Influence of nano-structural feature on electrolytic properties in Y$_2$O$_3$ doped CeO$_2$ system

Toshiyuki Mori$^{a, *}$, John Drennan$^b$, Yarong Wang$^a$, Graeme Auchterlonie$^b$, Ji-Guang Li$^c$, Anya Yago$^b$

$^a$Eco-energy Materials Group, Ecomaterials Center, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan
$^b$Centre for Microscopy and Microanalysis, The University of Queensland, St Lucia, Brisbane, Qld 4072, Australia
$^c$Advanced Materials Laboratory, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

Received 31 March 2003; accepted 7 May 2003

Abstract

Doped ceria (CeO$_2$) compounds are fluorite type 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 'low temperature operation (500–650 °C)' of solid oxide fuel cells (SOFCs). In this study, Y$_x$Ce$_{1-x}$O$_{2-x/2}$ ($x = 0.05, 0.1, 0.15, 0.2$ and $0.25$) fine powders were prepared using a carbonate co-precipitation method. The relationship between electrolytic properties and nano-structural features in the sintered bodies was examined. The micro-structures of Y$_{0.05}$Ce$_{0.95}$O$_{1.975}$, Y$_{0.15}$Ce$_{0.85}$O$_{1.925}$ and Y$_{0.25}$Ce$_{0.75}$O$_{1.875}$ as representative three specimens have been investigated in more detail with transmission electron microscopy (TEM). The big diffuse scattering was observed in the background of electron diffraction pattern recorded from Y$_{0.15}$Ce$_{0.85}$O$_{1.925}$ and Y$_{0.25}$Ce$_{0.75}$O$_{1.875}$ sintered bodies. This means that the coherent micro-domain with ordered structure is in the micro-structure. While Y$_{0.25}$Ce$_{0.75}$O$_{1.875}$ sintered body with low conductivity and high activation energy has big micro-domains, the micro-domain size in Y$_{0.15}$Ce$_{0.85}$O$_{1.925}$ with high conductivity and low activation energy was much smaller than that of Y$_{0.25}$Ce$_{0.75}$O$_{1.875}$. TEM observation gives us message that the size of coherent micro-domain with ordered structure would closely relate to the electrolytic properties such as conductivity and activation energy in the specimens. It was concluded that a control of micro-domain size in nano-scale in Y$_2$O$_3$ doped CeO$_2$ system was a key for development of high quality solid electrolyte in fuel cell application.

Keywords: Yttria doped ceria; Coherent micro-domain; Ordered structure; Diffuse scattering; Micro-structure; Electrolyte; Fuel cell application

1. Introduction

Oxide ion conductors are used in a variety of oxygen sensors [1], solid oxide electrochemical cells (SOECs) [2] such as membrane reactor and solid oxide fuel cells (SOFCs) [3,4]. Of particular interest is a development of SOFCs, which is the possibility of producing clean energy from a variety of fuels. It is an increasingly attractive prospect. The high quality electrolyte will decrease the operation temperature of the cells, and turn the large cell of SOFC system into the compact size. Yttria stabilized zirconia (YSZ) is the most common electrolyte used in such cells. However, the oxide ionic conductivity of YSZ is unsatisfactory level for the electrolyte of SOFCs in 'low' (500–650 °C) temperature operation. Accordingly, it is very important that high quality electrolyte with higher oxide ionic conductivity than that of YSZ is identified for a development of solid electrolyte in SOFCs in the low temperature operation.

Recently, samarium [5,6] or gadolinium [7,8] doped CeO$_2$ electrolyte is attracted much attention from the viewpoint of application in SOFC. It has been considered that these doped CeO$_2$ electrolytes exhibited high oxide ionic conductivity due to small association enthalpy between dopant cation and oxygen vacancy in fluorite lattice [9]. On the other hand, Y doped CeO$_2$ has relatively high electrical conductivity in whole doped-ceria series, although the association enthalpy between dopant cation and oxygen vacancy is a little
bit big. In addition, since \(Y_2O_3\) resource is in abundance, \(Y_2O_3\) doped \(CeO_2\) system has a special interest among doped ceria materials.

