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Characterization of Calcia Stabilized Zirconia Synthesis for Solid Oxide Fuel Cell Electrolytes through Precipitation Method

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Abstract

Indonesia has abundant natural resources which are potential to be converted into alternative renewable energy sources to offset the increasing future demand of electrical energy. One of them is Calcia (CaO) which is generally used to stabilize zirconia in order to form Calcia stabilized Zircon (CSZ). The latter is known as a solid electrolyte material in solid oxide fuel cell (SOFC). This fuel converts chemical energy into electrical energy with the advantage of having good impacts on the environment as well as a renewable fuel. An important part of SOFC is the electrolyte, in which ions flow from the cathode to the anode. The electrolyte is made from zirconia, which needs to be stabilized in a cubic phase to be able to flow the ions. Currently, Yttria has been widely used as a zirconia stabilizer in SOFC solid electrolytes. However, Yttria material is generally expensive and it is not widely available especially in Indonesia. Therefore, this research focused on producing CSZ from $Zr(OH)_4$ which was extracted from local zircon sand (ZrSiO4) and synthesized with CaO to produce CSZ powder by precipitation method. The CSZ powder was then transformed into pellets by compacting and sintering at the temperature of 1250˚C. CSZ powders and pellets were characterized using X-ray diffraction (XRD) testing to determine the crystal structure and Scanning Electron Microscopy with Energy Dispersive Spectroscopy to analyse the microstructure. The XRD test results on CSZ powders and pellets showed a pattern that was in accordance with that typically found for CSZ powders and pellets. Micro structural analysis showed that the porosities were still observed and there was an element of silicon impurity.

Keywords: CSZ, *fuel cell, pellet,* XRD, *precipitation*

I. INTRODUCTION

Solid oxide fuel cell (SOFC) is a renewable energy source that is formed through the reaction of chemical substances into electric energy. This new emerging fuel is lately preferred because of its superiority in terms of good environmental impact and renewable fuel. The SOFC is an electrochemical energy conversion based, that converts chemical energy into electrical energy [1,2]. It consists of 3 important components, namely anode, cathode and solid electrolyte. Electrolytes play an important role in a SOFC to facilitate ions flow from the cathode to the anode [3].

Currently, solid electrolyte materials in zirconia-based solid oxide fuel cells have been widely studied because they are considered as new emerging alternative fuel with promising research milestones [4-6]. Zirconia has polymorph properties which are influenced by temperature. The 3 polymorphs are: i) monoclinic that occur at lower temperature of 1170 ºC, ii) tetragonal occurs in the range of 1170-2370 ºC, and iii) cubic in the range of 2370-2700 ºC [7,8]. The most stable polymorphic phase is the one that has the lowest free energy under given conditions (i.e. composition, temperature, and pressure) [9]. The cubic phase is the most stable phase that is capable of flowing oxygen ions. In order to achieve a stable cubic phase at lower temperatures, the addition of an oxide is required. Calcia (CaO) is an oxide that was considered as the most suitable material as a zirconia stabilizer to produce the calcia stabilized zircon (CSZ). The required criteria for a good electrolyte are high ionic conductivity, high density, and minimum porosity at the grain boundaries [10]. This research focused on electrolytes made from the CSZ. The CSZ used is the result of previous process of $ZrSiO_4$ zircon sand extraction to obtain $Zr(OH)_4$. After getting the $Zr(OH)$, synthesis process was further conducted using the precipitation method to obtain CSZ electrolyte. Multi crystal structural characterization was further conducted using X-ray diffraction (XRD) and Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM-EDS) tests for CSZ powder and pellets. The study results revealed the characteristics of Calcia stabilized zircon synthesis to contribute to development of Solid Oxide Fuel Cell in the future.

