The effect of ZnO addition on the phase transformation, microstructure, and ionic conductivity of 8YSZ ceramics

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Abstract. In this paper the effect of zinc oxide (ZnO) addition on the phase transformation and ionic conductivity of 8 mol % Yttria-stabilised Zirconia (8YSZ) is investigated. Pure 8YSZ and ZnO doped YSZ ceramics are prepared using the solid state reaction method sintered at 1550^oC for 2 hours. The X-ray Diffraction (XRD) results reveal the presence of tetragonal, cubic and monoclinic phase of Zirconium dioxide (ZrO_2) for all undoped and doped YSZ sintered samples. The phase stability of tetragonal YSZ was found to be increased with the increase in ZnO addition. Minor fraction of monoclinic phase was found in pure YSZ sintered sample and the amount of monoclinic phase decreased with the increasing amount of Zn after sintering at 1550^oC for 2 hours. The fraction of cubic phase was also found to decrease with the increase in Zn concentration. The highest ionic conductivity of 1.03×10^{-3} S cm^{-1} was obtained at room temperature for samples with 3 mol% ZnO. Pure 8YSZ sintered sample on the other hand, yielded 9.88×10^{-4} S cm^{-1}.

1 Introduction

Solid oxide fuel cells (SOFCs) have attracted much attention in recent years due to their various potential advantages, including a wide variety of available fuels, inexpensive technology, good durability and highly efficient energy conversion [1–3]. Yttria-stabilized zirconia (YSZ) is the traditional electrolyte of the cell system. 8 mol% of Yttrium oxide (Y_2O_3) is one of the most explored compositions where the doping provides sufficient oxygen vacancies in fluorite ZrO_2 lattice thus, to ensure high ionic conductivity (σ) up to 0.1 S/cm. In addition, it also provide a stable cubic structure at 1000 ∘C as well as to obtain sufficiently high current densities and good power output.). Such high temperatures accelerate degradation of the fuel cell system and often lead to problems, such as solid reactions between the components, thermal degradation as well as thermal expansion mismatch. Furthermore, if the operation temperature of SOFC is to be decreased to 800∘C, the ionic conductivity of YSZ reduces to 0.044 S/cm which becomes insufficient for high SOFC performance due to very high ohmic losses [1].

Numerous studied have been carried out on yttria-stabilized zirconia (YSZ) as solid electrolyte materials and a key component of SOFC systems. Therefore, efforts have been

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exerted to reduce the operating temperature of such systems. In addition to solve the elevated cost of the sealing materials and interconnects, as well as the durability of the cells. Some experiments have reported the effect of dopants on the sintering, electrical, microstructure and mechanical properties of YSZ [2-4]. The ionic conductivity of YSZ are resulting from oxygen vacancies which depends on the type of dopant element and their amount [5]. Some dopant might increase and decrease the ionic conductivity level even though it could enhance the densification and reduce the sintering temperature. When ceria is doped with aliovalent oxides, such as Y_2O_3 and other rare-earth oxides the ionic conductivity increases significantly. However, an increasing amount of dopants tends to form a second phase due to solubility limits, resulting in the reduction of conductivity.

ZnO is well known not only as a semiconductor but also as a probable oxygen-ion conductor due to enrichment of oxygen vacancies at higher temperature. Although Liu and Lau already found that the small addition of ZnO was effective in reducing the sintering temperature and promoting the densification rate of the 8YSZ ceramics, but they are using co-precipitation method to synthesize 8YSZ [2]. Very recently, Gao et al. [6] synthesized $(Ce_{0.84}Y_{0.16}O_{1.92})_{1-x}(ZnO)_x$ electrolytes through a solid state reaction using ZnO as the sintering aid and they found the sintering temperature decreased from 1600 $^\circ$C (20 hours) to 1375 $^\circ$C (20 hours). However the addition of ZnO exhibited a slight detrimental influence on their conductivities.

