{Ce}_{0.85}\text{O}_{1.925}$ to $\text{Y}_{0.25}\text{Ce}_{0.75}\text{O}_{1.875}$. For a conclusion of relationship between dopant concentration and conducting properties of doped CeO_2 , an actual microstructure in doped CeO_2

should be taken into account. Based on the results of our micro-analysis, we concluded why the conductivity of $\text{Gd}_{0.25}\text{Ce}_{0.75}\text{O}_{1.875}$ was lower than $\text{Y}_{0.25}\text{Ce}_{0.75}\text{O}_{1.875}$. We briefly introduce our idea on the basis of our micro-analysis results. To conclude the relationships among microstructural features, conductivity, and dopant concentration, the comparison of the grain size dependence of Gd doped CeO_2 and Y doped CeO_2 was re-introduced in Fig.4 (a) to (d).

Figure 4 (b) grain size dependence of conductivity of Gd doped CeO_2 .^[26]

In the case of $\text{Gd}_{0.15}\text{Ce}_{0.85}\text{O}_{1.925}$ and $\text{Y}_{0.15}\text{Ce}_{0.85}\text{O}_{1.925}$, small amount of dopant was aggregated into micro-domains. The dopant concentration into micro-domain was 3 to 5% higher than that in the matrix (i.e. outside of micro-domain). And the size of micro-domain of $\text{Gd}_{0.15}\text{Ce}_{0.85}\text{O}_{1.925}$ would be smaller than that of $\text{Y}_{0.15}\text{Ce}_{0.85}\text{O}_{1.925}$. The authors will demonstrate micro-domain size difference between those Gd doped CeO_2 and Y doped CeO_2 using TEM pictures in Fig.5 and Fig.6. Based on our microanalysis results, relationship between dopant aggregation level and distance of two micro-domains was illustrated in Fig.4 (c) and (d). In those illustrations, a degree of oxygen vacancy ordering corresponds to dopant agglomeration level. The micro-domain size of $\text{Y}_{0.15}\text{Ce}_{0.85}\text{O}_{1.925}$ is bigger than $\text{Gd}_{0.15}\text{Ce}_{0.85}\text{O}_{1.925}$. And the total amount of aggregation of dopant in the small micro-domain area of $\text{Gd}_{0.15}\text{Ce}_{0.85}\text{O}_{1.925}$ is as

almost same as in the $\text{Y}_{0.15}\text{Ce}_{0.85}\text{O}_{1.925}$. Those results indicate that the degree of oxygen vacancy ordering into the micro-domain of Gd doped CeO_2 is higher than Y doped CeO_2 . In the microstructure of $\text{Gd}_{0.15}\text{Ce}_{0.85}\text{O}_{1.925}$, there are some clean areas among micro-domains.

Figure 4(c) and (d) dopant aggregation level into micro-domains of Y doped CeO_2 system (c) and Gd doped CeO_2 system (d).

Therefore, the oxide ion can easily diffuse into the heterogeneous micro-domain structure. On the other hand, the edges of micro-domain area are overlapped in the microstructure of $\text{Y}_{0.15}\text{Ce}_{0.85}\text{O}_{1.925}$ (as shown in Fig.4c). This is why the activation energy of Gd doped CeO_2 is lower than Y doped CeO_2 .

In the heavy dopant region (i.e. $\text{Gd}_{0.25}\text{Ce}_{0.75}\text{O}_{1.875}$), however, quite small micro-domains would be created between micro-domains of $\text{Gd}_{0.25}\text{Ce}_{0.75}\text{O}_{1.875}$. Then, the mobility of oxide ions in the microstructure of $\text{Gd}_{0.25}\text{Ce}_{0.75}\text{O}_{1.875}$ becomes low. The lowering of conductivity from $\text{Gd}_{0.15}\text{Ce}_{0.85}\text{O}_{1.925}$ to $\text{Gd}_{0.25}\text{Ce}_{0.75}\text{O}_{1.875}$ becomes big as compared with the degradation of conductivity from $\text{Y}_{0.15}\text{Ce}_{0.85}\text{O}_{1.925}$ to $\text{Y}_{0.25}\text{Ce}_{0.75}\text{O}_{1.875}$ (Fig.4a and 4b). As mentioned above, the relationship between dopant concentration and conducting properties of doped CeO_2 has to conclude on the basis of careful microanalysis of doped CeO_2 solid electrolytes.

