Effect of Sintering Conditions on the Microstructure and Electrochemical Properties of 6Scandia 1Ceria co-doped Zirconia (6Sc1CeZr)

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Abstract

The current work studies the effect of sintering conditions on the densification behavior, microstructure, and electrochemical performance of 6 mol% Sc$_2$O$_3$, 1 mol% CeO$_2$ co-doped ZrO$_2$ (6Sc1CeZr) for solid-state electrolyte applications. The physical properties and electrochemical performance of the specimen sintered at different temperatures ranging from 1000 °C to 1700 °C for 6 hours are examined through diffraction, microscopy, and Raman and electrochemical impedance spectroscopy. The activation energy and pre-exponential conductivity factor of the oxygen ions are calculated using a linear fit to the Arrhenius-type conductivity equation. We observe that samples sintered at 1500 °C for 6h show a lower c/a axial ratio for the tetragonal phase, highest relative density, and highest total conductivity among all samples investigated. The higher total conductivity is explained by the formation of a higher symmetric tetragonal phase and the simultaneous existence of the cubic and tetragonal phases (with higher symmetry), supported by the presence of the cerium ions partially replaced zirconium ions' sites.

Keywords: SOFC, Zirconia, 6Sc1CeZr, Ionic conductivity
Introduction

One of society's most significant challenges in engineering is the generation of energy from clean, efficient, reliable, and environmentally friendly sources. Fuel cells are one of the most efficient and effective solutions to this challenge. These electrochemical devices convert the chemical energy of fuel gas into electrical work with no need for combustion. Moreover, fuel cells can also be used for grid-scale renewable energy storage through high-efficiency conversion to chemical energy without CO₂ emissions. Fuel cells offer wide potential applications for electricity generation in residential, vehicular, and industrial settings [1, 2]. Among all types of fuel cells, Solid Oxide Fuel Cells (SOFCs) offer numerous advantages over conventional power generation systems such as high energy density and high efficiency (beyond 60% up to 90% with the addition of heat recovery cycles), no electrical fluctuation, and environmental noise [3].

The electronic current is generated in fuel cells by oxidation of the fuel gas at the anode and oxygen reduction at the cathode. Therefore, the electrical current is made possible by the flow of the ions from the anode to the cathode through the ion conductor membrane. The general mechanism of the current flow is explained via mass transport of oxide ions through the solid ion conductor electrolyte by introducing vacancies into the crystal structure and hopping of the charged species to the vacancies. Thus, ionic conductivity is increased significantly at elevated temperatures where sufficient energy allows ions to hop into and out of charged vacancies [4]. However, high temperatures also introduce thermal stresses, corrosion, increased system cost, and stack durability challenges. Therefore, there has been increased interest in reducing SOFC operating temperatures from the High Temperature (HT-SOFC) regime (800 °C to 1000 °C) down to the so-called Intermediate Temperature (IT-SOFC) regime (500 °C to 700 °C). It has been proposed that IT-SOFC materials could expand applications to large-scale stationary applications and smaller scale portable power/transportation markets [5, 6]. While Yttria-Stabilized Zirconia (YSZ) has been the most investigated membrane material for SOFCs, Scandia-Stabilized Zirconia (ScSZ) has shown almost 3-4 times higher ionic conductivity compared to that of YSZ (ex:10ScSZ (Sc₂O₃)₀.₁₀(ZrO₂)₀.₉₀ to 8YSZ). However, there is still a need to lower the operating temperature and increase the conductivity of scandia doped zirconia (ScSZ) electrolytes. Yashima and Badwal [7, 8] investigated the Sc₂O₃ – ZrO₂ mass system and discovered monoclinic, tetragonal, cubic, metastable tetragonal, and metastable rhombohedral phases exist from a range of 0 < Sc₂O₃ mol% ≤ 25. Of these phases, the cubic fluorite phase at 9.5 mol% Sc₂O₃ and the tetragonal phase (6 to 9 mol% Sc₂O₃) exhibit the highest and second-highest ionic conductivity. Increasing dopant levels has been shown to trigger the formation of the β – rhombohedral structure alongside the cubic phase, which decreases ionic conductivity. A study of ternary systems consisting of Sc₂O₃ – CeO₂ – ZrO₂ demonstrated that the addition of a small amount (≤ 2%) of a third component (here cerium oxide) can stabilize the higher ionic conductivity phases over a wider dopant range of Sc₂O₃. The reaction that creates oxygen vacancies in scandia ceria doped zirconia is expressed in the Kröger-Vink notation below.

