

Synthesis and Characterization of Sc and Y Co-doped Zirconia ($Zr_{0.84}Y_{0.08}Sc_{0.08}O_{1.92}$) Electrolyte Prepared by Sol-Gel Method

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Abstract: Y and Sc co-doped ZrO_2 [$Zr_{0.84}Y_{0.08}Sc_{0.08}O_{1.92}$ (4Sc4YSZ)] solid electrolyte was prepared via an alkoxide sol-gel route. 4Sc4YSZ was characterized by TG-DTA, XRD, SEM-EDS and AC impedance spectroscopy. XRD patterns showed that co-doping with Y and Sc resulted to the successful stabilization of the highly conductive cubic phase with a lattice parameter of 5.12 Å. Y and Sc dopants are well-distributed within the ZrO_2 particles as evidenced by EDS elemental maps. Total conductivities from 500 °C to 700 °C were determined from AC impedance spectroscopy and an activation energy of 1.31 eV (500-650 °C) was calculated. Even at a low sintering condition of 1200 °C for 5 h, a promising conductivity of 109 mS/cm was achieved for 4Sc4YSZ at 700 °C which is higher than the conductivity of typical 8YSZ solid electrolyte.

Keywords: Co-doped ZrO_2 , ionic conductivity, solid electrolyte; sol-gel; Y and Sc doped ZrO_2 .

1. Introduction

Solid oxide electrolysis cell (SOEC) is recognized as a key enabling technology as we progress towards an economy that is fully dependent on clean renewable energy production and storage [1]. Currently, yttria-stabilized zirconia (YSZ) is considered as the state-of-the-art electrolyte material for SOECs [2]. Doping of ZrO_2 with Y_2O_3 results to the substitution of Zr^{4+} lattice positions with Y^{3+} . The resulting net negative charge can be compensated by defects such as a positively-charged oxygen vacancy (V_O). The migration of V_O then contributes to the ionic conductivity of ZrO_2 -based electrolytes. In Kröger-Vink notation, this can be written as



YSZ is stable in the highly-conductive cubic phase over a wide range of Y_2O_3 doping levels: from 7 mol% to 15 mol% Y_2O_3 [3]. However, the conductivity of YSZ deteriorates when the SOEC's operating temperature is lowered to intermediate temperatures (c.a. 700 °C). On the other hand, scandia-stabilized zirconia (ScSZ) has been known to have higher conductivity than YSZ [4]-[5]. Moreover, limited studies have been conducted on scandia-stabilized zirconia (ScSZ) as an electrolyte material.

The higher conductivity of ScSZ than YSZ means that acceptable conductivity levels can be achieved with

ScSZ even at intermediate operating temperatures. However, the desirable cubic phase of ScSZ is only attainable in a narrow range of temperature, and Sc₂O₃ doping level [6]. Therefore, to improve conductivity at intermediate temperatures while maintaining structural stability, both Y and Sc can be used as co-dopants in the ZrO₂ system. Irvine and co-workers demonstrated that the ternary system of (Y₂O₃)₂-(Sc₂O₃)_x-(ZrO₂)_{98-x}, which is co-doped with 2 mol% Y₂O₃ and 8-11 mol% Sc₂O₃, prepared by ball-milling successfully stabilized the cubic phase [7]. Furthermore, to promote the desired stoichiometry and chemical composition, the sol-gel synthesis method was used in this study since it allows homogeneous mixing at the atomic level [8], [9].

In this study, Y and Sc co-doped ZrO₂ was synthesized via an alkoxide sol-gel route and the thermal, structural, morphological, and electrical properties of the pellet sintered at 1200 °C were investigated.