To make sure the validity of our conclusion, bright field image and dark field image were displayed in Fig.5. In Fig.5, some brighter areas in the dark field images were much darker in the bright field images. Those contrast changes in both images mean that the chemical composition and local structure in the brighter areas in the dark field images are different from the matrix area of Y doped CeO_2 sintered body.

Figure 5 Dark field image and bright field image recorded from $\text{Y}_{0.25}\text{Ce}_{0.75}\text{O}_{1.875}$ sintered body with low conducting property.

To compare the size and distribution of micro-domains of $\text{Y}_{0.25}\text{Ce}_{0.75}\text{O}_{1.875}$ and $\text{Gd}_{0.25}\text{Ce}_{0.75}\text{O}_{1.875}$, dark field image and bright field image recorded from $\text{Gd}_{0.25}\text{Ce}_{0.75}\text{O}_{1.875}$ are shown in Fig.6. The microstructural feature of Gd doped CeO_2 was similar to Y doped CeO_2 . But brighter areas in the dark field image recorded from $\text{Gd}_{0.25}\text{Ce}_{0.75}\text{O}_{1.875}$ was much smaller than that of $\text{Y}_{0.25}\text{Ce}_{0.75}\text{O}_{1.875}$. Since this type argument is based on preliminary observation of microstructure, we compared the size of micro-domain using high resolution TEM. This TEM observation basically agreed with our preliminary observation. Based on those data, it is concluded that micro-domains size and its distribution are different in the microstructure of

Figure 6 SEM image, bright field (a) and dark field (b) images recorded from $\text{Gd}_{0.25}\text{Ce}_{0.75}\text{O}_{1.875}$ sintered body.

each doped CeO_2 system. Those are changed by the dopant content. And relationship between dopant content and micro-structural features was summarized as follows. In the dilution region of dopant content (i.e. less than 10%), size of micro-domain is quite small. But the size of micro-domain becomes big when dopant content is more than 20% or 25%. Also the super-lattice is observed when dopant content is over 40% or 50% in doped CeO_2 system.

Moreover, the ordered structure of oxygen vacancy in the microstructure would be changed by the dopant content in doped CeO_2 . To conclude the influence of oxygen vacancy ordering on conducting properties in the heterogeneous micro-domain structure of doped CeO_2 , we already started a simulation of ordered oxygen vacancy structure using our simulation method. The authors will touch on this matter in the sections of Fig.9, Fig.10 and Table 1 in this paper.

Those results suggest that sintered bodies of CeO_2 with tri-valent cation are still in a non-equilibrium state. The authors will discuss why the heterogeneous microstructure at atomic scale is observed in doped CeO_2 sintered bodies latter. Before that, we must conclude what is micro-domain. What is the different between micro-domain area and matrix area of the grain in the materials? To clarify those points, we compared microstructures into two specimens. One is $\text{Y}_{0.25}\text{Ce}_{0.75}\text{O}_{1.875}$ sintered at 1100°C , another one is $\text{Y}_{0.25}\text{Ce}_{0.75}\text{O}_{1.875}$ sintered at 1450°C (Fig.7).

Figure7 Ce and Y element mappings and SAEDPs recorded from $\text{Y}_{0.25}\text{Ce}_{0.75}\text{O}_{1.875}$ sintered at 1450°C and 1100°C . Black arrows indicate aggregation of Y and Ce elements in the sintered bodies. ^[32]

In the specimen sintered at 1100°C , there were no some interesting micro-structural features. It looks homogeneous. But aggregation of dopant cation Y was clearly observed in the specimen sintered at 1450°C . Y concentration in the micro-domains was about 30%, while Y concentration in the matrix was about 25%. Also

a big diffuse scattering was observed in the background of SAEDPs recorded from the specimen sintered at 1450°C. It is concluded that the short range ordering of oxygen vacancy in the heterogeneous microstructure of doped CeO_2 creates those big diffuse scattering in the background of SAEDPs. Usually, the short range ordering of oxygen vacancy will be in one unit cell or half cell size. If the ordering of oxygen vacancy made a long chain and gather it into micro-domain area, an ordered structure line can be observed in the XRD profile by Bragg diffraction of X-ray analysis. Therefore, we conclude that there are so many small clusters consisted of oxygen vacancy and dopant cation in the microstructure. Many small oxygen vacancy clusters were gathered into the micro-domain area. Then the diffuse scattering comes up in the background of SAEDPs. In the section of our simulation, the authors will explain this point. Based on our observation results, we propose the following micro-domain formation process.

