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ELECTRICAL PROPERTIES OF VARIOUS COMPOSITION OF YTTRIUM DOPED-ZIRCONIA PREPARED FROM LOCAL ZIRCON SAND

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ABSTRACT

Doping yttrium ions, Y^{3+} into ZrO_2 produced Yttria-Stabilized Zirconia, YSZ. Various amount of yttrium ions could provide different ionic conductivity. This research investigated electrical conductivity of various YSZ composition, i.e., 4.5; 8.0 and 10% mol yttrium in ZrO_2. The ZrO_2 powder used was synthesized from zircon sand, a side product of tin mining plant, Bangka Island, Indonesia. Structural investigation on the prepared YSZ found that yttrium ion doping has changed the crystal structure of ZrO_2 from monoclinic to cubic, even though the monoclinic and tetragonal are also still exist. The Y^{3+} doping changed the cell parameter of ZrO_2 crystal. It indicates that the Y^{3+} entered into the ZrO_2 structure and produced vacancy sites. The highest ionic conductivity is provided by 8% mol Yttrium doping or 8YSZ, i.e., 2.74×10^{-4} $S.cm^{-1}$ at 700°C with an activation energy of 0.741 eV.

Keywords: Electrical conductivity; Various composition; YSZ; Zirconia; Zircon sand

1. INTRODUCTION

Indonesia has tin ore abundant spread over Pulau Karimun, Singkep, in some of the Sumatera lands, and also in Bangka Island, Riau islands, until to the West Kalimantan (Poernomo, 2012). Among of those, Bangka island has the largest Tin abundant with a side product is zircon sand ($ZrSiO_4$). Zircon, $ZrSiO_4$, is a stable molecule due to the strong bond between zirconia and silica. Some methods to extract zirconium from zircon are caustic fusion or with soda ash (El-Barawy et al., 2000), heat plasma dissociation (Ananthapadmanabhan et al., 1993), thermal decomposition (Pavlik et al., 2001), caustic fusion (Rahmawati et al., 2016) and mechanochemical processing (Puclin et al., 1995).

Zirconia, ZrO_2, is an important ceramics material due to its strengths and the high melting point temperature (2700°C). In addition, zirconia also has oxygen ions conductivity, low thermal conductivity, high flexibility, and high corrosion resistance (Rivai & Takahashi, 2010). Zirconia is used as a material for the oxygen sensor, fuel cell material, thermal barrier coating, and some high-temperature applications. Tetragonal zirconia has high mechanical strength; meanwhile, cubic zirconia has high ionic conductivity (Shackelford & Doremus, 2008). The addition of some metal oxides such as MnO, NiO, Cr_2O_3, Fe_2O_3, Y_2O_3, and Ce_2O_3 could stabilize tetragonal

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and cubic phase of zirconia at room temperature (Munggaran et al., 2014). Our previous research on preparing ZrO_2 from Indonesian zircon sand found a Zr content of 72.1% and the presence of some impurities such as sodium oxide, Na_2O at 14.71% and also silica, SiO_2 at 3.03%. The sodium oxide is known as the remains of sodium hydroxide reactant to mix with zircon, $ZrSiO_4$, sand. Meanwhile, the silica content refers to the silica network in zircon sand as the raw material (Rahmawati et al., 2016).

A high ionic conductivity of the material is required to develop a solid oxide fuel cell, SOFC. Cubic zirconia is known to has highest ionic conductivity. However, the structure is not stable at room temperature. Doping of yttrium ions into zirconia is known to stabilize the cubic structure at room temperature and increase the ionic conductivity due to the formation of oxygen vacancies when Zr^{4+} is replaced by Y^{3+} (Shakthinathan et al., 2012). Low yttrium concentration might produce tetragonal zirconia that has good mechanical strength. Meanwhile, a high concentration of yttrium dopant might produce cubic structure zirconia that has high ionic conductivity (Shackelford & Doremus, 2008). The ionic conductivity depends on the size and concentration of the dopant, in which yttria is the most common dopant for stabilizing the cubic phase of zirconia. When the Y_2O_3 content increases, the crystal structure of ZrO_2 transforms from monoclinic to tetragonal and further transforms to the cubic phase when the yttria addition up to 8 mol% (Sharma et al., 2016). When the ZrO_2 is prepared from $ZrSiO_4$ sand as a side product of tin mining plant, it is known that the addition of Y_2O_3 also transforms the structure to cubic, as confirmed by peaks at 2θ of 30.8°, 34.92°, 50.15°, and 59.52° which are in agreement with the YSZ standard diffraction ICSD #75316. However, the monoclinic ZrO_2 still exists as small peaks at 2θ of 27.91° and 31.09°, and tetragonal phase also present as small peaks at 2θ of 35.24° and 60.26° (Rahmawati et al., 2016).