2. Methodology

Y and Sc co-doped zirconia (Zr_{0.84}Y_{0.08}Sc_{0.08}O_{1.92} or 4Sc4YSZ) powder was prepared via an all-alkoxide sol-gel method using the following starting reagents: yttrium(III) isopropoxide (Y(OⁱPr)₃, Sigma-Aldrich, 99%), scandium(III) isopropoxide, Sc(OⁱPr)₃, Sigma-Aldrich, 99%), and zirconium(IV) n-butoxide, Zr(OⁿBu)₄, Kojundo, 99%). In an Ar-filled glovebox, stoichiometric amounts of the precursor alkoxide reagents were dissolved in 2-methoxyethanol (Sigma-Aldrich, 99.8%) with processing similar to these references [10], [11]. Using a hotplate, the alkoxide solution was heated at 130 °C under reflux for 15 min with magnetic stirring. A mixture of 1:1 volumetric ratio of deionized water to 2-methoxyethanol was then slowly added to the heated solution with continued heating until a viscous gel formed. The gel was aged in an oven at 150 °C for 30 min and then dried at 180 °C for 4 h. Dried powders were ground for 1 h before it was calcined in air at 600 °C for 2 h. Disc-shape pellets were obtained by uniaxial compression of as-calcined powders at 20 MPa for 3 min followed by sintering at 1200 °C for 5 h in a muffle furnace.

Thermal analysis was performed using a Netzsch STA2500 Regulus thermogravimetric and differential thermal analyzer (TG/DTA) under O₂ gas flow. XRD patterns were obtained at room temperature on a Rigaku High Resolution Smartlab X-ray diffractometer using Cu-Kα radiation (λ = 1.5406 Å) from 2θ range of 20° to 90° with a scan rate of 5°/min. Relative density of sintered pellet was determined using the Archimedes' method. Sintered pellet was characterized for its microstructure using a Hitachi SU-8320 field-emission scanning electron microscope (FE-SEM). With the same FE-SEM equipment, EDS elemental maps were obtained with a Horiba X-maxN 50 mm² window x-ray detector. Conductivity measurements were performed using EIS technique with Biologic VMP-300 Potentiostat/Galvanostat system from 7 MHz to 0.5 Hz from 500 °C to 700 °C at 50 °C interval under laboratory air atmosphere.

3. Results and Discussion

In order to determine the temperature at which unwanted sol-gel by-products can be degraded, the as-synthesized 4Sc4YSZ powders were subjected to TG/DTA testing. From the TG/DTA curve shown in Fig. 1, the first weight loss region with an 11.1% change in weight occurred below 120 °C and it can be attributed to the removal of physisorbed moisture. This also corresponds to the first small endothermic peak in the DTA curve. The second weight loss region occurred in the temperature range of 200-350 °C with around 12.4% change in weight. This corresponds to the degradation of organic compounds and this second region corresponds to the broad exothermic peak at c.a. 280 °C in the DTA curve. Minimal weight loss occurred after 600 °C which can be attributed to residual organic impurities. Hence, 600 °C was used as the calcination temperature prior to pelletizing and sintering.

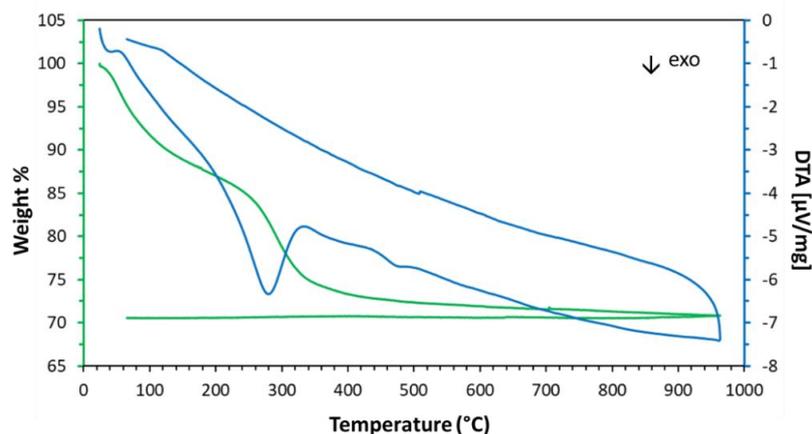


Fig. 1. TGA (green) and DTA (blue) curves of the as-synthesized 4Sc4YSZ under O₂ gas flow.

