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Characterization of Calcia Stabilized Zirconia as a solid Electrolyte Made through a sol gel Method in Solid Oxide Fuel Cell

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Abstract -- Solid Oxide Fuel Cell (SOFC) is a solid-state energy conversion device which produces electricity through the conversion of chemical energy directly to electrical energy. The research was carried out to characterize Calcia Stabilized Zirconia (CSZ) that was made using sol gel method. In this study, the production of CSZ pellets consisted of three steps. First step was the extraction of ZOC ($ZrOCl_28H_2O$) and second step was the production of $Zr(OH)_4$ and the last step was dissolution of $ZrOH_4$ into HCl and then adding CaO to get CSZ powder. The CSZ powder was then pressed to form pellets, followed by sintering at 1200 ºC for 3 hours. The characterization was conducted using X ray diffraction to analyze the presence of impurities as well as the formation of cubic phase and scanning electron microscope was used to observe the pores in the microstructure. From the XRD data and SEM analysis, it can be concluded that the Calcia Stabilized Zirconia as a solid electrolyte in SOFC using sol gel method gave promising results.

Keywords: Solid oxide fuel cell, Yttria stabilized zirconia, calcia stabilized zirconia, solid electrolyte

I. INTRODUCTION

Solid oxide fuel cell (SOFC) is sustainable energy resources that convert chemical energy directly to electrical energy. SOFC have a considerable potential to be applied to power generation sectors, portable and transport applications [1,2]. Compared to conventional power generation, solid oxide fuel cells have an advantage of operating at high efficiencies and able to run on a range of fuels, from the conversion of solar hydrogen to methanol, to the conversion of biomass to gasified coal [3]. Moreover, SOFC also provide a clean, environmental-friendly, and economical option for energy generation, especially for combined heat and power, small-scale, stand-alone as well as remote applications [4]. The basic components of the SOFC are a solid ceramic electrolyte and two electrodes (the anode and the cathode). Each component of the SOFC serves several functions and must meet certain requirements such as proper stability and conductivity, dense electrolyte to prevent gas mixing, porous anode and cathode to allow gas transport to the reaction sites and chemical compatibility with other components [5]. The electrolyte plays an important role as it allows oxygen ion (O_2^-) mobility from one electrode to the other in order to maintain the overall electrical charge balance [3]. The essential requirements for the electrolyte material are: good oxygen ion conductivity, similar thermal expansion coefficients to the other components, low electronic conductivity, ease of densification and stability, which is unreactive towards other components used in the SOFC. The most commonly used material which meets these requirements is yttria-stabilized zirconia (YSZ). Previous research had paid much attention on the electrolyte such as reducing the YSZ electrolyte thickness [6,7] and finding a candidate for SOFC electrolyte [8-10]. It has been reported that the solid electrolyte for the SOFC made of Calcia Stabilized Zirconia (CSZ) gave promising results [10,11]. Another research concluded that by mixing ZrO_2 with metallic oxides such as CaO, great molecular stability can be obtained [12]. Calcia can stabilize zirconia to become CSZ in a cubic phase, which is the most stable phase to allow the flow of Oxygen ions. On top of that, calcia has high oxygen ion conductivity. CSZ has an advantage as it can be operated at a lower temperature if it is combined with other materials with high ionic conductivity. Ionic conductivity is highly affected by the sintering condition of an electrolyte. Sintering condition will have an impact on the characteristics of the electrolyte produced. Microstructure with high density is one of the crucial factors which determine ionic conductivity. Several criteria required by an electrolyte include: high density with minimum porosity, high ionic conductivity as well as good chemical stability to electrode. This research focused on calcia as an alternative electrolyte material where zircon material is synthesized with CaO to produce CSZ using Sol-gel method. Characterization of CSZ was carried out using XRD to observe the formation of crystal structure, SEM to examine the porosity and SEM-EDS to obtain quantitative data analysis for the impurities.

II. EXPERIMENTAL METHOD

The production of CSZ was initiated by the extraction of ZOC ($ZrOCl_28H_2O$) which was obtained through grinding 100 gr of zircon sand ($ZrSiO_4$) along with 180 gr of NaOH. Calcination was the conducted for 3 hours at 700 ºC. After the mixture was cooled, further grinding was carried out in order to become powder. 20 gr of the powder was taken to be mixed with 150 ml of aquades. The process was then followed by heating for 30 minutes at 150 ºC while stirring. Mixture was

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then left to form sediment. After sedimentation occurred, water was taken out and 300 ml of aquades was used to wash the sediment, which was then heated at 150 ºC. This process was repeated for 6 times until the solution and sediment could not be separated. The experiment was followed by checking the pH, which needs to be within the range of 6 – 7.

