

Electrical Conductivity and Physical Characterizations of Y-TPZ Electrolyte in HT-SOFC

Abeer Farouk Al-Attar^{1*}, Saad B. H. F¹, Fadel A. Hashim¹ and Mohammad J. Eshraghi²

¹Department of Materials Engineering, University of Technology Al-Sinaa' Street, 10066, Baghdad, Iraq.

²Semiconductors Department, Materials and Energy Research Center, Meshkindasht, Karaj, Iran.

ABSTRACT

In this work, Y2O3-stabilized tetragonal polycrystalline zirconia (Y-TPZ) nanoparticles used to prepare electrolyte pellets for solid oxide fuel cell operated at high temperature (HT-SOFC) compacted by cold press method with various applied pressure and sintered at 1823^o K. Electrical conductivity of sintered electrolyte measured at 723^oK. Phases of sintered specimens were determined by X-ray diffraction (XRD). The DC electrical conductivity of electrolyte measured to be 3.32 x 10⁴S/m. XRD results show that Tetragonal zirconia phase has obtained. Crystallite size calculated based on Williamson-Hall method, which was found to be between 26 nm to 43 nm. Lattice parameter calculated by Rietveld refinement method. The physical characterization including the density of electrolyte investigated that obtained maximum density reached to 6.395 g/cm³. The maximum electrical conductivity at 723^o K measured to be 3.32 x 10⁴S/m. XRD results obtained tetragonal zirconia phases formed with crystallite size between 26 nm to 43 nm.

Keywords: SOFC, Pressure Effect, Electrical Conductivity, Physical Properties, Y-TPZ.

1. INTRODUCTION

In the recent decades, there is more focus in the usage of alternative for conventional energy production methods. One of the most attractive methods is SOFC [1], Which is an advanced technology for promising energy source in both stationary and portable applications including converting chemical energy to electrical power by electrochemical reactions [2,3]. According to the literature review, SOFCs operating at high operating temperature ranges (600°C~1000)°C, could achieve energy efficiency up to 85%. When combined with gas turbines higher efficiencies up to 85% could be achieved by SOFC, while engines and modern thermal power plants can achieve only 30% efficiency [3]. In SOFC, technology there is flexibility in fuel chose. The design of SOFC is simple; moreover, usage of precious noble metals is not necessary. SOFC have shown low emissions in exhaust gases because of converting of produced carbon monoxide to carbon dioxide at the high operating temperature [4]. It is worth noting that SOFC in comparison to other Fuel Cell types, is an all-solid-state fuel cell based on a solid oxide electrolyte [4,5]. Also, SOFC has shown environmental friendly due to very low levels of NOx and SOx emissions and silence in running temperatures [3,4].The choice of electrolyte material determines the running temperature of FC and prevents anode and cathode electrical contact by blocking the electrons. In addition, the electrolyte used to facilitate the flow of charged ions from one electrode to the other to maintain the overall charge balance. One of the most common materials utilized as an electrolyte for SOFC is yttrium (III) oxide stabilized zirconia (YSZ) due to its ability to conduct oxygen anions [5], as well as high ionic conductivity and high thermal stability. Because of its unique characteristics, recently there are great researchers focused on the electrical conductivity of YSZ electrolyte [6]. The motivations of present work are to investigate the effect of compaction pressure on the electrical conductivity of Y-TZP as an

* Corresponding Author: bero6058@gmail.com

electrolyte for SOFC applications which according to our knowledge there is a little report on this issue.

This work aims to manufacture Y-TPZ electrolyte for solid oxide fuel cell working at high temperature (HT-SOFC) at various compaction pressures to investigate the compaction pressure effect on electrical and physical properties of the electrolyte.

2. MATERIAL AND METHODS

A 3 mol% yttria-stabilized zirconia (TPZ) nanopowder supplied by Hongwu International Group Ltd, China, and Polyethylene glycol supplied by Reagent World, Inc, USA, used as raw materials as received. Raw materials examined by XRD and SEM to determine their phases and particle size. The XRD patterns have been taken with cobalt $\lambda_{\text{Co-K}\alpha 1} = 1.78901 \text{ \AA}$ radiation tube operating at 40 kV and 30 mA. The crystallite size estimated by Williamson-Hall method as obtained in eq.1 [7].

$$B \cos(\theta) = \frac{K \times \lambda}{\text{Size}} + 4 \text{Strain} \sin(\theta) \quad (1)$$

Where B= width of the peak, K = shape factor (1), and λ = wavelength of Co- $\text{k}\alpha$ radiation. Particle size and chemical composition investigated using scanning electron microscopy (SEM) images and electron dispersive spectroscopy (EDX). The average crystallites size and lattice parameters were estimated by the Rietveld method using Maud software [8,9]. The powders mixed with polyethylene glycol (PEG) as a binder and compacted to 4 code groups specimens with different applied pressures for each group: (191, 446, 573, 955) MPa.