In general, the easy sinterable powders were prepared for fabrication of dense sintered bodies using soft chemical process (i.e. co-precipitation method, sol-gel method, hydrolysis method and so on). In the case of preparation of solid solution such as trivalent or di-valent cation doped CeO_2 system, nano-level inhomogeneity would be still in the calcined powders which are prepared by means of the soft chemical process. In the homogeneous grain growth specimen which is fabricated at lower temperature, the heterogeneity in the grain of sintered body is still low level. In the heterogeneous grain growth specimens which is fabricated at higher temperature such as 1450°C, however, the heterogeneity is increased by the development of aggregation of dopant in the grain. Then the micro-domain was clearly formed into the grain of doped CeO_2 sintered bodies. Since this microstructural change in doped CeO_2 sintered body was subtle, relationship between electrolytic properties and nano-structural features has not been examined well. To decrease the nano-level inhomogeneity in the calcined powders, a long time anneal of powders at higher temperature would be effective. But such long annealed powders will lose the good sinterability. That means that processing route for fabrication of fine solid electrolyte powders and dense sintered bodies has to be carefully designed on the basis of microanalysis results. The authors believe that a design of high quality solid electrolytes on the basis of careful microanalysis marks a major breakthrough in the fuel cell field.

For development of our design concept, we must think about the concentration of oxygen vacancies into micro-domain and among the micro-domains in the fluorite matrix of doped CeO_2 . For our discussion, we need simulation of ordering or clustering of oxygen vacancy in the micro-domain and among the micro-domains. Also we need to discuss about the degree of

crystallographic order of the dopant atoms and oxygen vacancies in the microstructure. The authors will touch this point in the section of simulation.

In addition, to design the oxide ionic conductors for fuel cell application, we must think about the influence of the redox state of Ce on conducting properties. This argument is important for a design of doped CeO_2 oxide ionic conductor. Therefore, the authors will explain our results and idea in the parts of Fig.11 to Fig.14.

Before those discussions, we will explain the degree of oxygen vacancy ordering into micro-domain. To analyze it, the oxygen vacancy ordering into the micro-domain was observed by means of electron energy-loss spectroscopy (EELS) analysis method. O K-edge spectra recorded from micro-domain area and matrix area of $\text{Y}_{0.25}\text{Ce}_{0.75}\text{O}_{1.875}$ sintered body were shown in Fig.8. Figure 8a shows us that peak B height is much taller than that of peak C. This oxygen vacancy ordering in Ce doped Y_2O_3 and Y_2O_3 on Si was observed using X-ray photoelectron spectroscopy,²⁷ X-ray Absorption Spectroscopy²⁷ and EELS²⁸ before. Those previous works suggested that the degree of oxygen vacancy into Y_2O_3 can be characterized using O K-edge spectra. Since their ideas are quite interesting and explain the microstructural features well, we try to use same characterization method to understand of the micro-domain structure in the doped CeO_2 . As shown in Fig.8(a), the peak B height was quite different between micro-domain area and matrix area.

Figure 8 EELS oxygen K-edge spectra recorded from micro-domain area and matrix area of $\text{Y}_{0.25}\text{Ce}_{0.75}\text{O}_{1.875}$ sintered body and HR-TEM image for EELS analysis. Sintering temperature: 1450°C. [32]

This microanalysis leads us to conclude that the degree of oxygen vacancy is higher than the matrix area of fluorite structure. To confirm the

actual oxygen vacancy structure of micro-domain, however, a simulation of the oxygen vacancy structure in the micro-domain area and in the matrix area among micro-domains is required.

To conclude the oxygen defect structure into and between the micro-domains in doped CeO_2 , we tried to simulate SAEDPs using Mott-Littleton two-region approach.