II. METHODOLOGY

Foremost step of the research was the production of CSZ. It was started with extracting ZOC ($ZrOCl_2 8H_2O$) obtained by grinding 100 grams of local $ZrSiO_4$ and 180 grams of NaOH using the caustic fusion method with calcination for 3 hours at 700 °C. Furthermore, the grinding was carried out until it became a powder. Then 20 grams of the powder were mixed with 150 ml of distilled water. This process was repeated 6 times to ensure that the solution and sediment could not be separated anymore, and to reach the pH of 6-7. The next step was to produce $Zr(OH)_4$ by drying process in the furnace at the temperature of 110 °C. After drying, then leaching process was carried out using a magnetic stirrer for 2 hours, using 5M HCl at 90 °C then it was cooled down to the room temperature for a night until a sodium silicate precipitate was formed. The process was then followed by filtration to obtain a $ZrClO_2$ solution. The $ZrClO_2$ solution obtained from the extraction process was then precipitated by adding ammonia until the yellow colour of the solution turned afterwards. The next step was washing using distilled water until the sediment was formed. This process was repeated until the pH 8.5-9 of the solution was reached. The filtrate was taken from the filtration process, and followed by drying in a furnace at 150 ° to be converted into $ZrOH_4$ powder.

The process of producing CSZ through the precipitation method was carried out by mixing 5.7 grams of $ZrOH_4$ which was previously dissolved with 5M HCl and 0.45 grams of CaO. Note that the 0.45 grams of CaO had been dissolved in advance with 20 ml 1M HCl. The mixing process was carried out using a magnetic stirrer at the temperature 90 °C. Then ammonia was added until the yellow colour of the solution turned white and formed sediment, and was allowed to settle. The next stage was the filtration stage to obtain sediment. The sediment was then calcined at 800 °C for 3 hours to obtain the CSZ powder. Pelletized CSZ was made from CSZ powder by compacting it, then sintering at 1250 °C for 3 hours. The synthesized materials of CSZ pellets were characterized by powder XRD and microstructure analysis for CSZ pellets by performing SEM-EDS.

III. RESULTS AND ANALYSIS

III.1 Sample Analysis of $Zr(OH)_4$

Fig. 1 shows the XRD pattern of the $Zr(OH)_4$ powder test results which was made as a starting material for CSZ production while Fig. 2 presents the standard XRD pattern for $Zr(OH)_4$ powder.

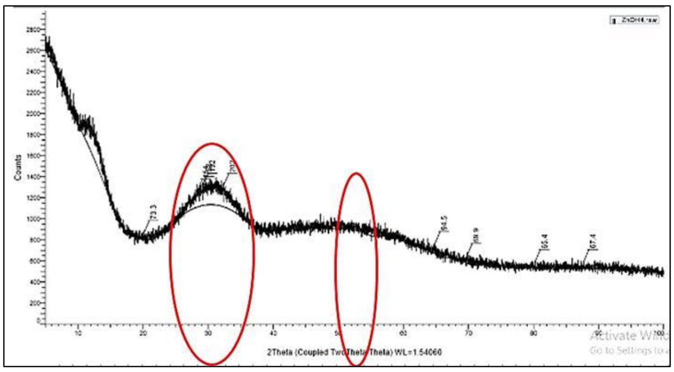

Fig.1 XRD pattern of $Zr(OH)_4$ Powder.

By comparing the results presented in both figures (see red circles in Fig.1 and Fig. 2), it can be seen that there are peaks similar to the standard XRD pattern of $Zr(OH)_4$, i.e, at the peak of 30° and 53° which are indicated by red circles.

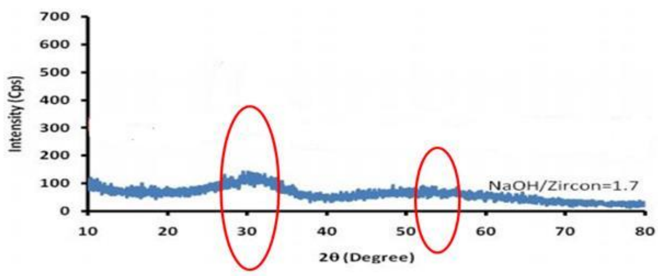

Fig. 2 XRD standard pattern of $Zr(OH)_4$ powder (indicated by red circle).

