



Doping Calcia and Yttria into Zirconia Obtained from by Product of Tin Concentrator to Improve its Ionic Conductivity

Fitria Rahmawati¹, Bambang Prijamboedi¹, Syoni Soepriyanto² & Ismunandar¹

¹Inorganic and Physical Chemistry Research Group, Faculty of Mathematics and Natural Sciences, Institut Teknologi Bandung, Jl. Ganesha 10 Bandung 40132

²Department of Metallurgical Engineering, Faculty of Mining and Petroleum Engineering, Institut Teknologi Bandung, Jl. Ganesha 10 Bandung 40132

Email: ismu@chem.itb.ac.id

Abstract. Zirconia has been prepared from Zircon concentrate by caustic fusion methods. Zircon is a by product from tin ore concentration plant at Bangka island of Indonesia. Yttria Stabilized-Zirconia (YSZ) was prepared by introducing the 8 % mol yttrium oxide into zirconia and sintered at 1500 °C for 5 hours. In order to obtain constant oxygen vacancy of 8 % mol in Zirconia, an appropriate amount of Yttria and Calcia were introduced into Zirconia and the mixtures were heated at 1350 °C for 5 hours. Elemental composition was determined by SEM/EDX and XRF and lattice parameters were determined using X-ray diffraction method. Ionic conductivity was measured by complex impedance spectroscopy. The results show that doping of Yttria into Zirconia (YSZ) and Calcia-Yttria into Zirconia (CYZ) allows phase transformation of Zirconia from tetragonal with space group P42/nmc into cubic Fm3m and enhance the ionic conductivity. However, the prepared materials are porous and have not met the requirement for the electrolyte material yet.

Keywords: *electrolyte material; CYZ; SOFC; YSZ; zircon.*

1 Introduction

Yttria Stabilized- Zirconia (YSZ) is widely used as the electrolyte for solid oxide fuel cell (SOFCs) since it exhibits sufficient ionic conductivity at operating temperature as high as 1000 °C [1]. However, a considerable interest in the mixed dopant effect on the ionic conductivity in several ternary systems containing ZrO₂ and Y₂O₃ [2-4] has arisen. Some authors [5-7] found that partial replacement of Y₂O₃ by CaO in the system of ZrO₂-Y₂O₃ may enhance the ionic conductivity at higher temperature (> 1127 °C). Even at the operating temperature around 1000 °C, the mixed CaO/Y₂O₃-stabilized ZrO₂ (CYZ) also exhibits ionic conductivity comparable to that of YSZ. Thus the ternary system ZrO₂-Y₂O₃-CaO might be more attractive than other ternary systems, due to the lower cost of CaO compared to other trivalent oxides such as Sc₂O₃ and Yb₂O₃. Gong *et al.* [8] found that the migration energy, E_m , and dissociation energy, E_a ,

for CYZ are higher than those for YSZ but lower than those for calcia stabilized zirconia (CSZ). At temperature over than 700 °C, the conductivity of CYZ increases more rapidly than that of YSZ. It has been noted by Gong *et al.* [8] that the pre-exponential factor of CYZ, $\ln \sigma_0$, is 19.65 S cm⁻¹ at 600-800 K, meanwhile the pre-exponential factor of YSZ is 16.84 S cm⁻¹ at the same temperature. The high pre-exponential factor of CYZ mainly due to its higher oxygen vacancies concentration compared to YSZ.

Bucko, *et al.* [9] synthesized CYZ using hydrothermal method from co-precipitated zirconia hydrogels and found that samples with 8 % mol oxygen vacancies, obtained from substitution of Calcium and Yttrium with ratio below 50:50, were composed of the cubic phase only. This cubic phase can be obtained with heat treatment at 1300 °C. This is exceptional, since based on binary phase diagram of Y₂O₃-ZrO₂, the fully cubic phase of Y₈SZ (8 % mol of Y₂O₃ doping into ZrO₂) could only be achieved at heating temperature more than 1500 °C [10]. It has been found also by Bucko, *et al.* [9] that the substitution of Calcia (CaO) for Yttria (Y₂O₃) as well as Yttria for Calcia in the Zirconia solid solutions results in an enhancement of ionic conductivity. In 8 % mol oxygen vacancy of CYZ where the ratio of CaO:Y₂O₃ is 10:90 (8C10Y90), introduction of Calcia produced the maximum enhancement of bulk and grain boundary conductivity.

