Synthesis and Characterization of Gadolinium doped Cerium (\(\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}\)) by using Various Carbonates as a Precipitant

Ade Utami Hapsari 1, Jarot Raharjo 1, Hanif Yuliani 1, I.G. Agung Suradhamika 2, Damish 1, Retna Deca Pravitasari 1, and Desiana P. Sari 3

1 Centre for Materials Technology, Agency for the Assessment and Application of Technology, Bldg. 224 PUSPIPEK, Serpong, South Tangerang 15314, Indonesia.
2 Laboratory For Ceramic Based Creative Industry, Agency for the Assessment and Application of Technology, Jl. By Pass Ngurah Rai, South Denpasar, Bali, Indonesia
3 Department of Physic Engineering, Faculty of Engineering, Surya University, Tangerang, Indonesia

*Corresponding author: ade.utami@bppt.go.id

Abstract. Gadolinium-doped cerium (\(\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}\), GDC) as an electrolyte in IT-SOFC has higher performance in nano-sized than the other sized. Carbonate was known as a precipitant agent that could affect the morphology and size of the particle. In this study, the effects of various carbonates as a precipitant agent on the synthesis of GDC by co-precipitation method were investigated. Cerium in the form of \(\text{Ce(NO}_3\text{)}_3.6\text{H}_2\text{O}\) (cerium nitrate hexahydrate) used in the synthesis process. Three types of carbonates, i.e. ammonium carbonate, potassium carbonate, and sodium hydrogen carbonate, namely GDC1, GDC2, and GDC3, respectively, was used as a precipitating agent. The GDC powder resulted was then characterized by X-Ray Diffraction (XRD), Fourier Transform Infra Red (FTIR), Particle Size Analysis (PSA), and Scanning Electron Microscopy (SEM). The carbonates variation affected the physical properties and the formed particle of GDC. GDC2 showed the optimum carbonate that produces electrolyte GDC with better properties as an IT-SOFC electrolyte based on physical properties.

Keywords: co-precipitation, \(\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}\), IT-SOFC, various carbonate

1. Introduction

Unlike most generating systems, solid oxide fuel cells (SOFC) do not generate vibration and produces little or no emissions of \(\text{NO}_x\) and \(\text{SO}_x\) [1]. So it can be said that SOFC is a technology with low pollution that can produce electricity electrochemically with high efficiency. SOFC currently has a high operating temperature of more than 800 °C [2]. This high SOFC operating temperature causes many problems to arise during SOFC operations, such as metal corrosion, cell component damage, long start-up times, high electrolytic sintering temperatures, and undesirable interfacial diffusion. High operating temperatures will also make the system require expensive high-temperature materials, resulting in high production costs [3].

Some of the problems arising from the high operating temperature of SOFC encourage the need for SOFC development that works at lower temperatures or so-called intermediate temperature solid oxide...
fuel cells (IT-SOFC). One is to develop an alternative electrolyte with high ionic conductivity at a temperature of 500-800 °C [4]. Gadolinium-doped cerium (GDC) is a potentially electrolytic material in IT-SOFC because of its transport and redox properties. Co-precipitation method is the most common method for GDC powder synthesis. This method is known for its ability to produce nano-sized GDC powders at low cost, easy procedure with short reaction time, and mass production capability [3]. Compared to other synthesis methods, the co-precipitation method uses a lower sintering temperature than the solid state reaction method that reaches 1700-1800°C. Currently, the development of nano-size in SOFC technology is the main target because nanostructures can improve performance on SOFC [5].

In the co-precipitation method, precipitant is an important factor affecting the characteristics of the final product [6]. Mostly, research to synthesize GDC powder by co-precipitation method using ammonium carbonate as its precipitation agent. However, the method of co-precipitation with ammonium carbonate is still not optimal because the size of the resulting particles is still large (~100 nm) [7] and agglomeration [8]. Besides ammonium carbonate, several other types of carbonates which can be used as precipitation agents in the synthesis of co-precipitation methods are potassium carbonate and sodium hydrogen carbonate. It was reported that the synthesis of CeO₂ nanoparticles using potassium carbonate and potassium hydroxide as its precipitating agent with a particle size of approximately 25 nm [9]. Sodium hydrogen carbonate is also one of the precipitant precursors ever used in the synthesis of MgCO₃ powder and successfully produces a powder with a high surface area [8]. Powder with small particle size has a high surface area which will affect the sintering process and increase ionic conductivity of the material. Powder with small particle makes it possible to produce thin electrolytes. Thin electrolytes have lower ohmic resistance, which allows the operation of SOFC at lower temperatures [10] and improves SOFC performance [11]. When the electrolyte thickness decreases, the maximum power density of the cell increases [10].

