Electrical conductivity of zirconia and yttrium-doped zirconia from Indonesian local zircon as prospective material for fuel cells

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Abstract. In this research, zirconium dioxide, ZrO₂, was synthesized from high-grade zircon sand that was founded from Bangka Island, Sumatra, Indonesia. The zircon sand is a side product of Tin mining plant industry. The synthesis was conducted by caustic fusion method with considering definite stoichiometric mole at every reaction step. Yttrium has been doped into the prepared zirconia by solid state reaction. The prepared materials were then being analyzed by X-ray diffraction equipped with Le Bail refinement to study its crystal structure and cell parameters. Electrical conductivity was studied through impedance measurement at a frequency range of 20 Hz- 5 MHz. Morphological analysis was conducted through Scanning Electron Microscopy (SEM) equipped with Energy Dispersive X-ray (EDX) for elemental analysis. The results show that the prepared yttrium stabilized zirconia, YSZ, was crystallized in the cubic structure with a space group of P42/NMC. The sintered zirconia and yttrium stabilized zirconia at 8 mol% of yttrium ions (8YSZ) show dense surface morphology with a grain size less than 10 µm. Elemental analysis on the sintered zirconia and 8YSZ show that sintering at 1500 °C could eliminate the impurities, and the purity became 81.30%. Impedance analysis shows that ZrO₂ provide grain and grain boundary conductivity meanwhile 8YSZ only provide grain mechanism. The yttrium doping enhanced the conductivity up to 1.5 orders. The ionic conductivity of the prepared 8YSZ is categorized as a good material with conductivity reach 7.01×10⁻³ at 700 °C. The ionic conductivities are still lower than commercial 8YSZ at various temperature. It indicates that purity of raw material might significantly contribute to the electrical conductivity.

1. Introduction
Zirconia is metal oxide for multifunctional applications such as for ceramics, due to the ability to reflect light and a good ceramics coating [1], for catalysts, due to its good thermal stability [2] and its high surface area [3]. It is also a potential material for electrolyte and electrode of fuel cells [4-7]. Zircon sand is a potential raw material for zirconia production. Zircon sand in Bangka Island Indonesia is siding product of tin mining plant that has low economic value. Therefore, some researchers such as Soepriyanto and Hidayat [8] did the effort to increase zircon (ZrSiO₄) concentration through flowsheet modification in...
separation method. It can increase zircon concentration from 20% to 98%. The commercial zircon usually contains of 66wt% min. ZrO$_2$ + HfO$_2$, 32-33 wt% (weight%) of SiO$_2$, 0.1 wt% TiO$_2$ dan 0.1 wt% max. Fe$_2$O$_3$ [9]. Zircon is very stable chemical compound due to the strong bond between zirconia and silica in its molecule. Therefore, the zircon extraction must be initiated by the chemical bonds break down. Alkali fusion method is a more favorable technique than traditional chlorination breakdown [10].

A variety of synthesis method is also being explored and developed for the production of stabilized and nonstabilized nanoscale zirconia particles. The methods are thermal decomposition [11-12], sol–gel [13], precipitation [13, 14], emulsion precipitation [15], hydrothermal [16], reverse microemulsion [17], and mechanical milling [18]. Since 1960, the caustic fusion method showed that zircon ore could be fused at 600 °C with the mixture of NaOH and water. The product is a hydrolyzed zirconate, which was further treated using HCl to form a zirconium oxychloride before precipitation [19]. Manivasan et al. [19] used a slight variation on this caustic fusion process and used nitric acid to form a zirconyl nitrate, which can be precipitated. The use of ball milling as a mean for breaking down loose agglomerates is also explored. Rahmawati et al. [4] have applied caustic fusion method as it was conducted by Soepriyanto and Hidayat [8] to produce ZrO$_2$ from zircon sand from Bangka Island, Indonesia. However, the synthesis did not follow the stoichiometric amount of each reagent, such as the zircon sand was crushed with solid NaOH at the same weight of the mixture. The produced ZrO$_2$ then was doped with yttrium and combined it with LSGM-8282. It found that the prepared YSZ is still non homogeneous and consist of high silica content. Even though the caustic fusion method still provides low purity of zirconia, however caustic fusion or alkali fusion is a simple non-expensive method to produce zirconia from zircon concentrate, ZrSiO$_4$ [20]. Therefore in this research, the caustic fusion method is conducted by applying a definite mole ratio at each reaction step based on the stoichiometric reaction. The prepared materials were sintered at a different temperature to study the effect of sintering temperature to its crystal structure and conductivity. Comparison to the commercial product was also conducted to study the prospect ability of the prepared materials.