In this paper, two types of doped-Zirconia, Y₂O₃-ZrO₂ (YSZ) and CaO-Y₂O₃-ZrO₂ (CYZ), were prepared using solid state reaction method. The Zirconia was prepared by caustic fusion of ZrSiO₄, a side product of Tin Mining in Bangka Island, Indonesia. This study also aims to increase value of this ZrSiO₄.

2 Experimental

Zirconia (ZrO₂) was prepared by caustic fusion of Zircon (ZrSiO₄), i.e by reacting Zircon with NaOH, followed by acid leaching and precipitation of ZrO₂ by addition of ammonia solution, as has been described by Soepriyanto, *et al.* [11]. Doping of Y₂O₃ and (CaO-Y₂O₃) to create 8 % mol vacancy were carried out by solid state reaction, i.e. by introducing certain amounts of Yttria and Calcia-Yttria into the Zirconia powder. The mixed powder was ground and fired at 1350 °C for 5 hours for CYZ and 1500 °C for 5 hours for YSZ. The obtained powder was then pressed by Cold Isostatic Pressure at 200 MPa to form discs. The discs were then sintered at 1500 °C for 3 hours.

The synthesized materials were characterized by powder X-ray diffraction. Refinement on XRD data was carried out by using Le Bail method implemented in RIETICA program in order to analyze their structures. Morphology and

elemental composition analyses were performed by Scanning Electron Microscope (SEM) equipped with EDX. Elemental analysis was also carried out using X-ray fluorescent (XRF). Ionic conductivities of the samples were measured by electrochemical impedance measurement using Agilent E4980A Precision LCR meter in the frequency range of 20 Hz - 2 MHz and at temperature range of 200 °C - 500 °C. The data from impedance measurement were fitted using ZView program to define of grain resistance (R_g) and grain boundary resistance (R_{gb}).

3 Results and discussion

The XRD patterns of ZrO_2 , YSZ and CYZ are presented in Figure 1. XRD pattern of ZrO_2 showed broad peaks, indicating the small size of ZrO_2 particles. There is no secondary phase observed in the XRD pattern of ZrO_2 . Doping of Yttria and Calcia-Yttria into ZrO_2 allow to enhance the crystallinity of material, as evident from the sharp peaks observed in XRD patterns of YSZ and CYZ. Secondary phase were found in YSZ sample and it were identified as different structure of crystal, the peaks at 28.312° and 31.624° . Meanwhile, in sample of CYZ (with 10:90 weight ratio of Calcia and Yttria), there is no indication of the presence of second phase, eventhough the sintering temperature of this CYZ is only at 1350 °C, which is lower than sintering temperature of YSZ, 1500 °C.

Le Bail profile refinement of XRD data of ZrO_2 produced by caustic fusion of $ZrSiO_4$, proceed successfully with tetragonal system and space group of $P42/nmc$. The obtained cell parameters are listed in Table 1. The small value (below 10%) of R_p and R_{wp} , 2.645% and 3.011%, respectively, indicate that the good fitting was achieved. Elemental analysis using XRF showed that the ZrO_2 contained 1.77% Silica and 5.76% Titania.

XRD analysis of YSZ and CYZ showed that there was phase transformation of ZrO_2 from tetragonal to cubic system with introduction of Yttria and Calcia-Yttria into Zirconia. Le Bail refinement of XRD data of YSZ and CYZ could be carried out successfully with cubic structure and $Fm3m$ space group. Cells parameters of ZrO_2 , YSZ and CYZ and other parameter from the refinement results are listed in Table 1. Again, good fitting were achieved as evident from the small value of R_p and R_{wp} for both materials. As expected, the R_p and R_{wp} values of YSZ are higher than those of CYZ (the values are listed in Table 1), due to the presence of monoclinic structure in YSZ.

