Fabrication and electrochemical characterization of SOFC single cell with 6Yb4ScSZ electrolyte powder by tape-casting and co-sintering

Hyeon-Jong JEON, Kyeong-Joon KIM, Min Young KIM, Seung-Woo CHOI, Moo Sung LEE,* Mi Young OH** and Ho-Sung KIM†

Korea Institute of Industrial Technology (KITECH), 6, Cheondan-gwagiro 208-gil, Buk-gu, Gwangju 500–480, Republic of Korea
†Chonnam National University, 300, Tonghong-Dong, Buk-gu, Gwangju 500–757, Republic of Korea
**R&D Education Center for Fuel Cell Materials & Systems, Chonbuk National University, Jeonju 561–756, Republic of Korea

Nanocrystalline Yb-doped scandia-stabilized zirconia (6Yb4ScSZ) powders are prepared using co-precipitation process. The effects of calcination treatments on factors such as phase evolution, crystallite size, and specific surface area are investigated. The synthesized electrolyte powders have a high specific area of 25 m²/g, nanocrystalline size of 17 nm and ionic conductivity of 0.7 S cm⁻¹ at 800°C, which is 2.3 times higher than that of the 8 mol% ScSZ electrolyte. The electrolyte powder layer consists of nanocrystalline 6Yb4ScSZ powders calcined at 850°C, is fabricated by tape casting and co-sintering. The open-circuit voltage of the SOFC single cell is approximately 1.07 V at 800°C, indicating negligible leakage of fuel through the electrolyte layer. As a result, power density of 1.30 W cm⁻² is obtained at 2.0 A cm⁻² and 800°C due to the drastic reduction of ohmic resistance in the SOFC cell.

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1. Introduction

Solid oxide fuel cell (SOFC) is generally composed of three components: an electrolyte (8-mol% Y₂O₃-stabilized ZrO₂ [YSZ]), an anode (Ni/YSZ cermet), and a cathode (perovskite based on LaSrMnO₃ [LSM]). The SOFC is conventionally operated at high temperatures between 900 and 1000°C due to the low ionic conductivity of YSZ below 800°C. However, high operating temperatures lead to serious problems such as physical and chemical degradation of component materials in the SOFC.

Therefore, the SOFC must be operated at intermediate temperatures (ITs) below 800°C. To accomplish this, two different approaches have been taken: (a) the development of an electrolyte with greater ionic conductivity than YSZ, even at low temperatures, and (b) the reduction of the thickness of the electrolyte layer (e.g., less than 10 µm).

In general, oxygen ionic conductors such as YSZ and 1Ce10ScSZ, 11ScSZ used in SOFC single cell are applied to the anode and cathode as well as the electrolyte to provide a reaction site for triple-phase boundaries and a path of ionic conductivity. Scandia stabilized zirconia (ScSZ) electrolyte shows highest conductivity among all zirconia-based electrolytes and hence provides a unique opportunity of lowering the operating temperature of SOFC. However, ScSZ-based electrolyte has a higher cost than any other currently available stabilized zirconia electrolytes. It is recommended that Yb and Sc-doped stabilized zirconia electrolytes should be developed to reduce the fabrication cost of cell and stack for IT-SOFC, keeping the high ionic conductivity of ScSZ solid electrolyte and the high power density of single cell.

Many methods have been used to synthesize zirconia-based electrolyte powders, including sol-gel process, co-precipitation, mechanical alloying, and spray pyrolysis. However, the chemical synthesis of 6Yb10ScSZ as electrolyte materials has not been recognized. Among the various synthesis processes, wet-chemical methods such as co-precipitation processes have significant advantages including lower cost, the production of nanocrystalline powders, and the sintering activity of electrolyte over conventional solid-state reactions.

