Preparation and conductivity measurement of 7-8 mol % YSZ and 12 mol % CSZ for electrolyte SOFC

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Abstract. The study of 7YSZ (93% ZrO$_2$-7%Y$_2$O$_3$), 8YSZ (92% ZrO$_2$-8%Y$_2$O$_3$), and CSZ (88% ZrO$_2$-12% CaO) as SOFC electrolytes have been carried out successfully. 7YSZ and 8YSZ powders were prepared by solid state reaction method of mixed Y$_2$O$_3$ and ZrO$_2$ followed by calcination at 1350 °C for 1 hour, while CSZ was commercial products. Pellets of 7YSZ, 8YSZ, and CSZ were prepared by 1.2 gr, pressed at 40 MPa and sintered at 1550 °C for 4 hours. Rietveld refinement revealed that 7YSZ comprised 47.27% monoclinic, 52.65% cubic, and 0.008% Y$_2$O$_3$ cubic, while 8YSZ comprised 48.45% monoclinic, 49.32% cubic, 2.23% Y$_2$O$_3$ cubic and CSZ has 88% ZrO$_2$ and 12% CaO. Ionic conductivity and activation energy were obtained from Cole-Cole Plot of impedance, the activation energy of 7YSZ=1.03eV, 8YSZ=0.96eV and CSZ=0.78eV.

1. Introduction

Fuel cells are energy conversion devices that produce electricity through an electrochemical process (1)(2). Fuel cells behave the characteristics of environmentally friendly (low pollutant emissions), has resistant to corrosion, has high operating temperature (600°C-1000°C), fast reaction kinetics, has the highest conversion among others (45-65 %) (2-7) and relatively high conversion efficiency (45 % to 60 %) (2). There are several types of fuel cell, theses include polymer electrolyte membrane (PEM) cell, alkaline electrolyte cell (AFC), phosphoric acid cell (PAFC), molten carbonate cell (MCFC) and solid oxide ceramic cell (SOFC) (1).

The SOFC is composed of anode, cathode and electrolyte (2)(3)(8). Electrolytes needs high ionic conductivity, has high stability (chemical, phase morphology, dimension) to environmental change, fully dense and thermal expansion almost the same as the other ceramic fuel cells (2)(8)(9). YSZ/CSZ is often used as an electrolyte because it fulfill the requirements above, has high ionic conductivity, chemically stable and mechanically stable (10,11). The research on YSZ and CSZ as electrolyte has been carried out by several researchers, among other are Joong Sun Park, et al (2012), Gong, et.al (2000) and Badwal, et.al (1992). Joong Sun Park, et al (2012) has reported that the activation energy of YSZ was 1.04 eV while Gong, et.al (2000) has reported the activation energy of 12 CSZ with sintering temperature 1650°C for 4 h was 1.1 eV while Badwal,et.al (1992) has reported the activation energy of...
8 YSZ was 1.1 eV at 400-500°C (12,13). In this study will be assessed CSZ and YSZ for SOFC electrolyte, preparation of powder, structure characterization and conductivity of sintered pellet of YSZ/CSZ.

2. Experimental

YSZ was synthesized by solid state reaction method. Raw material were ZrO\(_2\) (Zirconium oxide Purum, D30926 Sigma - Aldrich GmbH) and Y\(_2\)O\(_3\) (Yttrium Oxide, 99.999 % RED Puratrem 93-3925). The composition were 93 mol % ZrO\(_2\) and 7 mol % Y\(_2\)O\(_3\) (7YSZ) and 92 mol % ZrO\(_2\) and 8 mol % Y\(_2\)O\(_3\) (8YSZ) Zirconia and yttria were milled using a planetary mill Pulverisette 5 with a milling speed of 150 rpm for 4 hours to 8 YSZ and 7 YSZ were milled with a milling speed of 250 rpm for 4 hours. The result of mixing powder were calcined at 1350°C for 1 hours. Meanwhile, the CSZ were commercial product by Henan Winna Industrial-China. 7YSZ, 8 YSZ and CSZ powder, 1.2 gr each, were pressed using uniaxial die of 40 Mpa then sintered at 1550°C for 4 hours. The Density of sintered pellet were measured by Archimedes method. All sintered samples were examined by X-ray diffraction of Cu K\(\alpha\) radiation from 2\(\theta\)=20° to 70°. Phase identification was carried out using software Match!2, while quantitative analysis using software rietica by Rietveld method. Electrical characterization were measured by Solartron Impedance Analyzer.

3. Results and discussions

3.1 YSZ Powder

XRD pattern of calcination of mixed Y\(_2\)O\(_3\) and ZrO\(_2\) are shown in Figure 1. Based on the results of qualitative analysis using software Match!2, there were 3 phase detected: Zirconia cubic phase, Zirconia monoclinic phase and yttria oxide phase. This means that a long which this treatment the substitution of Y\(^{3+}\) to Zr\(^{4+}\) sites was not finished. Furthermore quantitative analysis by Rietveld method give results that percentage of phases is shown in Table 1. The cubic phase detected by XRD was a result of defect reaction of Y\(^{3+}\) ions incorporate in Zr sites.

\[
Y_2O_3 + ZrO_2 \rightarrow 2Y'_Zr + 3O^X_O + 3V^{**}_O
\]

\( (1) \)

![Figure 1. XRD pattern 7YSZ and 8YSZ after calcination at 1350°C for 1 hour.](image)

| Sample | Cubic phase (%) | Monoclinic Phase (%) | Yttria Phase (%) |
|--------|----------------|----------------------|-----------------|
| 7 YSZ  | 52.65          | 47.27                | 0.008           |
| 8 YSZ  | 49.32          | 48.45                | 2.23            |
Table 1 show that the cubic phase of 8 YSZ has lower percentage (49.32%) than 7 YSZ (52.65%). This fact should be caused by different milling process in which 7 YSZ carried out by 250 rpm compared to 150 rpm for 8 YSZ, both 4 hours milling time. Therefore, it can be concluded that our material is partially stabilized zirconia.

