Synthesis and characterization of 8YSZ/5GDC composite and dissimilar-bulk by sonochemistry assisted sol-gel method

A K Rivai\textsuperscript{1}, N Shabrina\textsuperscript{2} and A R Setiawan\textsuperscript{2}

\textsuperscript{1}Center for Science and Technology of Advanced Materials, BATAN, Kawasan PUSPIPTEK Gedung 71, Tangerang Selatan, Banten 15314
\textsuperscript{2}Material Science Department, FTMD, ITB, Ganesha No.10 Bandung 40132

Email: rivai.abukhalid@batan.go.id

Abstract. Synthesis and characterization of 8YSZ (8\%mol Y\textsubscript{2}O\textsubscript{3} – ZrO\textsubscript{2}) and 5GDC (5\%mol Gd\textsubscript{2}O\textsubscript{3} – CeO\textsubscript{2}) combination in the form of composite and dissimilar bulk using sonochemistry assisted sol-gel method have been done. 8YSZ and 5GDC powders were produced from sol-gel route method. Each of the powder was then ultrasonicated for 30 hours with 25kHz±50Hz of frequency and 39\% of amplitude. Toluene was used as a solution for the ultrasonication process. 8YSZ/5GDC composite was made by mixing the powders of 50\%:50\% in weight, and afterward compacted become a pellet. 8YSZ/5GDC dissimilar bulk was made by connected between 8YSZ pellet and 5GDC pellet at a flat part, and afterward re-compacted become a single pellet. Then, the pellets were sintered at 1400°C of temperature for 3 hours. The results showed that the ionic conductivity of the composite is higher than the dissimilar bulk.

1. Introduction

Yttria-Stabilized Zirconia (YSZ: Y\textsubscript{2}O\textsubscript{3}–ZrO\textsubscript{2}) ceramic is widely used in various fields, such as thermal barrier coating (TBC) for high temperature materials \cite{1}, oxygen sensor for nuclear reactors\cite{2, 3}, and Solid Oxide Fuel Cell (SOFC) \cite{4} because of its superior characteristics. SOFC is an electrochemical cell that converts the chemical energy of the fuel into the electrical energy without any combustion process \cite{4}. Development of SOFC is directed for lowering their operating temperature in order to reduce the fabrication costs and to expand the area of application of this technology. Lowering the operating temperatures of solid oxide fuel cells (SOFCs) from conventional 900–1000°C to the intermediate temperature range of 600–700°C allows a wider selection of materials for SOFC components, a better thermal integrity of the cells, and thus a longer life time of the cells \cite{4}. Electrolyte materials with higher ionic conductivity are needed in order to improve the SOFC efficiency at lower operating temperatures. YSZ is a conventional electrolyte material with high ion conductivity of 0.1 S/cm at 1000°C; however, its high operation temperature significantly limits its applications due to the materials’ thermomechanical degradation and raises the overall cell costs because of the ceramic interconnects required at high operation temperatures \cite{4}. This material reacts with cathode LSM (lanthahum strontium manganite) at higher temperature producing insulating phases such as La\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7} and SrZrO\textsubscript{3} at the cathode-electrolyte interface \cite{5}. It blocks the ion migration. In addition, the ionic conductivity of YSZ in the intermediate operating temperature (600°C) is low.

GDC (Gadolinia-Doped Ceria: Gd\textsubscript{2}O\textsubscript{3}–CeO\textsubscript{2}) has been considered as one of the most promising electrolyte materials for the development of intermediate temperature SOFCs because of its high ionic...
conductivity [6, 7]. Furthermore, the reduction of ceria also causes lattice expansion of the ceria electrolyte at the anode side. However, Ce$^{4+}$ reduces to Ce$^{3+}$ under reducing anode atmosphere at elevated temperatures. This induces an electronic conductivity which decreases an ionic conductivity and destabilizes the chemical reactivity. One proposed approach to prevent the OCV (open circuit voltage) drop and to improve the chemical and mechanical stability of doped ceria electrolytes in reducing atmospheres is to coat a thin YSZ film on the anode side of a doped ceria electrolyte [4, 7-9]. Since the ionic conductivity of YSZ is lower than GDC at an intermediate temperature, the YSZ film as an electronic and hydrogen blocking layer should be adequately thin to minimize its contribution to the total electrolyte resistance.

In this paper, we develop a simple, rapid and cost-effective method based on the sonochemistry assisted sol-gel method processing. The sol-gel technique has been widely used in recent years to form fuel cell components with enhanced microstructures for SOFCs [10]. However, the sol-gel method also has some disadvantages such as a complex synthesis route; the quality of the coating was influenced much by many process parameters. Furthermore, the typical gels show inherently large shrinkage, usually 20–25 vol%, which will introduce huge shrinkage and stresses during drying/heating process. Therefore, the sol-gel process also needs further development to deposit micro-structured materials in a selective area such as the triple-phase boundary of a fuel cell [10].

The alternative potential method that does not required mixing with other substance is the sonochemistry method. This method offers some advantages, such as simple and rapid preparation, direct and precise control of stoichiometry, homogeneity and high purity [11]. As an assisted method, the sonochemistry method is very useful to support with other synthesis methods [11-13].