The next stage to produce $Zr(OH)_4$ is the drying process inside a furnace at a temperature of 110 ºC. This process was followed by leaching for 2 hours, using HCl 5M at 90 ºC and then left at room temperature for 1 night to form sodium silicate sediment. The filtered solution went through crystallization process in a furnace at 70 ºC, until it was fully crystalized and produced $ZrOCl_2HCl$. Aquades were added to the $ZrOCl_2HCl$ crystal and further crystallization process was conducted in a furnace at 70 ºC until ZOC ($ZrOCl_28H_2O$) was produced. ZOC obtained from the extraction process was dissolved in HCl while heating process took place. Ammonia was also added until the yellow color turned into white. The experiment was continued by washing process using aquades. The solution was then left to form sediment. The process was repeated until the solution reached a pH of 8 – 9. The filtrate obtained from the filtration process, was dried at 150 ºC in order for ZOC to turn into $ZrOH_4$.

The production of CSZ was carried out by dissolving 5.7 gram of $ZrOH_4$ into HCl and then adding 0.45 gram CaO, which had been previously dissolved with 20 ml HCl. The experiment was then followed by the addition of 4.2 gr citric acid. After all the substances had been dissolved, heating process was conducted at 120 ºC until gel was formed. The temperature was the increased to 800 ºC for 3 hours to produce CSZ powder. CSZ pellets were formed by pressing method, followed by sintering at 1200 ºC for 3 hours. The results can be seen in Fig. 1.

Fig. 1 CSZ pellets made by sol gel method.

Characterization was carried out on ZOC and CSZ pellets, including crystal structure analysis using X-Ray Diffractometer (XRD) along with micro structure analysis using Scanning Electron Microscope-EDS.

III. RESULTS AND DISCUSSION

A. Analysis of ZOC sample

The X ray diffraction on ZOC is presented in Fig. 2.

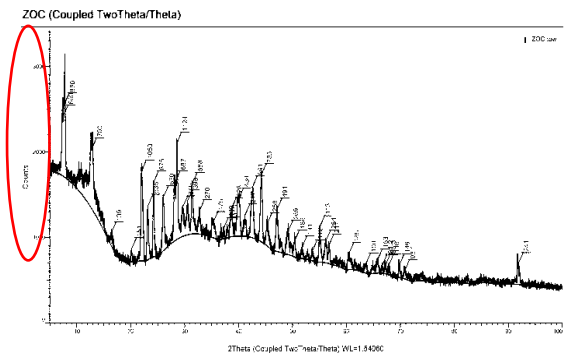


Fig. 2 X ray diffraction test results of ZOC sample.

The result from XRD test on ZOC (Fig. 2) was then compared to XRD of pattern ZOC in Fig. 3.

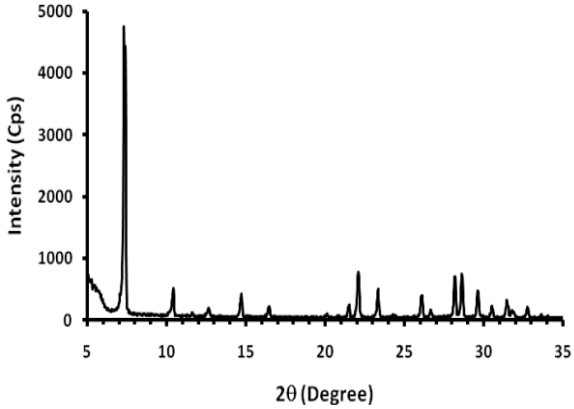


Fig. 3 X Ray Diffraction pattern of ZOC powder [1].

It can be seen that from both XRD graphs, the presence of ZOC substance was detected. This is indicated by the red circle in Fig. 2. However, the XRD result on ZOC sample created shows many peaks which indicate that there is a significant amount of impurities. The SEM – EDS results on ZOC samples can be seen in Figs. 4 and 5.