2. Experiment

ZrO$_2$ was synthesized by caustic fusion method. NaOH (99%) 30 g solid and 33 g of High-Grade Zircon were grounded in mortar and pestle for 2 hours. Weight ratio was determined from mol calculation based on the chemical reaction in equation (1).

$$\text{ZrSiO}_4(s) + 4 \text{NaOH}(s) \rightarrow \text{Na}_2\text{ZrO}_3(s) + \text{Na}_2\text{SiO}_3 + 2 \text{H}_2\text{O}(g)$$

(1)

The mixture is then dissolved in 120 mL of 5 M HCl solution during the acid leaching process to produce ZrOCl$_2$. Acid leaching was conducted at 85 °C for 30 minutes. The produced zirconium oxychloride then being reacted with ammonium hydroxide 1 M until pH of the solution reaches 9. This step was conducted to produce zirconium hydroxide, Zr(OH)$_4$. The addition of ammonium hydroxide was conducted under stirring at 80 °C. After 24 hours aging, zirconium hydroxide deposit was filtered and washed with hot water until reach neutral pH (pH=7) condition. The residue then was heated at 150 °C for 3 hours and being calcined at 800 °C for 5 hours to produce zirconia powder.

Doping yttrium ions into zirconia were conducted by solid state reaction between Y$_2$O$_3$ and the prepared ZrO$_2$ at definite mol amount to produce Y$_{0.08}$Zr$_{0.92}$O$_{2.9}$ (8YSZ) and followed by calcination at 1000 °C for 5 hours. The powder was analyzed by X-ray Diffraction, XRD (Bruker D8) equipped with Le Bail refinement to study its crystallinity, crystal structure and its cell parameters. The X-ray fluorescence, XRF (BRUKER S2 Ranger) analysis was conducted for elemental analysis. Surface morphology and elemental content were analyzed by Scanning Electron Microscopy, SEM/EDX (FEI Type Inspect S50).

Sintering of the prepared materials was conducted at 1500 °C for 5 hours. The conductivity analysis was conducted through calculation of conductivity from impedance data that was measured by LCR meter (GW Instek LCR-8105G, frequency range 20 Hz – 5 MHz) at 400 – 700 °C. Conductivity value was calculated by using equation (2). Capacitance value was used to determined the conductivity type, whether grain (∼0.1 pF), grain boundary (∼1.4 nF) or electrode-electrolyte interface (> 1 uF) [21].
$$\frac{1}{\sigma} = \frac{1}{R} \frac{l}{A} \quad (2)$$

$\sigma$ is specific conductivity (S cm$^{-1}$), $R$ is resistance ($\Omega$), $l$ is the thickness of pellet (cm), and $A$ is area of active electrode (cm$^2$).

The Arrhenius plot of conductivity to temperature was provided to analyze the activation energy of ionic conduction and the pre-exponential factor that correlates with the number of vacancies which potentially contribute to the ionic conductivity of the material. The plot followed Arrhenius equation (3).

$$\sigma = \sigma_0 \exp \frac{-E_a}{kT} \quad (3)$$

The $\sigma_0$ is the pre-exponential factor, the $E_a$ is the activation energy, $k$ is Boltzmann constant, and $T$ is temperature.