A. Analysis of CSZ Powder

The result of XRD analysis on CSZ powder is shown in Fig. 3.

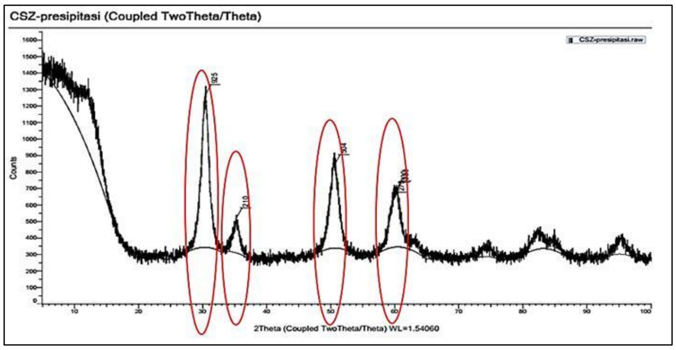

Fig. 3 XRD pattern of CSZ powder.

The pattern of XRD test results in Fig. 3 was then compared to the standard CSZ powder as shown in Fig. 4.

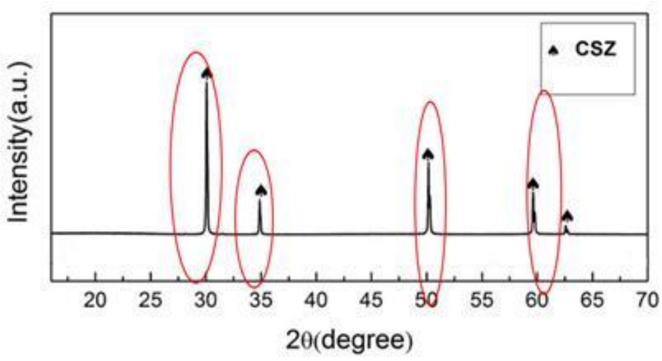

Fig. 4 XRD standard pattern of CSZ powder.

The analysis of XRD pattern by comparing the XRD pattern of CSZ synthesized powder with the precipitation method in Fig. 4 shows the similarity of the patterns to the standard

XRD pattern of CSZ powder, which occurs at the peaks of 30°, 35°, 50°, and 60°.

B. Analysis of CSZ Pellet

The XRD pattern of CSZ pellet is presented in Fig. 5. This result was then compared again to the standard XRD pattern for the CSZ pellet as shown in Fig. 6.

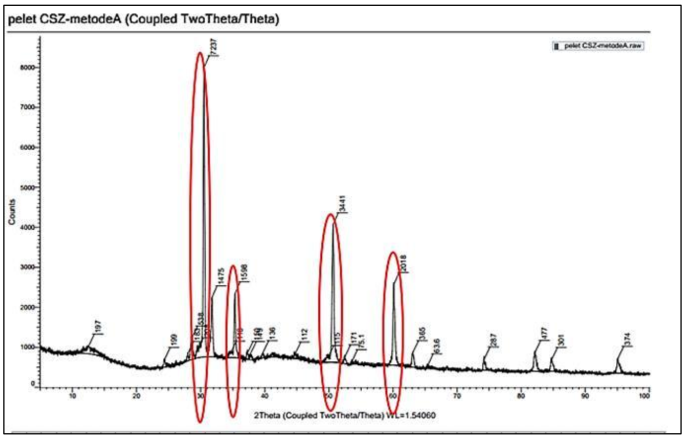

Fig. 5 XRD pattern of CSZ Pellet.