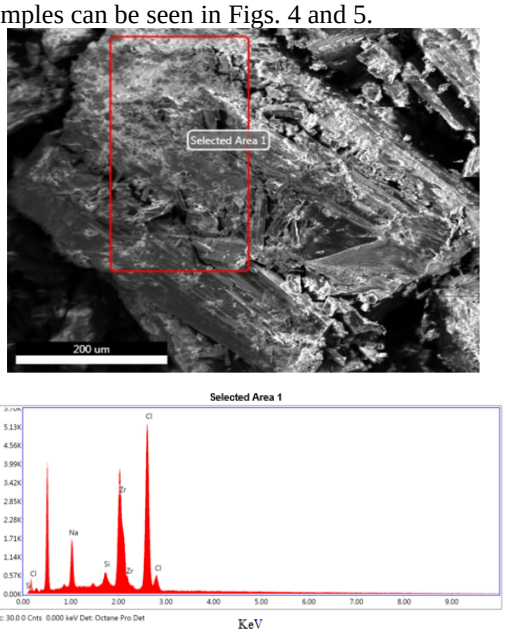
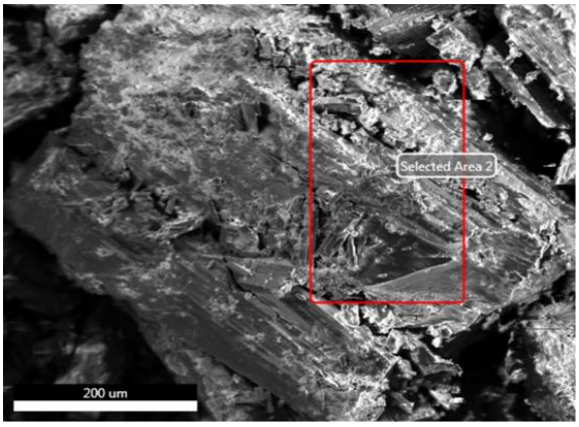


Fig. 4 SEM-EDS analysis of ZOC sample on selected area 1.

Table 1. Quantitative analysis of SEM-EDS on selected Area1

Element	% Weight
Na	9.38
Si	2.18
Zr	40.89
Cl	47.55



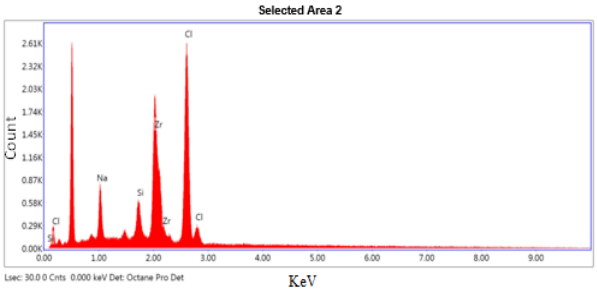


Fig. 5 SEM-EDS analysis of ZOC sample on selected area 2.

Table 2. Quantitative analysis of SEM-EDS of ZOC sample on selected Area 2

Element	% Weight
Na	8.66
Si	4.57
Zr	40.93
Cl	45.83

Tables 1 and 2 show the percentage of each element which can be found in the sample. Zr and Cl are compounds which were used to from ZOC, whereas Na and Si were impurities, which need to be removed, when the sum of percentage of both impurities reaches more than 10 %wt. To remove impurities found in ZOC sample, sedimentation process was conducted using ammonia, which caused NaCl or excess salt to disappear and turn into $Zr(OH)_4$.

B. Analysis of $Zr(OH)_4$

Analysis of $Zr(OH)_4$ using XRD is presented in Fig. 6.

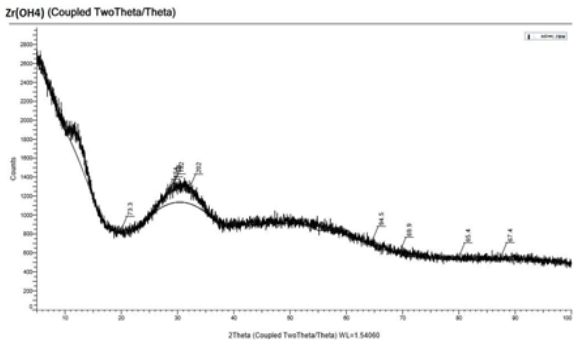


Fig. 6 X-Ray Diffraction result of $Zr(OH)_4$ sample.