The result is different when the commercial ZrO_2 is used, in which doping of > 7 mol$^{\%}$ produced the single cubic phase, while a 2–6 mol% Y_2O_3 content gives a partially stabilized (Sharma et al., 2016). Other researcher found 8–10 mol% Y_2O_3 that result in a fully cubic phase (Ochrombel et al., 2010). Meanwhile, for YSZ nanowire, the 4–10 mol% Y_2O_3 doping level produces a dominated cubic phase (Liu et al., 2017). Crystal structure may affect the ionic conductivity. Meanwhile, because of the different purity grade, the similar amount of yttrium doping to ZrO_2 that was prepared from Indonesian zircon sand and to the commercial ZrO_2 may produce a different crystal structure. Therefore, this research investigates their electrical properties in accordance with the Y_2O_3 dopant amount. For the commercial grade zirconia, it is found that the highest conductivity level of $(ZrO_2)_{1-x}(Y_2O_3)_x$ electrolyte is obtained when x is 0.08 (Kharton et al., 1999). This research is going to understand if the 71.53±0.76% purity of ZrO_2 and the presence of some impurities will affect the electrical conductivity as well.

2. EXPERIMENTAL METHODS

Yttrium stabilized-zirconia, YSZ, was prepared at the various composition of yttrium content, i.e., 4.5%, 8%, and 10% mol. The yttrium dioxide, Y_2O_3, (Aldrich) was used as yttrium ions precursor. Meanwhile, ZrO_2 was synthesized from Indonesian local zircon sand, procured as a side product of Tin Mining Plant in Bangka Island, Indonesia, and it was pre-concentrated in Laboratory of Metallurgy, Faculty of Mining and Oil Engineering, Institut Teknologi Bandung. XRF analysis on the zircon sand concentrate found that the concentrate consists of some elements, i.e., Zr, Si, Na, S, Al at 64.10%, 14.67%, 11.61%, 1.85%, and 1.33%, respectively, and some other small content elements at 6.44%.

Zirconia, ZrO_2 was synthesized by caustic fusion method (Soepriyanto et al., 2005; Rahmawati et al., 2012) in which the zircon sand concentrate, $ZrSiO_4$, was crushed with NaOH at a ratio of $ZrSiO_4$: NaOH 1:4. The mixture was then heated at 800°C to produce a greyish white powder.

The powder then was leached with distilled water at a volume ratio of 1:10 of powder to water, and followed by filtration. Next step was to leach residue of filtration with 3.5 M of HCl at a volume ratio of 1:10, means that 1 gram of residue was dissolved in 10 mL HCl, at 80^{o}C, and under stirred condition. The result was a cloudy yellow solution that produced a clear yellow solution after filtration. The yellow solution is $ZrOCl_2.6H_2O$ (ZOC). Zirconia, ZrO_2, was precipitated from ZOC by slowly added 3 M of NH_4OH. A white precipitate was produced. After decantation and heating at 800^{o}C for 5 hours, a white powder of ZrO_2 was founded. Our previous research on the caustic fusion of this Bangka Island zircon sand produced a zirconia powder at 71.53 ± 0.76% of purity (Rahmawati et al., 2014).

