

SYNTHESIS OF NANOCRYSTALLINE $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ SOLID ELECTROLYTE BY POLYMER COMPLEX METHOD

Patthamaporn Timakul^{1,2}, Yuichiro Kuroki², Tomoichiro Okamoto², and Masasuke Takata^{2*}

Received: August 22, 2012; Revised: January 16, 2013, 2013; Accepted: January 22, 2013

Abstract

Gadolinium-doped ceria (GDC) is to date the most promising solid electrolyte to replace the standard yttria-stabilised zirconia as an electrolyte for solid oxide fuel cells (SOFCs) operating at intermediate temperature. In order to synthesize the electrolyte material used at an intermediate temperature, nanocrystalline GDC powder with a composition of $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ was successfully prepared by the polymer complex (PC) method. The observation by transmission electron microscopy (TEM) revealed that the prepared nanocrystalline GDC powder had an average particle size of 5.5 nm after calcination at 400°C for 2 h. The x-ray diffraction (XRD) patterns of the calcined powders showed a pure cubic fluorite phase. For the electrical property, the total conductivity of the $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ pellets sintered at 1400°C for 4 h was found to be 1.52 S/m at 600°C with the activation energy (E_a) of 0.75 eV in the temperature range of 300-600°C, which results are in the same range as commercial powders produced by combustion spray pyrolysis. This study shows that the simple and low cost PC method could be a good candidate for making nano-sized GDC electrolyte for SOFCs.

Keywords: Polymer Complex Method, Nanocrystalline Powder, GDC Electrolyte, Electrical Conductivity

Introduction

A solid oxide fuel cell (SOFC) is an electrochemical device which can generate electricity with high efficiency and in an environmentally friendly manner compared with traditional electrical generators (Singhal, 2003). However, this specific type of fuel cell has to operate at high temperature between 850-1000°C, which requires a long time and consumes energy at the start up. Current interest in SOFCs is shifting towards lower operating temperatures because of the advantages with regards to fuel cell stack components and a decrease in material costs for the balance of plant construction, which

¹ National Metal and Materials Technology Center, 114 Thailand Science Park, Pathumthani, Thailand. E-mail: patthamt@mtec.or.th

² Department of Electrical Engineering, Nagaoka University of Technology, 1603- Kamitomioka, Nagaoka, Niigata 940-2188, Japan. E-mail: takata@vos.nagaokaut.ac.jp

* Corresponding author

can both reduce structural problems and potentially enhance lifetime (Leng *et al.*, 2004).

One of the concepts to reduce the SOFC operating temperature to an intermediate range about 500-700°C is the replacement of the standard ZrO₂-based electrolyte by other higher ionic conductivity materials such as ceria-based compounds (Leng *et al.*, 2004; Zhang *et al.*, 2004; Fergus, 2006). Ceria doped with rare earth elements has attracted considerable attention due to its high ionic conductivity at a much lower temperature compared with ZrO₂-based ones. Samarium- and gadolinium-doped ceria exhibited the highest ionic conductivity among ceria compounds, showing approximately 0.1 Scm⁻¹ at 700°C (Ralph *et al.*, 2001).

A wide variety of processes has been used for the synthesis of ceramic powders. Solid state techniques require a high calcination temperature above 1000°C for a homogeneous phase formation, whereas wet chemical processes offer high purity, homogeneous composition, and fine powder at lower temperature (Fuentes and Baker, 2009). The polymer complex (PC) method allows an easy control over the final stoichiometry, a low processing temperature, and no intermediate grinding (Kakihana *et al.*, 1999; Kakihana and Yoshimura, 1999; Popa and Kakihana, 2002).

In this work, a simple PC method was employed to synthesize nanocrystalline gadolinium-doped ceria (GDC) powder. The structural and physical characterization was investigated employing thermogravimetric and differential thermal analysis (TG-DTA), X-ray diffraction (XRD), transmission electron microscopy (TEM), and scanning electron microscopy (SEM). Furthermore, the electrical properties of the sintered body prepared by different heat treatments were studied by impedance spectroscopy. For the purpose of comparison, the commercial GDC powder produced by spray pyrolysis was also investigated.