In this work, the effect of ZnO addition on sinterability, microstructure, phase transition and ionic conductivity in commercial 8YSZ powders were investigated using solid state reaction. The aim is to determine whether the addition of ZnO in 8YSZ with large particle size and high impurity content could also improve densification and give positive impact to ionic conductivity.

2 Methodology

2.1 Sample preparation.

ZnO (1, 2, 3 mol%) was added to the 8YSZ powders using mortar and pestle followed by calcinations process. The calcined powders were die-pressed into cylindrical pellets (12 mm in diameter) at 6 tonne pressure by Automatic hydraulic press, model 3890.4NE000. The green pellets were sintered at temperatures 1550∘C in the air for 2 hours and subsequently cooled to room temperature.

2.2 Characterization.

Phase analysis was performed on the sintered pellet. The crystalline phase of all samples was examined using XRD (XRD, D/max-III, Rigaku) with CuKα radiation with an applied voltage of 40 kV and current of 40 mA. The XRD data were collected over the range of 2h = 20°-80° with a step size of 0.02° and a count time of 0.3°/min. The microstructure of the ceramics was investigated using SEM with an applied voltage of 30 kV (model JEOL JSM-6460LA SEM) and the energy dispersive. The oxide ionic conductivity of the materials was measured using electrochemical impedance spectroscopy based on sintered pellets.. Both sides of the pellets were coated with platinum (pt) using sputter coater prior characterized as electrodes and fired at   600 ∘C for 30 min before measurement to ensure good bonding. The AC impedance spectra were made using impedance analyser, model Agilent 4294A at 300 °C. The testing was conducted at frequency range from 4 Hz to 5 MHz

3 Results and discussion

3.1 Phase composition and crystal structure

The XRD patterns of 8YSZ and ZnO doped 8YSZ samples sintered at 1550°C for 2 h are shown in Figure 1. The XRD pattern has been indexed with the help of ICDS card and it confirms that all samples mainly comprises a combination of tetragonal (ICSD 98-002-0789) and cubic phase (ICSD 98-003-2797). Closed observation on the XRD pattern revealed the presence of small fraction of monoclinic phase (ICSD 98-010-8439) phase which can be characterized by a peak at $2\theta=28.2^{o}$. Yttria and ZnO based phase has not been detected which confirms the well incorporation of ZnO ions into the 8YSZ matrix.

Increases the dopant concentration to 3 mol% of ZnO resulted in increasing the formation of tetragonal phase and reduces the formation of monoclinic phase. It is very difficult to distinguish between tetragonal and cubic zirconia structure. The assignment of cubic and tetragonal structures, based solely on the x-ray diffraction analysis, can be misleading because the cubic and tetragonal structures (a0=0.5124 nm for cubic, and a0=0.5094nm and c0=0.5177 nm for tetragonal structures) are very similar as demonstrated in simulated ICSD paten shown in Figure 2.
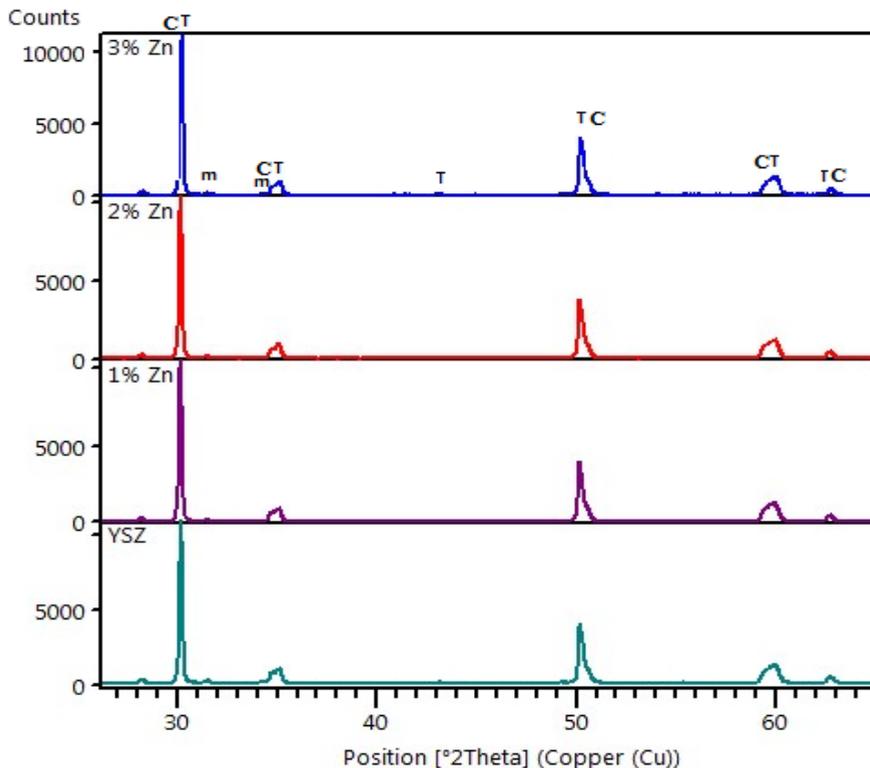
Fig. 1. XRD pattern of the 8YSZ ceramics with the addition of ZnO (1, 2, 3 mol%) sintered at 1550°C for 2 h in air (c:cubic, t:tetragonal, m:monoclinic).