In the simulation of F.Ye who is one of authors,²⁰ the clusters of oxygen vacancy and dopant cation were assumed into micro-domain of Gd doped CeO_2 . In this idea, the micro-domain consists of group of the clusters. Most simple oxygen vacancy cluster is $2\text{Gd}_{\text{Ce}}'-1\text{V}_\text{o}''$. One oxygen vacancy is associated with two dopant Gd^{3+} . In this work, electrically neutral clusters were assumed by the combination of one to four oxygen vacancies and two to eight Gd^{3+} cations. (i.e. $2\text{Gd}_{\text{Ce}}'-1\text{V}_\text{o}''$, $4\text{Gd}_{\text{Ce}}'-2\text{V}_\text{o}''$, $6\text{Gd}_{\text{Ce}}'-3\text{V}_\text{o}''$, and $8\text{Gd}_{\text{Ce}}'-4\text{V}_\text{o}''$). The binding energy (ΔE) of electrically neutral clusters is calculated by the following equation.

$$\Delta E = \sum E_{\text{isolated}} - E_{\text{cluster}}$$

where E_{cluster} is the energy of a defect cluster, E_{isolated} is the sum of the defect energies of the corresponding isolated defects Gd_{Ce}' and V_o'' . A higher binding energy means the high stability of cluster in the matrix of simple fluorite. For the simulation of short range ordering structure, stability of five types of short range ordering of oxygen vacancy cluster types were re-introduced in Fig.9 and Table 1. In this simulation, The helical chain of type 1 is most stable in all types of oxygen vacancy cluster chains. This type 1 oxygen vacancy cluster chain would be major in the micro-domain. But the authors conclude that so many short oxygen vacancy cluster chains gather into the micro-domain. Then the stability of micro-domain area would be increased in the matrix of fluorite by the formation of huge group of oxygen vacancy clusters. Now we simulate the defect structure consists of oxygen vacancy clusters among micro-domains. After we develop this simulation works, it is expected that oxygen defect structure of doped CeO_2 solid electrolytes will be clarified in the viewpoint of crystallography. In our next step, we are going to simulate a diffusion of oxide ion in this nano-heterogeneous structure for a design of high quality doped CeO_2 solid electrolyte. Our challenge of the design of doped CeO_2 on the basis of micro-analysis of actual microstructure will provide us a great opportunity of breakthrough of fuel cell technology.

Since the most stable oxygen vacancy cluster structure was type 1, we used this type 1 for the calculation of SAEDP. Calculated SAEDP and observed SAEDP were compared in Fig.10. There was no diffuse scattering in the background of calculated electron diffraction pattern on the basis of simple fluorite structure (Fig.10a). On the other hand, the diffuse scattering came up in

the background of calculated electron diffraction pattern on the basis of short range ordering model (type 1) as shown in Fig.10b. Also Fig. 10b almost agreed with observed electron diffraction pattern (Fig.10c).

Similar x-ray diffuse scattering²⁹ and neutron diffuse scattering³⁰ was observed into the Y_2O_3 stabilized ZrO_2 before. Also influence of the diffuse scattering of the stabilized ZrO_2 on long time aging was observed by TEM.³¹ Those analysis suggest that the diffuse scattering is appeared by the short range ordering of oxygen vacancy in the fluorite lattice. It would be attributable to phase separation of tetragonal zirconia and cubic zirconia at micro-scale. On the other hand, in the case of doped CeO_2 sintered bodies, the aggregation of dopant cation in the grain provided the diffuse scattering into the background of electron diffraction patterns.

Those results clearly tell us that a combination of ultimate analysis, simulation and processing route design will give us a new design paradigm for development of high quality doped CeO_2 solid electrolytes. And we conclude that a control of nano-inhomogeneity in doped CeO_2 is a key for design of high quality solid electrolytes for fuel cell application.

Figure 9 Type of defect clusters in Gd doped CeO_2 , (a): $2\text{Gd}_{\text{Ce}}'-1\text{V}_\text{o}''$, $4\text{Gd}_{\text{Ce}}'-2\text{V}_\text{o}''$, and (b): $6\text{Gd}_{\text{Ce}}'-3\text{V}_\text{o}''$, $8\text{Gd}_{\text{Ce}}'-4\text{V}_\text{o}''$.^[20]

Table 1 Binding energies of clusters.