Materials and Methods

GDC Powder Synthesis and Pellet Preparation

The PC method was employed to prepare nanocrystalline Ce_{0.9}Gd_{0.1}O_{1.95} (GDC) powder. Metal nitrate solutions Ce(NO₃)₃·6H₂O (99.99%, Aldrich) and Gd(NO₃)₃·6H₂O (99.9%, Aldrich) were used. Each nitrate was individually dissolved in distilled water in the desired amount and the solution was then mixed. Citric acid (99.5%, Wako) used as a chelating agent and PEG600 (Wako) used as a polymerization agent were added to the nitrate solution. The gel was obtained after heating the solution at 80°C for 4 h to remove excess water and to convert it into a gel. The gel was then heated at 250°C until nanocrystalline GDC powder was obtained. Figure 1 represents a flowchart of the nanocrystalline GDC powder synthesized by the PC method.

The powder was calcined at 400-900°C for 2 h and then pressed into pellets (10 mm ϕ) followed by a cold-isostatic press at 200 MPa. The pellets were then sintered at 600-1400°C for 4 h. In this step, the commercial powder was also fabricated into pellets using the same procedure and sintering conditions in order to compare them with our PC method derived powders. The commercial powder used in this study was GDC produced by spray-pyrolysis from Praxair (UK).

Sample Characterization

TG-DTA of the gel precursor prepared by the PC method was carried out at a heating rate of 5°C/min up to 1000°C using TG-8120 (Rigaku). The particle size of the GDC powders was determined by TEM. The phase identification was investigated by XRD (Rigaku; MultiFlex) using Cu-K α radiation. The microstructure of the pellets was investigated using SEM (JSM-5510, JEOL Ltd., Tokyo, Japan). The grain size determination was performed by the linear intercept method. The ionic conductivity measurement was performed using an

HP 4192A LF Impedance Analyzer. The impedance measurement was measured by the 2-probe method over the frequency range of 5 Hz - 10 MHz. Silver electrodes were coated on both sides of the pellets which were then fired at 800°C for 2 h to ensure the electrical contacts. The measurements were then taken under air atmosphere starting at 600°C down to 300°C with heating and cooling rates of 3°C/min and with a dwell time of 1 h before each measurement.

Results and Discussion

GDC Powder Characterization

Figure 2 illustrates the TG-DTA plots of the GDC dried gel. From the result, it is found that there are 3 distinct weight losses in the temperature ranges from (i) room temperature to 150°C, (ii) 150-250°C, and (iii) 250-317°C. The first one could be ascribed to the release

of H₂O. The second one might be related to the decomposition of the polymer complex. The third one showed a steep weight loss which might be related to the burn-out of residual organic compounds. A small endothermic peak at around 115°C is attributed to the dehydration of the gel powder. One sharp and strong exothermic peak at 303.8°C corresponded to the burn-out of residual organic compounds along with the formation of metal oxides. No more weight loss, endothermic or exothermic was found in the temperature range from 317-1000°C.

Figure 3 (a, b, c, d, e) shows the TEM nanostructure images of the PC method derived powder calcined at various temperatures, and also 3(f) for the commercial powder (spray pyrolysis). The results showed that at 400°C calcination the PC derived powders obtained the smallest particle size of about 5.5 nm. The particle size increased from 5.5-70 nm as calcination temperatures