3. Results and discussion

The caustic fusion of zircon occurs within each step as listed in reaction equations (4) – (6). The decomposition reaction with sodium hydroxide follows equation (1) [10]. Acid leaching with hydrochloric acid was proceeded as described in equation (4) to form ZrOCl$_2$. Then ZrOCl$_2$ was reacted with ammonium hydroxide to form zirconium hydroxide (equation (5)).

\[ n\text{Na}_2\text{ZrO}_3 + 4n\text{HCl} \rightarrow n\text{ZrOCl}_2 + n\text{NaCl} + n\text{H}_2\text{O} \quad (4) \]
\[ \text{ZrOCl}_2 + n\text{H}_2\text{O}_{(aq)} + 2\text{NH}_4\text{OH}_{(aq)} \rightarrow \text{Zr(OH)}_4_{(s)} + 2\text{NH}_4\text{Cl}_{(aq)} + (n-1)\text{H}_2\text{O}_{(l)} \quad (5) \]

Zirconium oxide was formed during calcination at 800°C for 5 hours, as it is described in equation (6).

\[ 2\text{Zr(OH)}_4 \rightarrow t\text{-ZrO}_2 + m\text{-ZrO}_2 + 4\text{H}_2\text{O} \quad (6) \]

Zirconium oxide was formed during calcination at 800°C for 5 hours, as it is described in equation (6). X-ray diffraction analysis of the initial HG Zircon and the prepared ZrO$_2$ produced diffraction equipped with the Le Bail refinement have been studied in our previous paper [22]. The Le Bail refinement shows that the prepared ZrO$_2$ was crystallized in tetragonal structure with a space group of $P4_2/NMNC$ with cell parameters $a=b=3.592(1)$ Å and $c=5.192(2)$ Å. The cell volume is 67.00(4) Å$^3$ with an angle $\alpha=\beta=\gamma=90^\circ$. The refinement proceeded well at % residual of $R_p$ 5.51% and $R_{wp}$ of 6.75%. XRF analysis shows that the concentration of ZrO$_2$ in the prepared powder is 72.17%. Some impurities are still present such as sodium oxide and silica [22].

Yttrium doping was conducted by solid state reaction of Y$_2$O$_3$ with the prepared ZrO$_2$. The XRD pattern is depicted in Figure 3 in comparison with standard 8YSZ ICSD #90885. XRD patterns show that the mixture of Y$_2$O$_3$ with ZrO$_2$ without calcination has many peaks with low crystallinity. After being calcined at 1000 °C for 2 hours, some peaks were disappeared and the diffraction has many sharp peaks that indicate high crystallinity. However, comparison of the calcined sample with standard diffraction of 8YSZ ICSD #90885 shows four peaks that are not in agreement with the standard. The presence of sodium oxide and silica as it was shown by elemental analysis may confirm that the unidentified peaks are related to sodium oxide and silicon dioxide as it is described in Figure 1.

The morphological analysis shows that the sintered ZrO$_2$ has dense surface morphology with a grain size less than 10 µm as it is described in Figure 2. EDX analysis confirms that the sintered ZrO$_2$ has a high content of Zr i.e. 81.30% weight (Figure 4(b)), and there are no impurities detected. It indicates that some impurities might be released while sintering at 1500 °C for 5 hours, such as the sodium oxide was melted at 1132 °C. Meanwhile, the silicon dioxide is still present due to the compound has high melting point, i.e., 1600 °C.
**Figure 1.** XRD pattern of the mixture of $\text{Y}_2\text{O}_3$ and $\text{ZrO}_2$ without calcination, the prepared 8YSZ after being sintered at 1500 °C, and the XRD pattern of standard 8YSZ from ICSD #90885, standard diffraction of $\text{SiO}_2$ and standard diffraction of $\text{Na}_2\text{O}$. Sign o refers to the YSZ peaks, □ refers to the disodium oxide and Δ refers to the silicone dioxide.

**Figure 2.** (a) SEM image of the prepared zirconia that was sintered for 5 hours at 1500 °C.

**Figure 2.** (b) EDX result of the prepared zirconia that was sintered for 5 hours at 1500 °C.
Meanwhile, 8YSZ shows more dense surface morphology with grain size around 10 µm. However, the morphology is less dense than the commercial 8YSZ. SEM images are described in Figure 3. EDX analysis (Figure 4) shows that the prepared 8YSZ content of 68.25% weight and yttrium of 11.02% weight.