\[
Sc₂O₃^{2zrO₂} \rightarrow 2Sc^{zr} + V_0^- + 3O_0^\chi
\]

\[
CeO₂^{zrO₂} \rightarrow Ce^{zr} + 2O_0^\chi
\]
In this case, alloying the zirconia with ceria (with fluorite structure, but higher cation radius) will not result in the creation of additional positively charged vacancies but will facilitate the stability of the cubic structure. The stabilization of the cubic phase arises from applied lattice strain due to the presence of large cerium ions on the host lattice sites. This substitution assists formations of the higher-symmetry cubic phase by lowering the c/a ratio in the tetragonal phase, thus resulting in higher ionic conductivity [9]. Since the cubic fluorite structure attracts the most interest for investigation, numerous studies have been done on the influence of the microstructure and lattice strain on the ionic conductivity of fluorite structures. However, there are still regions that have been only poorly investigated within the tetragonal crystal structures in Sc₂O₃ – CeO₂ – ZrO₂ system. Improved mechanical performance of 6Sc1CeZr comparing to 10Sc1CeZr in addition to the lower production cost due to a reduction in costly Sc₂O₃, make 6Sc1CeZr an attractive candidate for investigation for SOFC applications.

In this work, we explore the crystal structure, microstructure, and total conductivity of 6Sc1CeZr samples (oxide composition (Sc₂O₃)₀.₉₆(CeO₂)₀.₀₁(ZrO₂)₀.₉₄, with the stoichiometry of Sc₀.₁₂Ce₀.₀₁Zr₀.₈₇O₂₋_δ), synthesized at various sintering temperatures to determine optimal processing conditions. We hypothesize that sintered samples below coarsening and at the highest densification temperature will result in the highest measured ionic conductivity by lowering the grain and grain boundary resistivity and increasing the cubic phase conductivity.

**Experimental**

6Sc1CeZr powder was prepared by Daiichi Kigenso Kagaku-Kogyo Company (DKKK, Osaka, Japan). The particle size of the 6Sc1CeZr powder was measured using Polarization Intensity Differential Scattering (PIDS) (L230 Beckman Coulter, U.S.) for as-received powder as well as after wet ball milling in ethanol for 5h at 300 rpm (Fritsch, Germany) using zirconia media. The ceramic slurry then dried at 40 °C for 5h and then at 100 °C overnight. Then powder was compacted and pelletized by uniaxial die pressing (Carver, U.S.) at 150 MPa followed by cold isostatic pressing (CIP) (Autoclave Engineers, U.S.) at 220 MPa. The green pellets were sintered in air at temperatures between 1000 °C and 1650 °C with increments of 100 °C, for 6 hours by the conventional sintering method in a Carbolite box furnace. The samples' density was measured employing the gravimetric buoyancy method using distilled water (T_{Dw}=295 K) as the immersion medium and pycnometer density measurement exploiting helium gas (Ultrapyc 5000, Anton Paar). X-ray diffraction (XRD) patterns were obtained using Bruker D2 Phaser with Cu Kα monochromatic radiation (λ = 1.5418 Å) in 20 scanning range from 10 to 80 degree with a scan step size of 0.01° and counting rate of 1 second per scan step. Crystal domain size was estimated using the Scherrer equation from XRD diffraction peaks using the full width at half maximum (FWHM) of the (111) peaks. Samples were sectioned with a diamond saw (Allied HighTech) and fine polished to 200 nanometers (Buehler). Cross-sectional scanning electron microscopy and Elemental Dispersion Spectroscopy (SEM/EDS) were performed on an FEI Quanta 600 FEG microscope. The Average Grain Intercept method (AGI) was used to determine the grain sizes of the pellets at each sintering condition.
Electrochemical Impedance Spectroscopy (EIS) was performed using an impedance/gain-phase analyzer SI 1260 & electrochemical interface SI 1287 (Solartron, US). EIS was carried out on the samples in the air atmosphere to study the electrochemical properties of sintered samples. Platinum paste (Heraeus, Germany) was screen-printed on the sintered pellets (electrode thickness ≈ 20 µm) and fired at 950 °C for 1 hour as electrodes. The conductivity of the sintered samples was measured in the temperature range from 300 °C to 800 °C from 1MHz to 1Hz. The total conductivity of all samples was determined by x-axis intercept in Nyquist plots obtained from EIS data at high frequency (1 MHz).

