# Effect of alumina addition on the microstructure and grain boundary resistance of magnesia partially-stabilized zirconia

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Sanghyeon Yoon [a], Chester J. Van Tyne [b], Heesoo Lee [a],*

[a] School of Materials Science & Engineering, Pusan National University, Jangjeon-dong, Geumjeong-gu, Busan 609-735, Republic of Korea
[b] Advanced Steel Processing and Products Research Center, Department of Metallurgical and Materials Engineering, Colorado School of Mines, Golden, CO 80401, United States

ABSTRACT

The electrical properties of 9 mol% MgO–ZrO$_2$ (Mg-PSZ) with 1 mol% Al$_2$O$_3$ and the mechanisms for electrical degradation were investigated using structural, morphological, and electrochemical analyses. The addition of Al$_2$O$_3$ caused an increase in both the monoclinic and the Mg-rich phases at the grain boundaries in the Mg-PSZ. Coarse grains larger than 20 $\mu$m and an intergranular layer composed of the Mg-rich phase were identified in a specimen sintered at 1600 °C. This specimen exhibited a minimum of ionic conductivity (4.98 $\times$ 10$^{-4}$ S cm$^{-1}$ at 700 °C) due to the grain boundary resistance (245 $\Omega$ cm$^2$), which dominated the overall resistance. A similar trend was observed over the entire temperature range (600–1500 °C). An intergranular siliceous impurity (SiO$_2$) was present in conjunction with the Mg-rich phase. This impurity and the Mg-rich phase acted as a barrier layer for oxygen ion diffusion. The presence of the intergranular phases (i.e. the monoclinic and Mg-rich phases) contributed to the degradation of the ionic conductivity in Mg-PSZ with an Al$_2$O$_3$ addition.

## 1. Introduction

Zirconia-based solid electrolytes have been used in practical applications of solid oxide fuel cells (SOFC), in oxygen sensors, and in oxygen pumps, due to their excellent ionic conductivity, mechanical strength, and thermal stability [1,2]. Magnesia partially-stabilized zirconia (Mg-PSZ), which exhibits better mechanical and thermal properties than yttria-stabilized zirconia (YSZ), can be used in oxygen-permeating membranes for removing oxygen from molten steel as a high temperature application [3,4].

These materials are usually fabricated through compaction under high pressure (approximately 200 MPa) followed by sintering at high temperatures (above 1500 °C) to obtain a dense body. A dense body is desirable, because its ionic conductivity is closely related to its relative density [5]. Additives such as Al$_2$O$_3$, Fe$_2$O$_3$, SiO$_2$, and TiO$_2$ have been used as sintering aids in order to improve the density of these types of electrolytes [6,7].

Electrolytes with satisfactory conductivity must have reduced grain boundary resistance, as well as improved density. The grain boundary resistance of an electrolyte can increase due to the presence of a siliceous phase situated at the grain boundary. The siliceous impurity (even at a level of only one hundred ppm) forms a high-resistance film, which causes a blocking layer for oxygen ion diffusion. This film can reduce the grain boundary conductivity [8]. Because of this barrier film, the grain boundary resistance can become approximately two orders of magnitude higher than that of the intra-grain resistance [9].

When Al$_2$O$_3$ is added to the electrolyte, the siliceous films at the grain boundary form around the additive. The grain boundary resistance decreases with the addition of Al$_2$O$_3$, since the Al$_2$O$_3$ acts as a scavenger of the siliceous phase [10–12]. However, Verkerk et al. and Guo have reported detrimental effects of Al$_2$O$_3$ addition on the ionic conductivity of these electrolytes [7,13]. Their explanation is that both the intra- and inter-granular resistances are influenced by the type and concentration of the substituted dopants, the impurity concentration of the starting materials, and the sintering temperature [9]. Other studies have been performed that have attempted to reduce the grain-boundary resistance of these zirconia based electrolytes, particularly in Y$_2$O$_3$–ZrO$_2$ and CaO–ZrO$_2$ systems [10,11,14]. Research on the effects of Al$_2$O$_3$ on the electrical property of MgO–ZrO$_2$ systems is absent from the literature. It is necessary to understand the scavenging behavior and the mechanism for electrical degradation of the MgO–ZrO$_2$ system that contains Al$_2$O$_3$ in order to produce better oxygen-permeating membranes.