Type	Chain of clusters	Distance of $\text{Vo}^{**}-\text{Gd}_{\text{Ce}}$	Distance of $\text{Vo}^{**}-\text{Vo}^{**}$	n=1	ΔE (eV)			
					2	3	4	
1	Curved	$\langle 311 \rangle/4$	$\langle 110 \rangle/2$	0.75	1.42	2.24	3.56	
2	Curved	$\langle 111 \rangle/4$	$\langle 110 \rangle/2$	0.57	1.28	2.04	2.81	
3	Straight	$\langle 311 \rangle/4$	$\langle 110 \rangle/2$	0.75	1.42	2.03	2.83	
4	Straight	$\langle 111 \rangle/4$	$\langle 110 \rangle/2$	0.57	1.28	1.93	2.51	
5	Curved	$\langle 311 \rangle/4$	$\langle 111 \rangle/2$	0.75	1.46	2.29	3.18

Figure 10 a: [110] calculated electron diffraction pattern on the basis of simple fluorite structure, b: [110] calculated electron diffraction pattern on the basis of type I cluster structure, c: [110] observed electron diffraction pattern.

Influence of nano-inhomogeneity on macro-scale properties of doped CeO_2 electrolytes

To let our design concept mature, the authors have been extensively investigated the influence of nano-structural features on conducting properties in Gd -,^[21, 26, 32-36] Sm -,^[33,37,38] Y -,^[18,19,39-41,45] Yb -,^[42] La -,^[38,43] Ho -,^[44,45] Dy -,^[46,47] Tb -,^[48-52] doped CeO_2 electrolytes. For development of doped CeO_2 , the semi-conducting property has to be depressed. Ho -, and Tb doped CeO_2 are known as semi-conductors which dominant carrier in conduction phenomena is hole or electron. However, Ho -, and Tb -doped CeO_2 systems have a wide single phase region of fluorite. In general feeling, the oxide ionic conductor consists of simple fluorite structure. Why did those doped CeO_2 systems show the semi-conducting property? To conclude the influence of microstructural features on semi-conducting property of doped CeO_2 , we observed the micro-structural features of Ho -, and Tb -doped CeO_2 specimens sintered at 1450-1500°C. The microstructural features of Ho -, and Tb -doped CeO_2 are quite different as compared with Gd -, Sm -, and Y -doped CeO_2 . The microstructural features of Tb doped CeO_2 was demonstrated in Fig.11. The small precipitation in

the microstructure was observed in this figure. Tb M-edge peak from precipitation area was much higher than outside of precipitation area. The Tb content in the small precipitation area (i.e. white dashed line area of TEM image in Fig.11) was approximately 9atm.% higher than that in the matrix area (i.e. fluorite structure area). Also a big change of Ce M-edge peak was observed in this figure. In the matrix area, Ce M-edge peak has small shoulder as shown in Fig.11.

Figure 11 (a): HR-TEM image recorded from $\text{Tb}_{0.1}\text{Ce}_{0.9}\text{O}_{1.95}$ sintered body, (b) HR-TEM image and (c) EELS Tb and Ce M-edge spectra recorded from $\text{Tb}_{0.25}\text{Ce}_{0.75}\text{O}_{0.875}$ sintered body.^[50]

It is because Ce^{4+} M-edge peak has this type small shoulder. But Ce^{3+} does not have this shoulder peak. This indicates that Ce^{3+} content into the small precipitation area was much higher than that in the matrix area. Based on those microanalysis results, it is concluded that tri-valent cations (i.e. Tb^{3+} and Ce^{3+}) were aggregated into the small precipitation area. And this suggests that a high level oxygen vacancy ordering is around small precipitation area. However, it is very hard to observe those subtle changes of microstructure using standard X-ray diffraction analysis.

As mentioned above, it is concluded that the oxide ionic conductivity and semi-conducting property in doped CeO_2 are conspicuously influenced by the subtle changes of microstructure at atomic scale in the specimens.

To maximize the potential of doped CeO_2 system in our work, dense Dy doped CeO_2 specimens were fabricated using conventional sintering (CS) and pulsed electric current sintering (PECS) methods. Usually, we have fabricated CS specimens with heterogeneous grain growth. To fabricate the homogeneous grain growth specimen, dense sintered bodies were fabricated using PECS method. The microstructures of PECS specimens were shown

in Fig.12 (b) and (c). To calculate mean grain size, we scanned 500 grains in SEM pictures of sintered body and calculated mean grain size using those data.