Results & Discussion

1. Particle Size Analysis

Figure 1 shows particle size analysis of the initial 6Sc1CeSZ powder as-received from DKKK and after ball-milling, using Polarization Intensity Differential Scattering (PIDS). The purpose of the ball milling was to obtain high density and consequently better conductivity by preparing smaller particles with narrower size distribution. It can be seen that the initial powder's PSA consist of 3 peaks at 10 µm, 30 µm and agglomerates of the size 55 µm, with more than 55% of the particles have a diameter less than 10 µm. After ball milling, PSA shows two peaks with maxima at 300 nm and the second maxima at 3 µm with an overall particle range of 100 nm to 10 µm with no sign of the presence of the agglomeration. The obtained narrow distribution serves the goal of achieving the highest density and packing factor.

![Figure 1. Particle size distribution for 6Sc1CeZr before and after ball milling.](image)

2. Density Measurement

Figure 2 shows the apparent densities versus sintering temperatures. The density graph shows a sigmoidal dependence of the density on sintering temperature with a plateau around 1500 °C, indicating the saturation limit of the densification process. The densification plateau occurrence
depends on several factors such as particle size of the powder (fig. 1), particle packing, heating rate (here 3 °C /min), and sintering atmosphere (air) [10].

It can be observed from figure 2 that upon increasing the sintering temperature from 1000 °C to 1400 °C relative densification increases. Conventionally sintered pellets at 1500 °C and 1600 °C show the highest densification followed by a plateau as expected. Sintering at higher temperatures (T ≥ 1500 °C) resulted in excessive grain growth in pellets derived from the confinement of intermittent pores, mostly at the 3- and 4-grain boundaries interfaces as discovered by electron microscopy (fig. 3).

![Figure 2. Samples’ density, grain size, and pore size as a function of sintering temperature.](image)

### 3. SEM

Figure 3 shows the backscattered and secondary electron cross-sectional SEM to analyze the microstructure of the sintered pellets. Using the mean linear intercept method (ASTM standard E112-13) and ImageJ, the grain size of the SEM micrographs was determined [11].

Politova et al. discussed that the co-doping of the Sc₂O₃−ZrO₂ system is prone to lower achievable density [12]. This phenomenon occurs owing to the slower rate of cation diffusion in this system. Therefore, in SEM micrographs, for all samples, even those sintered at elevated temperatures for a longer time, residual porosity at the 3- and 4-grain boundaries junctions has been observed to some extend [13]. The Energy-dispersive spectroscopy of the samples, as can be found in figure 3, doesn’t show any specific elemental change for all samples and the presence of Zr, O, Sc, and Ce was observed without any sign of segregation on dopants at grain boundaries.
4. XRD

XRD spectra of the sintered pellets at 1000 °C to 1650 °C for 6 hours were collected at room temperature and presented in figure 4. The diffraction peaks were characterized using monochromated Cu Kα radiation with wavelength $\lambda = 1.5418$ Å. The lattice constant was calculated from the XRD peaks using the Rietveld method implemented with GSAS-II software [14], and average crystallite size was determined using the Scherrer equation:

$$\tau = \frac{\kappa \lambda}{\beta \cos \theta}$$

(1)

Where $\tau$ is the mean size of the ordered (crystalline) domains, which may be smaller or equal to the grain size, which may be smaller or equal to the particle size, $\kappa$ is shape factor (typically 0.94), $\lambda$ is the wavelength of radiation, $\beta$ is the line broadening at half the maximum intensity (FWHM), $\theta$ Bragg's angle [15, 16, 17].

To do so, a Gaussian function was fit to the high-intensity peaks of (111). The calculated crystallize size and the lattice parameter can be found in table 1.
From the XRD patterns (fig. 5) and Raman spectroscopy data (fig. 6), it can be observed that 6 mol% of Sc$_2$O$_3$ couldn't fully stabilize the zirconia structure to form and maintain the cubic fluorite crystal structure. Depending on sintering temperature and time, three phases of cubic, tetragonal and monoclinic were detected. In samples sintered at higher temperature ($T > 1500 \, ^\circ C$) for 6 hours, the minority monoclinic phase has been detected (fig. 5).

