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Short Communication

High-performance thin film solid oxide fuel cells with scandia-stabilized zirconia (ScSZ) thin film electrolyte



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ABSTRACT

A high-performance thin film solid oxide fuel cell (TF-SOFC) was fabricated using a scandia-stabilized zirconia (ScSZ) thin film electrolyte deposited on an anodized aluminum oxide supporting structure. The crystallinity and ionic conductivity were evaluated of the ScSZ film that was deposited by sputtering at room temperature. No phase transformation of ScSZ film was observed during heating to the TF-SOFC operation temperature of 500 °C. The oxygen ion conductivity of the ScSZ film was determined to be 0.00024 S/cm at 500 °C on polycrystalline Al₂O₃. The maximum power density of the TF-SOFC including the 280 nm thick ScSZ thin film electrolyte was measured to be 227 mW/cm² at 500 °C.

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Introduction

Solid oxide fuel cells (SOFCs) are considered to be promising power generation devices due to various advantages

including high efficiency and fuel flexibility [1–13]. Due to the poor ionic conductivity of electrolytes, SOFCs are generally operated at high temperatures (>800 °C). However, such high operation temperatures cause problems such as thermal degradation and material selection, thereby obstructing the

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commercialization of SOFCs. Therefore, thin film SOFCs (TF-SOFCs) fabricated by using thin film techniques have been investigated to lower the operation temperatures [3–7,10]. Typical TF-SOFCs are composed of nanometer-scale electrodes and electrolytes to compensate for their poor ionic conductivity at low temperatures (350–550 °C) [3–7,10]. Among TF-SOFCs, nanoporous anodized aluminum oxide (AAO)-based TF-SOFCs have been studied in which membrane electrode assemblies (MEAs) are fabricated on anode supporting structures to secure mechanical stability and large-area fabrication capability [3,5–7,10]. The use of AAO as the supporting microstructure for the MEA allows the preparation of thin, mechanically stable, dense electrolytes of high ionic conductivity and minimum thickness to maximize performance.

Stabilized zirconia, prepared by adding aliovalent dopants such as Y or Sc to zirconia, has high oxygen ion conductivity and superior chemical stability, making it the most typical oxygen ion conducting electrolyte, not only for SOFCs but also for solid oxide electrolyzers, oxygen pumps, and oxygen sensors [1–10,14,15]. Among the various stabilized zirconia, scandia-stabilized zirconia (ScSZ) of fluorite phase is known to have high oxygen ion conductivity because of the similar ionic radii of the Sc³⁺ dopant ion (0.87 Å) and the Zr⁴⁺ host ion (0.84 Å); Sc³⁺ leads to less steric blocking than other dopants such as Y³⁺ (0.94 Å) [16–21]. However, the similar ionic radii of Sc³⁺ and Zr⁴⁺ allows seven different types of phases owing to the low barrier to the redistribution of dopants, significantly affecting the properties of ScSZ [18,20,22]. Many studies on the properties of ScSZ films prepared by various processes have been conducted to allow their use as electrolyte materials for SOFCs [16–23].

In this study, we deposited ScSZ films at room temperature by a sputtering method, and investigated the crystallinity and ionic conductivity of the resulting ScSZ films. Also, for the first time, we applied ScSZ as the thin film electrolyte in an AAO-based TF-SOFC and measured the electrochemical characteristics. The results may help to widen the applications of ScSZ films and TF-SOFCs for various applications.

Experimental

To fabricate ScSZ thin films, a commercial ceramic ScSZ target (6.8 mol% Sc₂O₃, Adventech, Korea) and a sputtering system equipped with a radio frequency (RF) power source were used. Crystal structures of as-deposited and heat-treated ScSZ films were investigated by glancing-mode X-ray diffraction (XRD) using an X'pert Pro (PANalytical, Netherlands) with a Cu K α source. Electrochemical characterization of the ScSZ film and fuel cell performance measurements were conducted by using a custom-built station on a temperature-controlled heating stage. Pt pads (4 × 0.5 mm²) with a thickness of approximately 100 nm were deposited on the ScSZ films with a 300 μ m gap in a planar fashion by the DC magnetron sputtering technique. To characterize the ScSZ films, electrochemical impedance spectroscopy (EIS) measurements were performed at 450–550 °C by using potentiostats (FAS2, Gamry Instruments Inc., USA).