Figure 12 SEM images and grain size distributions recorded from (a) CS and (b) PECS $\text{Dy}_{0.25}\text{Ce}_{0.75}\text{O}_{1.875}$ specimens. Sintering temperature: 1150°C.

In the case of CS specimen, the grain size distribution in the sintered body is quite broad (Fig.12(a-2)). On the other hand, we successfully fabricated dense PECS specimens which had a quite sharp grain size distribution as shown in Fig.12(c-2). In the case of CS specimen, the compact body is heated by heat elements in the furnace. In this case, the compact body is heated from outside of specimen. On the other hand, PECS specimen is fabricated by the applied direct current. In the case of PECS specimen, almost all grain boundaries can be homogeneously heated by means of this sintering method. Then we can expect homogeneous grain growth in the specimen during the sintering process. Since we can clearly see the difference of grain size distribution between CS and PECS specimens, we concluded that nano-inhomogeneity in the PECS specimen was improved as compared with CS specimen.

The grain size dependence of electrolytic properties (i.e. conductivity, activation energy and oxygen partial pressure (P_{O_2}) dependence of conductivity) of $\text{Dy}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ sintered body were shown in Fig.13.^[47] The activation energy of sintered bodies was calculated using the data of temperature dependence of conductivity from 400 to 600°C. The P_{O_2} was changed by the oxygen, air, argon, humidified hydrogen and hydrogen gas flow. The oxygen partial pressure was checked by the external ZrO_2 oxygen gas sensor which is heated at 800°C. The conductivity of Dy doped CeO_2 was conspicuously enhanced by the improvement of heterogeneity of microstructure. Also the change of activation energy of sintered bodies corresponded to the change of conductivity. To conclude why the conductivity

was improved in the Dy doped CeO_2 sintered bodies, the P_{O_2} dependence of conductivity was examined. The P_{O_2} dependence of conductivity was constant in relation to measured P_{O_2} as demonstrated in Fig.13(b). This indicates that the improvement of conductivity of PECS specimens is attributable to an enhancement of oxide ionic conductivity in homogeneous microstructure at micrometer scale.

Figure 13 (a): average grain size dependence of conducting properties (i.e. conductivity and activation energy), (b): oxygen partial pressure dependence of conductivity of $\text{Dy}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ sintered body.^[47]

Also this suggests that the heterogeneity of microstructure at micrometer scale is linked to the heterogeneity of microstructure at nano-scale.

Figure 14 demonstrates the relationship

between the heterogeneity of microstructure and the conductivity in Dy doped CeO₂ specimens.

Figure 14 Schematic diagram of conducting property at 500°C vs. micro-structural feature of Dy doped CeO₂ sintered specimens. ^[47]

The TEM observation in Fig.14 shows us that the size of micro-domain was minimized in PECS specimen. This result clearly indicates that we can maximize the potential of doped CeO₂ solid electrolytes by means of a control of nano-inhomogeneity of micro-structure of doped CeO₂. Now the detail micro-structural features in PECS specimen and doped CeO₂ thin film devices are under observation. And we try to understand the relationship between nano-scale inhomogeneity and macro-properties such as electrolytic property using doped CeO₂ system. In the near future, we expect that we will be able to develop our simulation method and predict an ideal microstructure of doped CeO₂ solid electrolytes which has high oxide ionic conductivity and excellent long time durability for fuel cell application.

Summary

In our short review, we re-introduced a part of our recent results about microanalysis of microstructure, simulation of oxygen defect structure and processing route design for an improvement of macro-property in doped CeO₂ solid electrolytes. Many small micro-domains with ordered structure of oxygen vacancy coexisted into the fluorite structure. The electrolytic properties of doped CeO₂ become low by the formation of big micro-domains. And we successfully decreased the size of micro-domains in our materials and improved the electrolytic properties of doped CeO₂. Based on our all experimental results, it is expected that micro-domain size in doped CeO₂ will be minimized into sub-nano scale and the electrolytic properties will be maximized by means of the combination of ultimate analysis, simulation and processing route design. The authors believe that the aforementioned combination approach will provide us a great opportunity for future innovative works in our

fuel cell field.