Table 1. Calculated lattice parameters and crystallite size from XRD data by Rietveld refinement.

| Sintering Temperature [°C] | Lattice Parameter, c [Å] | Lattice Parameter, a [Å] | Crystallite Size [nm] | $c/a$  | XRD analysis |
|---------------------------|--------------------------|--------------------------|-----------------------|-------|--------------|
| 1650                      | 5.115                    | 3.651                    | 89                    | 1.401 | t + c + [m]  |
| 1600                      | 5.113                    | 3.597                    | 82                    | 1.421 | t + c        |
| 1500                      | 5.111                    | 3.593                    | 77                    | 1.421 | t + c        |
| 1400                      | 5.109                    | 3.595                    | 75                    | 1.419 | t + c        |
| 1300                      | 5.106                    | 3.597                    | 72                    | 1.415 | t            |
| 1200                      | 5.105                    | 3.593                    | 65                    | 1.421 | t            |
| 1100                      | 5.105                    | 3.592                    | 51                    | 1.422 | t            |
| 1000                      | 5.104                    | 3.593                    | 28                    | 1.422 | t            |
Figure 5. XRD spectra of the first two peaks of sample sintered at 1650 °C with the corresponding phases indicates the simultaneous presence of cubic, tetragonal and monoclinic phases.

The monoclinic phase formation depends on the primary sample preparation methods, the sintering conditions, and even following mechanical treatments such as surface polishing/grinding [18]. Using Rietveld refinement, the volume fraction of the monoclinic phase was calculated to be in the range of $X_m < 7\%$. 
Kim observed that the degree of tetragonality of the cell (c/a ratio) plays a crucial role in the phase transition in zirconia systems in a way that ZrO\textsubscript{2} solid solution stability increase by a decrease in tetragonality toward unity and vice versa [19]. Adding less than 2% of CeO\textsubscript{2} brings higher symmetry to the Sc\textsubscript{2}O\textsubscript{3}−ZrO\textsubscript{2} system. The ionic radii of Zr\textsuperscript{4+}, Ce\textsuperscript{4+}, and Sc\textsuperscript{3+} are 84, 111, and 87 pm. The presence of a small amount of Ce\textsuperscript{4+} dopant will decrease in c and increase in a = b lattice parameter in a way that contributes to the stabilization of the unit cell. Cubic and tetragonal zirconia have similar XRD patterns, making it difficult to determine the phase assembly only by exploring XRD data. To attain a better understanding of the phase presence and phase transition, Raman spectroscopy was utilized. Figure 6 represents the Raman spectra with cubic phase indicated by 620 cm\textsuperscript{-1} peak and tetragonal peaks at lower wavenumbers, which is in good agreement with the literature. In samples sintered at 1650 °C for 6 hours, a trace of monoclinic phase has been detected, indicating the formation of the Baddeleyite phase [20, 21, 22].
5. EIS

EIS data could be fitted to semicircles corresponding to mass transport and ionic conductivity through the grains, grain-boundary, and electrodes effect at high, intermediate, and low frequencies. It has been proven that a significant inductive load effect resulted from the leads and instrument induction always presents in high-frequency data points. The main transport properties of the ion conductor membranes are represented in the high-frequency regime of the EIS data. Therefore, it is crucial to subtract the inductive load effect from the obtained data to eliminate the instrumentation and leads resistance [23].

This inductance appears as an imaginary part of the impedance data in the positive direction of the imaginary part of the impedance axis (direction), as shown in fig. 7. It is noteworthy that, unlike the samples' behavior, there is a non-considerable dependence of inductance on temperature. At low temperatures, the effect of the inductance is not effective although it is present, but in high temperatures, the inductance effect is obvious as the highest frequency data points lying below the x-axis (fig. 7-center).

The fitting in this manuscript is restricted to the high-frequency regime of the impedance spectra after subtracting the lead inductance. Figure 8 shows the impedance spectra of the 6Sc1CeZr sintered at 1500 °C for 6 hours obtained over the frequency range of 1MHz to 1Hz in the temperature range from 700 °C to 800 °C.