Therefore, this study aims to determine the optimal conditions for the use of carbonate compounds as precipitation agents to produce GDC powder with small particles and monodisperse.

2. Experiment

The materials used in this study were gadolinium (III) nitrate hexahydrate (Gd(NO₃)₃.6H₂O, Sigma Aldrich, 99.9%), cerium (III) nitrate hexahydrate (Ce(NO₃)₃.6H₂O, Sigma Aldrich, 99%), ammonium carbonate ((NH₄)₂CO₃, Sigma Aldrich), potassium carbonate (K₂CO₃, Sigma Aldrich), sodium hydrogen carbonate (NaHCO₃, Sigma Aldrich), and aquadest.

The synthesis of GDC10 powder uses 0.4514 gram Gd(NO₃)₃.6H₂O and 3.9808 gram Ce(NO₃)₃.6H₂O which is dissolved into 100 mL of distilled water (solution A), then some carbonate (ammonium carbonate, potassium carbonate, and sodium hydrogen carbonate, namely GDC1, GDC2, and GDC3) is dissolved in aquadest for mixing into solution A drop-by-drop while stirring with a magnetic stirrer at room temperature until precipitation occurs, resulting in a white solution. White solution then dried in an oven with a temperature of 110 °C for 24 hours. The dried sample was calcined at 900 °C for 90 minutes.

The resulting GDC powder is then characterized using x-ray diffraction (XRD), Fourier Transform Infra-Red (FTIR), particle size analysis (PSA), and scanning electron microscopy (SEM) to determine its physical properties.

3. Results and discussion

3.1. Fourier Transform Infra-Red (FTIR)

Figure 1 shows spectral bands of different types of carbonate precipitates. This spectral band showed the same type. The existence of the spectral beam found at 700, 1127, 1300, 1472, 1630, 2360, 2979, 3300, and 3700 cm⁻¹.

In the FTIR graph, the spectrum below 700 cm⁻¹ is the peak for organometallic compound GDC (finger print) products. In this research, there is a spectrum in the range of 700 cm⁻¹. The spectrum band
in the region 850 - 400 cm\(^{-1}\) indicates the presence of a Ce-O bond [12]. This indicates Ce-O as an organometallic compound product and GDC is already formed.

\[\text{Figure 1. FTIR results of Powder GDC from different types of carbonates}\]

\[\text{Figure 2. XRD patterns of Powder GDC from different types of carbonates}\]

While the spectra above 700 cm\(^{-1}\) is a type of functional group absorption of organic compounds that indicate the presence of impurities. Impurities can be either synthesis or by-products. In this research, there are some spectra above 700 cm\(^{-1}\) that is in area 1127, 1300, 1472, 1630, 2979, 3300, and 3700 cm\(^{-1}\). This indicated that in the range 3000-3700 cm\(^{-1}\) and 1630 cm\(^{-1}\) are respectively associated with the hydroxyl group (\(-\text{OH}\)) [13] and the H-O-H bonds indicating the presence of water molecules in the sample [14]. This is commonly found when the material is hygroscopic.

Around 1270-1450 cm\(^{-1}\) are vibrations of the C-O, C-H [15] and O-H groups [9]. Sometimes there are also N-H bonds with typical characteristic graphic characteristics as shown in Figure 1. Overall, there is no impurity from the GDC synthesis reaction. The existence of the N-H bond formed is possible because there is still a nitrate bond with the rest of the carbonate molecule so as to produce a by-product of nitrate ((\(\text{NH}_4\))\(_2\)\(\text{NO}_3\), \(\text{K}_2\text{NO}_3\), \(\text{NaHNO}_3\)).

Sintering treatment at 900 °C temperature is expected to eliminate impurities and by-products because the value of boiling point has been passed ((\(\text{NH}_4\))\(_2\)\(\text{NO}_3\) = 210 °C, \(\text{K}_2\text{NO}_3\) = 400 °C, \(\text{NaHNO}_3\) = 380 °C). Therefore, it is necessary to wash the process of synthesis before drying.

3.2. X-ray diffraction (XRD)

Figure 2 show the XRD graph of GDC in various carbonates. The diffraction patterns of all samples show that only one phase is formed with a cubic fluorite crystal structure. All the peaks corresponding to the composition Ce\(_{0.90}\)Gd\(_{0.10}\)O\(_{1.95}\) (GDC10) indicate that Gd succeeded in doping into the Ce lattice [16]. There is no other detected crystal phase for all GDC samples indicates that only one phase (phase) of material and material has a high homogeneity [17]. The sharper peak intensity indicates that the sample has a larger crystal size, while the wider peak (peak broaden) width indicates that the sample has a smaller crystal size [18].

All GDC samples have diffraction patterns that are very similar in both width and height of intensity, so it can be predicted that the crystallite size of the three GDC samples should not be much different.
The result of calculation of crystallite size of each GDC sample using the Scherrer equation [19] shown in Table 1.