Herle et al. [10] reported that excellent conduction properties were observed (i.e. high ionic conductivity \((-0.63 \text{ s/cm at } 700 ^\circ \text{C}\)) low activation energy \((70 \text{ kJ/mol})\) and very small grain boundary resistance) through the examination of sintering behavior and ionic conductivity of \(Y_xCe_{1-x}O_2\) \((x = 0.1–0.33)\) specimens. Tian and Chan [11] investigated the conducting property in \(Y\) doped \(CeO_2\) thin film. They concluded that space charge layer around grain boundary strongly affected conductivity. On the other hand, Adler and Smith [12] simulated conducting property in \(Y\) doped \(CeO_2\) system and pointed out that the simulation result deviated from simple crystal structure of defect fluorite. While good conducting properties in \(Y\) doped \(CeO_2\) system were reported before, the influence of micro-structure on the conducting property has not been clarified yet.

The authors have prepared fine \(Y_2O_3\) doped \(CeO_2\) powders using carbonate co-precipitation method and examined its siterability before [13,14]. The carbonate co-precipitation method was useful method for preparation of fine \(Y_2O_3\) doped \(CeO_2\) powders and sintered bodies with high density.

In the present study, the authors examined the relationship between electrolytic properties and micro-structure for a design of micro-structure in \(Y_2O_3\) doped \(CeO_2\) solid electrolyte. In order to investigate the influence of micro-structure on electrolytic properties, \(Y_xCe_{1-x}O_2\) \((x = 0.05, 0.1, 0.15, 0.20, \text{ and } 0.25)\) was prepared using carbonate co-precipitation method. The micro-structures in the sintered bodies were investigated in detail with transmission electron microscopy (TEM). These were sectioned and 3 mm discs were removed from the central region of each specimen by ultrasonic drilling. These discs were then mechanically ground to a thickness of approximately 100 \(\mu\text{m}\). The final thinning to electron transparency was achieved by ion beam milling. In order to avoid reduction of doped \(CeO_2\) by ion beam milling. Ar ion beam was irradiated using cold stage in liquid nitrogen. TEM observation was performed with gun voltages of 400 and 200 keV (JEOL 4010 and JEOL 2010).

2.2. Sample characterization

The crystal phase in the sintered bodies was identified using X-ray diffraction (XRD, Cu Ka, 40 kV, 40 mA) and selected area electron diffraction pattern. An electron diffraction pattern was calculated using the software CarRine Crystallography version3.1 (presented by Bou-dias and D. Monceau). For detailed examination of the micro-structure, three representative specimens were selected for analysis using TEM. An impurity such as \(SiO_2\) in the grain boundary was checked by TEM equipped with X-ray energy-dispersive spectrometer (XEDS). Ion beam thinned specimens were used for TEM observation. These were sectioned and 3 mm discs were removed from the central region of each specimen by ultrasonic drilling. These discs were then mechanically ground to a thickness of approximately 100 \(\mu\text{m}\).

2.3. Measurement of electrical properties

Electrical conductivity of the sintered specimens was measured by dc three-point measurements at 400–700 \(^\circ\text{C}\) in air. Platinum electrode was applied to both sides of the sintered bodies at 1000 \(^\circ\text{C}\) for 1 h in air. The dimensions of the samples were 10 mm in diameter and 2 mm in thickness for three-point measurements. The activation energy was calculated using the data of conductivity at the temperature ranging from 400 to 700 \(^\circ\text{C}\).