The graph in Fig. 6 was then compared to the graph of $Zr(OH)_4$ in Fig.7 as a reference.

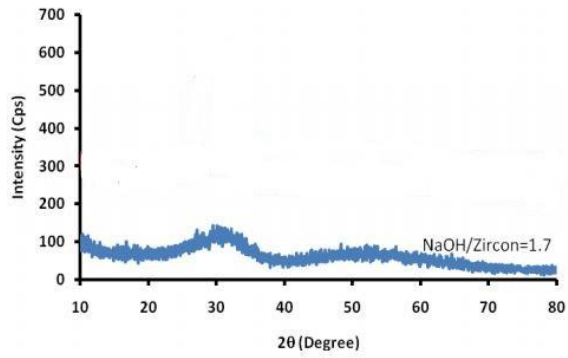


Fig.7 X ray diffraction pattern of $Zr(OH)_4$ sample [13]

From the analysis that was conducted by comparing graph obtained from the experiment using Zr(OH)4 sample (Fig. 6) with the standard (Fig.7), it can be seen that both graphs show similar patterns which indicate the sample was created according to the reference.

C. Analysis of Calcia Stabilized Zirconia (CSZ)

Analysis of CSZ powder was carried out using XRD, the results can be seen in Fig. 8.

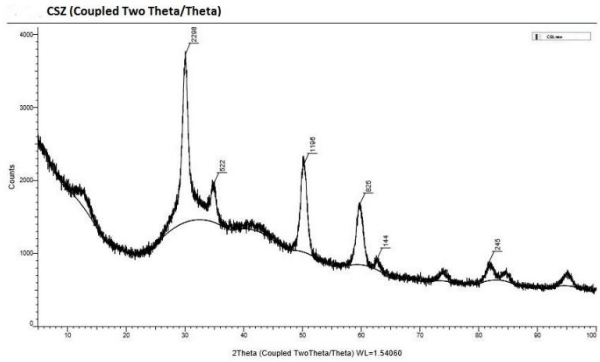


Fig. 8 X ray diffraction test results of CSZ powder.

From the XRD test result of CSZ powder, a graph in Fig.8 was then compared to the reference, which is presented in Fig. 9.

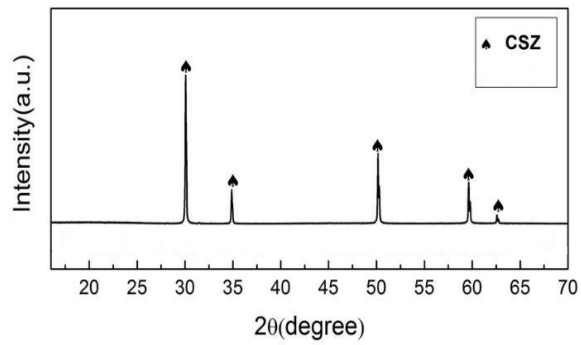


Fig. 9 X ray diffraction pattern Of CSZ powder.

The comparison between the graph obtained from the CSZ powder sample test (Fig. 8) and the standards (Fig.9) shows a similar pattern, which indicates that CSZ powder corresponds to XRD pattern. CSZ characterization in the form of pellet was conducted using XRD and the results can be seen in Fig. 10.

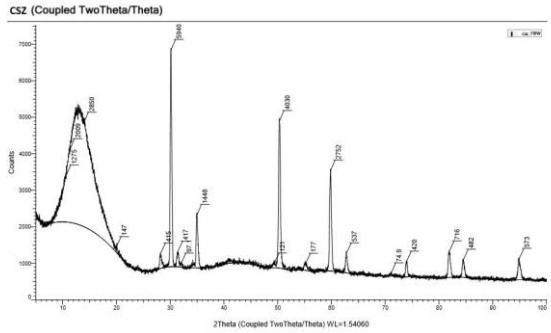


Fig. 10 X-Ray Diffraction test results of CSZ pellets.

From XRD testing for CSZ pellet, a graph, as presented in Fig. 10 was obtained was then compared to Fig. 11, which is the X ray diffraction pattern of CSZ. Both graphs were then compared to see any correlation.

