Preparation and characterization of RHA based ceramic membrane for gas leak testing in SOFC seals

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Abstract. Solid Oxide Fuel Cell (SOFC) systems show great potential in future power generation applications. SOFC has many advantages, including high efficiency, low emission, and flexible modular structure. SOFC is an electrochemical device that converts fuel into electricity directly. If hydrogen gas is used, it will produce electricity and waste products in the form of heat and water vapor. The complete SOFC module system consists of a furnace, cell stack, fuel and oxygen. Several parameters that affect SOFC performance are fuel flow rate, furnace temperature, cell material, and collector current. SOFC consists of anode, electrolyte, cathode, and current collector. These parameters have a correlation with each other in building a SOFC system, resulting in a good cell and optimal output voltage. SOFC based on electrolyte material yttria stabilized zirconia (YSZ) operates at working temperatures between 600 to 1,000°C, so all materials used must be able to withstand these temperatures. In the empirical case to separate each function of the components in the fuel cell, a sealant is needed. The sealant function prevents fuel and oxidant leakage in the stack and electrically isolates the cells in the stack. So the other sealant material requirements are to have thermal and chemical compatibility with other cell components, chemically and physically stable at high temperatures and have good mechanical strength. The composition of the material (RHA, CaO, Al₂O₃, MgO and BaO) with six formulations (F1-F6) which was determined as a gas leak test specimen through a synthesis process using the ball mill method for 12 hours resulted in a grain variation between 3.808 um – 19.631 um. The production of gas leak test specimens was successfully carried out by molding which was designed to be effective using a material weight of 1.5 grams with a 96% PVA binder as much as 20% by weight. The size of the specimen obtained in the form of a membrane with a thickness of 1-1.1mm. The preparation of the test material can be continued in the next gas leak test process.

1. Introduction
The main challenge in implementing solid oxide fuel cells (SOFC) is the development of a suitable sealant material as an air and fuel separator. Several approaches have been used to achieve adherence to the required prerequisites, including problems of mechanical integrity and stability. This applies to rigid seals where no load is applied during operation and compressive seals where a load is applied during operation. The most common approach is to use rigid glass or glass-ceramic seals, the properties of which can be specifically designed for use in SOFCs through variations in the composition of the glass.
However, ceramic materials are inherently brittle, so the development of metal, metal-ceramic, and ceramic-ceramic composite sealants, in both Rigid and Compressive configurations, has been developed.

The use of multi-phase seals allows for improvement of factors, such as wettability, interfacial fit, strain reduction, increased density against gas leakage and seal stability[1]. Meanwhile the design requirements for the seal are high electrical insulation; low production costs; Thermal compatibility with other cell components; chemically and physically stable at high temperatures; leak resistant; chemically compatible with other components and has good mechanical strength [2]. The development of the SOFC sealant material composition has been carried out. SOFC cells are currently being manufactured using ceramic materials with a process that uses relatively high temperatures between 500 – 1000°C. In the cell and reaction chamber for sealing gaps and hooks, seals are used. The sealant is made of ceramic material that is able to withstand temperature cycle loads, the coefficient of expansion must be in accordance with the electrode material, not easy to crack and has a high resistivity [3].

It is a challenge to develop and utilize local materials. Steele et al. divides seals into three categories: rigid bonded sealing, compressive sealing, and compliant bonded sealing. In particular, rigid bonded seals are the most common and are usually made of glass (pyrex) or glass-ceramic materials [4]. Currently the best candidate is SiO$_2$ glass. Several studies on SOFC seals use glass-based materials (SiO$_2$ SrO La$_2$O$_3$ Al$_2$O$_3$ L$_2$O$_3$) [2, 5, 6, 7, 8, 9, 10, 11].

In this study, a sealant material based on RHA will be developed which is obtained through the RH extraction process by synthesizing other materials to strengthen seal performance. The white ash obtained from burning this raw material at medium temperature contains 87 ± 97% silica in amorphous form and a number of metal impurities such as iron (Fe), manganese (Mn), calcium (Ca), sodium (Na), potassium (K), and magnesium (Mg) which affect the purity and color of silica can be removed by pre-treatment with hydrochloric acid, sulfuric acid or nitric acid before combustion [15].