3. Results and discussion

Fig. 1(a) shows the relationship between \(Y\) content in doped \(CeO_2\) electrolytes and the electrical conductivity of the five specimens at the temperature ranging from 400 to 700 \(^\circ\text{C}\). The conductivity of \(Y\) doped \(CeO_2\) electrolytes was maximized at the composition around \(x = 0.15\) in \(Y_xCe_{1-x}O_2\) system in whole measurement temperature. Fig. 1(b) summarizes the \(Y\) content dependence of activation energy in the \(Y\) doped \(CeO_2\) electrolytes. The activation energy of \(Y\) doped \(CeO_2\) electrolytes was minimized at the composition around \(x = 0.15\) in \(Y_xCe_{1-x}O_2\) system. These results indicates that mobility of oxide ion maximized at the composition around \(x = 0.15\) in \(Y_xCe_{1-x}O_2\) system.
In addition, the activation energy in the present work (i.e. 65 kJ/mol) was lower than the previous reported activation energy (i.e. approximately 70 kJ/mol) in Y doped CeO$_2$ electrolytes. The author concluded that the electrolytic properties strongly depend on the micro-structure in the sintered body. In order to conclude why the conductivity and activation energy in Y doped CeO$_2$ electrolytes has optimum value around $x = 0.15$ in Y$_x$Ce$_{1-x}$O$_{2.5}$ the crystal phases and micro-structures in the representative three specimens such as $x = 0.05$, 0.15 and $x = 0.25$ in the composition of Y$_x$Ce$_{1-x}$O$_{2.5}$ were characterized using XRD and TEM.

Fig. 2 displays the XRD profiles of representative three sintered bodies. The representative three specimens Y$_{0.05}$Ce$_{0.95}$O$_{1.975}$, Y$_{0.15}$Ce$_{0.85}$O$_{1.925}$, and Y$_{0.25}$Ce$_{0.75}$O$_{1.875}$ consisted of fluorite structure and no other phases were observed in XRD patterns.

To conclude the influence of impurity in the grain boundaries on conducting properties, isolated impurity such as SiO$_2$ in the grain boundary of representative three specimens was analyzed using XEDS experimentation. Fig. 3(a)–(c) presents XEDS profiles of triple points and bulk of representative three specimens Y$_{0.05}$Ce$_{0.95}$O$_{1.975}$, Y$_{0.15}$Ce$_{0.85}$O$_{1.925}$, and Y$_{0.25}$Ce$_{0.75}$O$_{1.875}$, respectively. These figures indicate that the composition around triple point is equal to that in bulk. Isolated impurity such as SiO$_2$ in the grain boundary was undetectable of EDS analysis. The grain boundaries of aforementioned three specimens were very clean. Therefore, it is concluded that the composition dependence of ionic conductivity is reflected in changes of micro-structure in the grain.

Fig. 4(a) and 4(b) displays the selected area electron diffraction patterns, $[110]_F$ and $[112]_F$ recorded from Y$_{0.05}$Ce$_{0.95}$O$_{1.975}$ sintered body. In order to analyze the observed diffraction pattern, calculated diffraction pattern of $[110]_F$ and $[112]_F$ are displayed in Fig. 4(g) and 4(h), respectively. The selected area electron diffraction patterns recorded from Y$_{0.05}$Ce$_{0.95}$O$_{1.975}$ showed a simple fluorite pattern, no other information of micro-structural feature was observed. As shown in Fig. 4(c) and 4(d), however, Y$_{0.15}$Ce$_{0.85}$O$_{1.925}$ sintered body has a big diffuse scatter in the background of electron diffraction pattern. This result indicates that coherent micro-domain with ordered structure exists in the fluorite lattice. Since the interface between micro-domain and fluorite lattice was coherent, it is concluded that the very important micro-structural feature did not come up in the XRD patterns of Fig. 2 (b) and 2(c).

Moreover, Y$_{0.25}$Ce$_{0.75}$O$_{1.875}$ has very small extra spots in the electron diffraction pattern recorded from the grain in the sintered body, as displayed in Fig. 4 (e) and 4(f). These results give us message that Y$_{0.05}$Ce$_{0.95}$O$_{1.975}$ consisted of simple fluorite structure and other representative two specimens consisted of fluorite lattice and coherent micro-domain with ordered structure. In addition, the small extra spots in Fig. 4(e) and 4(f) indicates that the size of
micro-domain in the $Y_{0.25}Ce_{0.75}O_{1.875}$ sintered body is much bigger than that in the $Y_{0.15}Ce_{0.85}O_{1.925}$ sintered body. These micro-structural features are subtle change. It is very hard to observe them from general observation using XRD analysis. The author concluded that this subtle change in the micro-structure gives the electrolytic properties big changes.