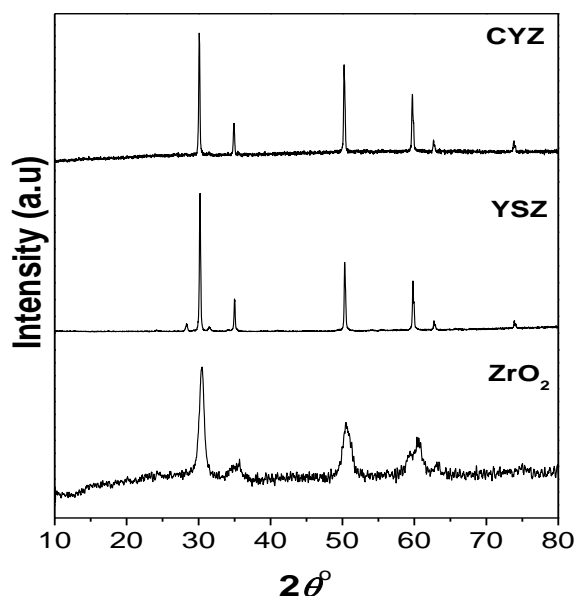


Figure 1 XRD patterns of ZrO_2 prepared from caustic fusion of ZrSiO_4 , YSZ (8 % mol of Yttria) and CYZ (8 % mol of vacancy).

Table 1 Cell parameters of ZrO_2 , YSZ and CYZ as determined using Le Bail method.

Parameters	ZrO_2	$\text{Y}_{0.08}\text{Zr}_{0.92}\text{O}_{2-\delta}$ (YSZ)	$\text{Ca}_{0.008}\text{Y}_{0.072}\text{Zr}_{0.862}\text{O}_{1.84}$ (CYZ)
a (Å)	3.60(1)	5.134(2)	5.150(3)
b (Å)	3.60(1)	5.134(2)	5.150(3)
c (Å)	5.22(2)	5.134(2)	5.150(3)
R_p (%)	2.645	9.697	4.828
R_{wp} (%)	3.011	7.611	6.210
χ^2	0.063	0.374	0.483

SEM photographs of YSZ and CYZ are given in Figure 2. These images indicate that the materials are not homogenous and still porous. There were two different morphologies appeared in SEM images, large grain and small ones. EDX analysis on the small grain showed that this region contains Silica as high as 2.97% of its total mass. This is 1.2% higher than the value obtained from XRF measurement. Presumably Silica was segregated in this part, i.e. in the area between the grain boundary of YSZ or CYZ.

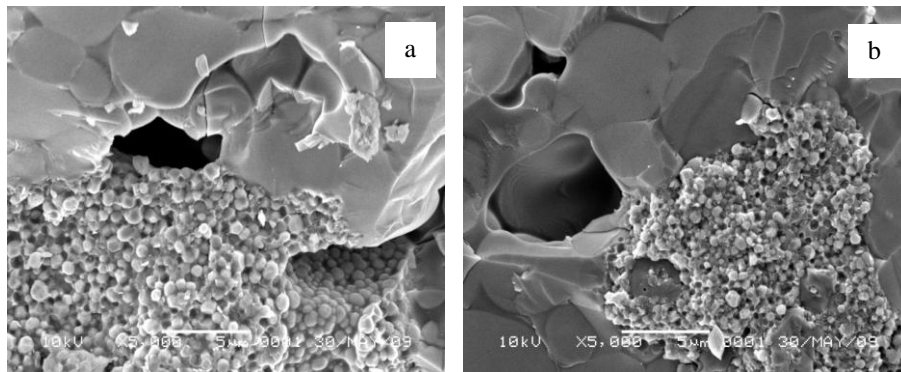


Figure 2 SEM photographs of (a) YSZ and (b) CYZ.