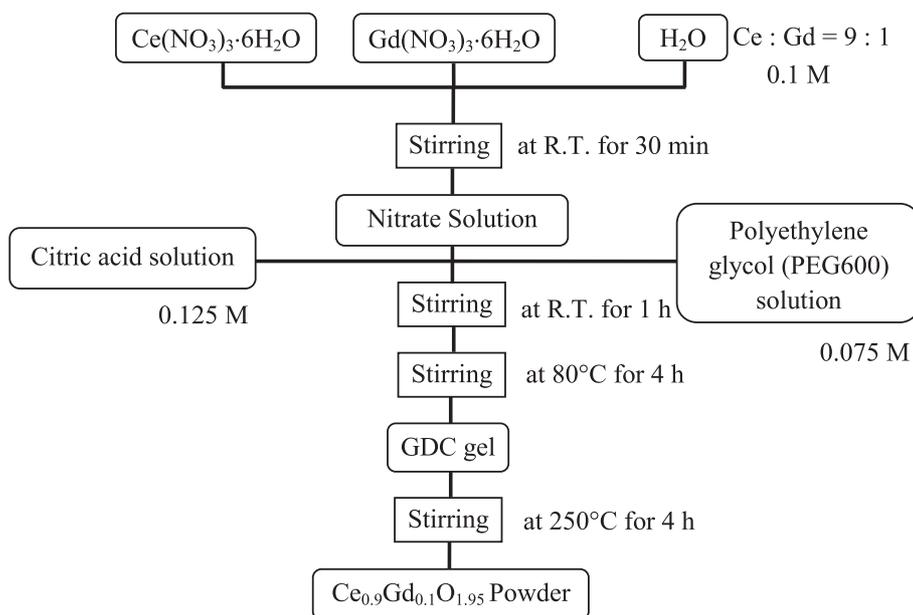


Figure 1. Flowchart illustrating the PC route of nanocrystalline GDC powder

increased from 400-900°C. The as-received commercial powder showed a particle size of 22 nm.

The X-ray diffraction patterns of the GDC powder from the PC method calcined at 400-900°C, and also the patterns of the commercial powder, are presented in Figure 4. They all were characterized to be the peaks of pure cubic fluorite structure. The intensity of the main diffraction peaks increased as calcination temperatures increased indicating a more well-defined crystal structure and the growth of the crystallite size. The diffraction peaks of the 400°C calcined powder were

relatively broad, indicating the smallest crystallite size (Huang *et al.*, 1998; Fuentes *et al.*, 2009), compared to other calcination temperatures which is in a good agreement with the results from the TEM observation. Therefore, we chose this calcined temperature of 400°C to be carried on to sintering.

GDC Pellet Characterization

The SEM fracture surfaces of the sintered pellets derived from the PC method at 600-1400°C for 4 h are shown in Figure 5. The grain size was increased, as the sintering temperature increased from 70-447 nm. Figure 6 shows the fracture surface of the commercially-derived samples sintered at 600-1400°C. The grain size increased from 70 to 520 nm. From the relation between the sintering temperature and the grain size in Figure 7, it could be concluded that the PC method derived powder prepared in this study has a smaller grain size compared to the commercial powder in all sintering temperatures. The density of the GDC pellets from both the PC method and the commercial powder increased as the sintering temperature increased as shown in Figure 8. The densities of the pellets sintered at 1400°C were 90 and