| Oxide   | Function                              |
|---------|---------------------------------------|
| Al$_2$O$_3$ | Provides viscosity control through crystallization rate |
| B$_2$O$_3$ | Reduces Tg, Ts, and viscosity and increases wettability |
| BaO     | Reduces Tg and Ts, and increases CTE in glass-ceramic |
| CaO     | Reduces Tg and Ts, and increases CTE in glass-ceramic |
| MgO     | Reduces Tg and Ts, and increases CTE in glass-ceramic |
| La$_2$O$_3$ | Used as viscosity modifier and long term CTE stabilizer |
| CuO     | Improves surface adherence             |
| MgO     | Improves surface adherence             |
In this research model, heat is generated from an electric furnace whose temperature can be adjusted from 0 – 1000 °C. The ideal SOFC output voltage without loss, for one cell can produce 1.1 volts and current in the mA scale [27]. SOFC itself has a high efficiency because the fuel is converted directly into electricity, if at low temperatures it produces waste products in the form of water (H\textsubscript{2}O), if at high temperatures it is in the gas phase. The heat used to generate the working temperature of the SOFC can utilize flue gas or geothermal heat etc. The heat source generated in this research model comes from an electric furnace. In real applications, using an electric furnace becomes inefficient. This electric furnace is a model that in the future can be used to see the performance of a single SOFC cell. In the development of sealant materials, it can be seen from the performance of the resulting SOFC cells. Because currently SOFC is still a problem at high temperatures, namely the optimal temperature is 800 – 900°C degrees.

2. Experimental Design
2.1 Plant Structure
The general structure is shown in Figure 1. The SOFC system consists of several components. The main components are SOFC cells, electric furnaces, hydrogen cylinders, oxygen cylinders, gas supply lines, valves, data acquisition devices and computer.

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Planar SOFC systems usually use techniques to seal the cell stacks by glass joining or pressure sealing, as shown in Figure 2. Glass was originally used because it is easy to manufacture and apply. The first requirement for rigid seals is that the thermal expansion of the seal must match the thermal expansion of the cell components to which it is connected. [28, 29].
Figure 2. Separate view of planar system SOFC components [30]

High pressure can result from a thermal gradient or mismatch of thermal expansion between the glass material and the cell during heating and cooling. Fully stabilized zirconia has a relatively high coefficient of thermal expansion (CTE) for ceramics (10–11 × 10⁻⁶K⁻¹), but this CTE is lower than that of ordinary metals [30]. Glass seals have the property of becoming brittle after melting and cooling. This makes it very susceptible to cracking due to tensile stress. Sealing glass does not crystallize when cooled, cracks formed due to thermal cycling can "self-healing" if periodically heated to temperatures near the melting point of the glass. Glass has a relatively low strength when compared to polycrystalline ceramics. The amorphous structure of some glasses with high CTE often tends to crystallize when held at high temperatures for a long time, and the CTE will change. This has led to the use of special compositions to form purposefully made crystal glasses, also known as glass-ceramic [30, 31].

In this study, in particular, we will observe how the synthesis of materials as a reliable sealant is carried out. Through the SOFC electric furnace at the Mechanical Engineering Lab, Diponegoro University specimens can be tested for gas leaks. The challenge given as a novelty is how to design the sealing specimen according to the construction of the available SOFC electric furnace as shown in Figure 3. There are two things that are the focus of this research, the first is the preparation and characterization of the material to be synthesized and the second is the specimen production process.

Figure 3. Cell or Sealant Specimen Holder

The part of the furnace used for testing is in the form of a chamber that is connected to the supply of oxygen and hydrogen gas. The center of the chamber is the place where the cell specimen / sealant is used as a fuel and oxygen seal. On both sides of the cell placement section, it can be removed because there is a locking sleeve in the middle. This SOFC stack holder is 57 cm long and the locking shroud is 6 cm. In the locking sleeve there is a cavity to accommodate a SOFC cell with a diameter of 28 mm, as shown in Figure 3.
3. Methodology
The main activity is the process of determining the composition and synthesis of materials and the second is the production of specimens according to construction. In determining the composition of the material using the RHA basis which is associated with SiO2 with other materials, namely CaO, Al2O3, MgO and BaO. Specimen production includes the design and manufacture of moldings, testing of molding functions, determination of material weight, determination of binder composition, and specimen printouts. The function of the specimen sealant made is to prevent gas leaks from both fuel and oxygen. The planar coin shape approach according to the fuel cell structure at the plant is intended to ensure that the entire surface of the plane can really be solid and able to withstand gas leaks at operating temperature.

Figure 4. Flowchart Of Making Gas Leak Test Specimen

The flow process for making test samples on the sealant material is shown in Figure 4. Beginning with determining the composition of the sealant material with reference to the YSZ zirconia electrolyte-based SOFC material. The composition of the base material and the treatment when mixing various oxides used the ball mill process according to previous experiments [32]. Material characterization is in the form of particle size measurement.

The second stage is to carry out a test sample production process according to the plant structure as shown in Figure 4. In this printing process a PVA binder is used and pressing at a pressure of 4 MPA is carried out in preparing samples for material hardness tests, with shapes and sizes different samples. This stage requires finding a new formula with a variable amount of PVA mass. The next process is to conduct a visual study of the resulting sample whether it is technically feasible to proceed to the furnace process. In achieving the second research objective, an experimental device was developed.