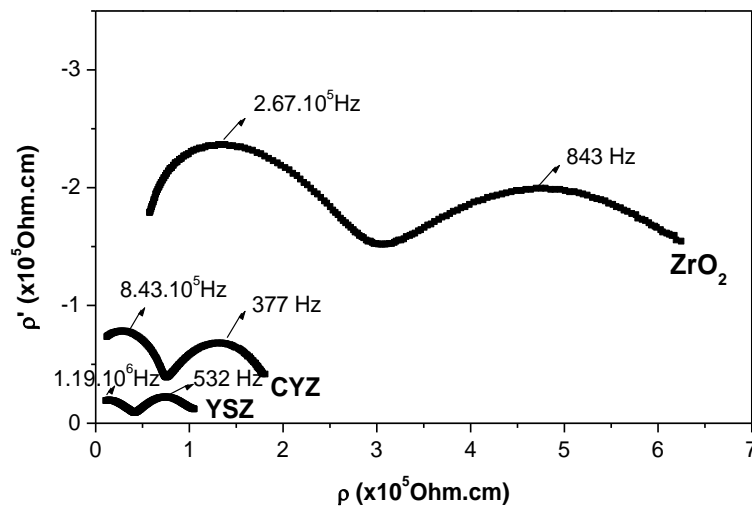


Figure 3 Impedance spectra of YSZ, CYZ and ZrO_2 at $350^\circ C$, frequency is expressed in Hertz (Hz).

The raw impedance data of ZrO_2 , YSZ and CYZ are plotted in Figure 3. These impedance data were taken at $350^\circ C$ and in the frequency range of 20 Hz-2 MHz. The two well-defined arcs have been observed. These arcs have capacitance values around ~ 0.1 pF and 1.4 nF, which are related to the grain and grain boundary impedance, respectively [12]. We could see in Figure 3 that

doping Yttria and Calcia-Yttria into Zirconia could reduce the impedance value significantly. The impedance data could be well fitted with a series circuit model of resistor-CPE (Constant Phase Element) and resistor-capacitor. CPE itself is non ideal behavior of the double layer capacitor on real cells. This model component represents several factors such as the porous-electrode effect associated with a distributed resistance/capacitance networks in the equivalent circuits and associated with electrode interface inhomogeneity [13].

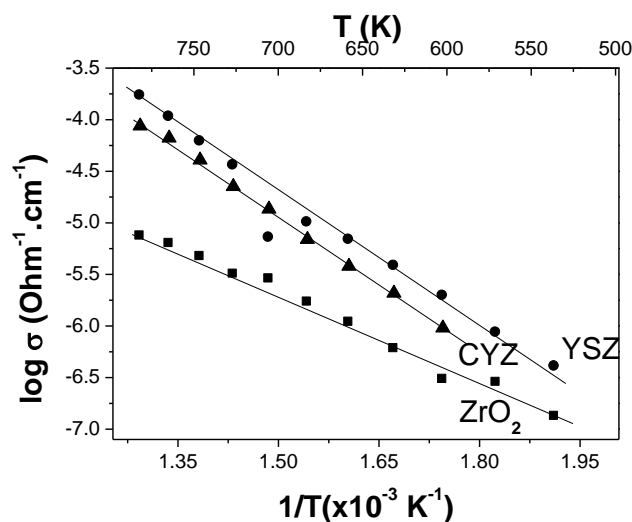


Figure 4 Plot of total conductivity of prepared materials of ZrO₂, YSZ and CYZ.