The compacted pellets have cylindrical shape 0.01 m in diameter and 0.01 m thick. Finally, sintering performed in two steps. The first sample semi-sintered at 1173^oK for 4 hours. These semi-sintered specimens polished to reduce their thickness down to around (0.89-1.07) mm. Finally, polished sample sintered at 1823^oK for 4h in the air. The DC electrical conductivity test performed with two GWINSTEK GOM 8145 digital multimeters in two-point probe configuration using Pt mesh at both sides of electrolyte to collect current from the electrolyte in the temperature range of 293^oK to 723^oK. Silver paste used for making electrical contact on both sides of pellets. The density of sintered pellets carried out according to ASTM (C373-17).

3. RESULTS AND DISCUSSION

XRD pattern of starting material 3YSZ is shown in Figure (1). As it can be seen strong peaks of Y-TPZ are dominant while very small peaks related to ZrO₂, and Y₂O₃ phases also exist in the pattern.

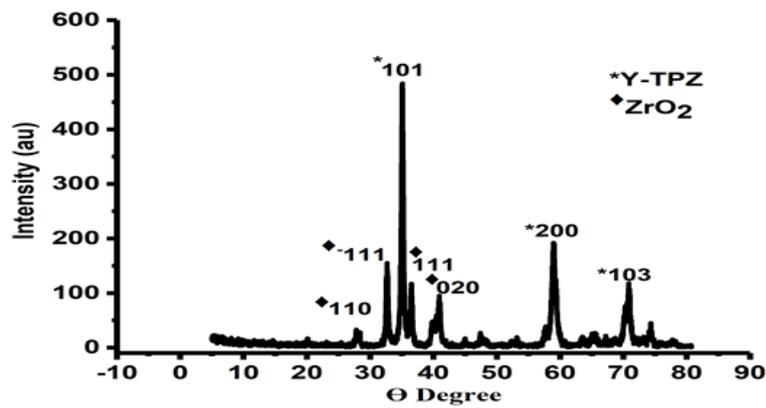


Figure 1. XRD pattern of as received Y-TZP.

Micrographs of Y-TPZ raw material taken by Scanning Electron Microscope is shown in Figure (2). As it can be seen the average particle size of powders are approximately 40-90 nm without any special shape.

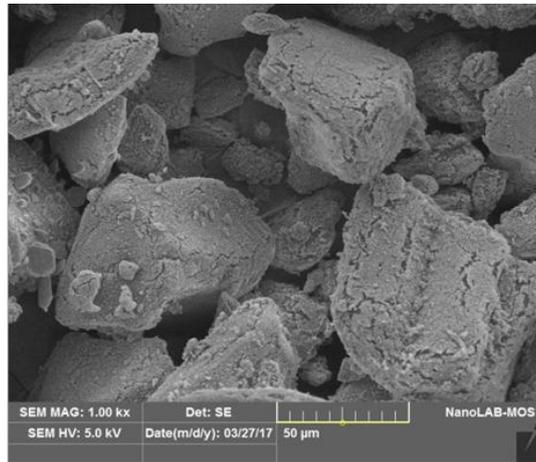


Figure 2. SEM images of Y-TPZ particles.

EDX spectrum of Y-TZP particles is shown in Figure (3). The elemental composition percentage of yttrium and zirconium are exposed around 2.91% and 95.12 respectively as seen in Table (1).