Fig. 2 shows the XRD patterns of as-calcined and as-sintered 4Sc4YSZ. Even with just after calcination at 600 °C, it was found that all the XRD peaks can already be indexed to the cubic structure with a calculated lattice parameter of 5.13 Å which is in good agreement with the reference lattice parameter for 8YSZ (PDF# 04-015-2373, $a = 5.142$ Å). The estimated grain size according to Scherrer's equation is about 132 Å. Furthermore, no new phase resulted from the doping of 4 mol % Sc₂O₃ as evidenced by the XRD patterns. Upon sintering at 1200 °C, 4Sc4YSZ retained its cubic structure with a calculated lattice parameter of 5.12 Å. The observable peak splitting in the XRD pattern of as-sintered 4Sc4YSZ is associated with the K α 1 and K α 2 doublet. The lattice parameter of as-sintered 4Sc4YSZ is expected to be smaller than 8YSZ since Sc³⁺ has a smaller ionic radius than Y³⁺. Most importantly, this result suggests that co-doping with 4 mol% Sc and 4 mol% Y were able to stabilize the cubic structure of the parent ZrO₂ lattice.

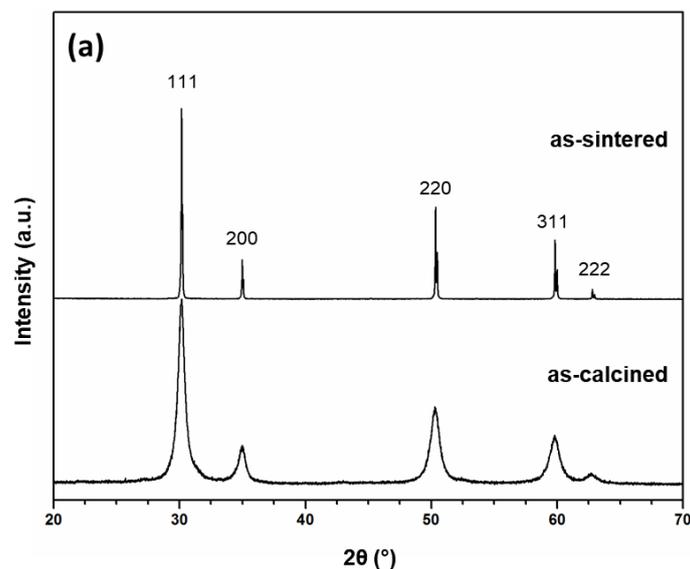


Fig. 2. XRD patterns of as-calcined and as-sintered 4Sc4YSZ.

The sintered pellet showed a relative density of 98.3% with respect to theoretical density. Morphological analysis of the fractured surface of as-sintered 4Sc4YSZ revealed micron-size grains (Fig. 3). Furthermore, large aggregates appeared along with smaller particles (Fig. 4a). EDS elemental map (Fig. 4) shows well-distributed Sc and Y dopants in the ZrO₂ particles. Dark portions in the elemental maps are not voids in the microstructure but they are due to the surface roughness or the difference in heights of the specimen's

surface features.