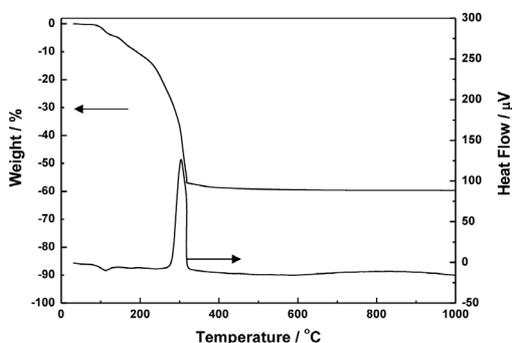


Figure 2. TDA and DTA plots for GDC precursor derived from the PC method

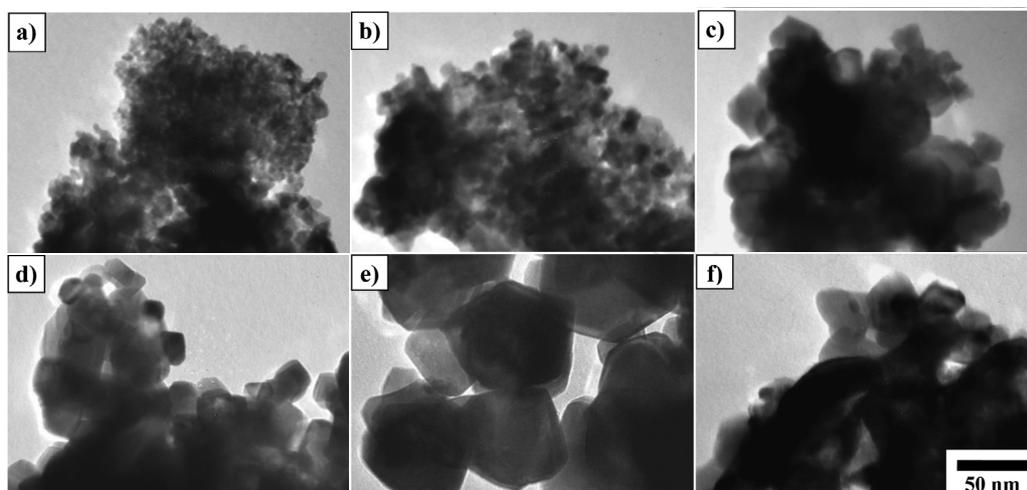


Figure 3. TEM nanostructure images of the PC method derived $Ce_{0.9}Gd_{0.1}O_{1.95}$ powder calcined at a) 400°C, b) 600°C, c) 700°C, d) 800°C, e) 900°C for 2 h, and, f) commercial powder (spray pyrolysis)

96% of theoretical density for the PC method and commercial powder, respectively. Relative densities of the sintered PC powder were lower than those of the commercial powder.

The electrical conductivity of the GDC sample was conducted over the temperature range of 300°C to 600°C. Figure 9 shows the impedance plot at 500°C. The contributions of the grain interior, grain boundary, and electrode can be identified in the plots at high, intermediate, and low frequencies, respectively. The impedance spectra were fitted to the

equivalent circuit inserted in Figure 9.

The resistance of the electrolyte GDC samples can be obtained from the electrical measurements and then converted to conductivity (σ) by consideration of the specimen geometry:

$$\sigma = L / AR \quad (1)$$

where L is the distance between 2 electrodes which is the thickness of the measured sample, A is the area of the electrode, and

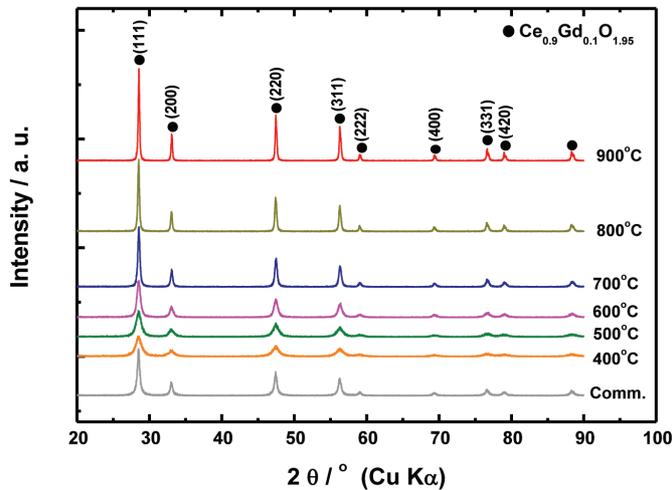


Figure 4. XRD patterns of the PC method derived $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ powder calcined at 400°C to 900°C for 2 h and the commercial powder (spray pyrolysis)