Fig. 5(a), (b) and (c) demonstrates lattice images at high magnification of aforementioned three specimens. There are no micro-domains in the $Y_{0.05}Ce_{0.95}O_{1.975}$ sintered body which does not have diffuse scatter in the background of electron diffraction pattern. Since the content of oxygen vacancy in this specimen is very low level ($\delta = 2.5$ at.$\%$), it is concluded that the conductivity in this specimens was low level too. On the other hand, $Y_{0.25}Ce_{0.75}O_{1.875}$ sintered body with diffuse scatter and extra spot in the diffraction pattern has big micro-domain with irregular shapes. The size of micro-domain seems to be over 10 nm units. Several micro-domains combined each other to form continuous and large micro-domain. And the micro-domain with ordered structure would lower the mobility of oxide ion and the electrolytic properties in the specimen. In addition, the authors concluded that the crystal structure of micro-domain is c-type like structure as same as $Y_2O_3$. Usually, the lower valance cation such as Y was dissolved into tetra valance Ce site to create oxygen vacancy. However, there is a size misfit of cation between Y and Ce in the fluorite structure of specimen. The big lattice distortion would be introduced in the crystal. In order to minimize the lattice distortion in fluorite lattice, micro-domain would be formed in the lattice. In this study, the micro-domain size was minimized in the $Y_{0.15}Ce_{0.85}O_{1.925}$ sintered body with high conductivity and low activation energy. The size of micro-domain was approximately 5 nm units in the grain of $Y_{0.15}Ce_{0.85}O_{1.925}$ sintered body. Therefore, the author concluded that the composition around $x = 0.15$ in $Y_xCe_{1-x}O_2$ system contributes to minimize the lattice distortion and maximize diffusion of oxide ion in the fluorite lattice of the specimen.

4. Conclusions

The relationship between micro-structure and electrolytic properties was examined in $Y_2O_3$–CeO$_2$ system. Y doped CeO$_2$ specimens which were prepared using co-precipitation method shows maximum conductivity and lowest activation energy at the composition around $x = 0.15$ in $Y_xCe_{1-x}O_2$ system. To conclude the reason why the conductivity and activation energy in Y doped CeO$_2$ electrolytes has optimum value around $x = 0.15$ in $Y_xCe_{1-x}O_2$ system, the crystal phases and micro-structures in the representative three specimens such as $x = 0.05, 0.15$ and $x = 0.25$ in the composition of

---

Fig. 3. XEDS profiles in triple point and bulk of (a) $Y_{0.05}Ce_{0.95}O_{1.975}$ sintered body, (b) $Y_{0.15}Ce_{0.85}O_{1.925}$ sintered body, and (c) $Y_{0.25}Ce_{0.75}O_{1.875}$ sintered body. X: Cu (this element is contamination from sample holder in ion milling process).
$Y_{1-x}Ce_{x}O_{2-x}$ were characterized using XRD and TEM. The micro-analysis of specimens indicates that the size of coherent micro-domain in $Y_{0.15}Ce_{0.85}O_{1.925}$ sintered bodies is smaller than that in $Y_{0.2}Ce_{0.8}O_{1.9}$ sintered body. In the electron diffraction pattern recorded from $Y_{0.2}Ce_{0.8}O_{1.9}$ sintered body, the very small extra spots which means the growth of micro-domain came up in the diffuse scatter. This micro-structural feature is subtle.
Fig. 4 (continued)
Fig. 5. TEM observation of micro-structure in (a) $Y_{0.05}Ce_{0.95}O_{1.975}$ sintered body, and micro-domain in (b) $Y_{0.15}Ce_{0.85}O_{1.925}$ sintered body, and (c) $Y_{0.25}Ce_{0.75}O_{1.875}$ sintered body. Dashed line indicates a micro-domain in the lattice.