The tetragonal structure can be distinguished from the cubic structure by the presence of the characteristic splitting peak at $2\theta \cong 34^{o}$, 50°, 59°, such as (002) (110), (021) (112) and (121) (013), and etc., whereas the cubic phase exhibits only single peaks at all of these

positions. Due to the broadening of the peak, the two polymorph might overlap, thus crystal structure refinement using whole profile fitting method or Rietveld method to determine the present of either one or both polymorphs. Table 1 demonstrates phase quantification using Rietveld Method and presents the phase composition for all sintered undoped and doped 8YSZ samples.
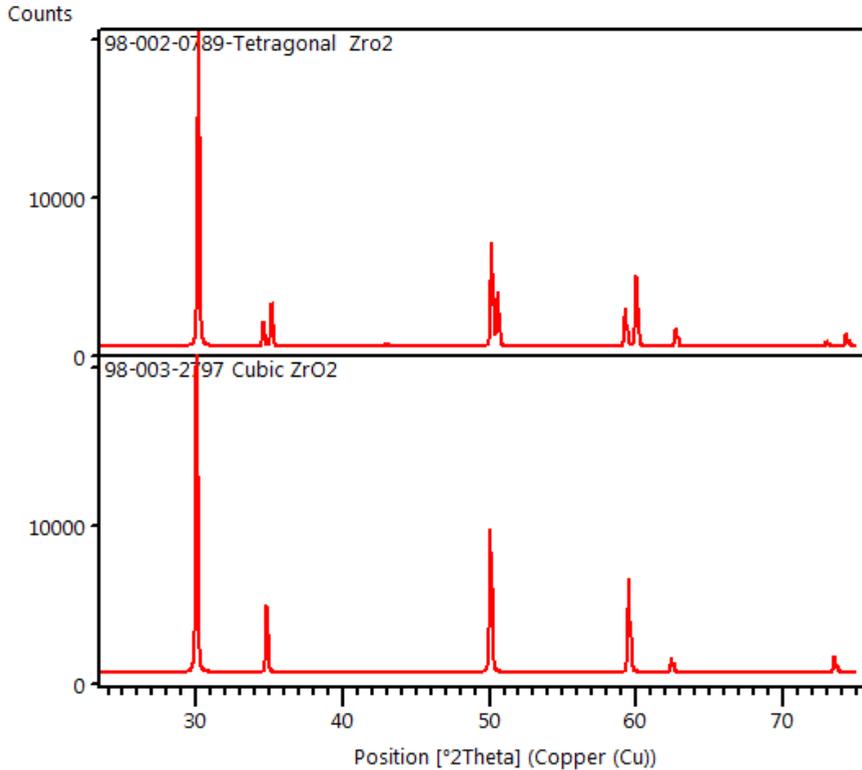
Fig. 2. Simulated pattern of ICSD data of cubic and tetragonal fluorite structure.