Yttrium ions doping was conducted with Y_2O_3 as yttrium source. A mixture of Y_2O_3 and ZrO_2 was crushed for 2 hours in a pestle at a stoichiometric ratio to produce a 4.5%, 8% and 10% mol of yttrium. Calcination was at 1000^{o}C for 2 hours, then followed by sintering of its green pellets at 1500^{o}C for 5 hours. X-ray diffraction analysis equipped with Le Bail refinement was used to identify the peaks in comparing with YSZ standard diffraction, and also to analyze its crystallinity, crystal structure, and its cell parameters. The prepared materials also were analyzed by SEM to understand their surface morphology. The MeasureIT software (free edition) was used to analyze the average particle size from SEM images. Meanwhile, the electrical conductivity was analyzed with LCR meter (GW Instek) to study their impedance plot and their electrical conductivity. The impedance was measured at 20–5 MHz at 300–700^{o}C. The impedance curve was fitted with Origin 6.0 program (free edition), and the conductivity value was calculated by Equation 1.

$$\kappa = \frac{1}{R}\frac{A}{l} \tag{1}$$

where κ is the specific conductivity (Ohm^{-1}.cm) (S.cm), R is the resistance that was determined from impedance measurement equipped with the fitting process (Ohm), A is the area of the active electrode (cm^2), and l is the thickness of material (cm).

3. RESULTS AND DISCUSSION

The material characterization has been conducted on the prepared YSZ at 4.5%, 8%, and 10% of mol yttrium ions. The analysis by X-ray diffraction equipped with le bail refinement and the results have been published in our previous paper (Rahmawati et al., 2016). The yttria-stabilized zirconia at 4.5%, 8%, and 10% produced from zircon sand were crystallized in the same structure, i.e., cubic, tetragonal, and monoclinic with the space group of *F M 3 M, P 42/ N M C z,* and *P1 21/C 1,* respectively. The specific peaks of ZrO_2 are identified at 2θ~30.30°; 34.70°; 35.24°; 50.34° and 60.26°. Meanwhile, a peak at 2θ~28.36° confirms the presence of monoclinic phase ZrO_2 based on ICSD#157403 (Rahmawati et al., 2016).

Impedance measurement at 20–5 MHz for 4.5 YSZ produce impedance curves as plotted in Figure 1. The Figure 1 shows that the impedance curve of 4.5 YSZ is in a semicircle at 400, 500, 600, and 700^{o}C. The impedance values decrease as the temperature increase. A similar trend also can be seen in Figure 2 for 8 YSZ, in which the impedance value decreases as the temperature increases. However, at 400^{o}C, the 8 YSZ shows a two semicircle curve of impedance (Figure 2). Those two semicircle indicates that the ionic conductivity of 8 YSZ consists of grain conduction and grain boundary conduction (Li et al., 2003). The impedance value of 8 YSZ is lower at various temperature, in which at 600^{o}C the impedance of 8 YSZ is around 600 Ohm, which is 5 times lower of 4.5 YSZ impedance value. Meanwhile, the 10 YSZ shows a similar trend of impedance curve with 8 YSZ, in which at 400^{o}C the impedance curve consists of two semicircles indicating grain and grain boundary conductivity. However, the impedance value of 10 YSZ at various temperature are higher than the impedance of 8 YSZ. As it can be seen in Figure 3 that the impedance of 10 YSZ at 600°C is around 3500 Ohm, meanwhile the impedance of 8 YSZ is around 600 Ohm.