Based on the calculation of crystallite size values, the best use of carbonate type as precipitant is potassium carbonate because it produces the smallest crystal size followed by ammonium carbonate and sodium hydrogen carbonate of 4.08 nm and 6.93 nm. The calculation results for all GDC samples correspond to readings of the width and height of the intensity of the diffraction pattern, having a diffraction pattern that is very similar in both width and height of intensity, thus having a crystalline size not much different.

| Name Sample | Crystallite Size (nm) |
|-------------|-----------------------|
| GDC1        | 4.08                  |
| GDC2        | 3.47                  |
| GDC3        | 6.93                  |

3.3. Particle Size Analysis (PSA)

The distribution and particle size of GDC materials are characterized using a particle size analyser (PSA) with the principle of dynamic light scattering (DLS). The surfactants used are triton x and acetyl acetone. Figure 3 showed the number distribution graph from PSA. Figure 3 shows the sample GDC1 having an average particle size of 22.0552 nm. Each particle size average for GDC 2 and GDC3 is 369.8 nm and 27.524 nm. The average value of the smallest particle diameter for each sample was GDC potassium carbonate of 369.8 nm. This is proportional to the XRD results where the smallest crystallite size is obtained in potassium carbonate samples (3.47 nm).

There is still the possibility of agglomeration in the sample because of the nano-sized sample. This is seen from the presence of a number of nanoparticles measuring 161.5 nm in the ammonium carbonate sample. As we know that materials with nanoparticles tend to agglomerate. A fairly high average particle size in GDC samples is possible because high calcinations temperatures of 900 ºC are used during the sample synthesis process. The particle size increases with the increase of the calcinations temperature [2]. The average particle size of GDC is much larger than the size of the crystallites. This indicates that the GDC powder formed has a polycrystalline structure wherein one particle there is more than one crystal inside [20].

The number distribution graphs of GDC1 show that the sample has a very wide particle size distribution meaning that GDC1 powder has a polydisperse system. This indicates that the average value of the particle size obtained does not represent the actual value. While in GDC2 and GDC3 powders, the graph of the distribution number appears to have a monodisperse system, which means that all particles have the same size.

3.4. Scanning Electron Microscopy (SEM)

Characterization of Scanning Electron Microscopy (SEM) aims to look at the morphology of GDC powders. The results of SEM characterization on GDC samples at 10,000x magnification with precipitant variations of ammonium carbonate, potassium carbonate, and sodium hydrogen carbonate are shown in Figure 4. Each sample indicates the occurrence of agglomeration. Synthesis of GDC using ammonium carbonate and sodium hydrogen carbonate results in the morphology of particles in the form of flakes, whereas when using potassium carbonate a more oval morphology is obtained [21].
4. Conclusion
The Gadolinium doped cerium (Ce$_{0.9}$Gd$_{0.1}$O$_{1.95}$, GDC) powders was synthesized by co-precipitation method of raw material of cerium (III) nitrate hexahydrate (Ce(NO$_3$)$_3$.6H$_2$O and various carbonates as precipitating agent. GDC phase formed is a cubic fluorite crystalline structure of the smallest crystallite size is obtained on GDC2 with potassium carbonate, which is 52.49 nm. All GDC has a polycrystalline structure and still agglomeration of each type of precipitant. Various carbonates as precipitate agent could affect the shape of the formed GDC 10 particles. Number distribution of PSA showed that GDC2 with potassium carbonates as a precipitate produces the smallest particle size 369.8 nm even though GDC1 with ammonium carbonates as a precipitate can produce a number of 161.5 nm sizes particles. This indicates that ammonium carbonate and potassium carbonate have the potential as a precipitate agent to produce GDC nano powder.

Acknowledgement
The authors gratefully acknowledge the financial support given by the Ministry of Research, Technology, and Higher Education, Republic of Indonesia via “INSINAS-2018”, and the Centre for Materials Technology, Agency for the Assessment and Application of Technology (BPPT) through the development of rare-earth materials program.
References

[1] Singhal, S. C. 2013. Solid Oxide Fuel Cells: Facts and Figures, Past, Present and Future. In J. T. Irvine & P. Connor (Eds.), Solid Oxide Fuels Cells: Facts and Figures, Green Energy and Technology, pp. 1-25. London: Springer London.

[2] Raharjo, Jarot, et al. 2017. Synthesis and characterization of uniform-sized cubic ytterbium scandium co-doped zirconium oxide (1Yb10ScSZ) nanoparticles by using basic amino acid as organic precursor. International Journal of Hydrogen Energy 42, pp. 9274-9283.