![Figure 3](image_url)

**Figure 3.** SEM images of the prepared 8YSZ (a) and (b) at different magnification and SEM image of commercial 8YSZ (c)

![Figure 4](image_url)

**Figure 4.** EDX result of the prepared 8YSZ from zircon concentrate

| Element | Wt%  | At%  |
|---------|------|------|
| O       | 18.26| 54.31|
| Si      | 02.47| 04.18|
| Y       | 11.02| 05.90|
| Zr      | 68.25| 35.60|
The prepared 8YSZ that was sintered at 1500 °C has diffraction peaks that in agreement with the standard diffraction of ICSD #90894 (Figure 5). The refinement results that the prepared 8YSZ has a cubic structure with cell parameters of $a=b=c=5.1442$ Å with a cell volume of $136.14(2)$ Å$^3$. The residual factors are $R_p 6.27\%$ and $R_{wp} 13.5\%$.

**Figure 5.** The diffraction patterns of 8YSZ after sintering at 1500 °C

**Figure 6.** The Nyquist plots of imaginary impedance ($Z''$) to the real impedance ($Z'$) of the prepared ZrO$_2$ at various temperature.
Figure 7. Impedance plots of the prepared 8YSZ at various temperature.

Impedance analysis at 400 – 700 °C for ZrO₂ and 8YSZ produce Nyquist plots as it is described in Figure 6 and 7. Zirconia shows two semicircles that indicate migration of charge carriers might occur through different mechanisms such as grain and grain boundary conduction or electrolyte-electrode interface. Meanwhile, the prepared 8YSZ shows two semicircles at 300 °C and 400 °C, and the curve became single semicircle at 500 °C and above. Fitting on impedance plot confirms that the resistance value decreased as the temperature increase. Capacitance values confirm that zirconia provides grain
resistance only at 300 °C and provide grain and grain boundary resistance at temperature 400 C and above. These were confirmed by capacitance values that listed in Table 2. Calculation of conductivity with equation (1) shows that the prepared zirconia shows good ionic conductivity that is higher than $1 \times 10^{-4}$ S.cm$^{-1}$ [23] at a temperature higher than 500 °C. Meanwhile, at 300 – 400 °C the ionic conductivity values are lower than $1\times10^{-4}$ S.cm$^{-1}$. Therefore, it is not suitable to be applied as an electrolyte for the fuel cell.

Doping of 8% mol yttrium into the prepared zirconia could increase ionic conductivity values at about two orders. Therefore, the material become suitable for the electrolyte in fuel cell even at 400 °C, due to the ionic conductivity is $2.92 \times 10^{-4}$ S.cm$^{-1}$; which categorized as good electrolyte [23]. The conductivity values are listed in Table 2. At temperature above 400 °C, the ionic conductivity was dominated by grain boundary conductivity, as confirmed by their capacitance values (Table 2). At 300 – 500 °C the ionic conductivity values are lower than the commercial 8YSZ. The ionic conductivity of the prepared 8YSZ become higher than the commercial 8YSZ at above 500 °C. The Arrhenius plot in Figure 8 shows clearly the conductivity trendline of the materials. It indicates that the 8YSZ that was prepared from Indonesian zircon sand might provide better performance for the high-temperature solid oxide fuel cell than the commercial one.

![Figure 8](image)

**Figure 8.** Plot Arrhenius of the prepared ZrO$_2$, YSZ and the commercial YSZ (YSZc)

Arrhenius plot also can be used to study the energetic of ionic migration inside crystal structure. The conductivity plot of each material shows only a single slope. The slope might consist of activation energy of ionic hoping and the activation energy of ionic migration. Rahmawati et al. [4] also found the only single slope of 8YSZ. Meanwhile, Zhang et al. [24] found two slopes of Arrhenius plot of nanosize 8YSZ. A slope at 600-700 °C with greater value than slope at 700-1000 °C. The temperature of conductivity measurement that only until 700 °C, might become a factor that cause the prepared 8YSZ only shows one slope. It means that if the measurement proceeds up to higher than 700 °C, the Arrhenius plot might consist of two slopes.
The activation energies of the prepared 8YSZ and commercial 8YSZ are 1.002 eV and 1.094 eV, respectively. These are consistent with the result of Madani et al. [25] who found activation energy of 1.08 eV for 9.5% mol YSZ and activation energy of 1.14 eV [24]. Meanwhile, Gong et al. [26] found 0.91 eV at measurement temperature higher than 650 °C. The activation energy of the prepared 8YSZ is lower than the commercial 8YSZ. It indicates that ions might migrate easier in the crystal structure of the prepared 8YSZ. However, the pre-exponential factor of commercial 8YSZ is three times higher than 8YSZ from local zircon. Pre-exponential factor is representing the number of vacancies, as it can be seen in equation (7) and (8) for Frenkel and Schottky defect, respectively [27]. It indicates that commercial 8YSZ has high vacancies concentration than the 8YSZ from zircon sand. It probably of the presence of impurities inhibits the formation of oxygen vacancies.