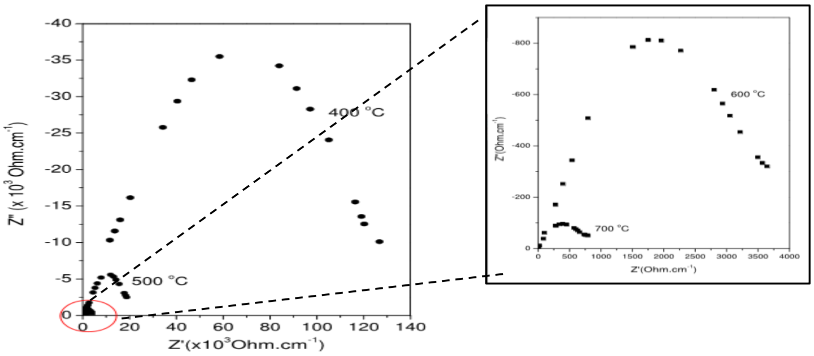

Figure 1 Nyquist plots of 4.5 YSZ at 400°C, 500°C, 600°C, and 700°C

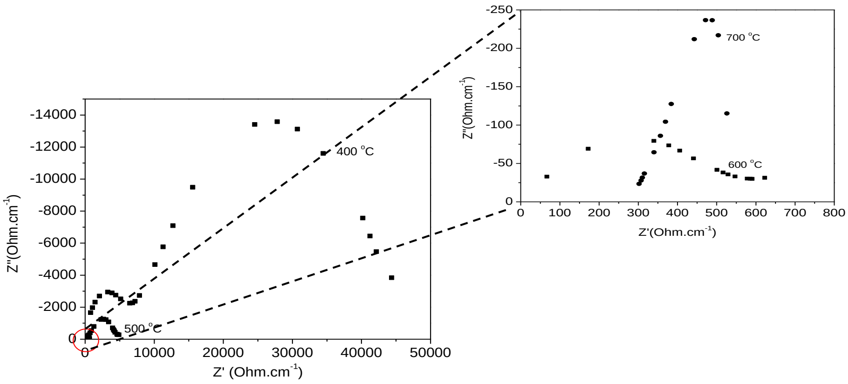

Figure 2 Nyquist plots of 8 YSZ at 400°C, 500°C, 600°C, and 700°C

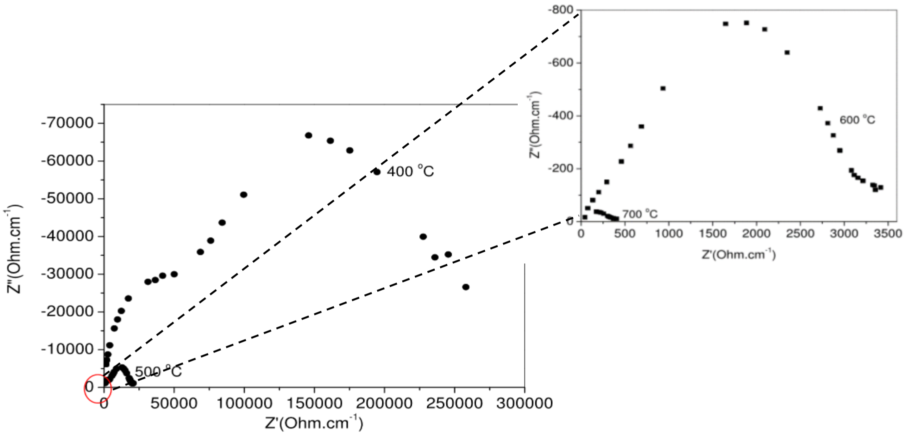

Figure 3 Nyquist plots of 10 YSZ at 400°C, 500°C, 600°C, and 700°C

Curve analysis continued by conductivity calculation found that 8 YSZ has the highest conductivity (Table 1). This result is in agreement with the result on commercial zirconia, in which the highest conductivity also found at 8 YSZ (Ramamoorthy et al., 1999). Based on refinement result on X-ray diffraction data, it is known that the cell volume of a cubic phase of 8

YSZ is highest than 4.5 YSZ and 10 YSZ. The cell volume of 8 YSZ is 137.551392 $Å^3$. Meanwhile, the cell volume of 4.5 YSZ and 10 YSZ are 135.408920 $Å^3$ and 136.834610 $Å^3$, respectively. The diffraction data was refined successfully with the standard input data of ICSD#75316, a cubic zirconia with a space group of *Fm3m*. A high cell volume may allow oxygen ions to migrate easier than in a small cell volume crystal structure. The ionic conductivity also in correlation with the porosity of the sintered material, in which high porosity of material can cause low ionic migration due to losing contact between grains. Therefore it will require a higher temperature to move the ions between grains (Munggaran et al., 2014).

Morphological analysis by scanning electron microscope on the various composition of YSZ found that the grain size of 8 YSZ is 2.021± 0.716 µm, which is larger than the grain size of 10 YSZ, i.e., 1.529 ± 0.498 µm with more pores existed inside, as it can be recognized in SEM image as the dark holes (Rahmawati et al., 2016). SEM images of the prepared materials and its magnification (30% magnification) are depicted in Figure 4.