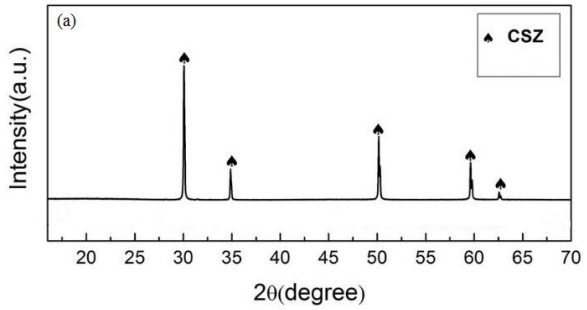


Fig. 11 X ray diffraction pattern of CSZ pellets.

Analysis was carried out by comparing the graph obtained through experiment using CSZ, with its standard. Fig. 11 (a) was used to indicate the material used in the experiment was CSZ whereas Fig. 11 (b) was used to compare crystal structure of both the sample and the reference. The result shows similar patterns which indicates that CSZ (Calcia Stabilized Zirconia) corresponds to its standard. Based on the crystal structure comparison, CSZ sample has a cubical shape. Cubic phase in an electrolyte indicates a good ionic conductivity, which suggests that the CSZ sample has this characteristic. The SEM – EDS results on ZOC samples can be seen in Figs. 12 and 13.

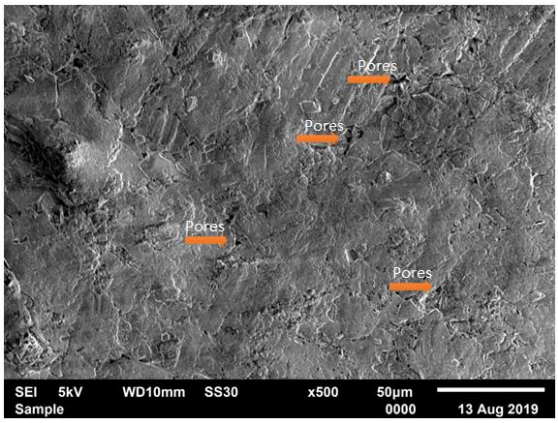


Fig.12 A scanning electron image of CSZ microstructure.

From the Fig. 12, it can be seen that there is a significant amount of pores. This was due to the presence of trapped air during heating process which led to the formation of pores.

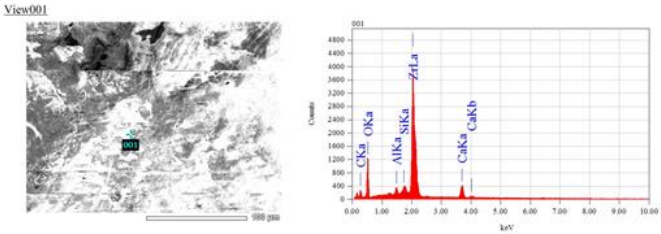


Fig.13 SEM-EDS analysis of CSZ.

Table 3. Quantitative analysis of SEM-EDS of CSZ on selected Area in Fig. 13.

Element	% Weight
Zr	38.47
Ca	2.56
Si	0.48
Al	0.86
O	40.59
C	17.04

Based on the results obtained from SEM-EDS quantitative analysis on CSZ sample (see Table 3), it can be seen that there was a decrease in the amount of impurities (see Tables 1 and 2 for the impurities e.g.: Na and Si). Furthermore, the sum of percentage of impurities (in wt.%) is still within the acceptable threshold e.g.:2% [13].

IV. CONCLUSIONS

From the data and analysis of the tests results and analysis, the conclusions are drawn as follows:

- The use of Calcia as a solid electrolyte in SOFC using sol gel method with the parameter used in this research can be implemented and gave promising results.
- CSZ ceramic made using sol-gel method had a tendency to have high porosity level.
- Addition of calcia to CSZ ceramic created a cubical crystal structure which had a positive impact on the increase of ionic conductivity.

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Meilinda Nurbanasari is a Professor. She obtained her BE in the field of Metallurgical Engineering from University of Indonesia. She received her Master Degree from Institut Teknologi Bandung, Indonesia and she was awarded her PhD from the Materials Science and Engineering from the University of Sheffield, UK. Currently, she is an academic staff at the Mechanical Engineering Department, Institut Teknologi Nasional, Bandung, Indonesia. She is also a reviewer of some international journals and appointed as Editorial Board Member of Journal of Metallic Materials Research.

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