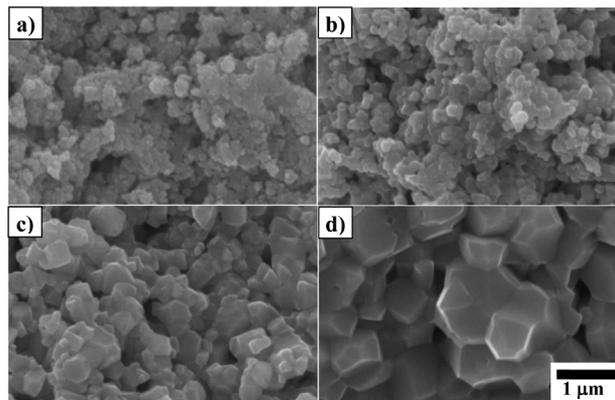


Figure 5. SEM micrograph of fracture surfaces of the PC method derived $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ pellets sintered at a) 600°C, b) 1000°C, c) 1200°C, d) 1400°C for 4 h

R is the resistance of the sample. In general, the oxygen ionic conductivity of a solid electrolyte can be expressed as the following empirical equation (Kilner, 2000; Steele, 2000):

$$\sigma_i T = \sigma_0 \exp\left(\frac{-E_a}{k_B T}\right) \quad (2)$$

where E_a is the activation energy for conduction, k_B the Boltzmann constant, T the absolute temperature, and σ_0 the pre exponential term (Kilner, 2000; Steele, 2000).

The Arrhenius plot of the grain interior (GI) conductivity of the GDC samples from the PC method and commercial powders is shown in Figure 10. At every sintering

temperature, the GI conductivity of the PC powder is in the same range as the GI conductivity of the commercial powder. Figure 11 illustrates the relationship between conductivity and relative density of the GDC samples from the PC method and commercial powders. When compared at the similar density, the conductivity of the PC derived sample was higher than that of the commercial one, which indicated that the the PC derived sample potentially has high conductivity. This trend showed that a PC derived sample can be prepared with lower density; however, the electrical conductivity is higher than the commercial powder.

Table 1 shows the comparison of the

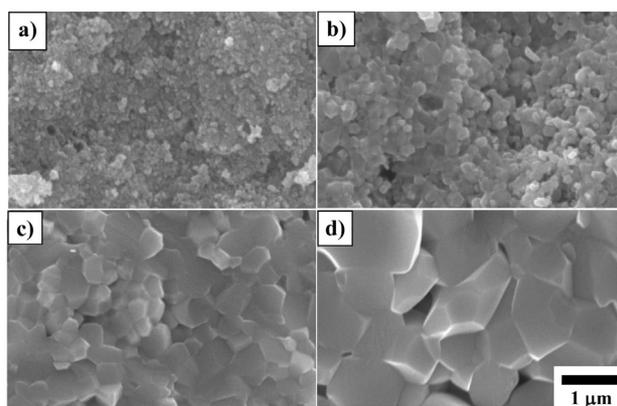


Figure 6. SEM images of fracture surfaces of the commercially derived $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ pellets sintered at a) 600°C, b) 1000°C, c) 1200°C, d) 1400°C for 4 h