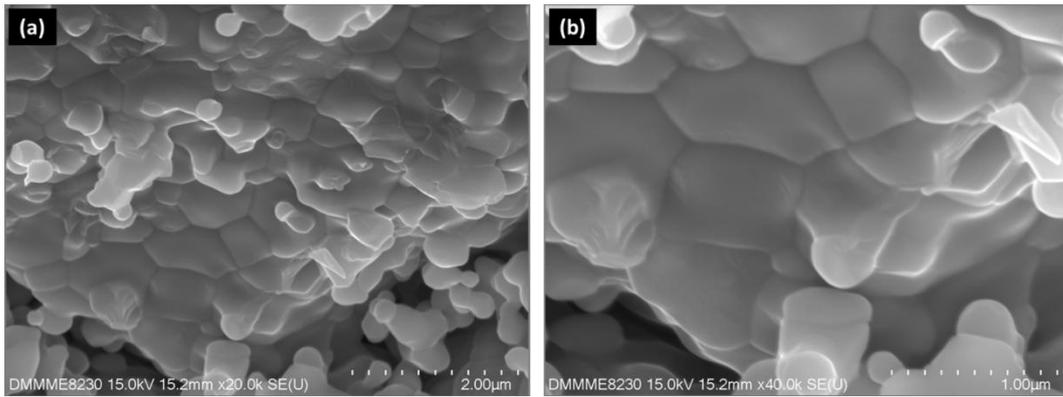


Fig. 3. FE-SEM images of fractured surface of 4Sc4YSZ pellet sintered at 1200 °C for 5 h shown at different magnifications: (a) 20,000x and (b) 40,000x.

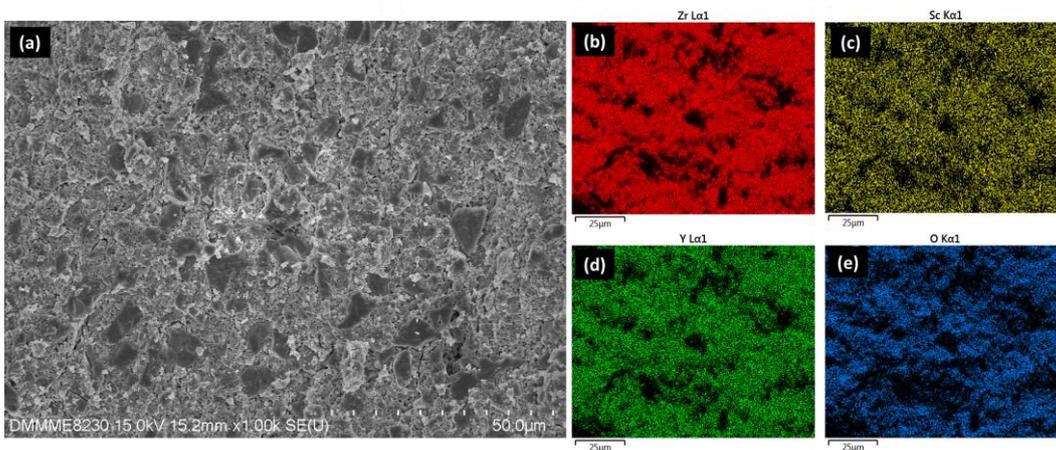


Fig. 4. (a) FE-SEM image at 1,000x magnification of fractured surface of 4Sc4YSZ pellet sintered at 1200 °C for 5 h. Corresponding EDS data of location in (a) showing elemental maps for (b) Zr, (c) Sc, (d) Y and (e) O.

The conductivity of 4Sc4YSZ was determined by measuring its impedance via EIS. Fig. 5a shows a representative impedance result for 4Sc4YSZ in a Nyquist type plot measured at 700 °C. At 700 °C, the grain (bulk) and grain boundary resistance contributions can no longer be resolved. The observed small high-frequency arc part can be attributed to the contribution of the grain boundary resistance while the larger low-frequency arc corresponds to charge transfer resistance at the specimen-electrode interface. It can be said that the nature of the conducting species is ionic due to this impedance arc at the specimen-electrode interface since the electrode is a Pt metal [12]. In other words, there is barrier to the migration of conducting species from the specimen to the Pt electrode.

The total conductivity was determined by fitting an equivalent circuit (inset in Fig. 5a) to the Nyquist plots. In the temperature range of 500 °C to 700 °C, conductivity of 4Sc4YSZ increased with increasing temperature (Fig. 5b) which is indicative of non-metallic conduction behavior. Moreover, an activation energy (E_a) of 1.31 eV (500-650 °C) was calculated. This E_a is a further evidence that the nature of the dominant conducting species is ionic. However, there is an observable change in the Nyquist plot's slope beyond 650 °C and the determination of E_a at temperatures above 650 °C can be a subject of further studies.