To prepare a MEA, a commercial AAO template was used as a substrate [5–7,10]. A 300 nm Pt anode was sputtered onto a bare AAO by using direct current (DC) sputtering with the power of 200 W under the pressure or 0.67 Pa (Ar). The ScSZ thin film electrolyte was sputtered onto the Pt anode by using radio frequency sputtering with the power of 50 W under 0.67 Pa (Ar/O₂ (3% O₂) gas). Finally, a 150 nm-thick, Pt cathode with 1 mm [2] area was sputtered onto the ScSZ thin film electrolyte by DC sputtering (100 W, 12 Pa). A glass sealant paste (CP4010, Aremco, USA) was used to ensure gas tightness. An Ag paste (597-A, Aremco, USA) and Ag wire were used for anode current collection. Stainless steel micro-probe (Lenno, Korea) was used for cathode current collection [24]. The cross-sectional structure of the TF-SOFC was evaluated by focused ion beam scanning electron microscopy (FIB-SEM, Quanta3D, FEI, USA). The surface morphology of the cathode and electrolyte were evaluated by field emission scanning electron microscopy (FESEM, SUPRA55VP, Carl-Zeiss, Germany) and atomic force microscopy (AFM, Park system, Korea). EIS and performance measurements of the TF-SOFC were conducted at 500 °C and 550 °C by Solartron 1287/1260 (Solartron, UK).

Results and discussion

Before they were applied as thin film electrolytes for TF-SOFCs, 6.7 mol% Sc₂O₃-stabilized zirconia (Sc: 4.45 at%, Zr: 31.06 at%) films were deposited on cleaned Si wafers and polycrystalline Al₂O₃ to investigate their properties. As previously mentioned, ScSZ has seven different phases and easily transforms among them due to the similar ionic radii of the host and the dopant. Thus, the properties of ScSZ films are extremely sensitive to preparation and thermal history [18,20,22]. In this study, ScSZ thin film electrolyte based TF-SOFC was fabricated at room temperature, and then, operated at 500 °C. Therefore, the crystallinity and crystallite orientation of as-deposited and post-annealed (500 °C for 1 h) ScSZ films were examined by XRD to confirm transformation of crystal structure (Fig. 1); both film types showed cubic crystal structure, consistent with previously reported results

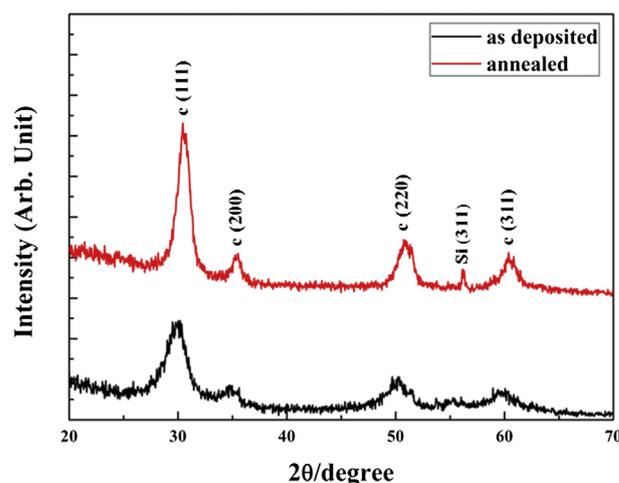


Fig. 1 – XRD spectra of as-deposited and post-annealed (500 °C) ScSZ films.

[18,21–23]. Compared with as-deposited ScSZ, the post-annealed ScSZ films had clearer and sharper XRD peaks, which indicated almost identical but improved crystal structure. This result implies that ScSZ electrolyte prepared by sputtering can maintain their cubic crystal structure during 1 h of operation; there was no clear evidence of phase transition in the 500 °C post-annealed ScSZ films. We speculate that the annealing temperature used, which is the same as the operating temperature, was not high enough and the time was not long enough to cause phase transformation in the ScSZ films.

In-plane conductivity calculations of ScSZ films on polycrystalline Al_2O_3 were performed based on EIS measurements; Arrhenius and Nyquist plots are shown in Fig. 2. The activation energy (E_{act}) for conduction of oxygen ions was determined based on the slope of the Arrhenius plot. The EIS results are matched with equivalent fitting curves (one semicircle) except at low frequency range which is slightly asymmetric like previously reported results (Fig. 2a) [18,19]. The resistance of the ScSZ film decreased as the temperature was increased. The in-plane conductivities of films were within the range of previously reported results (Fig. 2b) [16,18,25]. The activation energy for conduction, E_{act} , was determined to be 1.02 eV; this was in good agreement with previous reports by Virbukas et al. (e-beam technique, 0.88–1.01 eV) and Ksapabutr et al. (electrostatic spray deposition, 1.09 eV) [23,26]. The ionic conductivity and E_{act} results indicated that ScSZ thin films of cubic fluorite phase were successfully prepared on a polycrystalline Al_2O_3 by RF sputtering at room temperature, and that these films maintained their crystal structure during conductivity measurements in a temperature range including the TF-SOFC operation temperature.