3.2 CSZ Powder
CSZ powder was a commercial product. Therefore, it needs to examine the percentage of calcia in the powder. For that purpose the powder than examined by EDX analysis, Figure 2. The EDX results gives ~12 atomic % of Ca (12 CSZ). Furthermore, Rietveld analysis of XRD data gives 74.64% cubic phase and 25.36% monoclinic phase. The cubic phase detected by XRD was a result of defect reaction.

$$\text{CaO} \quad \text{ZrO}_2 \quad \rightarrow \quad \text{Ca}_2\text{Zr}^\sigma \text{O}_6 + \text{V}_O^{**}$$

(2)

Figure 2. (a). EDX pattern of CSZ (b). XRD pattern of CSZ.

3.3 Sintering
The relative density of all the samples were measured by Archimede’s method. The result are shown in Table 2. It seen that the relative density vary for each samples. The possible explanation of the relative density variation was the percentage of cubic phase for each composition, as depicted in table 3. The higher cubic percentage, the sample become more dense.

| Sample | Relative Density |
|--------|-----------------|
| 7 YSZ  | 93.80%          |
| 8 YSZ  | 96.70%          |
| 12 CSZ | 88.20%          |

Table 2. Relative density all samples

Figure 3 are shown XRD pattern of sintered pelet samples. Based on the qualitative analysis using software Match!2, 8 YSZ present single phase (cubic phase) while the 7 YSZ and 12CSZ samples are bi phase (cubic phase and monoclinic phase). Further, quantitative analysis using Rietveld method, the percentage of each phases a shown in Table 3.
It can be seen that the percentage of cubic phase for sintered pellet samples (1550°C, 4 h) are increased compared to the percentage of cubic phase of calcined powder (1350°C, 1 h). At 1550°C, the energy for diffusion at Y$^{3+}$ to replace Zr$^{4+}$ is sufficiently. As for 8YSZ, Y$^{3+}$ sufficiently stabilized the cubic phase. Besides, 8 YSZ lattice parameters for the cubic phase has smaller than 7YSZ, this was due to the amount of the Y$^{3+}$ was substituted Zr$^{4+}$ on 8YSZ more than the 7 YSZ. Similarly for the 12 CSZ, the lattice parameter is the smallest ones, it is because the radius of Ca$^{2+}$ is smaller than radius Zr$^{4+}$ and Y$^{3+}$.

3.4 Electrical Properties
The cole-cole plot of impedance for sample are shown in figure 4. For YSZ, the curves show 3 semicircle which are grain impedance, grain boundary impedance and electrode impedance while for 12 CSZ show grain impedance and unclear the rets. Then, evaluation the grain impedance for each powder, Figure 5 show Arrhenius plot of ln conductivity versus $\frac{1}{T}$. Furthermore, this the deduced activation energy for grain conductivity in table 4.

| Sample | Cubic Phase (%) | Monoclinic Phase (%) | Cubic Phase | Monoclinic Phase |
|--------|-----------------|----------------------|-------------|------------------|
| 7 YSZ  | 86.24           | 13.76                | 5.1434 (8)  | 5.167 (3)        |
| 8 YSZ  | 100             | 0                    | 5.1385 (1)  | -                |
| 12 CSZ | 84.64           | 15.46                | 5.1210 (1)  | 5.155 (2)        |

Figure 3. Diffraction pattern a). 8 YSZ b). 7 YSZ, and c). 12 CSZ at sintering 1550°C for 4 hours.

Figure 4. Cole cole plot (a). 7 YSZ and 8 YSZ at 450°C (b). 12 CSZ at 450°C.
Table 4. Activation energy from grain

| Sample  | Activation Energy (Grain) (eV) |
|---------|-------------------------------|
| 7 YSZ   | 1.03                          |
| 8 YSZ   | 0.96                          |
| 12 CSZ  | 0.78                          |

The Activation energy were the minimum energy that oxygen vacancy defect to migrate. Figure 5 show that the linierity of fitting curves for the activation energy were depicted in table 4. The lower activation energy for 8 YSZ (0.96 eV) compared to 7 YSZ (1.03 eV) was clearly due to low concentration of $V_{\text{O}}^{\bullet\bullet}$ for 7 YSZ. The similar reason for 12 CSZ which have activation energy 0.78 eV. This result were similar to the reported by Badwal, et.al (2000). Eventhough 12 CSZ possed the lowest activation energy but the 12 CSZ more resistive than YSZ, while 8 YSZ exhibiting the most conductive when T=800° C.

4. Conclusion
Based on the result described precedenly, 8 YSZ has a single cubic phase, so that a fully stabilized cubic zirconia and has activation energy 0.96 eV. Therefore, 8 YSZ is good for electrolyte SOFC, while for 7 YSZ and 12 CSZ has 2 phases namely cubic and monoclinic , therefore these sample is still partially stabilized zirconia with energy activation of 7 YSZ and 12 CSZ are 1.03 eV and 0.78 eV respectively.

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