A maximum conductivity of 109 mS/cm was achieved at 700 °C which is a magnitude higher than the reported conductivity of pure 8YSZ (

Table 1). Hence, even if the microstructure was not totally densified, the 4Sc4YSZ sintered at 1200 °C showed a promising ionic conductivity compared to the typical 8YSZ electrolyte. Therefore, future studies on the optimization of the sintering condition to obtain dense microstructure can further increase the ionic conductivity of 4Sc4YSZ. It can be said that the co-doping technique is successful in improving the total conductivity of ZrO₂ electrolyte.

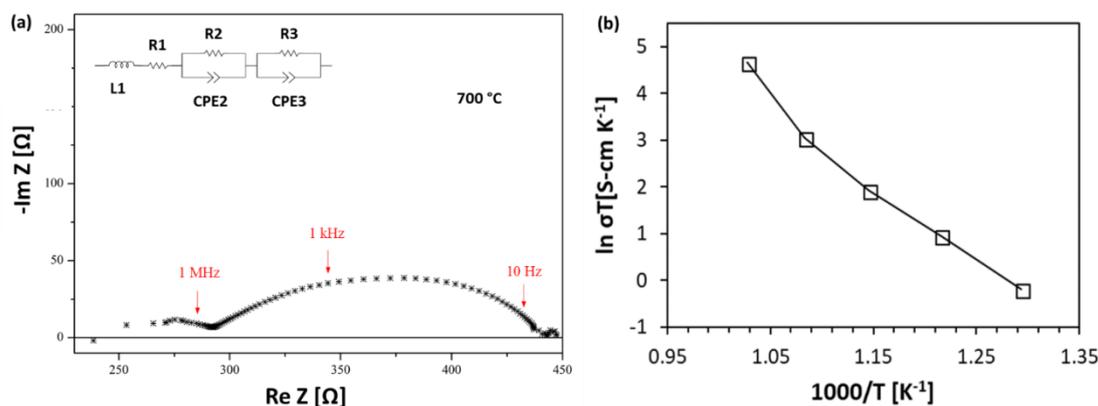


Fig. 5. (a) Nyquist impedance plot of as-sintered 4Sc4YSZ measured at 700 °C. equivalent circuit used to fit the Nyquist plot is shown as inset. (b) Arrhenius type plot of the total conductivity of as-sintered 4Sc4YSZ measured under air atmosphere.

Table 1. Comparison of Conductivity of 4Sc4YSZ, Pure 8YSZ, and Other Electrolytes Prepared Using Co-doping Technique

Material	Method	Sintering condition	Crystal structure	Conductivity [S/cm] at 700 °C	E _a [eV]	Ref
4Sc4YSZ	Sol-gel	1200 °C, 5 h	Cubic	0.109	1.31 (500-650 °C)	This study
8YSZ	Wet milling	1500 °C, 1 h	Cubic	~0.005	1.01 (300-800 °C)	[13]
8YSZ	Commercial	1050 °C, 5 m	Cubic	0.068	0.96 (300-700 °C)	[14]
MgYSZ	Wet milling	1500 °C, 1 h	Cubic	~0.015	0.92 (300-800 °C)	[13]
1Yb10ScSZ	Sol-gel	1550 °C, 5 h	Cubic	0.0063	0.67 (650-800 °C)	[15]

4. Conclusion

The effect on the structure, morphology, and conductivity of Y and Sc co-doped ZrO₂ were investigated. XRD revealed that the co-doping technique is successful in stabilizing the desired cubic structure without formation of new phases. EDS mapping showed the homogeneous distribution of Y and Sc dopants in the parent ZrO₂ lattice. Even if 4Sc4YSZ pellet was not totally densified when just sintered at 1200 °C, a promising conductivity of 109 mS/cm was achieved at 700 °C which is higher than the conductivity of pure 8YSZ electrolyte. A possible higher conductivity values for 4Sc4YSZ can be achieved with further optimization of the sintering condition.

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