Cross-sectional structure and surface morphology investigations of the MEA were performed by FIB-SEM, FESEM and AFM. A 280 nm thick, dense and defect-free ScSZ electrolyte was successfully deposited onto the Pt anode (Fig. 3a); this was confirmed again by observing the surface morphology of the ScSZ electrolyte (Fig. 3c). Interestingly, ScSZ thin film electrolyte was composed of fine nano-sized grains (Fig. 3d). Notably, the Pt cathode deposited under the pressure of 12 Pa showed dense morphology after measurements (Fig. 3b). We concluded that thermal degradation of the

Pt cathode occurred at 500 °C, causing a considerable loss of cathode polarization [10,11].

Electrochemical characterization of a TF-SOFC was conducted at 500–550 °C with 100 sccm H_2 . The open-circuit voltage (OCV) of the cell was measured to be 1.08 V at 500 °C and 1.04 V at 550 °C (Fig. 4a). This is close to the theoretical value for the SOFC, implying that the sputtered ScSZ electrolyte had no pinholes despite its relative thinness [5]. In addition, the maximum power density of the TF-SOFC was measured to be 227 mW/cm^2 (500 °C) and 334 mW/cm^2 (550 °C). These performance were considerably higher than those of similarly structured TF-SOFCs reported previously in which yttria-stabilized zirconia thin film electrolytes by various thin film techniques were used [5–7,10]. We speculate that the higher fuel cell performance was due to the higher ionic conductivity of the ScSZ electrolyte, due to the significant reduction in electrolyte thickness without pinholes. The high performance of the ScSZ films was also attributed partially to their high grain boundary density (Fig. 3d), because grain boundaries are well-known to be favorable sites for oxygen incorporation reactions [12,13,18]. EIS measurements were also conducted under different applied cell voltages (OCV, 0.7 and 0.5 V) to clarify the cell's electrode polarization resistance and ohmic resistance characteristics (Fig. 4b). The ohmic resistance (the X-axis intercept point at high frequency) was somewhat similar for the two applied cell voltage conditions (0.340 Ωcm^2 at 0.7 V, 0.256 Ωcm^2 at 0.5 V at 500 °C; Fig. 4b inset). Contrastingly, the low-frequency arc, corresponding to the electrode polarization resistance, was affected by the applied cell voltage (1.513 Ωcm^2 at 0.7 V, 1.018 Ωcm^2 at 0.5 V at 500 °C). According to previous studies, it is generally known that the low-frequency arcs in EIS are mainly related to the oxygen reduction reaction at the cathode due to sluggish reactivity, and are greatly affected by the applied cell voltage. Therefore, EIS measurements using different applied cell voltage conditions allowed the ohmic resistance and electrode polarization resistance of the TF-SOFC to be separated clearly. High electrode polarization resistance has been confirmed to be the main reason for performance reduction of TF-SOFCs [8,10–13].

To the best of our knowledge, this is the first report demonstrating an AAO based TF-SOFC based on a ScSZ thin

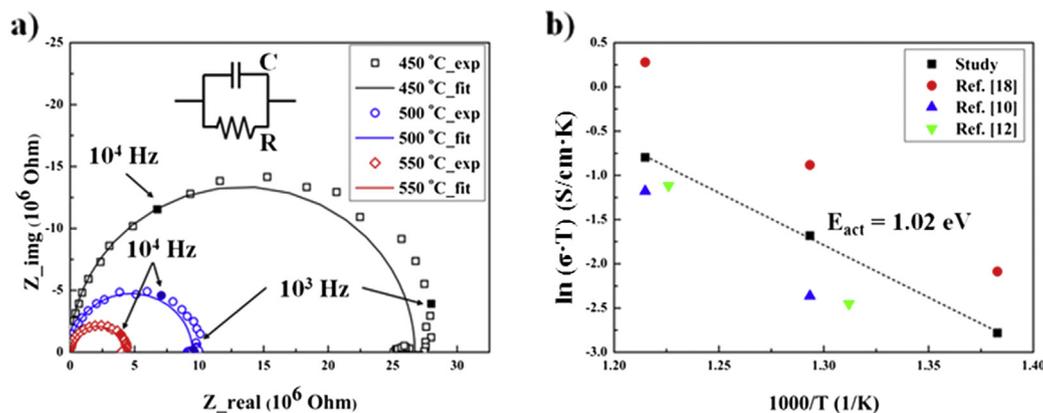


Fig. 2 – (a) EIS spectra of a ScSZ film measured at different temperatures, used to determine ionic conductivity. (b) Arrhenius plots of as-deposited ScSZ thin film on polycrystalline Al_2O_3 and results from the literature.