\[
\sigma_o = \frac{n_f}{\exp(-g_f / 2kT)}(a^2 q^2 / kT)\nu_o \quad (7)
\]

\[
\sigma_o = \frac{n_s}{\exp(-g_s / 2kT)}(a^2 q^2 / kT)\nu_o \quad (8)
\]

| Materials | Temperature (°C) | \(\sigma_{\text{grain}}\) (S.cm\(^{-1}\)) | \(\sigma_{\text{grain boundary}}\) (S.cm\(^{-1}\)) | CPE1 (F) | CPE2 (F) |
|-----------|------------------|------------------------------------------|-----------------------------------------------|---------|---------|
| ZrO\(_2\) | 300              | 7.74 \times 10^{-7}                     | -                                             | 1.63 \times 10^{-12} | -       |
|           | 400              | 9.15 \times 10^{-6}                     | 4.91 \times 10^{-6}                           | 3.44 \times 10^{-12} | 1.02 \times 10^{-9} |
|           | 500              | 2.07 \times 10^{-5}                     | 1.45 \times 10^{-5}                           | 2.71 \times 10^{-12} | 1.54 \times 10^{-9} |
|           | 600              | 1.90 \times 10^{-4}                     | 1.81 \times 10^{-4}                           | 2.19 \times 10^{-11} | 1.04 \times 10^{-8} |
|           | 700              | 9.74 \times 10^{-4}                     | 6.59 \times 10^{-4}                           | 1.03 \times 10^{-10} | 1.05 \times 10^{-8} |
| 8YSZ      | 300              | 1.96 \times 10^{-5}                     | 2.143 \times 10^{-6}                          | 2.39 \times 10^{-11} | 1.11 \times 10^{-10} |
|           | 400              | 2.92 \times 10^{-4}                     | 3.747 \times 10^{-5}                          | 3.77 \times 10^{-11} | 3.12 \times 10^{-9} |
|           | 500              | -                                         | 4.04 \times 10^{-4}                           | -       | 3.35 \times 10^{-8} |
|           | 600              | -                                         | 2.22 \times 10^{-3}                           | -       | 2.46 \times 10^{-8} |
|           | 700              | -                                         | 7.01 \times 10^{-3}                           | -       | 4.22 \times 10^{-8} |
| YSZc      | 300              | 3.07 \times 10^{-5}                     | 1.02 \times 10^{-5}                           | 2.857 \times 10^{-11} | 8.461\times 10^{-10} |
|           | 400              | 1.90\times 10^{-4}                      | 9.95\times 10^{-4}                            | 1.871 \times 10^{-11} | 1.650\times 10^{-9} |
|           | 500              | 1.79\times 10^{-3}                      | -                                             | 3.948 \times 10^{-10} | -       |

Table 3. The activation energy and pre-exponential factor of the prepared materials.

| Materials | Ea (eV) | pre exponential |
|-----------|---------|-----------------|
| ZrO\(_2\) | 0.732   | 0.202           |
| 8YSZ      | 1.002   | 3.082           |
| YSZc      | 1.094   | 10.348          |

4. Conclusion
Doping of yttrium ions into the prepared zirconia from zircon sand produced 8YSZ with the presence of small amount of silica, i.e., 2.47%. The ionic migration in zirconia structure contains grain and grain boundary, meanwhile after being doped with yttrium ions, the mechanism of migration at above 400 °C is
dominated by grain boundary conductivity. The ionic conductivity of 8YSZ is higher than $1 \times 10^{-4}$ S.cm$^{-1}$, which is categorized as a good electrolyte for the fuel cell.

Acknowledgement
Authors thank Ministry of Research and Technology for funding this research through INSINAs Research Project 2015.

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