Micro-domain size (nm) = f(dopant content, dopant segregation)

Fig. 6. Schematic image of relationship among micro-domain size, conductivity and activation energy.
change. The author believes that this subtle change in the micro-structure gives the electrolytic properties a big change. Fig. 6 illustrates the schematic image of relationship between the size of micro-domain and ionic conductivity in Y doped CeO$_2$ electrolytes. The author concludes that electrolytic properties strongly depend on a micro-structure at atomic level in Y doped CeO$_2$ electrolytes. It is expected that electrolytic properties in Y doped CeO$_2$ system would be improved when the size of micro-domain is in sub nano-level. On the other hand, micro-domain would be formed to minimize the lattice distortion in the crystal. And it is concluded that the lattice distortion is introduced into lattice by a segregation of dopant such as Y. Accordingly, the author expected that the micro-domain size is controllable in sub nano-scale by preparation of fine and homogeneous powder and the electrolytic properties will be improved in the controlled micro-structure.

References

[1] N. Yamazoe, N. Miura, Prospect and problems of solid electrolyte based oxygenic gas sensors, Solid State Ionics 86–88 (2) (1996) 987–993.
[2] S. Hamakawa, T. Hayakawa, T. Tsunoda, K. Suzuki, K. Murata, K. Takehira, Partial oxidation of propene to acrylaldehyde with an electrochemical membrane reactor coated with yttria stabilized zirconia, Electrochem. Solid State Lett. 1 (5) (1998) 220–221.
[3] N.Q. Minh, Ceramic fuel cells, J. Am. Ceram. Soc. 76 (3) (1993) 563–588.
[4] N.Q. Minh, A. Anumakonda, B. Chung, R. Doshi, J. Ferrall, J. Guan, G. Lear, K. Montgomery, E. Ong, J. Yamanis, Development of reduced temperature solid oxide fuel cell power systems, in: S.C. Singhal, M. Dokiya (Eds.), Solid Oxide Fuel Cells (SOFC VI), Proc. Sixth Int. Symp., Honolulu, 17–22 October, vol. 99-19, 1999, pp. 68–74.
[5] M. Gökicke, J.I. Gauckler, Engineering of solid oxide fuel cells with ceria-based electrolyte, J. Electrochem. Soc. 145 (2) (1998) 414–421.
[6] C. Milliken, S. Guruswamy, A. Khandkar, Evaluation of ceria electrolytes in solid oxide fuel cells electric power generation, J. Electrochem. Soc. 146 (3) (1999) 872–882.
[7] R. Doshi, V.L. Richards, J.D. Carter, X. Wang, M. Krumpelt, Development of solid oxide fuel cells that operated at 500°C, J. Electrochem. Soc. 146 (4) (1999) 1273–1278.
[8] B.C.H. Steele, Materials for IT-SOFC Stacks: 35 years R and D; the inevitability of gradualness?, Solid State Ionics 134 (1–2) (2000) 3–20.
[9] J.A. Kilner, C.D. Waters, The effects of dopant cation-oxygen vacancy complexes on the anion transport properties of non-stoichiometric fluorite oxides, Solid State Ionics 6 (3) (1982) 253–259.
[10] J.V. Herle, T. Horita, T. Kawada, N. Sakai, H. Yokokawa, M. Dokiya, Sintering behavior and ionic conductivity of yttria-doped ceria, J. Eur. Ceram. Soc. 16 (9) (1996) 961–973.
[11] C. Tian, S.-W. Chan, Electrical conductivity of (CeO$_2$)$_{1-x}$(Y$_2$O$_3$)$_x$ thin film, J. Am. Ceram. Soc. 85 (9) (2002) 2222–2229.
[12] S.B. Adler, J.W. Smith, Effects of long-range forces on oxygen transport in yttria-doped ceria: simulation and theory, J. Chem. Soc. Faraday Trans. 89 (16) (1993) 3123–3128.
[13] J.-G. Li, T. Ikegami, Y. Wang, T. Mori, Nano-crystalline Ce$_{1-x}$Y$_x$O$_{2-x/2}$ (x = 0, x = 0.35) oxides via carbonate precipitation: synthesis and characterization, J. Solid State Chem. 108 (2002) 52–59.
[14] Y. Wang, T. Mori, J.-G. Li, T. Ikegami, Low temperature synthesis of praseodymium doped ceria nano-powders, J. Am. Ceram. Soc. 85 (12) (2002) 3105–3107.