The present studies were conducted to investigate the fabrication and electrochemical characterization of 6Yb4ScSZ electrolyte powders prepared via co-precipitation process. The crystal structure, crystallite size, surface area, and morphology of the synthesized powders were investigated via XRD, BET and SEM. Moreover, thin electrolyte film layers of less than 10 µm were fabricated to reduce the electrical resistance of the synthesized 6Yb4ScSZ powder. Finally, the SOFC single cell using the synthesized 6Yb4ScSZ powders was fabricated by tape casting and co-sintering. Electrochemical evaluation of the SOFC single cell, including measurements of power density and impedance, were also conducted.

2. Experiment

2.1 Synthesis and characterization of 6Yb4ScSZ powders

6 mol% ytterbium and 4 mol% scandia-doped zirconia (6Yb4ScSZ) powders were synthesized via co-precipitation...
The general procedure for the synthesis of 6Yb4ScSZ powder is schematically shown in Fig. 1. Zirconium oxychloride (JUNSEI, Japan), Ytterbium nitrate (Aldrich, USA), and scandium nitrate (Beyond Chem, China) were used as the starting materials for the powders. These precursors were first dissolved in a fixed quantity of distilled water by stirring at room temperature. From this mixture solution, the Yb-doped Sc2O3–ZrO3 solid solution was precipitated by addition of ammonium hydroxide, which brought the pH value of the solution to around pH 9–10 during the chemical precipitation. The wet precipitation materials of the reactor were then matured at room temperature for 24 h without ammonia addition or pH control. The wet precipitation materials were collected by repeatedly filtering and washing through filter paper with deionized water and absolute ethanol to remove the free water and other impurities. The as-synthesized powders were then dried overnight in an oven at 110°C in air and were additionally calcined at different sintering temperatures, 500–1500°C for 2 h.

First of all, the thermal characteristics of the as-synthesized powders were analyzed using thermal analysis systems DSC (DSC823, Mettler Toledo, Switzerland) and TGA (TGA/SDTA851, Mettler Toledo, Switzerland). The as-synthesized powders were heated to 600 and 1200°C at a heating rate of 10°C min⁻¹, respectively.

The crystallite structures of the powder samples were identified at room temperature using an X-ray diffractometer (XPert Pro, PANalytical, Netherlands), employing CuKα radiation (λ = 1.5406 Å). The crystal system such as lattice parameters, crystal size, crystal volume, etc. was estimated according to the Rietveld refinement method.

The specific surface areas of the powders were characterized using the BET method (BET, ASAP2020, Micrometrics, USA). Moreover, the microstructure of the SOFC single cell was observed via field emission scanning electron microscopy (FESEM, HITACHI S-4700, Japan).

The electrical conductivities of the synthesized electrolyte powders were measured at temperature within the range of 500–900°C using the two-probe method and an oven cell (Keithley 2182, Neo-science, Korea), and the electrical conductivity was calculated as follows:

\[ \sigma = \frac{L}{(A \times R)} \]  

Where \( L \) is the length of the sample sheet, \( A \) is the area of the sample, and \( R \) is the ohmic resistance determined by AC impedance. In here, the specimen of pellet was fabricated by pressing in disc mold at 60 MPa for 20 min and then sintered at 1400°C for 10 h and then the pellet was prepared as specimen size of 80 mm of length, 10 mm of wide and 30 mm thickness for fixing between the platinum plates in the device of conducting measurement. Meanwhile, to compare with the synthesized 6Yb4ScSZ powder, the electrical conductivities of commercial 6Yb4ScSZ powder and YSZ were also measured by the same test method.