4. Result
According to the first step in the preparation of the specimen is the determination of the material composition. The material with fixed composition is CaO, Al2O3 while the variation composition is RHA (SiO2) as base, MgO and BaO. The following composition data is proposed in table 2.
Table 2. Material Composition

| Composition | RHA | CaO | Al₂O₃ | MgO | BaO | Total [%] |
|-------------|-----|-----|-------|-----|-----|-----------|
| F 1         | 90  | 5   | 5     | 5   | 5   | 100       |
| F 2         | 85  | 5   | 5     | 5   | 5   | 100       |
| F 3         | 85  | 5   | 5     | 5   | 5   | 100       |
| F 4         | 80  | 5   | 5     | 5   | 5   | 100       |
| F 5         | 75  | 5   | 5     | 10  | 5   | 100       |
| F 6         | 75  | 5   | 5     | 10  | 5   | 100       |

Each composition was mixed through the Ball Mill process for 12 hours to obtain a homogeneous mixture and sieved with a size of 250 mesh.

Grain size characterization based on measurements using the Laser Particle Sizer-LLPA-C10 tool produces data as shown in table 3.

Table 3. Particle Size

| Sample | DₐV | S/V | S/g | Surface Weighted Mean D[3,2] | Vol. Weighted Mean D[4,3] |
|--------|-----|-----|-----|----------------------------|--------------------------|
|        | µm | cm²/cm³ | cm²/g | µm                         | µm                       |
| F1     | 3.808 | 16,705.97 | 16,705.97 | 3.592 | 3.808 |
| F2     | 19.631 | 33,903.26 | 33,903.26 | 1.770 | 19.631 |
| F3     | 4.097  | 15,620.16 | 15,620.16 | 3.841 | 4.097 |
| F4     | 4.220  | 15,427.22 | 15,427.22 | 3.889 | 4.220 |
| F5     | 8.750  | 27,695.22 | 0.00    | 2.166 | 8.750 |
| F6     | 3.996  | 15,972.19 | 15,972.19 | 3.757 | 3.996 |

The manufacture of molding specimens with designs according to the construction of the SOFC furnace is made with brass material. Molding design and construction as shown in Figure 5. Molding needs to meet the requirements, easy to fill in the material, strong in the high pressing process and easy in the process of releasing the molded material. Molding can be used for a wide variety of specimen thicknesses.

Figure 5. Mold and Product Design
The next specimen production process is that each material composition is added with 96\% Polivinyl Alcohol (PVA) binder as an adhesive mixed using a magnetic stirrer for 10 minutes [33]. After mixing, the specimens were formed using a molding tool which was pressed with a hydraulic press with a power of 4 MPa. The results obtained are given in Table 4.

| Composition | Quality Specimen using PVA 96\% as binder |
|-------------|-------------------------------------------|
|             | 5\%                                      | 10\% | 15\% | 20\% |
| F1          | not good                                  | not good | good | good |
| F2          | not good                                  | not good | not good | good |
| F3          | not good                                  | not good | not good | good |
| F4          | not good                                  | not good | not good | good |
| F5          | not good                                  | not good | good | good |
| F6          | not good                                  | good | good | good |

The specimen production process is carried out using a Universal Testing machine with a pressure of 4 MPA and the results of a successful sample are shown in Figure 6.

![Figure 6. Pressing Process and Specimen Production Yield](image)

In order to obtain the thinnest possible specimen results obtained by experimenting with variations in the weight of the material. Table 5 shows the thickness variations obtained by varying the material weight of each composition.

| Composition | Specimen Thickness with Variations in Material Weight |
|-------------|---------------------------------------------------------|
|             | Material Weight                                         |
|             | (1 gr) (1.5 gr) (2 gr)                                  |
|             | mm mm mm                                                |
| F1          | failed 1-1.1 1.5-1.6                                    |
| F2          | failed 1-1.1 1.5-1.6                                    |
| F3          | failed 1-1.1 1.5-1.6                                    |
| F4          | failed 1-1.1 1.5-1.6                                    |
| F5          | failed 1-1.1 1.5-1.6                                    |
| F6          | failed 1-1.1 1.5-1.6                                    |
Based on the experiments conducted, the molding was successfully used to print specimens with a pressure of 4 MPa. The recommended use of 96% PVA binder is 20% [33] by weight of the material. Mixing the material with a binder with a magnetic stirrer for 10 minutes to get good homogeneity.