In this work, we have synthesized and investigated the combination of 8YSZ and 5GDC in the form of composite and dissimilar bulk by sonochemistry-assisted sol-gel method. In order to investigate the performance of the synthesized materials, the conductivity performance tests of 8YSZ/5GDC in the form of composite and dissimilar bulk have been observed.

2. Experiment

The powders of 8YSZ (8%mol Y$_2$O$_3$ – ZrO$_2$) and 5GDC (5%mol Gd$_2$O$_3$ – CeO$_2$) were synthesized by sonochemistry-assisted sol-gel method using Zirkonium(IV) oxide chloride-octahidrate, Yttrium(III) nitrate hexa-hydrate and cerium nitrate hexa-hydrate (Ce(NO$_3$)$_3$.6H$_2$O E.Merck), gadolinium(III) nitrate hexa-hydrate (Gd(NO$_3$)$_3$.6H$_2$O, Aldrich) as starting materials of 8YSZ and 5GDC. Each stoichiometric amounts of starting materials were dissolved in distilled water. An anhydrous citric acid (C$_6$H$_{12}$O$_7$ – E. Merck) was dissolved in water and then was added to the solution. NH$_4$OH was added to the solution to control pH=5. The solution was heating at 150°C until gel formed. The gel was calcined at 800°C for 4.5 hours until fine 8YSZ white powder and 5GDC yellow powder were formed. Then, each powder with toluene solution as a medium was ultrasonicated for 30 hours with the frequency of 25kHz±50Hz and 39% amplitude.

Combination of 8YSZ and 5GDC was done in the form of composite and dissimilar bulk using 50:50 mass compositions. The composite of 8YSZ/5GDC was made by mixing the powder of 8YSZ and 5GDC. Then, the mixing powder was compacted and sintered at 1400°C of temperature for 3 hours. The dissimilar bulk of 8YSZ/5GDC was made by compacting the piled up of the powder of 8YSZ and 5GDC. Then, the resulting pellet was also sintered using the same parameters.

In order to ensure the phase of each combination, an X-ray Diffraction characterization was carried out before and after sintering process. XRD data were collected with Cu Kα radiation in the range of 2θ from 10° to 120°.

The conductivity of the samples was conducted using EIS (Electrochemical Impedance Spectroscopy). Pt electrodes were coated on both sides of the dense samples. LCR - inductance (L), capacitance (C), and resistance (R) meter measurement was carried out in dry air in a temperature range 400-600°C in frequency range of 42 Hz to 5MHz using HIOKI-3522. The ionic conductivity, the bulk resistance (Rb) and grain boundary resistance (Rgb) were measured using EIS Spectrum Analyser Software using LevMarq fitting and Amplitude function. The ionic conductivity was
determined by the Arrhenius law subsection: \( \sigma_T = \sigma_0 \exp \left( \frac{-E_a}{kT} \right) \), where \( \sigma_0 \) is the pre-exponential factor, \( E_a \) is the activation energy (in eV), \( k \) is the Boltzmann constant and \( T \) is in kelvin.

3. Results and Discussion

The XRD technique was used to determine the crystal structure of the composite 8YSZ/5GDC. Spectra of 5GDC powders were obtained with the range of 20 from 10°-120° with 5°/s scanning rate. The black line in figure 1 indicated peaks belonging to GDC and YSZ before sintering. The analysis showed that the composite has been mixed well without any impurity. Diffraction patterns are matched with JCPDS 00-075-0161 for GDC which has a fluorite cubic crystal with space group Fm3m, and JCPDS 00-030-1468 for YSZ which also has a fluorite cubic crystal with space group Fm3m. After sintering, all the compositions exhibited a single-phase solid solution with a fluorite structure which is also similar before the sintering cases. However, there is a new found phase which indicated the reaction between 8YSZ and 5GDC after sintering process, as shown by the red line in figure. It means that there is a reaction and diffusion between 8YSZ and 5GDC during the sintering process at temperatures of 1400°C. This reaction occurred in whole sides in 8YSZ/5GDC composite. Differently in dissimilar bulk, the reaction occurred in the interface of 8YSZ/5GDC.

![Figure 1. X-ray diffraction pattern of composite 8YSZ/5GDC (red line) before sintering and (black line) after sintering in range 10-120° of 20.](image)

In order to investigate the reaction phenomena to its conductivity, the EIS was used to characterize the electrical behavior of them. The ionic conductivity measurement in combination 8YSZ/5GDC was conducted to determine the characteristics of its electrical properties in the form of composite and dissimilar bulk. Measurements were carried out at a temperature range of 400-600°C. The total impedance value was obtained by fitting the measured results with R series paralleled and the CPE (constant-phase elements) models.
Figure 2. Impedance plots of (a) composite 8YSZ/5GDC (b) dissimilar bulk 8YSZ/5GDC measured at temperature of 400-600°C

The Nyquist plot for both composite and dissimilar bulk of 8YSZ/5GDC showed the same trends that the resistance decreases with increasing of operating temperature. At a temperature of 400°C, the Nyquist plots of the dissimilar bulk of 8YSZ/5GDC generate no semicircle shape and tend to be random, so it become difficult to be fitted. This may be occurred because the ion oxide of the dissimilar bulk does not have enough energy to migrate in the operating temperature of 400°C.