* Corresponding author. Tel.: +82 51 510 2388; fax: +82 51 512 0528.
 E-mail address: heesoo@pusan.ac.kr (H. Lee).

The current study examines the effects of $Al_2O_3$ additions on the oxygen ion conductivity and the formation of an intergranular phase in a 9 mol% MgO partially-stabilized zirconia for use as an oxygen-permeating membrane. The formation of intergranular phases and the scavenging behavior were determined by structural, morphological, and electrochemical analyses.

## 2. Experimental procedure

Zirconia powder doped with 9 mol% MgO (Saint-Gobain ZirPro, MgZ02B) was used as a raw material and the impurity concentration for $SiO_2$ was 0.07 wt%. The $ZrO_2$ powder was mixed with 1 mol % of $Al_2O_3$ (Junsei Chemical Co. Ltd.) using a ball mill with zirconia balls for 24 h. The mixture was compacted into a cylindrical (20 mm in diameter) and a rectangular (length 60 mm, width 7 mm) using a steel die with a uniaxial pressure of 20 MPa. The specimens were then isostatically pressed at 200 MPa. The green bodies were sintered at 1500 °C and 1600 °C for 6 h in an ambient atmosphere. Table 1 gives the composition and sintering temperatures for the specimens.

Powder X-ray diffraction (XRD, Rigaku, Ultima-IV) of the sintered powders was performed at room temperature over a $2\theta$ range of 20–90° with a scan speed of 1°/min and a scan step of 0.02°/$2\theta$. The lattice parameters were evaluated using the whole pattern refinement module of PANalytical X-Pert Plus software. The shape of the XRD peak and the background were fitted to a pseudo-Voight function and a fifth-degree polynomial, respectively. A microstructural analysis using a scanning electron microscope (SEM, Hitachi, S-4800) was performed on the polished and thermally etched (at 1400 °C for 1 h) surfaces of the sintered bodies to characterize the surface morphology and the grain size.

The ionic conductivity was measured using a four-probe dc conductivity technique over the temperature range of 600–1500 °C. The specimens were cut into rectangular shapes ($2.5 \times 5.5 \times 40$ mm) and Pt wires wrapped around the specimens as an electrode prior to the electrical measurement. A Pt paste was applied to the electrode and notches, followed by calcination at 1000 °C for 1 h to ensure connection between the electrolytes and the electrode. Direct current was supplied by a current source (Keithley, 2400), and the corresponding voltage drop was measured using a multimeter (Agilent, 34401A). The grain and the grain-boundary resistances of the electrolytes were determined by ac impedance spectroscopy. A Pt paste over an area of 0.49 $cm^2$ was applied on both sides of the cylindrical specimens. Impedance spectra were obtained over the frequency range, $10^7$ Hz–$10^{-2}$ Hz, at an excitation voltage of 10 mV for temperatures ranging from 500 to 1000 °C using an IviumStat electrochemical analyzer (Ivium Technologies, IviumStat). The element distribution in the specimens was analyzed using electron probe microanalysis (EPMA, CAMECA SX-100) to observe the scavenging behavior.