Table 3. Phase composition of sintered 8YSZ ceramics doped with different amount of ZnO.

% molZnO	Tetragonal	Cubic	Monoclinic	Rwp
0	65.5	26.8	7.8	13.66
1	69.2	23.2	7.6	12.87
2	70.7	22.8	6.5	12.65
3	78.9	16.1	5.0	12.80

It is proposed that the cause of the stability of the tetragonal phase in these present studies is directly related to the particle size of the raw powders (8YSZ). In particular, during the heat treatment the Y_2O_3 doping can either diffuse into the ZrO_2 crystal lattice or segregate at grain boundaries, depending on how the yttrium atoms were combined with the zirconium atoms during the synthesis process. In this context, the presence of monoclinic phase even in sintered pure 8YSZ samples could be attributed to an inhomogeneous distribution of yttrium and zirconium ions due to the conditions used in each synthesis process, so that stabilization of the tetragonal phase is not possible.

3.2 Microstructure

Figure 3 displays the SEM photographs of $(YSZ)_{1-x}(ZnO)_x$ samples sintered at 1550^oC for different mol% of ZnO. The sample with 1 mol% ZnO was found to be porous despite being sintered at 1550∘C. In contrast to sample with undoped 8YSZ samples was dense with small closed pore left in the ceramic matrix (cant understand). This was resulted from the insufficient pore elimination The addition of ZnO inhibited the sintering process. ZnO has higher melting point which is 1975^oC [7]. The addition of Zno does not lead to an increase in the grain size[8]. The effectiveness of sintering aids depends on several factors, such as sintering temperature, viscosity, solubility and glass wettability. The main requirement for liquid sintering is that the liquid phase should wet the grains of the ceramics. Generally, the chemical reaction between sintering aids and ceramic particles can provide the best wetting condition[9].

Although Y. Liu et al. reported that ZnO-added samples experience viscous flow sintering which promotes the diffusivity rate of 8YSZ matrix, thus enhancing the densification and grain growth however, it also greatly depends on the type of initial raw materials used. During liquid phase sintering process, both solid and liquid are subject to rearrangement because of the unbalanced capillary forces. The sintering aids with low melting temperature would act as lubricant and the rearrangement of the particles proceeds in the direction of reducing porosity. This rearrangement is driven by an imbalance capillary pressure which is a result of initial raw materials used such as (1)particle size distribution, (2) irregular particle shape, (3) local density fluctuation in the powder compact, and (4) anisotropic materials properties which limits the wetting angles between particles.
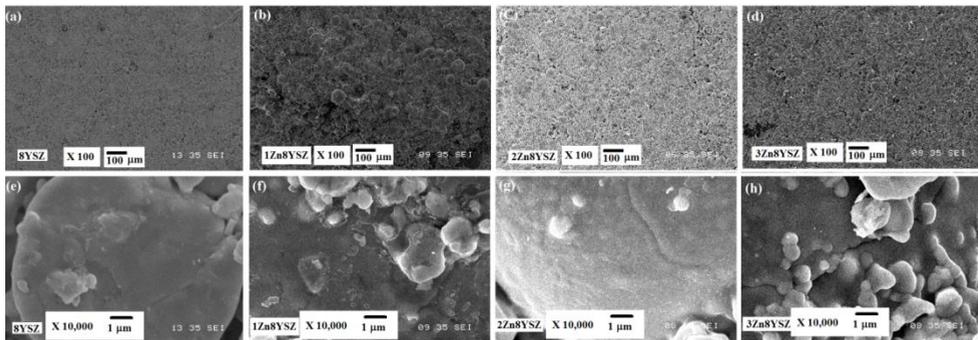
Fig. 3. SEM micrographs of ceramics samples at 1550^oC with X100 magnification: undoped 8YSZ(a), with 1 mol % ZnO (b), with 2 mol % ZnO (c), with 3 mol% ZnO (d) and ceramics sintered at 1550 °C for 2 h. with X 10,000 magnification: undoped 8YSZ(e), with 1 mol % ZnO (f), with 2 mol % ZnO (g), with 3 mol% ZnO (h)