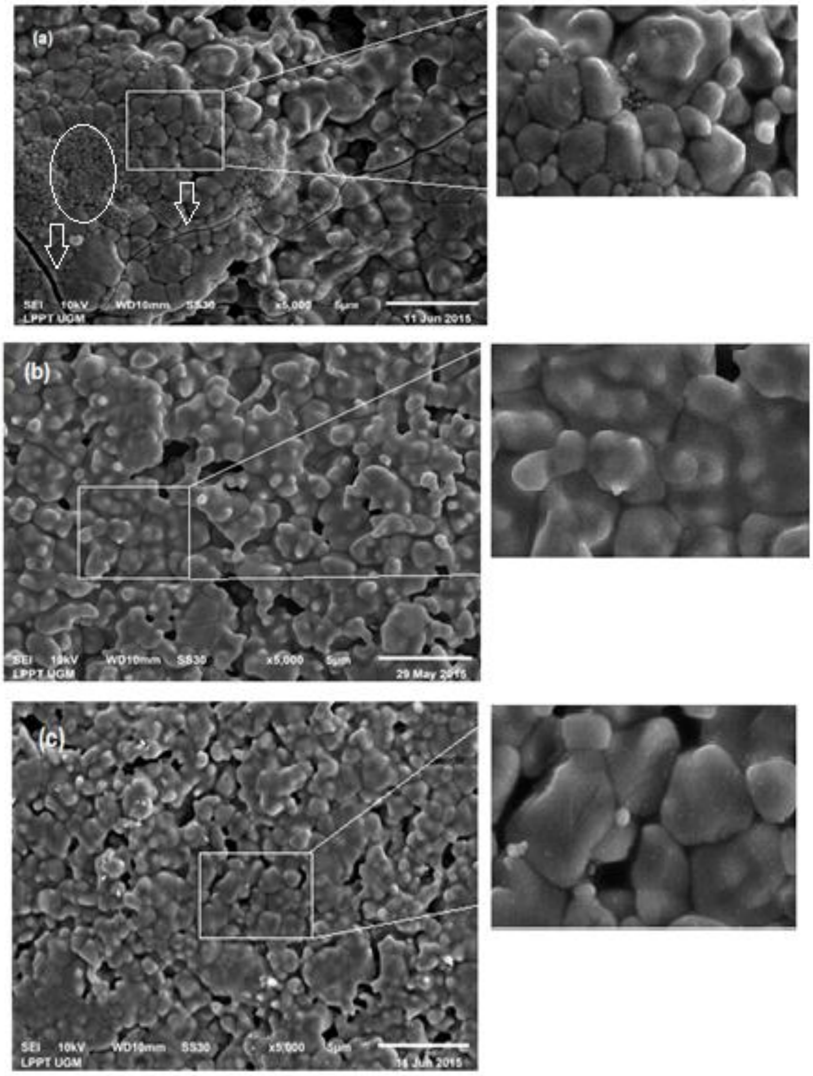

Figure 4 SEM images of 4.5 YSZ, the white circle is showing a blocking phase, and the white arrows are showing the crack lines (a), 8 YSZ (b), and 10 YSZ (c) and each 30% magnification

The morphology of 4.5 YSZ shows a heterogeneous surface with the presence of blocking phase as it is described in Figure 4. The blocking phase was also found when zirconia from zircon sand was combined with lanthanum gallate material, i.e., $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{2-\delta}$ (Rahmawati et al., 2012). The elemental analysis on the blocking point of 4.5 YSZ found that the blocking phase is a silica-rich phase, with 3.03% of silica content and 14.71% of sodium oxide. The sodium content might come from NaOH as destructive chemical. However, those sodium content would release when the material was heated at 1500^{o}C for 5 hours during the sintering process. Liu et al. (2014) also found such impurities when producing zirconia from Brazillian zircon. The sodium silicate is formed during mixing process between zircon sand and NaOH, and it hydrolized into H_2SiO_3 during water leaching. The Na_2ZrSiO_5 is also might produce during the caustic fusion process, which then reacts with HCl during acid leaching to produce $ZrO(OH)_2$-SiO_2 and $NaCl.ZrO(OH)_2$. As the final result, the composition of powder produced from Brazillian zircon sand are ZrO_2, SiO_2, and Na_2O were 57.169%, 6.77% and 7.049% , respectively (Liu et al., 2014). The nonhomogeneous content also caused a crack line in the 4.5 YSZ pellet after sintering at 1500^{o}C for 5 hours. The crack line (Figure 4) causes a loose contact between grains allowing high ionic migration resistant and low ionic conductivity.