5. Conclusion
The composition of the material (RHA, CaO, Al₂O₃, MgO and BaO) with six formulations (F1-F6) which was determined as a gas leak test specimen through a synthesis process using the ballmill method for 12 hours resulted in a grain variation between 3,808 μm – 19,631 μm. The grain size has not been found to be correlated with the quality of the production process. The results of the preparation of the gas leak test specimen were carried out by molding which was designed according to the effective electric furnace construction using a material weight of 1.5 grams with a 96% PVA binder as much as 20% by weight. Specimens can be produced with sizes above 1 mm, with 1.5 grams of material obtained 11.1mm membrane thickness. The preparation of the test material can be continued in the next gas leak test process. The preparation of the test material can be continued in the next gas leak test process.

[1] Fergus J W 2005 Journal of Power Sources 147 46–57
[2] Winiczewicz K C and Cooper J S 2005 Journal of power sources 140 280-296
[3] Mahato N, Banerjee A, Gupta A, Omar S and Balani K 2015 Progress in Materials Science 72 141-337
[4] Della V P, Kühn I and Hotza D 2002 Materials letters 57 818-821
[5] Luo L, Lin Y, Huang Z, Wu Y, Sun L, Cheng L and Shi J 2015 Ceramics International 41 9239-9243
[6] Wang S, Hsu Y and Hsieh Y 2015 International Journal of Hydrogen Energy 40 3338–3347
[7] Da-Silva M J, Bartolome J F, Antonio H and Mello-Castanho S 2016 Journal of the European Ceramic Society 36 631-644
[8] Partyka J and Leśniak M 2016 Ceramics International 42 8513-8524
[9] Zhang W, Wang X, Dong Y, Yang J, Pu J, Chi B and Jian L 2016 International Journal of Hydrogen Energy 41 6036-6044
[10] Li B, Li W and Zheng J 2017 Journal of Alloys and Compounds 725 1091-1097
[11] Wang S F, Lu H C, Liu Y X, Hsu Y F and Liu Z Y 2017 Ceramics International 43 613-620
[12] Nayak J P, Kumar S and Bera J 2010 NOC 356 1447–1451
[13] Rautanen M, Thomann O, Himanen O, Tallgren J and Kiviaho J 2014 Journal of Power Sources 247 243-248
[14] Silva D M J, Pontuschka W M, Bartolomé J F, Jasinski P, Karczewski J and Reis S T 2019 Journal of the European Ceramic Society 39 3103-3111
[15] Chen J, Chang F and Industries U (1991) Industrial & engineering chemistry research 30 2241–2247
[16] Osipova T, Wei J, Pećanac G and Malzbender J 2016 Ceramics International 42 12932-12936
[17] Sabato A G, Cempura G, Montinaro D, Chrysanthou A, Salvo M, Bernardo E and Smacchetto F 2016 Journal of Power Sources 328 262-270
[18] Sengodan S, Lan R, Humphreys J, Du D, Xu W, Wang H and Tao S 2018 Renewable and Sustainable Energy Reviews 82 761-780
[19] Lin D, Tan S, Lin F, Dong Z, Yan J, Tang D, and Zhang T 2018 Journal of the European Ceramic Society 38 4488-4494
[20] Weil K S 2006 Jom 58 37-44
[21] Yalcin N and Sevinc V 2001 Ceramics international 27 219-224
[22] Adam F, Nelson, J and Iqbal A 2012 Catalysis Today 190 2–14
[23] Abu R, Yahya R and Neon S 2016 Procedia Chemistry 19 189–195
[24] Azadeh M, Zamani C, Ataie A, and Morante J R 2018 Materials Today Communications 14 141-150
[25] Ma Z, Sun, W H, Zhu N, Li Z, Shao C and Hu Y 2002 Polymer international 51 349-352
[26] Darjat, Sulistyo, Triwiyatno A, Sumardi and Widiyantoro I 2020 Eastern-European Journal of Enterprise Technologies 103 68-76
[27] Ryan P O H, Suk-Won C, Whitney-Colella F B P 2006 Fuel Cell Fundamentals (Canada: John Wiley & Sons, Inc)
[28] Lara C, Pascual M J and Durán A 2004 Journal of Non-Crystalline Solids 348 149–155
[29] Elsayed H, Javed H, Sabato A G, Smeacetto F and Bernardo E 2018 Journal of the European Ceramic Society 38 4245-4251
[30] Fergus J, Hui R, Li X, Wilkinson D P and Zhang J 2016 Solid oxide fuel cells: materials properties and performance (London: CRC press)
[31] Ley K L, Krumpelt M, Kumar R, Meiser J H and Bloom I 1996 Journal of Materials Research 11 1489-1493
[32] An D, Guo Y, Zou B, Zhu Y and Wang Z 2011 Biomass and Bioenergy 35 1227-1234
[33] Nayak J P and Bera J 2009 Phase Transitions 82 879-888
[34] Nguyen X, Chang C and Jung G 2016 International Journal of Hydrogen Energy 3–10