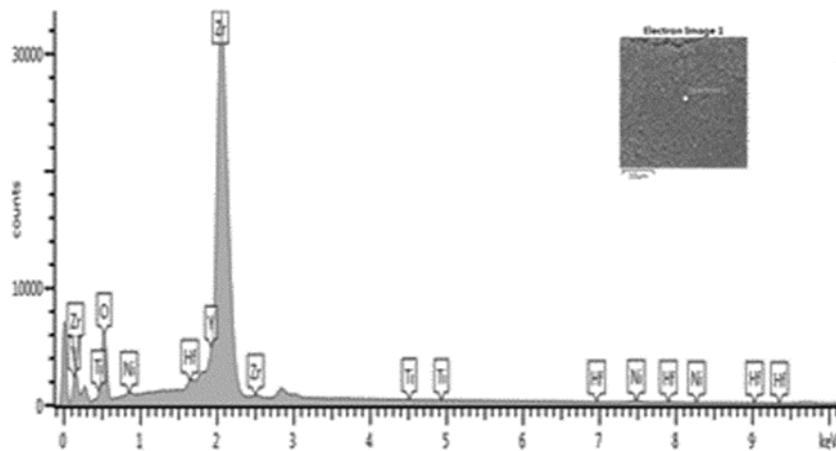


Figure 3. EDX spectrum of Y-TPZ.

Table 1 Element Wt% with spectra of EDX of Y-TZP particles

Element	O	Ti	Ni	Y	Zr	Hf	Total:
Wt%	45.88	0.00	0.56	2.91	49.24	1.41	100.00

Table (2) shows the crystalline parameters, estimated using Rietveld refinement method for all specimens. These data reveal that the compaction pressure has an effect on lattice parameter but cannot change the crystalline structure. The values of the a and c lattice parameters obtained by Rietveld refinement for all samples are very close to already reported values [10]. It is evident that increasing compaction pressure up to 382MPa results in an increase of lattice parameter as shown in Figure (4). In addition, it can be deduced that applying more pressure over 382MPa has an adverse effect on lattice parameter and other parameters, which will be discussed in the following. XRD patterns of sintered specimens in figures (5) shows that peaks sharpness increases by increasing applied pressure in three groups of the Y-TZP electrolyte.

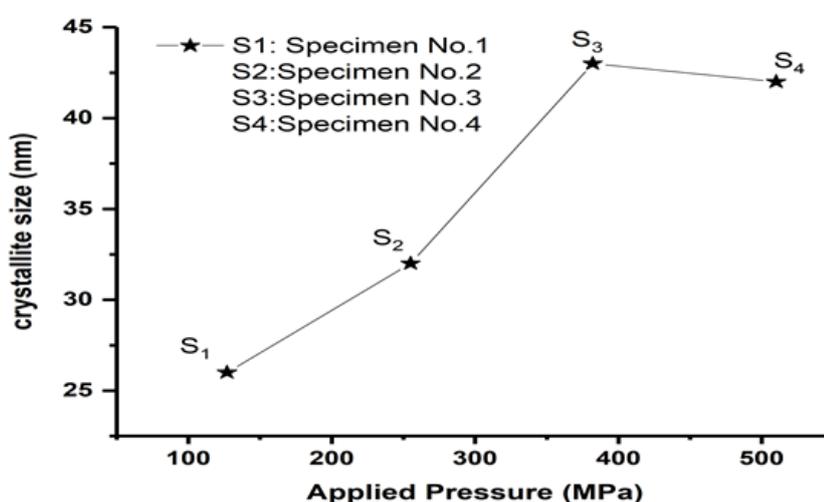


Figure 4. Relationship between crystallite size and applied pressure (MPa).

As it could be seen in Table (2) increasing applied pressure up to 382 MPa will cause the crystallite size to grow from 26 nm to 43 nm, however applying higher pressure has no effect on crystallite size.

Table 2 Pressure applied and density for four specimen code groups

Specimen Code	1	2	3	4
Pressure (MPa)	127	255	382	510
Density g/cm ³	5.897	6.388	5.985	6.395

The density of specimens are listed in the table (2). As it can be seen by increasing applied pressure from 191 MPa to 955 MPa the density of sintered sample increases from 5.897g/cm³ to 6.395 g/cm³, which could be due to the increase in contact surface area between particles of compaction specimens which has an effect on the density of electrolyte pellets. XRD patterns of sintered specimens suggest that all samples contains Zr_{0.963}Y_{0.037}O_{1.982} Tetragonal zirconia (Y-TPZ) phase that indicated zirconia crystal phase is relatively stable [11]. In addition, increasing compaction pressure of pellets the sharpness of peaks in XRD pattern increased in a comparison between groups of Y-TPZ electrolyte are visible in Figure 5.