Table 1 Conductivity of the various YSZ composition at various temperature

Materials	Temperature (^{o}C)	Conductivity (S.cm^{-1})
4.5 YSZ	300	1.95×10^{-7}
	400	2.96×10^{-6}
	500	1.03×10^{-5}
	600	8.84×10^{-5}
	700	2.24×10^{-4}
8 YSZ	300	3.14×10^{-7}
	400	5.76×10^{-6}
	500	5.86×10^{-6}
	600	4.55×10^{-5}
	700	2.74×10^{-4}
10 YSZ	300	2.21×10^{-8}
	400	2.40×10^{-6}
	500	1.70×10^{-5}
	600	1.67×10^{-5}
	700	1.98×10^{-4}

The Arrhenius plot between the specific conductivity and reverse of temperature can be used to determine the activation energy, Ea, of ionic migration (Figure 5). The Arrhenius equation is described in Equation 2 (Zhang et al., 2007).

$$\sigma T = \sigma_o \exp\left(\frac{-Ea}{kT}\right) \tag{2}$$

where Ea is the activation energy for ionic conduction, σ is the ionic conductivity, σ_o is the pre-exponential factor, k is the Boltzmann constant, and T is the temperature. The slope of linear regression line representing ($-\frac{Ea}{kT}$), by input the temperature and the Boltzmann constant, the value of E_a can be determined. The result is listed in Table 2, in which the activation energy of 8 YSZ is the lowest, i.e., 0.741 eV. It indicates that the ionic migration in 8 YSZ could proceed easier than in 4.5 YSZ and in 10 YSZ. The physical properties regarding the inter-grains connection and the cell volume might become the factors related to that ionic migration.

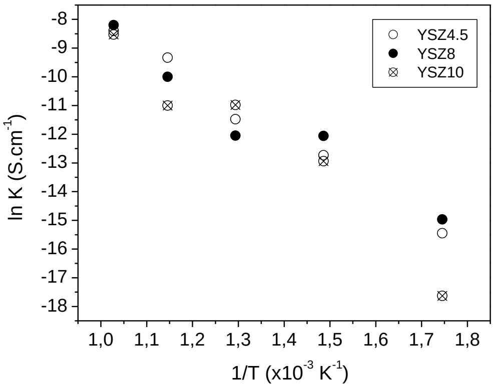

Figure 5 The Arrhenius plot of 4.5 YSZ, 8 YSZ, and 10 YSZ

Table 2 Activation energy, *Ea*, pre-exponential factor and regression coefficient of 4.5 YSZ, 8 YSZ and 10 YSZ

Materials	Activation Energy, Ea (eV)	Coef.of regression, R^2
4.5YSZ	0.846	0.991
8YSZ	0.741	0.932
10YSZ	0.999	0.935

4. CONCLUSION

The yttria-stabilized zirconia at 4.5 %, 8 %, and 10 % produced from zircon sand were crystallized in the same structure, i.e., cubic, tetragonal, and monoclinic with the space group of *F M 3 M*, *P 42/ N M C z,* and *P1 21/C 1*, respectively. The yttrium ion doping changed the cell parameter of ZrO_2. The highest ionic conductivity is provided by 8 mol% Yttrium doping or 8YSZ, i.e., 2.74 x 10^{-4} S.cm^{-1} at 700 ^{o}C with an activation energy of 0.741 eV. The activation energy is the lowest among the produced YSZ. It indicates that the ionic migration in 8YSZ could proceed easier than in 4.5YSZ and in 10YSZ.

5. ACKNOWLEDGMENT

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