From total resistivity, the sum of grain and grain boundary resistivity, the ionic conductivity values were calculated. Arrhenius plot of the ionic conductivity of the prepared materials were depicted in Figure 4. Arrhenius plot of the ionic conductivity of ZrO₂ and YSZ are almost linear. However, there is an anomaly in CYZ, i.e. the conductivity has outlier value around 700 K, which always present in subsequent measurement. It is found that ZrO₂ has the smallest activation energy, $E_a = 0.25$ eV. Meanwhile, the E_a values of YSZ and CYZ are 0.36 eV and 0.38 eV, respectively. The ionic conductivity of YSZ and CYZ are within in the range of electrolyte material, i.e. over 10^{-4} S.cm⁻¹ [14]. The enhancement of conductivity of doped-Zirconia could be explained by the phase transformation from tetragonal into cubic. It is well known that fully stabilized cubic zirconia has high ionic conductivity and has been actively investigated as an oxide ion conductor in solid oxide fuel cell [15,16]. The conductivity values of CYZ are lower than that of YSZ in the measured temperature range of

200°C-500°C. The values of total conductivities of materials are plotted in Figure 4. Some authors found [5-7] that partial replacement of Y_2O_3 by CaO in the system ZrO_2 - Y_2O_3 may enhance the ionic conductivity at temperature higher than 1400 K.

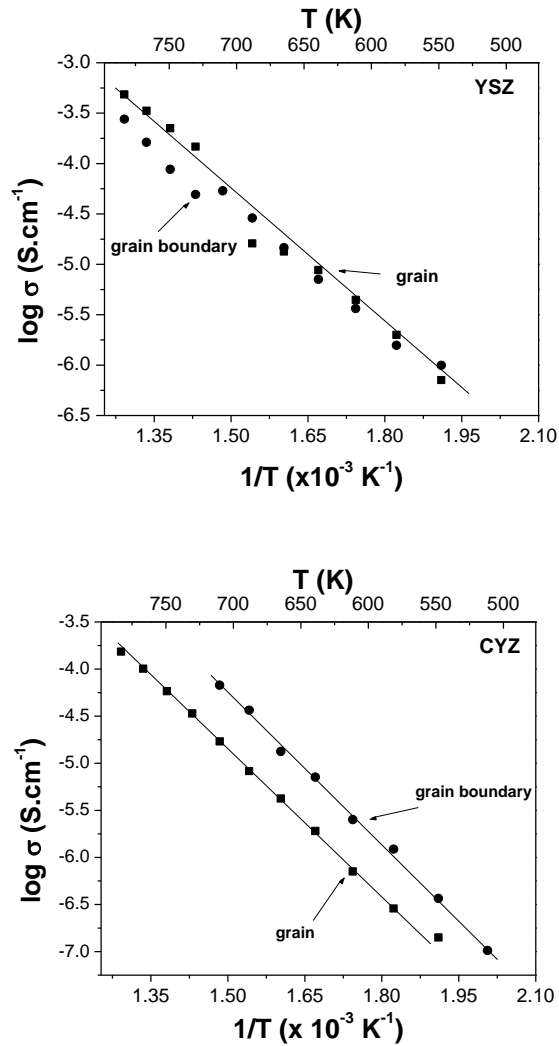


Figure 5 Arrhenius plots of grain and grain boundary conductivity of YSZ and CYZ samples.

In order to investigate the contribution of grain and grain boundary conductivity in the YSZ and CYZ, we plot the conductivities from those samples in separate figures, as shown in Figure 5. For the YSZ sample, we found that grain and grain boundary conductivity have similar values at temperature of 200 °C – 425 °C. At high temperature region, over 425 °C, it is found that grain boundary conductivity is lower than bulk or grain conductivity. Some authors [7,17] found that the grain boundary effect in YSZ based compound has been largely attributed to the existence of second phase, consisting mainly of oxides of Si, Al, Mg and Ca impurities in the grain boundary. However, the influence of grain boundary on the conductivity is small at high temperature [18]. Different behavior is observed in CYZ sample where the grain boundary conductivity is found to be larger than grain conductivity. We could add here, that the slope of grain boundary conductivity is larger than the slope of grain conductivity. Therefore there is a possibility to obtain higher conductivity of CYZ at high temperature by increasing the grain boundary conductivity, as stated by some authors [5-7].