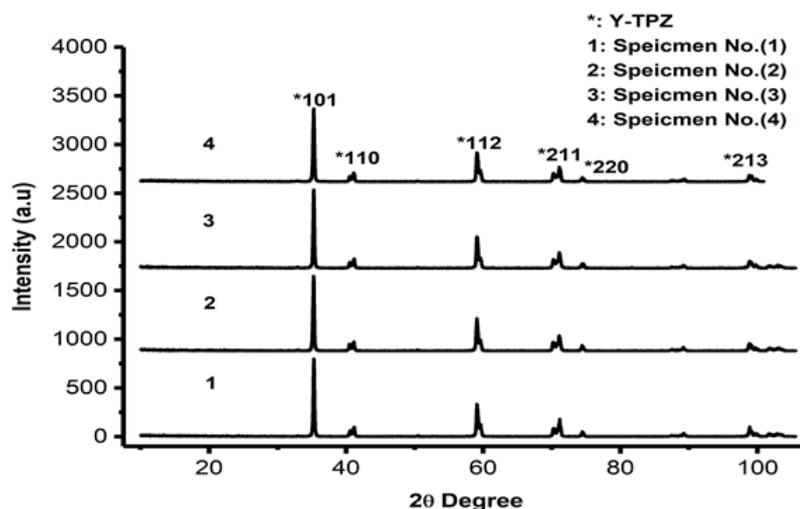


Figure 5. XRD pattern of sintered pellets, 1: specimen No.1, 2: specimen No.2, 3: specimen No.3, and 4: specimen No.4.

As seen in Table (3) increasing applied pressure up to 382 MPa will cause the crystallite size to grow from 26 nm to 43 nm, but applying higher pressures almost has no effect on crystallite size. This could be because of full densification of samples at 382MPa. The electrical resistivity increase by crystallite size growth is logical because ions undergo fewer grain boundaries during transfer in the bulk. A decrease in electrical conductivity in specimens prepared at higher applied pressures could be a reason of protons need space. This effect seems more significant for the jump rotational mode low temperature than for the jump-diffusion in high temperature [12], also decreasing of oxygen vacancy concentration, which would decrease conductivity [13] with high-applied pressure.

Figure (6) displays the results of electrical conductivity at the temperature range of 293⁰K to 723⁰K, measured by two-point probe method. It can be seen that electrical conductivity start to rise at about 550⁰K for all 4 groups due to increasing mobility of ionic conductor in the Y-TZP electrolyte during increasing the operating temperature. It can be observed that the electrical conductivity decreased with increased operating temperature also, the maximum value of electrical conductivity was 35000 S/m at 700⁰K, in sample compacted at 382 MPa. As shown in Table (2) electrical conductivity decreases by increasing applied pressure to values higher than 382 MPa.

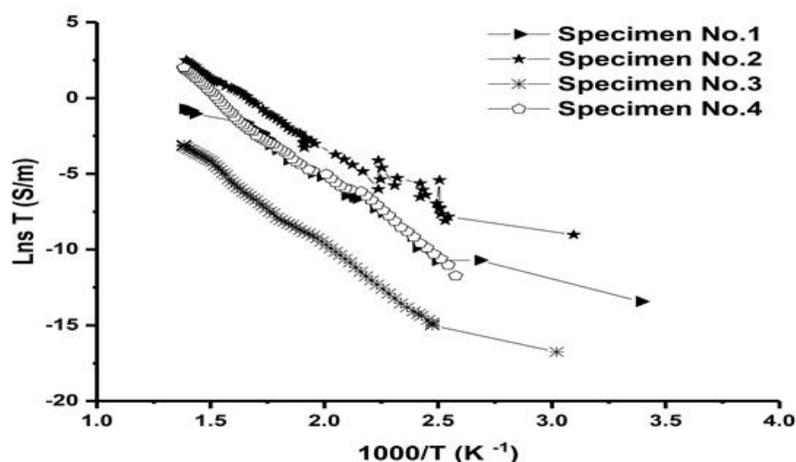
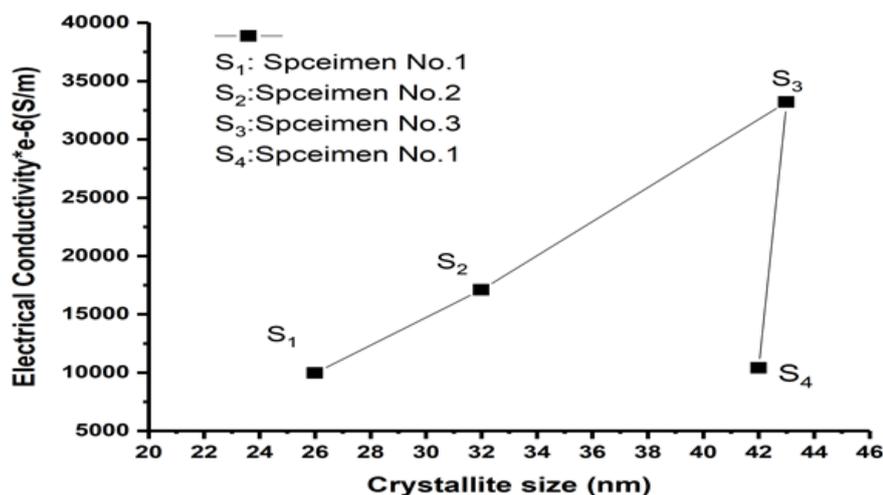