The SEM analysis shows the formation of individual particles' micro-sized spherical and irregular crystals with size of 0.5–40μm. They are partially fused to form hard agglomerates. Moreover, the structure of YSZ samples obtained at 800°C consisted of large-grained monolithic matrix, indicating good connectivity between the grains.

3.3 Ionic conductivity

Figure 4 shows the ionic conductivity of all investigated samples measured at room temperature as a function of frequency. Ionic conductivities of all undoped and Zn doped 8YSZ samples increase with increasing frequencies. Figure 5 demonstrate the ionic conductivity values of all undoped and Zn doped 8YSZ sintered samples measured at 5 MHz at room temperature. For $(8YSZ)_{1-x}(ZnO)_x$ (x = 1, 2, and 3 mol%), the ionic conductivity decreased from $9.884 \times 10^{-4} \, \Omega^{-1} \, cm^{-1}$ for undoped samples to x = 3.75 $\times 10^{-4} \, \Omega^{-1} \, cm^{-1}$ then increased to $1.03 \times 10^{-3} \, \Omega^{-1} \, cm^{-1}$ for 3 mol% ZnO addition,
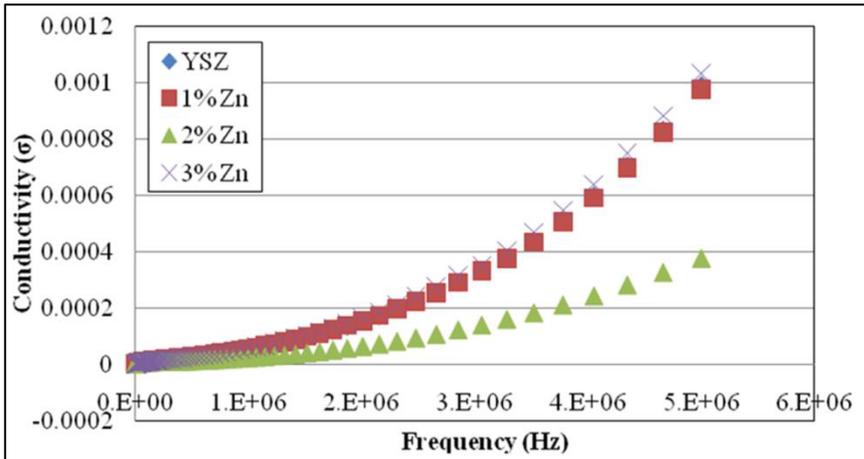
Fig. 4. Ionic conductivity of undopedand ZnO-doped 8YSZ ceramics measured at different frequency.
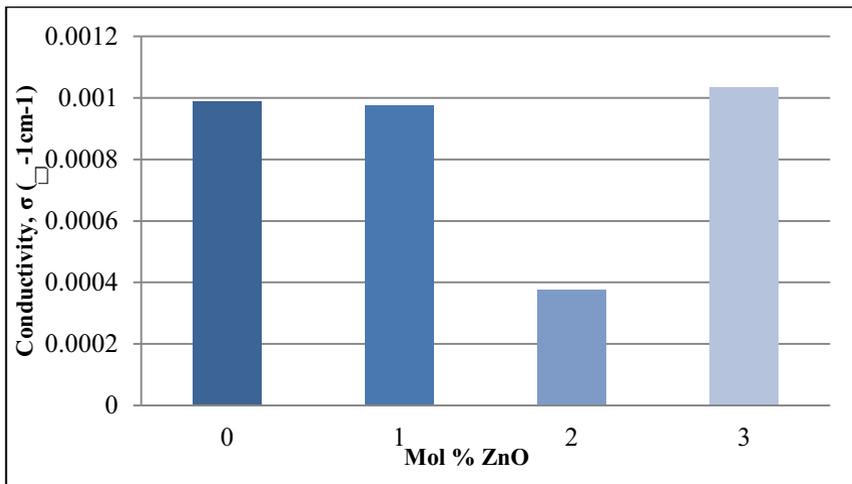
Fig. 5. Ionic conductivity of undoped and ZnO doped 8YSZ sintered samples measured at room temperature at frew 5 MHz.