Table 1. Resistance of bulk, grain boundaries and total of composite and dissimilar bulk of 8YSZ/5GDC at temperature range of 450-600°C

| Temp. (°C) | Rb (Ohm)   | Rgb (Ohm)   | Rtot (Ohm)  |
|-----------|------------|-------------|-------------|
|           | Composite  | Dissimilar  | Composite   | Dissimilar  | Composite   | Dissimilar  |
| 400       | 6.73 x10³  | -           | 6.38 x10²   | -           | 6.44 x10⁵   | -           |
| 450       | 6.10 x10³  | 9.72 x10³   | 2.17 x10⁵   | 1.00 x10⁶   | 2.23 x10⁵   | 1.97 x10⁶   |
| 500       | 5.24 x10⁵  | 2.21 x10⁵   | 9.72 x10⁴   | 5.92 x10⁵   | 1.02 x10⁶   | 8.13 x10⁵   |
| 550       | 4.79 x10⁴  | 1.00 x10⁵   | 4.85 x10⁴   | 2.41 x10⁵   | 5.33 x10⁴   | 3.41 x10⁶   |
| 600       | 8.65 x10²  | 8.01 x10⁴   | 5.23 x10⁴   | 1.32 x10⁵   | 5.32 x10⁴   | 2.12 x10⁶   |

Table 1 shows the value of Rb, Rgb, and Rtot for each composite and dissimilar bulk of 8YSZ/5GDC. It shows that resistance decreases with the increasing operating temperature of both the resistances of grains, grain boundaries and total. Then, the decreasing resistance causes higher ionic conductivity. The resistance of composite is smaller than dissimilar bulk. Thus, the value of ionic conductivity of composite is higher than dissimilar bulk.
Table 2. Ionic conductivity of composite and dissimilar bulk of 8YSZ/5GDC at a temperature range of 450-600°C

| Temperature (°C) | Total Conductivity | 8YSZ | 5GDC |
|------------------|--------------------|------|------|
|                  | Composite          | Dissimilar bulk |      |      |
| 400              | 6.38 x10^{-7}      | -    | 5.73 x10^{-6} | 1.38 x10^{-4} |
| 450              | 1.84 x10^{-6}      | 2.86 x10^{-7} | 4.97 x10^{-5} | 1.69 x10^{-4} |
| 500              | 4.02 x10^{-6}      | 6.93 x10^{-7} | 1.25 x10^{-4} | 2.00 x10^{-4} |
| 550              | 7.72 x10^{-6}      | 1.65 x10^{-6} | 4.39 x10^{-4} | 2.29 x10^{-4} |
| 600              | 7.73 x10^{-6}      | 2.65 x10^{-6} | 7.35 x10^{-4} | 8.56 x10^{-4} |

Table 2 shows the ionic conductivity of composite and dissimilar bulk of 8YSZ/5GDC. The reason of selecting the combination of 8YSZ/5GDC in the form of dissimilar bulk is to protect decreasing the ionic conductivity by using an electron blocking layer. The reduction of Ce^{4+} to Ce^{3+} in GDC has caused lower the ionic conductivity [14]. With the 8YSZ as an electron blocking layer, it is expected that the ionic conductivity will become higher. The result showed the ionic conductivity of composite is higher than dissimilar bulk in composition 50:50. It means that dissimilar bulk is not effective enough to increase the ionic conductivity.

The highest ionic conductivity on this combination system is in the form of composite 8YSZ/5GDC. However, the ionic conductivity value is still lower than the ionic conductivity of 8YSZ and 5GDC themselves. The phenomenon has also been found in another report [15], that the reactions occurred at whole side (for composite) and at the interface (for dissimilar bulk) exhibit lower ion conductivity results by almost two orders of a magnitude than that of YSZ and GDC themselves. It caused by an extensive inter-diffusion between 8YSZ and 5GDC solid solution.

The activation energy of the composite and dissimilar bulk is obtained through the line slope values in the figure 3 chart through the arrhenius equation. The obtained activation energy values for composite and dissimilar bulk were 0.316 eV and 0.388 eV, respectively. The activation energy of composite is lower than dissimilar bulk which is also supported by its higher ionic conductivity. The
activation energy value of the combination of 8YSZ/5GDC is located in the middle between the conductivity of 8YSZ and 5GDC themselves.

4. Conclusion
The combination electrolytes of 8YSZ and 5GDC in the form of composite and dissimilar bulk have been fabricated by sonochemistry-assisted sol-gel method. A new phase reaction formed between 8YSZ and 5GDC occurred after sintering process at temperature 1400°C. The ionic conductivity of composite is higher than dissimilar bulk. However, for both combinations, the ion conductivity is still lower than the both ion conductivity of YSZ and GDC themselves. The phenomenon occurred because of an extensive inter-diffusion between YSZ and GDC solid solution.

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