Figure 6. Relationship between electrical conductivity (σ) and temperature of 4 sintered pellets.

Table 3 Applied pressure, Lattice parameter, and electrical conductivity for four specimens code groups

Specimen Code	1	2	3	4
Pressure (MPa)	127	255	382	510
Crystallite size (nm)	26	32	43	42
a (Å)	3.6075	3.6080	3.6092	3.6087
c (Å)	5.1700	5.1715	5.1734	5.1716
Electrical Conductivity (S/m) at 723 ⁰ K	9.96E+03	1.71E+04	3.32E+04	1.04E+04

It can be noticed from relationship between electrical conductivity (σ) and crystallite size in Figure (7) that the maximum value of electrical conductivity was $3.32E+04$ at 43 nm. Therefore it could be deduced that there is a direct relationship in the group (1, 2, and 3), but an inverse relationship in the group (4) between crystallite size and electrical conductivity.

**Figure 7.** Relationship between electrical conductivity (σ) and crystallite size.

4. CONCLUSION

Nano Y-TZP used to prepare electrolyte of SOFC by with different applied pressure during compaction. It has been found that the by increasing applied pressure up to 382 MPa the electrical conductivity increases. Also increasing applied pressure up to 382 MPa results in an increase of crystallite size up to 43 nm. However, increasing applied pressure to higher values than 382 MPa almost has no effect on crystallite size. The electrical conductivity of pellets is also correlated to crystallite size of pellets. The maximum electrical conductivity achieved at 750⁰K was around $3.32E+04$ S/m. The results of XRD pattern shows that pure T-YZP phases obtained from sintered specimens. The maximum density achieved related to the pellets compressed at 510 MPa, which could be a result of high compression force.

REFERENCES

- [1] Y. M. A. Welaya, M. M. & N. R. Ammar, International Journal of Naval Architecture and Ocean Engineering **5.4** (2013) 529-545.
- [2] Y. M. A. Welaya, M. Mosleh, N. R. Ammar, Journal of Marine Science and Application **12.4** (2013) 473-483.
- [3] M. Pehnt, Life-cycle analysis of fuel cell system components, John Wiley & Sons, Ltd, Chichester **4.13** (2003) 1293-1317.
- [4] Yeqing Fu, PhD thesis, M.S.CEP, Massachusetts Institute of Technology, USA, (2014.)
- [5] Singhal SC, Science and technology of solid-oxide fuel cells. MRS Bull **25.3** (2000) 16-21.
- [6] S. Vatansever, F. Oksuzomer, S. Nacikoc, M. Somer, H. Deligoz, M. A. Gurkaynak, Materials Science-Poland **28.1** (2010) 85-91.
- [7] VD Mote, Y Purushotham & BN Dole, Mote *et al.* Journal of Theoretical and Applied Physics **6** (2012) 1-8.
- [8] Lutterotti L, Matthies S, Wenk HR. MAUD, International Conference on Textures of Materials (ICOTOM-12), Montreal, Canada, (1999)
- [9] Ferrari M, Lutterotti L., Journal of Applied Physics **76.11** (1994) 7246.
- [10] Cintia R. D.de F., Meirielle M. de G., Rodolfo B. da S., Jose A. P. da C., Joao M. S, Materials research Ibero-americanjournal of materials, ISSN 1980-5373 (2017) 1-7.
- [11] X. Liang, Y. Qiu, S. Zhou, X. Hu, G. Yu & X.Deng, Journal of University of Science and Technology Beijing **15.6** (2008) 764.
- [12] Q. Chen, A.Braun, A. Ovalle, C. D.Savaniu, T. Graule & N. Bagdassarov, Swiss Federal Laboratories for Materials Testing and Research, (2011) 5.
- [13] R. Fortes M & D. M. Pinatti F. S, Materials Research **19.1** (2016) 45-50.