The ionic conductivity of $(8YSZ)_{0.97}(ZnO)_{0.03}$ was observed to be much higher than that of pure 8YSZ samples (x = 0). The above analysis ascertained that YSZ with certain ratio of ZnO could improve the electrical property of 8YSZ electrolytes further. The study demonstrated that better electrical properties could be obtained with samples synthesized using 3 mol% ZnO .in this study. Although $(8YSZ)_{0.97}(ZnO)_{0.03}$ was still not well sintered as shown at the micrograph in Figure 3. The present of closed pores, indicate the samples

are not have fully densified microstructure. Thus, it can be concluded that sinterability of the specimens can be promoted further by increasing the sintering temperature or prolonging the holding time, whereas ionic conductivity may be improved by increasing the density.

The higher ionic conductivity for the $(8YSZ)_{0.97}(ZnO)_{0.03}$ samples could probably be attributed to the higher densification (as shown in Figure 3) and the more compact arrangement of crystal grains that favored the transportation of the carriers. In this study, doping with ZnO may cause two opposite effects. On the one hand, as a sintering aid, ZnO can reduce porosity and improve sinterability to effectively obtain a dense electrolyte material, leading to a decrease in activation energy of conduction and an increase in ionic conductivity. On the other hand, ZnO also shows a detrimental influence on conductivity when the amount added is not enough to enhance desification, which leads to an increase in the activation energy of conduction and a decrease in ionic conductivity. When the ZnO content (x) was at 0.2 mol %, the latter effect may be stronger than the former, resulting in lower ionic conductivity. However, when the dopant content (x) was at 3 mol.%, the former effect may be stronger than the latter, leading to higher ionic conductivity and lower activation energy for conduction. It is known that ZnO dissolves into the ZrO_2 can create the oxygen vacancies as the addition of $Y_2O_3 Y_2O_3 \rightarrow 2Y_{Zr}' + V_O^{\bullet\bullet} + 3O_O^x\}$ and $ZnO \rightarrow Zn_{Zr}'' + V_O^{\bullet\bullet} + O_O^x$ 3 mol % addition of ZnO causes an increase in bulk conductivity due to the increasing number of vacancies. If the concentration of the oxygen vacancy is too high, it might leads to the formation of high activation energy pathways for oxygen diffusion and the formation of ordered oxygen vacancy complexes at high Y concentrations thus, hinders the vacancy mobility. It has become evident that the atomic defect configuration of Y and oxygen vacancy complexes have a profound effect on the oxygen diffusion and transport in YSZ, and hence on the efficiency of solid electrolyte.

4 Conclusion

Un-doped and doped 8YSZ ceramic were successfully synthesized using the solid state reaction method. Structural characterization demonstrates the present of cubic, tetragonal and monoclinic phase for all doped undoped samples. The monoclinic phase decreased as the amount of ZnO increases. The surface textural and morphological property revealed the formation of fine grain in a matrix of large grain. The addition of ZnO on 8YSZ powders are not significantly enhanced the densification as previously reported which might due to large particle size of 8YSZ used in the present studies. For $(8YSZ)_{1-x}(ZnO)_x$ (x = 0,1,2,3 mol%), ionic conductivity was improved in comparison to pure 8YSZ, and the highest ionic conductivity was 0.001 S cm^{-1} measured at room temperature with x = 0.03. It was confirmed that an appropriate amount of ZnO could improve the ionic conductivity of 8YSZ electrolytes.

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