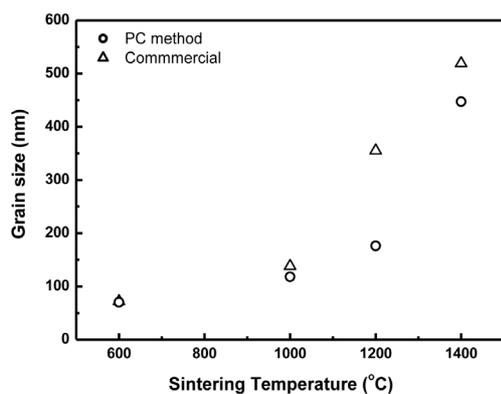


Figure 7. Relationship between sintering temperature and grain size

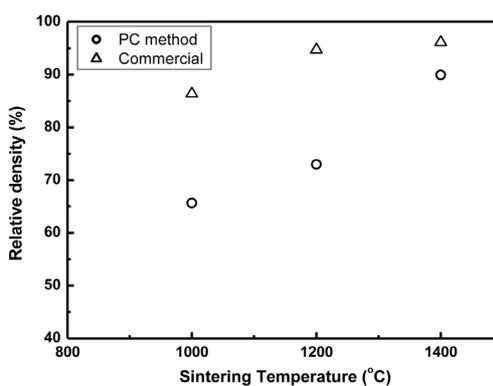


Figure 8. Relationship between sintering temperature and relative density

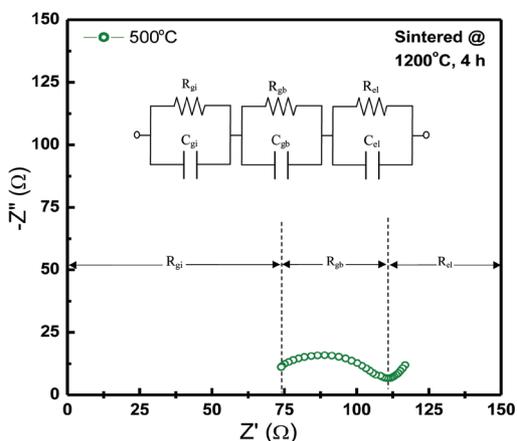


Figure 9. Impedance spectra plots of $Ce_{0.9}Gd_{0.1}O_{1.95}$ pellet by the PC method measured at $500^{\circ}C$

$Ce_{0.9}Gd_{0.1}O_{1.95}$ conductivity in this study to others. The total conductivity of the GDC pellets sintered at $1400^{\circ}C$ for 4 h is found to be $1.52 S/m$ at $600^{\circ}C$ with the E_a of $0.75 eV$ in the temperature range of $300-600^{\circ}C$; these results are in the same range as the commercial powder.

Conclusions

Nanocrystalline $Ce_{0.9}Gd_{0.1}O_{1.95}$ powder for an electrolyte material used at intermediate temperature solid oxide fuel cells was successfully synthesized via the PC method. The PC powder calcined at low temperature (at $400^{\circ}C$) is found to have smaller grain sizes after sintering compared to the commercial

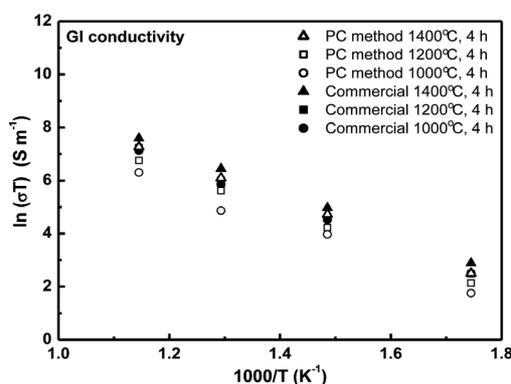


Figure 10. Grain interior conductivity of $Ce_{0.9}Gd_{0.1}O_{1.95}$ pellets measured at $300-600^{\circ}C$

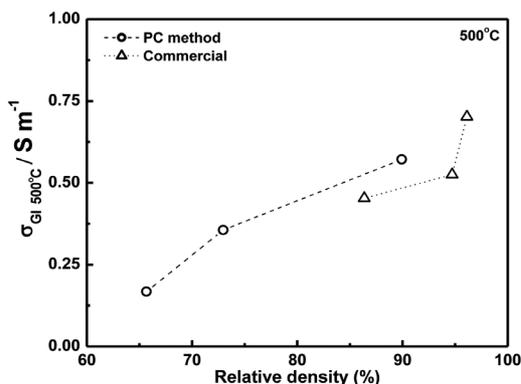


Figure 11. Relationship between conductivity and relative density of GDC samples

Table 1. The comparison of the $Ce_{0.9}Gd_{0.1}O_{1.95}$ PC method derived powder to the commercially made powder and powders made in the References

Sample	$\sigma_{total} 600^{\circ}C$ (S/m)	$E_a total$ (eV)
This work	1.52 ($1400^{\circ}C$, 4 h)	0.75
Commercial (spray pyrolysis)	1.75 ($140^{\circ}C$, 4 h)	0.77
Sol-gel (Tao <i>et al.</i> , 2009) (Tape casting)	1.7 ($1450^{\circ}C$)	0.49
Aerosol flame (Im <i>et al.</i> , 2008)	0.77 ($1400^{\circ}C$, 10 h)	Not applicable
Solid state (Zhang <i>et al.</i> , 2006)	1.2 ($1600^{\circ}C$, 5 h)	0.71

spray pyrolysis powder. The PC method derived powder has a potentially higher electrical conductivity. Due to the high electrical conductivities of the PC derived powder in this study, it is possible to reduce the operating temperature of SOFCs, so that less expensive materials, i.e. steels and copper could be employed as system components instead of ceramics.