The electrolyte material in SOFC should be dense enough so that the fuel and oxidant could not pass through the electrolyte. Water diffusion test on prepared materials and microstructure analysis by means of SEM analysis on low magnification (Figure 6) showed that the prepared materials are still porous and has not met the requirement for electrolyte material yet. Presumably Silica enrichment as stated above hinders the growth and densification of Zirconia. Better preparation method that could produce Silica free Zirconia from $ZrSiO_4$ is needed.

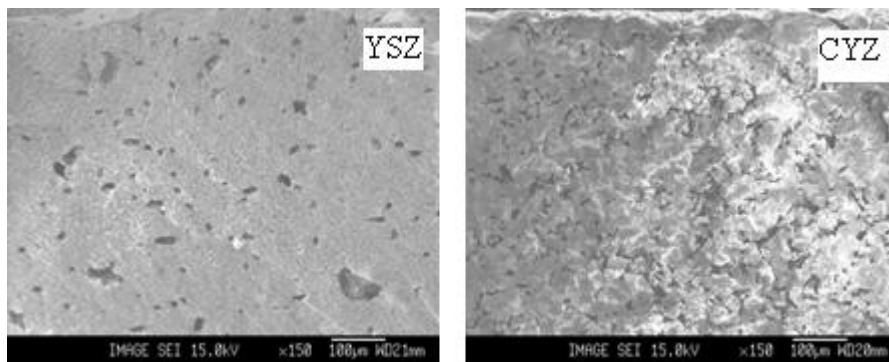


Figure 6 Microstructure images of SEM analysis of YSZ and CYZ with magnification 150x.

4 Conclusions

YSZ and CYZ prepared from $ZrSiO_4$ concentrate could have high ionic conductivity (above $10^{-4} \text{ S.cm}^{-1}$) at low temperature, 500 °C and has potential application in SOFC. Silica enrichment in the grain boundary decrease YSZ and CYZ conductivity. These impurities also result in porous structure of sintered prepared materials. At temperature range of 200 °C – 500 °C, the ionic conductivity of CYZ is found to be lower than YSZ due to the grain boundary effects. However, the grain boundary effects of YSZ are suppressed above 400 °C, implying that CYZ could have ionic conductivity comparable to or higher than YSZ at higher temperature.

Acknowledgements

This work was supported by Incentif Program by Ministry of Research and Technology, Indonesia, contract number 53/RT/Incentif/PPK/II/08 (February 15th, 2008) and 050/RT/D.PSIPTN/Incentif/PPK/I/2009 (January 20th, 2009). It was supported also by Riset KK ITB contract number 1501/K01.08/SPK/2009 January 30, 2009. Authors also gratefully acknowledge the help of Prof. G.M. Choi from Fuel Cell Centre, Department of Material Science and Engineering, Pohang University of Science and Technology, Pohang, South Korea.

References

- [1] Xu, D., Liu, X., Wang, D., Yi, G., Gao, Y., & Zhang, D., *Fabrication and Characterization of SDC-LSGM Composite Electrolytes Material in IT-SOFC.*, J. of Alloys and Compounds, **429**, pp. 292-295, 2007.
- [2] Corman, G.S., & Stubican, V.S., *Phase Equilibria and Ionic Conductivity in the System ZrO_2 - Yb_2O_3 - Y_2O_3* , Journal of American Ceramic Society, **68**, pp. 174-181, 1985.
- [3] Chiba, R., Ishii, T., & Yoshimura, F., *Temperature Dependence of Ionic Conductivity in $(1-x)ZrO_2$ - $(x-y)Sc_2O_3$ - yYb_2O_3 Electrolyte Material*, Solid State Ionics, **91**, pp. 249-256, 1996.
- [4] Kaneko, H, Jin, F., & Taimatsu, H., *Electrical Conductivity of Zirconia Stabilized with Scandia and Yttria*, Journal of American Ceramic Society, **76**, pp. 793-1975, 1993.
- [5] Li, Y., Tang, Z.L., Zhang, Z.T., & Gong, J.H., *Electrical Conductivity of Zirconia Stabilized with Yttria and Calcia*, Journal of Material Science Letter, **18**, pp. 443-444, 1999.
- [6] Gong, J.H., Li, Y., Tang, Z.L., & Zhang, Z.T., *Ionic Conductivity in the Ternary System $(ZrO_2)_{1-0.08x-0.12y}$ - $(Y_2O_3)_{0.08x}$ - $(CaO)_{0.12y}$* , Journal of Material Science, **35**, pp. 3547-3551, 2000.
- [7] Li, Y., Gong, J., Xie, Y.S., Tang, Z.L., & Zhang, Z.T., *Microstructural Dependence of Electrical Conductivity of $(ZrO_2)_{0.90}$ - $(Y_2O_3)_{0.04}$ - $(CaO)_{0.06}$*