[3] Joh, Dong Woo, et al. 2016. Sintering Behaviour and electrochemical performances of nano sized gadolinium-doped ceria via ammonium carbonate assisted co-precipitation for solid oxide fuel cells. Journal of Alloys and Compounds 682, pp. 188-195.

[4] Irvine, John T. S., Connor, Paul. 2013. Alternative Materials for SOFCs Opportunities and Limitations. In J. T. Irvine & P. Connor (Eds.), Solid Oxide Fuels Cells: Facts and Figures, Green Energy and Technology (pp. 163-). London: Springer London.

[5] Abdalla, Abdalla M., et al. 2018. Nanomaterials for solid oxide fuel cells: A review. Renewable and Sustainable Energy Reviews Volume 82, pp. 352-368.

[6] Huang, Y., Liu, T., Liu, M. 2013. The effect of precipitants on co-precipitation synthesis of MgO-ZrO2 powders. Advanced Materials Research Volume 788, pp. 132-135.

[7] Fan, L. Wang, C. Chen, M. Zhu, B. 2013. Recent development of ceria-based (nano) composite materials for low temperature ceramic fuel cells and electrolyte-free fuel cells. Journal of Power Sources Vol. 234, pp. 154-174.

[8] Zulfqar, Muzammal, et al. 2016. Investigations on Gadolinium doped ceria electrolyte prepared via sol-gel and co-precipitation routes for intermediate temperature solid oxide fuel cell (IT-SOFC) applications. Energy, Environment and Sustainable Development (EESD) 4th International Conference.

[9] Majid, F., Zarinkamar, M. 2015. Synthesis of nano-sized ceria (CeO2) particles via a cerium hydroxy carbonate precursor and the effect of reaction temperature on particle morphology. Journal of Ultrafine Grained and Nanostructured Materials Vol. 48, No. 1, pp. 5-10.

[10] Zuo, Chendong, Liu, Mingfei, Liu Meilin. 2012. Chapter 2 Solid Oxide Fuel Cells in Sol-Gel Processing for Conventional and Alternative Energy, by M. Aparicio, et al., 7-36. New York: Springer Science Business Media.

[11] Kim, Sun-Dong, Lee, Jong-Jin, Moon, Hwan, Hyun, Sang-Hoon, Moon, Jooho, Kim, Joosun, Lee, HaeWeon. 2007. Effects of anode and electrolyte microstructures on performance of solid oxide fuel cells. Journal of Power Sources. Volume169, Issue 2, pp.265-270.

[12] Wang, T & Sun, DC. 2008 Prepara on and characteriza on of nanometerscale powders ceria by electrochemical deposi on method. Mater Res Bull 43(7), pp 1754-1760.

[13] Accardo, et el. 2016. Electrical and microstructural characteriza on of ceramic gadolinium-doped ceria electrolytes for ITSOFCs by sol-gel route. J. Appl. Biomater Funct Mater 14 (1). Pp 35-41.

[14] Arabaci, A., Öksüzömerb, M. Faruk. 2012. Preparation and characterization of 10 mol% Gd doped CeO2 (GDC) electrolyte for SOFC applications. Ceramics International, Volume 38, Issue 8, pp. 6509-6515.

[15] Gondolini, et al. 2013. Effects of the microwave heating on the properties of gadolinium-doped cerium oxide prepared by polylol method. Journal of the European Ceramic Society 33, pp 67–77

[16] M.Jamshidijam, R.V.Mangalaraja, A.Akbari, Fakhrabadi, S.Ananthakumar, S.H.Chan. Effect of rare earth dopants on structural characteristics of nanoceria synthesized by combustion method. Powder Technology, Volume 253, February 2014, Pages 304-310

[17] Li,J-G.,Ikegami, T., Wang, Y.,Mori, T. 2002.a. Reactive Ceria Nanopowders via Carbonate Precipitation. Journal of The American Ceramic Society, 85 (9), 2376-2378.

[18] Theivasanthi, T., Alagar, M. 2012. Electrolytic Synthesis and Characterizations of Silver Nanopowder. Nano Biomedicine and Engineering, 4 (2), 58-65.
[19] Tok, A. I. Y, et al. 2004. Carbonate co-precipitation of Gd2O3-doped CeO2 solid solution nanoparticles. Materials Science and Engineering.

[20] Mahato, et. Al. 2015. Progress in Material Selection for Solid Oxide Fuel Cell Technology: A Review, Progress in Materials Science.

[21] Spiridigliozzi, L., et al. 2018. Engineered co-precipitation chemistry with ammonium carbonate for scalable synthesis and sintering of improved Sm0.2Ce0.8O1.90 and Gd0.16Pr0.04Ce0.8O1.90 electrolytes for IT-SOFCs. Journal of Industrial and Engineering Chemistry 59, pp. 17-27.