2.2 Fabrication process of SOFC single cell

The SOFC single cell of coin-type was designed with a shape having 24 mm of diameter and 11 mm of thickness as overall size, which is composed of an anode-support (NiO, YSZ) of 1.0 mm, an anode active layer (NiO, YSZ) of 20 μm, thin-film electrolyte (6Yb4ScSZ) of 8 μm and a cathode layer (LSM, YSZ) of 20 μm. Figure 2 illustrates the schematic fabrication process of the SOFC single cell composed of anode-supported electrolyte and cathode. The synthesized 6Yb4ScSZ powders, which were sieved for a certain size, mixed with a modifier, a binder, and a solvent (ethanol and toluene) as a percentage to prepare slurry for tape casting. A typical slurry mixture is about 30 to 35 wt% electrolyte powder and 20 to 24 wt% binder solution including modifier and solvents. Ball milling was conducted for 24 h to prepare
homogeneous slurry compositions. After ball milling, the slurry was coated on a PET film using a tape-casting machine at a maximum speed of 1.2 m min$^{-1}$ at 80°C. The compositions of the anode support and anode active layer were derived from a previous paper. Both of the anode films were also fabricated under the same conditions as the electrolyte layer in the tape casting process. The anode-supported electrolyte was fabricated by stacking and laminating 40–60 sheets of the 40–μm thick anode film, 1 sheet of the anode active film of 20–30 μm and 1 sheet of the electrolyte film of 8 μm. This laminating process was carried out at 80°C for 20 min under a pressure of 400 kgf cm$^{-2}$. The laminated anode-supported electrolyte films were co-sintered at 1400°C for 10 h.

The cathode layer was coated on the 6Yb4ScSZ electrolyte layer by screen printing using the paste mixture of powders and additives composed of LSM (La$_0.7$Sr$_0.3$MnO$_3$, Praxair, USA) and binder solution, followed by a final sintering stage at 1100°C for 3 h for SOFC single cell.

2.3 Electrochemical evaluation of SOFC single cell

A single cell of a coin-type was successfully installed in the SOFC evaluation system (Model FC5300, Chino Corp., Japan) to evaluate the power density and impedance. Before the test, the sealing status of the SOFC single cell was identified by checking the open circuit voltage (OCV). The current–voltage (I–V) characteristics were measured using an electric load (Model PLZ664WA, KIKUSUI, Japan) in the range of 700 to 800°C in humidified hydrogen (200 cm$^3$ min$^{-1}$ with 3 wt% H$_2$O) with a sufficient supply condition of fuel without considering fuel utilization for the anode side and in dry air (300 cm$^3$ min$^{-1}$) for the cathode side. Impedance evaluations of the SOFC single cell were also carried out under OCV conditions using AC impedance spectroscopy (Solartron 1260), with a frequency range of 0.1 Hz to 100 kHz and signal amplitude of 100 mV.

3. Results and discussion

3.1 Synthesis and properties of nanocrystalline 6Yb4ScSZ electrolyte powders

In order to investigate the thermal characteristics of the as-synthesized powders before XRD analysis, TGA and DSC analysis were carried out, as shown in Fig. 3. The bold line shows the curve of the TGA analysis, indicating the ratio of weight loss with heating temperature and the dotted line shows the curve of the DSC analysis, indicating an endothermic peak and exothermic peak. The endothermic peak corresponding weight loss at 120°C can be attributed to the decomposition of hydroxide and nitrate, including moisture and organic materials. The total weight loss of the solid precursor was about 18.6% at 600°C. Here, the exothermic peak, which may be estimated as the activation point for the crystallization of the ceramic precursor powders, was observed at 420°C. Therefore, the calcination treatment of as-synthesized powders was performed to review the behavior of powder crystal system at the temperature range of 500 to 1500°C. Figure 4 shows the XRD patterns of the as-synthesized powders and the powders calcined at different temperatures. As shown in the figure, the cubic structure (Fm-3m) was observed at all calcination temperature. The intensity and width of the main peaks such as (111), (022), and (113) simultaneously grew and narrowed with increase in the calcination temperature, with the peaks almost stabilized at above 800°C. Table 1 summarizes the detailed information of lattice constants and crystallite sizes of the 6Yb4ScSZ powders determined by XRD analysis according to the calcination temperature. It was found that the lattice constant showed almost identical value of 5.10707 to 5.10916 Å.