- Solid Electrolyte*, Material Science and Engineering B, **78**, pp. 140-144, 2000.
- [8] Gong, J., Li, Y., Tang, Z., Xie, Y., & Zhang, Z., *Temperature-Dependence of the Lattice Conductivity of Mixed Calcia/Yttria-Stabilized Zirconia*, Material Chemistry and Physics, **76**, pp. 212-216, 2002.
- [9] Bucko, M.M., *Ionic Conductivity of CaO-Y₂O₃-ZrO₂ Materials with Constant Oxygen Vacancy Concentration*, Journal of the European Ceramic Society, **24**, pp. 1305-1308, 2004.
- [10] Scott, H.G., *Phase Relationship in the Zirconia-Yttria System*, Journal of Material Science, **10**, pp. 1527-1535, 1975.
- [11] Soepriyanto, S., & Hidayat, T., *Synthesis on Nanocrystalline Zirconia from by Product of Tin Processing* in Proceeding International Conference on Mathematics and Natural Sciences (ICMNS), Faculty of Mathematics and Natural Sciences, Institute Teknologi Bandung, pp. 460-464, 2006.
- [12] Martin, P, Lopez, M.L., Pico, C., & Veiga, M.L., *Li_{(4-x)/3}Ti_{(5-2x)/3}Cr_xO₄ (0 ≤ x ≤ 0.9) Spinels: New Negatives for Lithium Batteries*, Solid State Sciences, **9**, pp. 521-526, 2007.
- [13] Barsoukov, E., & Macdonald, J.R., *Impedance Spectroscopy: Theory, Experiment and Applications*, 2nd ed., A John Wiley & Sons, Inc., pp. 492-493, 2005.
- [14] Agrawal, R.C., & Gupta, R.K., *Review Superionic Solids: Composite Electrolyte Phase- an Overview*, Journal of Material Science **34**, pp. 1131-1162, 1999.
- [15] Bucko, M.M., *Some Structural Aspects Ionic Conductivity in Zirconia Stabilized by Yttria and Calcia*, Materials Science-Poland, **24**, pp. 39-44, 2006.
- [16] Bonanos, N., Slotwinski, R.K., Steele, B.C.H., & Butler, E.P., *High Ionic Conductivity in Polycrystalline Tetragonal Y₂O₃-ZrO₂*, Journal of Material Science Letters, **3**, pp. 245-248, 1984.
- [17] Gong, J.H., Li, Y., Tang, Z.L., Xie, Y.S., & Zhang, Z.T., *Temperature-Dependence of The Lattice Conductivity of Mixed Calcia/Yttria-Stabilized Zirconia*, Material Chemistry and Physics, **76**, pp. 212-216, 2002.
- [18] Li, Y., Liu, M., Gong, J., Chen, Y., Tang, Z., & Zhang, Z., *Grain Boundary Effect in Zirconia Stabilized with Yttria and Calcia by Electrical Measurements*, Material Science and Engineering B, **103**, pp. 108-114, 2003.