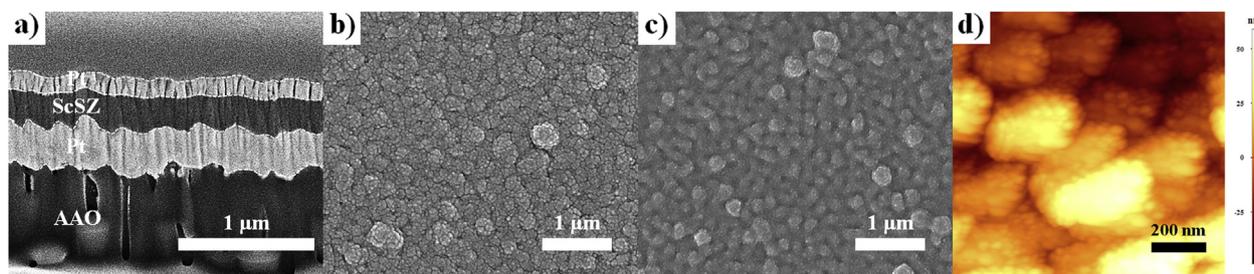


Fig. 3 – (a) Cross-sectional structure of the TF-SOFC. (b) Surface morphology of the cathode. (c) Surface morphology of electrolyte. (d) Surface topography of the electrolyte.

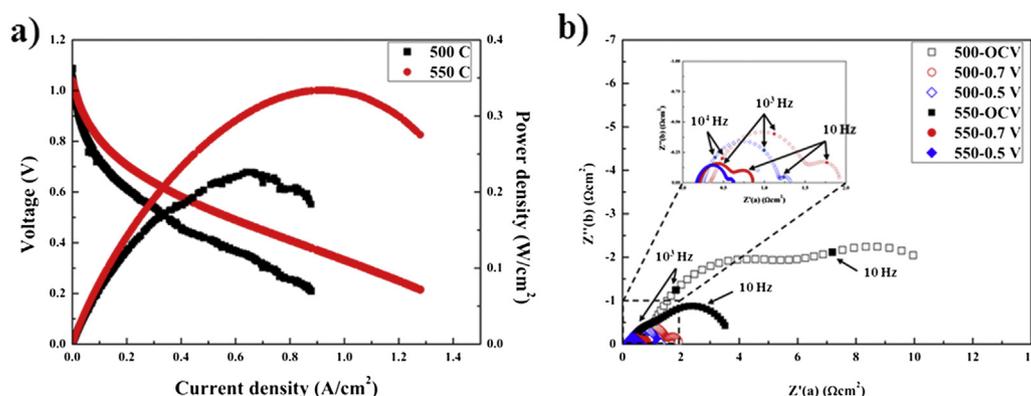


Fig. 4 – (a) Polarization curve and power density of the TF-SOFC with the ScSZ thin film electrolyte at 500–550 °C. (b) EIS results of the TF-SOFC.

film electrolyte by a vacuum process; additionally, this TF-SOFC showed higher performance than devices reported in earlier studies, and was operated without phase transformation of films. We expect that the results will provide insights in the design of high-performance TF-SOFCs for various applications.

Conclusions

In this study, 6.7 mol% ScSZ thin films were successfully prepared by RF sputtering. The films showed cubic crystal structure and their degree of crystallinity was improved after heat treatment at 500 °C; additionally, no phase transition to other crystal structures was observed. The ionic conductivity of a film on polycrystalline Al_2O_3 showed similar ion conductivity to that reported for previous studies in the range of 450–550 °C, and had the activation energy of 1.02 eV. Electrochemical characteristics of the AAO-supported TF-SOFC with 280 nm thick ScSZ electrolyte were examined at 500–550 °C. Its performance was measured to be 227 mW/cm² (500 °C) and 334 mW/cm² [2] (550 °C), respectively.

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