## 3. Results and discussion

Fig. 1(a) shows the X-ray diffraction patterns and lattice parameters of the sintered Mg-PSZ both with and without the $Al_2O_3$ powder. All specimens exhibit a mixture of cubic, tetragonal, and
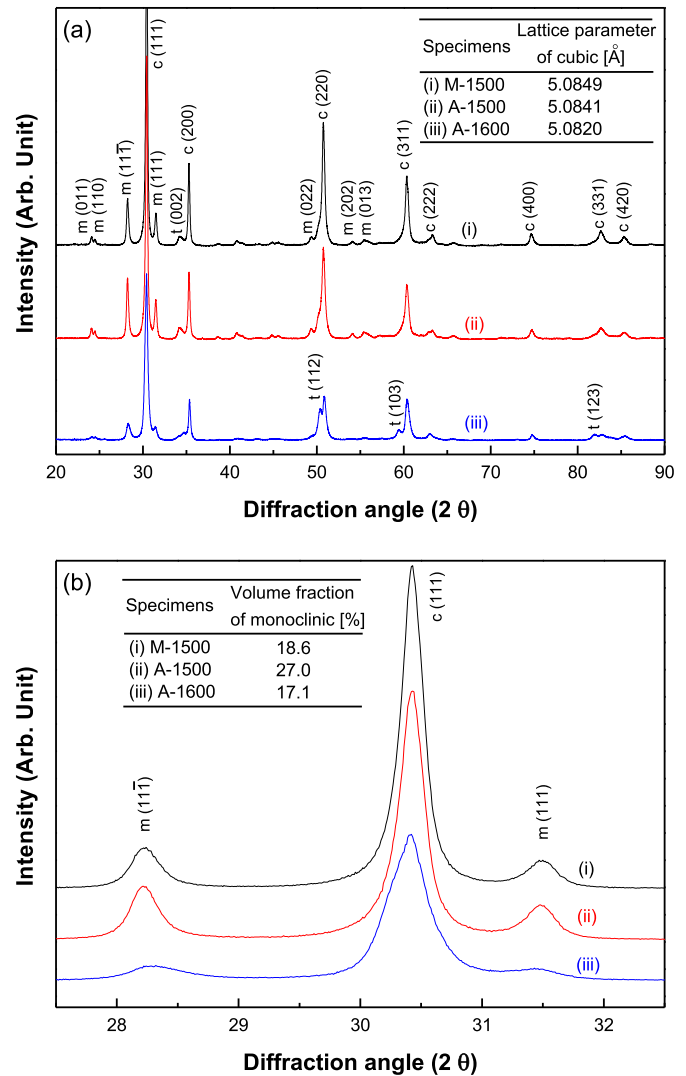
**Table 1**
Composition and sintering temperature of the specimens.

| Specimens | Composition | Sintering temperature (°C) |
|---|---|---|
| M-1500 | 9 mol% Mg-PSZ | 1500 |
| A-1500 | 9 mol% Mg-PSZ + 1 mol% $Al_2O_3$ | 1500 |
| A-1600 | 9 mol% Mg-PSZ + 1 mol% $Al_2O_3$ | 1600 |



**Fig. 1.** (a) X-ray diffraction patterns and (b) expanded XRD patterns in the $2\theta$ range of 27.5–32.5° of the Mg-PSZs: (i) Mg-PSZ, (ii) Mg-PSZ with $Al_2O_3$ sintered at 1500 °C, and (iii) Mg-PSZ with $Al_2O_3$ sintered at 1600 °C.

monoclinic phases, and no secondary phase was detected. The minor peaks within the $2\theta$ range of 38–47° and the peaks around 24° $2\theta$ were assigned to the monoclinic phase. Polyphase $ZrO_2$ is generally observed when the MgO content is below 13 mol% [15]. Fig. 1(b) shows the expanded XRD patterns in the $2\theta$ range of 27.5–32.5° for Mg-PSZs. For the A-1500 specimen, peaks at approximately 28.2° and 31.4° $2\theta$ that correspond to the monoclinic phase are increased, and the peak around 30.4° representing the overlapped cubic and tetragonal phases is diminished. The volume fraction of the monoclinic phase in Mg-PSZ was calculated by the following equation suggested by Potter and Heuer [16]:

$$V_m = \frac{I\left(11\bar{1}\right)_m + I(111)_m}{I\left(11\bar{1}\right)_m + I(111)_m + I(111)_{c+t}}$$

where $V_m$ is the volume fraction of the monoclinic phase and $I$ is the intensity of specific XRD peaks. The addition of $Al_2O_3$ causes an increase in the phase from 18.6% to 27.0%. It appears that the metastable cubic phase undergoes a decomposition reaction with the addition of $Al_2O_3$. In contrast, specimen A-1600 shows a