Figure 8 compares the impedance spectra for the sample acquired at 800 °C. The sample sintered at 1500 °C for 6H shows the least resistance among all other samples. As can be seen, the grain, grain boundary, and total resistivity have analogous behavior. Sample 1500 °C exhibit the best electrical property among others. This high electrical conductivity is attributed to the high achieved relative density and most minuscule contribution of grain boundary resistivity to the total resistivity as sintering temperature and initial sample preparation techniques. However, the bulk resistivity is not significantly dependent on grain size and sintering conditions, while two semicircles were observed in the low-temperature regime of the impedance plots. The high-frequency arc corresponds to the grain (bulk) resistance, and the
intermediate frequency semicircle corresponds to the grain boundary resistance component.

![Nyquist plot of EIS data measured from 700 °C to 800 °C on sample sintered at 1500 °C exhibiting the highest conductivity among all prepared samples.](image)

Figure 8. Nyquist plot of EIS data measured from 700 °C to 800 °C on sample sintered at 1500 °C exhibiting the highest conductivity among all prepared samples.

It is well known that the microstructure influences the total electrical conductivity. Figure 8 shows the total conductivity of the samples over the entire measured temperature range, determined by extrapolation of the data to the $Z'$ (real part) in the high-frequency regime with subtracting the lead impedance. The data points were fit to an Arrhenius type conductivity equation:

$$\sigma = \frac{\sigma_0}{T} \exp \left( - \frac{E_a}{k_B T} \right)$$

(2)

Where $\sigma_0$ is the pre-exponential factor in S cm$^{-1}$ K, $T$ is temperature, $E_a$ is activation energy, and $k_B$ is Boltzmann constant. In low densified samples, an increased number of pores maintained due to the lower diffusion rate required for sintering along the grain boundaries presumably has resulted in a decrease in total conductivity from 1000 °C to 1300 °C.
Table 2 Calculated activation energy and pre-exponential factor of the sintered samples obtained from linear fit to the conductivity data using conductivity equation

| Sintering temperature | $E_a$ (eV) | $\sigma_0$ (Scm$^{-1}$K$^{-1}$) |
|----------------------|------------|---------------------------------|
| 1650 °C              | 0.68       | 1.274 x 10$^3$                  |
| 1500 °C              | 0.61       | 1.224 x 10$^3$                  |
| 1400 °C              | 0.58       | 5.324 x 10$^3$                  |
| 1100 °C              | 0.53       | 8.103 x 10$^3$                  |
| 1000 °C              | 0.57       | 2.344 x 10$^3$                  |

Figure 8 shows that for all samples sintered from 1000 °C to 1500 °C the total conductivity increased. Samples sintered at 1500 °C achieved near theoretical density without excessive coarsening and this sample also exhibits the highest conductivity, while conductivity slightly decreased for samples sintered at higher temperatures than 1500 °C. These samples show an almost identical density to that of specimens sintered at 1500 °C but with larger grain sizes. Therefore, it can be concluded that samples sintered at 1400 °C and 1500 °C show the highest conductivity for dwell time of 6 hours. The difference in the conductivity values was explained by the grain size and porosity analysis. The sample sintered at 1500 °C, has the highest grain size but almost similar (in the same range) to the samples sintered at lower temperatures in the densification region of the density plot (fig. 2), while specimens sintered at 1600 °C and above, by reaching the density plateau, the densification process is stopped and coarsening happened, leading the formation of huge trapped pores at the 3 and 4 border grain boundaries (for instance,
sample sintered at 1650 °C, has pores with the pore size of almost 1.2 μm). Thus, the high conductivity of the samples sintered at 1500 °C is attributed to the large grain size, and a quite low pore sizes at the final stage of densification process, before coarsening happens. Therefore, it is noted that the total conductivity of the 6Sc1CeZr, increased to almost ln(σT)=3 [S.cm-1.K] where the grainsize reached 5.45 μm. For samples sintered at 1650 °C, it seems that the grain growth and increase in the grain and pore sizes, no longer increase the ionic conductivity of the samples and there should be scattering of ions at the grain boundaries, causing the reduction in the measured conductivity.

**Conclusions**

The effect of the microstructure of 6 mol% scandia, 1 mol% ceria co-doped zirconia was investigated by different physical and electrochemical characterization methods under controlled sintering temperature. It is found that the sample sintered at 1500 °C shows the best total electronic conductivity, which is predominantly related to the density and sensitivity to the grain size of the electrolyte. The total conductivity is influenced by both intergranular and intragranular conductivity in the electrolyte. Therefore, microstructures fully densified with suitable grain sizes are essential prerequisites to achieving the best performance and efficiency for solid-state ionic conductors.

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