Acknowledgments

The authors gratefully acknowledge the financial support of the Japanese Government (Monbukagakusho) Scholarship for the Doctoral Program of the International Graduate Course for Continuing Professional Development.

References

- Fergus, J.W. (2006). Electrolytes for solid oxide fuel cells. *J. Power Sources*, 162:30-40.
- Fuentes, R.O. and Baker, R.T. (2009). Structural, morphological and electrical properties of $Gd_{0.1}Ce_{0.9}O_{1.95}$ prepared by a citrate complexation method. *J. Power Sources*, 186:268-277.
- Huang, K., Feng, M., and Goodenough, J.B. (1998). Synthesis and electrical properties of dense $Ce_{0.9}Gd_{0.1}O_{1.95}$ ceramics. *J. Am. Ceram. Soc.*, 81:357-62.
- Im, J.M., You, H.J., Yong S.Y., and Shin, W.S. (2008). Synthesis of nano-crystalline $Gd_{0.1}Ce_{0.9}O_{2-x}$ for IT-SOFC by aerosol flame deposition. *Ceram. Int.*, 34:87-881.
- Kakahana, M. and Yoshimura M. (1999). Synthesis and characteristics of complex multicomponent oxides prepared by polymer complex method. *B. Chem. Soc. Jpn.*, 72:1427-1443.
- Kakahana, M., Arina, M., Yoshimura, M., Ikeda, N., and Sugitani, Y. (1999). Synthesis of high surface area $LaMnO_3^{3+d}$ by polymerizable complex method. *J. Alloy. Comp.*, 283:102-105.
- Kilner, J.A. (2000). Fast oxygen transport in acceptor doped oxides. *Solid State Ionics*, 129:13-23.
- Leng, Y.J., Chan, S.H., Jiang S.P., and Khor, K.A. (2004). Low-temperature SOFC with thin film GDC electrolyte prepared in situ by solid-state reaction. *Solid State Ionics*, 170:9-15.
- Popa, M. and Kakihana M. (2002). Synthesis of lanthanum cobaltite ($LaCoO_3$) by the polymerizable complex route. *Solid State Ionics*, 151:251-257.
- Ralph, J.M., Schoeler, A.C., and Krumpelt, M. (2001). Materials for lower temperature solid oxide fuel cells. *J. Mater. Sci.*, 36:1161-1172.
- Singhal, S.C. (2003). *High Temperature Solid Oxide Fuel Cells: Fundamentals, Design and Applications*. Elsevier Advanced Technology, Oxford, UK.
- Steele, B.C.H. (2000). Appraisal of $Ce_{1-x}Gd_xO_{2-y/2}$ electrolytes for IT-SOFC operation at 500°C. *Solid State Ionics*, 129:95-110.
- Tao, Y., Shao, J., Wang, J., and Wang, W.G. (2009). Morphology control of $Ce_{0.9}Gd_{0.1}O_{1.95}$ nanopowder synthesized by sol-gel method using PVP as a surfactant. *J. Alloy. Comp.*, 484:729-733.
- Zhang, T.S., Ma, J., Kong L.B., Hing P., and Kilner, J.A. (2004). Preparation and mechanical properties of dense $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ ceramics. *Solid State Ionics*, 167:191-196.
- Zhang, T.S., Ma, J., Cheng, H., and Chan, S.H. (2006). Ionic conductivity of high-purity Gd-doped ceria solid solutions. *Mater. Res. Bull.*, 41:563-568.