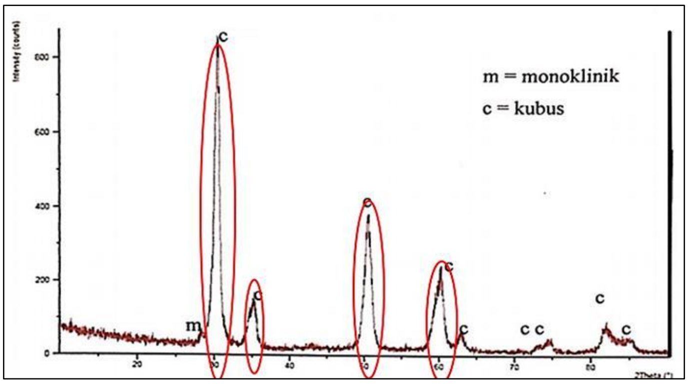

Fig. 6 XRD Standard Pattern of CSZ Pellet.

Based on the comparison between the XRD pattern and the standard XRD pattern of the CSZ pellet, it is obviously seen that the CSZ pellet has a cubic phase according to the standard pattern (indicated by red circles).

C. SEM-EDS Analysis of CSZ Pellet

SEM-EDS results from the CSZ pellet sample are presented in Figs. 7a,b, 8 and 9 below.

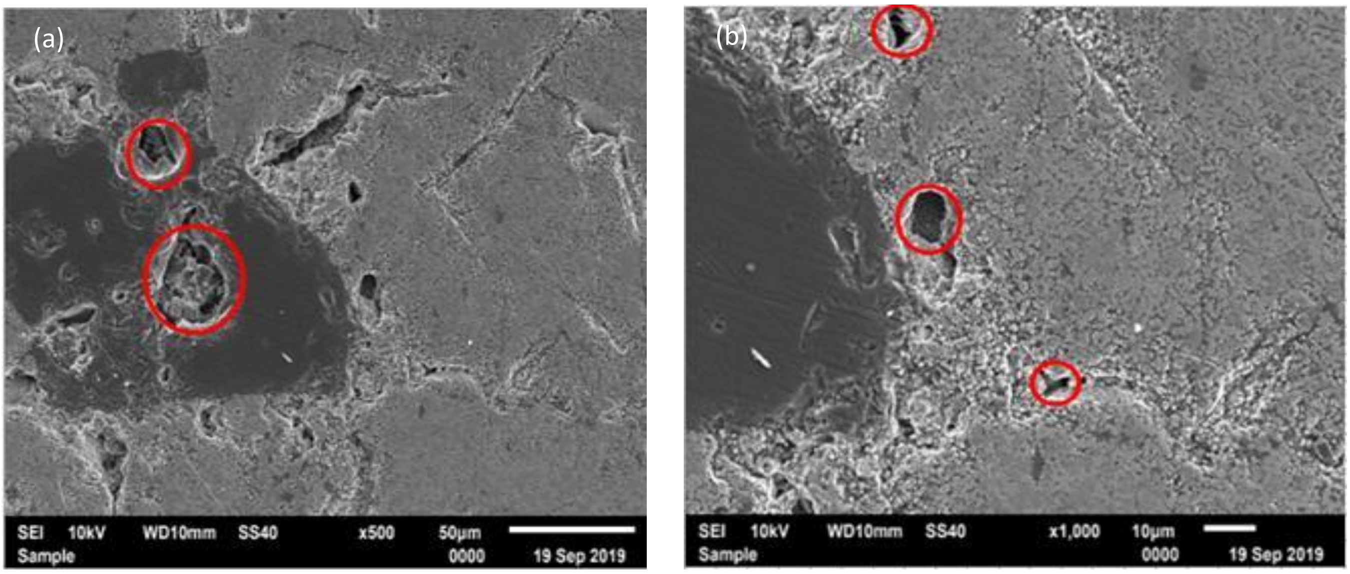

Fig. 7 SEM Images of CSZ Pellet.