![Fig. 3. TGA and DSC curve of as-synthesized 6Yb4ScSZ electrolyte powder.](image)

![Fig. 4. XRD patterns of the electrolyte 6Yb4ScSZ powders.](image)

| Table 1. Physical characteristics of 6Yb4ScSZ powders calculated from XRD patterns |
| --- | --- | --- |
| Calcination temperature (°C) | Lattice constant (Å) | Crystalline size $d_{XRD}$ (nm) |
| 500 | 5.10773 | 7 |
| 600 | 5.10707 | 8 |
| 700 | 5.10784 | 12 |
| 800 | 5.10838 | 17 |
| 900 | 5.10871 | 36 |
| 1000 | 5.10857 | 51 |
| 1100 | 5.10855 | 81 |
| 1200 | 5.10911 | 154 |
| 1300 | 5.10902 | 204 |
| 1400 | 5.10916 | 176 |
| 1500 | 5.10879 | 147 |
on all samples, forming the cubic structure of 6Yb4ScSZ powders. The crystallite size was calculated according to the Rietveld refinement method. The crystallites, which were detected for all samples, increased gradually from 7 to 81 nm in the range of 500 to 1100°C, and finally grew rapidly to 154 nm at 1200°C, showing the maximum crystalline size of 204 nm at 1300°C and after that, it just tend to be down again.

Figure 5 shows the SEM images of 6Yb4ScSZ powder prepared by calcination at the different temperature of 800, 850, 900 and 1000°C. As shown in the figure, the powders exhibited well-crystallized nanocrystallites with a homogeneous, spherical and primary particle size of about 20–60 nm, which is similar to the crystallite size obtained from XRD analysis. In here, as the calcination temperature increased from 850 to 900°C, the particle size of powders suddenly increased from 20 to 50 nm. Therefore, the nanocrystalline powders calcined at 850°C were used for the fabrication of thin film electrolyte layer. The specific surface areas were measured using BET analysis to obtain information about the granularity of the synthesized powder. As a result, the specific surface area of the as-synthesized powders was 250 m² g⁻¹, with the value decreasing to 19 m² g⁻¹ at the calcination temperature of 850°C. Thus, nanocrystalline 6Yb4ScSZ powders with less grain growth and high specific surface area could be fabricated by our chemical synthesis process.

Figure 6 shows the cross section of pellet specimens using commercial 6Yb4ScSZ powder (a, b) and the synthesized 6Yb4ScSZ powder (c, d), respectively. The pellet specimen with the synthesized 6Yb4ScSZ powder showed denser microstructure and thinner impurities layer of grain boundary as compared with the commercial 6Yb4ScSZ powder as shown in the figure, indicating the high ionic path between grains.

Figure 7 shows the electrical conductivity of the synthesized 6Yb4ScSZ powder prepared via co-precipitation process, compared to the conductivity of the commercial 6Yb4ScSZ and YSZ powders. The ohmic resistance of the 6Yb4ScSZ powders was measured using the AC impedance method at a range of 500–900°C and then the electrical conductivities were 0.07, 0.10 and 0.13 S cm⁻¹ at 800, 850 and 900°C, respectively. On the other hand, the conductivity of commercial YSZ and 6Yb4ScSZ powders were 0.03 and 0.05 S cm⁻¹ at 800°C, respectively. Therefore, it is confirmed that the synthesized powders showed a great ionic conductivity more than commercial material of identical chemical composition due to the nanocrystalline 6Yb4ScSZ powder, which made a dense structure of the electrolyte without impurities layer of grain boundary.