References

- [1] N.Yamazoe and N.Miura, *MRS Bull.*, 24(6), 37-43(1999).
- [2] U.Nigge, H.D.Wiemhofer, E.W.J.Romer, H.J.M. Bouwmeester, T.R.Schulte, *Solid State Ionics*, 146(1-2), 163-174(2002).
- [3] A.Hashimoto, T.Hibino, M.Sano, *Electrochemical and Solid State Letters*, 5(2), H1-H3(2002).
- [4] N.Izu, W.Shin, I.Matsubara, N.Murayama, *Sensors and Actuators B-Chemical*, 101(3), 381-386(2004).
- [5] T.Hibino, K.Ushiki, Y.Kuwahara, and M.Mizuno, *J.Chem.Soc.-Faraday Transactions*, 92(21), 4297-4300(1996).
- [6] H.Uchida, N.Osada, and M.Watanabe, *Electrochemical and Solid State Letters*, 7(12), A500-A502(2004).
- [7] J.Udagawa, P.Aguiar, N.P.Brandon, *Journal of Power Sources*, 180(1), 46-55(2008).
- [8] S.C.Singhal, "Science and technology of solid oxide fuel cells", *MRS Bull.*, 25(3), 16-21(2000).
- [9] B.C.H.Steel, *Nature*, 414(15), 345-352(2001).
- [10] R.M.Ormerod, *Chemical Society Reviews*, 32(1), 17-28(2003).
- [11] I. Riess, *Journal of Power Sources*, 175, 325-337(2008).
- [12] M.Sucipta, S.Kimijima, and K.Suzuki, *Journal of the Electrochemical Society*, 155(3), B258- B263(2008).
- [13] H.Yahiro, Y.Baba, K.Eguchi and H.Arai, *Journal of the Electrochemical Society*, 135(8), 2077-2080(1988).
- [14] V.Buttler, C. R. A. Catlow, B. E. F. Fender, and J.H.Harding, *Solid State Ionics*, 8, 109-113(1983).
- [15] J.Kilner, *Solid State Ionics*, 129, 13-23(2000).
- [16] M.Mogensen, N.M.Sammes, G.A.Tompsett, *Solid State Ionics*, 129(1-4), 63-94(2000).
- [17] V. Esposito, and E. Traversa, *Journal of the American Ceramics Society*, 91(4), 1037-1051(2008).
- [18] T.Mori, J.Drennan, Y.Wang, G.Auchterlonie, J.G.Li, and A.Yago, *Science and Technology of Advanced Materials*, 4, 213-220(2003).
- [19] D.R.Ou, T.Mori, F.Ye, M.Takahashi J.Zou and J.Drennan, *Acta Materialia*, 54, 3737-3746(2006).
- [20] F.Ye, T.Mori, D.R.Ou, A.N.Cormack, R.J.Lewis, and J.Drennan, *Solid State Ionics*, 179(35-36), 1962-1967(2008).
- [21] T.Mori, J.Drennan, D.R.Ou, and F.Ye, *International Journal of Nuclear Research (NUKLEONIKA)*, 51, S11-S18(2006).
- [22] R.Gerhard-Anderson and A.S.Nowick, *Solid State Ionics*, 5, 547-550(1981).
- [23] J.A.Kilner, *Solid State Ionics*, 8, 201-207(1983).
- [24] J.Faber, C.Geoffroy, A.Roux, A.Silverstre and P.Abelard, *Appl.Phys.A*, 49, 225-232(1989).
- [25] J.C.Boivin and G.Mairesse, *Chem. Mater*, 10,

2870-2888(1998).

[26] T.Mori, R.Buchanan, D.R.Ou, F.Ye, T.Kobayashi, J.Zou, and J.Drennan, *J. Solid State Electrochemistry*, 12(7-8), 841-849(2008).

[27] L.Douillard, M.Gautier, N.Thromat, M.Henriot, and M.J.Guittet, 49(23), 16171-16180(1994).

[28] A.Travols, N.Boukos, G.Apostolopoulos, and A.Dimoulas, *Applied Physics Letters*, 82(3), 4053-4055(2003).