The SEM microstructure images in Figs. 7a and 7b show that the CSZ pellet sample has an inhomogeneous microstructure with porous regions or defects as indicated by red circles (Figs. 7). Because of these defects, the density of the pellet became lower, although it appeared to have higher density in the defect-free regions. The defects in the pellets are attributed to the agglomeration of fine CSZ particles. The agglomeration of ultra-fine primary particles due to surface forces, liquid, or a solid bridge is a common phenomenon which in turn leads to poor compaction and inhomogeneous densification during sintering [11,12]. Other possible factors that cause the defects are: powder synthesis method, particle size distribution, and post-processing of the powders. The synthesis method determines various powder characteristics including phase purity and homogeneity of the dopant concentration [12]. The selected zone for SEM-EDS analysis of the CSZ pellet is shown in Fig. 8 and the results of the qualitative and quantitative analyses using SEM-EDS of CSZ pellet are presented in Fig. 9 and Table 1, respectively.

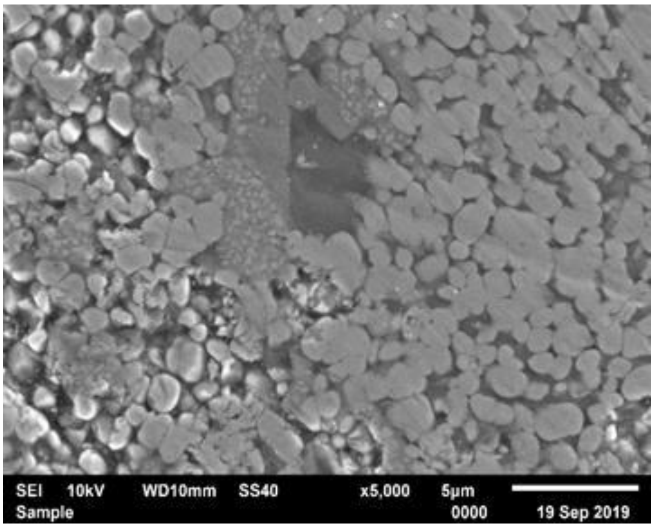

Fig. 8 SEM image of surface CSZ pellet with EDS analyses of selected zone.

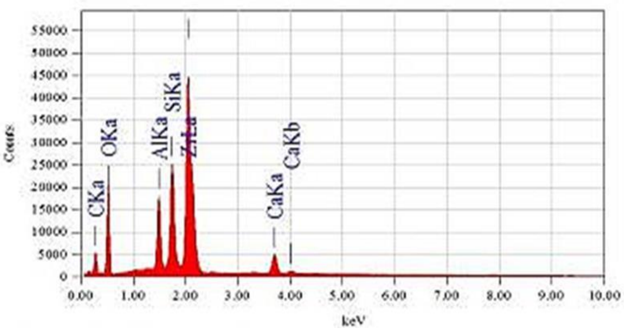

Fig. 9 SEM-EDS qualitative analyses of CSZ pellet.

Table 1. SEM-EDS quantitative analysis of CSZ pellet.

Elements	% mass
Zr	28.77
Ca	1.74
Si	5.11
Al	3.75
O	37.55
C	23.08

Qualitative analysis of SEM-EDS in Fig. 9 on the small grains (see Fig. 8 for selected zone) clarifies the presence of a number of elements, namely C, O, Al, Si, Zr and Ca. Meanwhile, quantitative analysis of SEM-EDS on the same selected area in Table 1 shows that this region contains impurity of silica of 5.11% of its total mass while the standard guided that the content should be below 1 %. Presumably, Silica was segregated in this area and the inhomogeneity of the chemical composition that occurs in CSZ pellets could be caused by the poor compaction of the CSZ powder which in turn led to the density gradients in the green pellets.

IV. CONCLUSIONS

Based on the aforementioned data analysis and findings, the following conclusions were drawn as follows;

1. $Zr(OH)_4$ which was made as a starting material for the manufacture of CSZ obtained from the extraction process of the caustic fusion method was observed to be able to produce good $Zr(OH)_4$.
2. The CSZ powder produced through the synthesis process of the precipitation method was in accordance with the standard XRD pattern which was indicated by 2θ peaks formed at 30, 35, 50, 60 degrees.
3. CSZ pellets made with a composition of 82:12 % molarity by the synthesis process of precipitation method were able to form a cubic phase, with the, which did not wash or decrease the pH.

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