3.2 Fabrication and electrochemical evaluation of SOFC single cell

In order to evaluate the performance of an SOFC single cell using the synthesized electrolyte powder calcined at 850°C, thin electrolyte film was prepared by tape-casting process and then applied to the SOFC single cell as stated earlier. Figure 8(a) showed cross-section image of the SOFC single cell assembly using the synthesized 6Yb4ScSZ powders. Moreover, the cross-sectional morphologies of the electrolyte layer were observed to investigate the microstructure as shown in the Fig. 8(b). In here,
thin electrolyte layer of 5 μm was successfully observed in the SOFC single cells. Both the anode and cathode layers adhered well to the electrolyte layer with a tiny closed-pore structure and the active layer showed a microstructure with the effective formation of the three-phase boundary. However, Fig 8(b) showed that the electrolyte layer is not perfectly dense and uniform due to the agglomeration of powders in the slurry mixture for the tape-casting process. Therefore, it is recommended that the nano powder mixture with a high surface area should be either dispersed more sufficiently or decrease the surface area of powder to be applied on the PET film by the tape-casting process. As expected from the previous results, the electrolyte film layer showed a continuous and crack-free morphology in the SOFC single cell.

Electrochemical tests to determine the I-V curve and the impedance of the SOFC single cell were performed at 700, 750 and 800°C, respectively. Figure 9 shows the I-V characteristics of the SOFC single cell. The single cell had an OCV value of approximately 1.07–1.09 V, which is close to the theoretical value calculated using the Nernst equation. However, a high OCV value indicated that a dense structure was well formed in the electrolyte layer without gas leak, and that the fuel gas leakage was negligible for the SOFC single cell. This result indicates that electrolyte layers using nano powders with a high surface area can be produced by a tape-casting process without warpage or cracks.

As a result of the test, the power density of the SOFC single cell was 0.8, 1.0 and 1.3 W cm⁻² at 2.0 A cm⁻², 700, 750 and 800°C, respectively. Figure 10 shows the impedance characteristics of SOFC single cell. The Ohmic resistances were determined to be 0.08, 0.07, 0.06 Ω cm² at 700, 750 and 800°C respectively. The Ohmic resistances were determined to be 0.08, 0.07, 0.06 Ω cm² at 700, 750 and 800°C respectively, in which they showed little differences with the operating temperature. However, the polarization resistances were 0.9, 0.6 and 0.4 Ω cm² at 700, 750 and 800°C respectively. Therefore, this SOFC single cell was assumed to exhibit good power density due to the low Ohmic resistance as compared with that previously reported for 1Ce10ScSZ electrolyte.\(^{15}\)

4. Conclusions

Nanocrystalline 6Yb₄ScSZ electrolyte powders were successfully prepared via co-precipitation process. These powders were then utilized to fabricate the anode-supported electrolyte of an SOFC single cell. 6Yb₄ScSZ electrolyte powders with spherical shapes, high surface area, and nanocrystalline structures were prepared using the starting materials of ytterbium nitrate, zirconium oxychloride, and scandium nitrate. All of the 6Yb₄ScSZ powders, the calcined powders, showed a typical cubic structure. Calcination treatment of the as-synthesized 6Yb₄ScSZ powders showed some good effects such as a high specific area, nanocrystalline size and a high conductivity. Moreover, nanocrystalline 6Yb₄ScSZ powder with less grain growth and high specific surface area could be fabricated by the calcination treatment at 850°C.

The tape-casting process using the nanocrystalline 6Yb₄ScSZ electrolyte powder was successfully applied to the fabrication of an anode-supported electrolyte for an SOFC single cell. Characterization of the SOFC single cell demonstrated that the 6Yb₄ScSZ electrolyte film was crack-free and dense, with good adhesion occurring between the anode and the cathode. The power density of the SOFC single cell with the 6Yb₄ScSZ electrolyte was about 1.3 W cm⁻² at 2.0 A cm⁻² and 800°C. This value suggests that our tape-casting with thin film and co-sintering technique using the nanocrystalline 6Yb₄ScSZ electrolyte powder has the potential for application in IT-SOFCs fabrication.

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References