[29] T.R.Welberry, R.L.Withers, J.G.Thompson, and B.D.Butter, *Journal of Solid State Chemistry*, 100, 71-89(1992).

[30] T.Proffen, R.B.Neder and F.Frey, *Acta Cryst.*, B52, 59-65(1996).

[31] Junya Kondoh, Shiomi Kikuchi, Yoichi Tomii and Yasuhiko Ito, *Journal of the Electrochemical Society*, 145(5), 1536-1550 (1998).

[32] D. R. Ou, T. Mori, F. Ye, J. Zou, G. Auchterlonie and J. Drennan, *Electrochemical and Solid-State Letters*, 10(1), 1-3(2007).

[33] R.Buchanan, T.Mori, Y.Wang, D.R.Ou, F.Ye, and J.Drennan, *Transactions of the Materials Research Society of Japan*, 30(4), 955-958(2005).

[34] T.Mori T, and J.Drennan, *J.Electroceramics*, 17(2-4), 749-757(2006).

[35] D.R.Ou, T.Mori, F.Ye, J.Zou, and J.Drennan, *Physical Review B*, 77, article number 024108-1 – 024108-8(2008).

[36] F.Ye, T.Mori, D.R.Ou, J.Zou, G.Auchterlonie, and J.Drennan, *Solid State Ionics*, 179(21-26), 827-831(2008).

[37] T.Mori, J.Drennan, Y.Wang, J.G.Li, and T.Ikegami, *Journal of Thermal Analysis and Calorimetry*, 70(2), 309-319(2002).

[38] T.Mori, J.Drennan, J.H.Lee, J.G.Li, and T.Ikegami, *Solid State Ionics*, 154, Special Issue Part B, 461-466(2002).

[39] Y.Wang, H.Kageyama, T.Mori, H.Yoshikawa, and J.Drennan, *Solid State Ionics*, 177(19-25), 1681-1685(2006).

[40] D.R.Ou, T.Mori, F.Ye, T.Kobayashi, J.Zou, G.Auchterlonie, and J.Drennan, *Applied Physics Letters*, 89(17), 1911-1913(2006).

[41] D.R.Ou, T.Mori, F.Ye, J.Zou, and J.Drennan, *Electrochemical and Solid-State Letters*, 10(1), 1-3(2007).

[42] F.Ye, T.Mori, D.R.Ou, M.Takahashi, J.Zou, and J.Drennan, *Journal of the Electrochemical Society*, 154(2), B180-B185 (2007).

[43] T.Mori, J.Drennan, Y.Wang, J.H.Lee, J.G.Li, and T.Ikegami, *Journal of the Electrochemical Society*, 150(6), A665-A673(2003).

[44] D.R.Ou, T.Mori, F.Ye, J.Zou, G.Auchterlonie, and J.Drennan, *Journal of the Electrochemical Society*, 154(7), B616-B622 (2007).

[45] D. R. Ou, T. Mori, F. Ye, J. Zou, and J. Drennan, *Renewable Energy*, 33, 197-200(2008).

[46] Y.Wang, T.Mori, J.G.Li, and J.Drennan, *Journal of the European Ceramic Society*, 25(6), 949-956(2005).

[47] T.Mori, T.Kobayashi, Y.Wang, J.Drennan,

T.Nishimura, J.G.Li, and H.Kobayashi, *Journal of the American Ceramic Society*, 88(7), 1981-1984(2005).

[48] F.Ye, T.Mori, and D.R.Ou, *Journal of Nanoscience and Nanotechnology*, 7(7), 2521-2525 (2007).

[49] F.Ye, T.Mori, D.R.Ou, J.Zou, and J.Drennan, *Materials Research Bulletin*, 42(5), 943-949(2007).

[50] F.Ye, T.Mori, D.R.Ou, J.Zou, G.Auchterlonie, and J.Drennan, *Journal of Applied Physics*, 101(11), article number: 113528-1 –113528-5(2007).

[51] F.Ye, T.Mori, D.R.Ou, J.Zou, and J.Drennan, *Materials Research Bulletin*, 43(3), 759-764(2008).

[52] F. Ye, T. Mori, D. R. Ou, J. Zou and J. Drennan, *Renewable Energy*, 33, 331-335(2008).

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