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Atomic layer deposition of yttria-stabilized zirconia thin films for enhanced reactivity and stability of solid oxide fuel cells

Joonho Park [a], Yeageun Lee [a], Ikwhang Chang [b], Gu Young Cho [a], Sanghoon Ji [b], Wonyoung Lee [c, **], Suk Won Cha [a, b, *]

[a] Department of Mechanical and Aerospace Engineering, Seoul National University, Gwanak-ro 1, Gwanak-gu, Seoul, 151-744, Republic of Korea
[b] Graduate School of Convergence Science and Technology (GSCST), Seoul National University, Gwanggyo-ro 145, Yeongtong-gu, Suwon, 443-270, Republic of Korea
[c] School of Mechanical Engineering, Sungkyunkwan University, Seobu-ro 2066, Jangan-gu, Suwon, 440-746, Republic of Korea

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ABSTRACT

We report the advantages of atomic layer deposition (ALD) for the fabrication of yttria-stabilized zirconia (YSZ) electrolyte. The reactivity and stability of anodic aluminum oxide (AAO)-based thin-film solid oxide fuel cells (SOFCs) are improved by applying ALD YSZ electrolyte. The fuel cell fabricated by ALD shows a peak power density of 154.6 mW cm^{-2} at 450 °C, whereas the fuel cell fabricated by sputtering demonstrates a peak power density of 66.2 mW cm^{-2}. The amorphous and nanogranular microstructure of the ALD YSZ film is ascribed for a significant improvement in the cathodic reactivity of the AAO-based thin-film fuel cells. Moreover, the smooth and uniform surface of the ALD YSZ electrolytes mitigates the agglomeration of the Pt cathode layer, and thus the thermal stability of the thin-film fuel cell is remarkably improved at 450 °C.

1. Introduction

Solid oxide fuel cells (SOFCs) are promising candidates for next-generation energy sources due to their high efficiency and environmental friendliness [1–4]. Traditional SOFCs are generally operated at temperatures as high as 1000 °C in order to obtain sufficient ionic conductivity of their solid-state electrolyte materials, for instance, yttria-stabilized zirconia (YSZ) and gadolinium-doped ceria (GDC). Such high operating temperature, however, causes recurring problems related to stable operation of the SOFCs, such as thermal stress, material selection issues, and sealing problems [5,6]. Therefore, extensive researches have been conducted to lower the operating temperature through the use of new materials, structures, and fabrication processes.

In line with these efforts, thin-film SOFCs have been developed to compensate for the low ionic conductivity of zirconia-based electrolyte materials at lower temperatures, through the shortening of the ionic conduction path [7]. Recently, freestanding membranes with a thickness of less than 100 nm were employed as electrolytes, showing a peak power density of 0.4–1.3 W cm^{-2} at 400–450 °C [8–10]. However, such thin freestanding structures will inevitably undergo thermomechanical issues [11,12]. Alternatively, nanoporous templates have been suggested as substrates to support thin-film fuel cells for greater mechanical stability and more efficient gas delivery. It has been demonstrated that the electrical and microstructural degradation of thin-film fuel cells supported by nanoporous anodic aluminum oxide (AAO) can be significantly mitigated even at elevated temperatures [13].

Currently, several groups have demonstrated successful results when attempting to fabricate thin-film SOFCs onto AAO substrates without any gas leakage using various deposition techniques [13–18]. Although wet-chemical deposition processes are superior in terms of cost-efficiency and scalability for fabricating thin films, macro-defects can still be observed on thin films deposited by these processes [19]. In contrast, vacuum-assisted deposition techniques are used to deposit thin layers of material atom-by-atom or molecule-by-molecule onto a solid surface. Therefore, these techniques can be utilized to produce full-density thin films without

* Corresponding author. Department of Mechanical and Aerospace Engineering, Seoul National University, Gwanak-ro 1 Gwanak-gu, Seoul, 151-744, Republic of Korea.
** Corresponding author.
E-mail addresses: pjh1304@snu.ac.kr (J. Park), cuplus@snu.ac.kr (Y. Lee), eugeneviper@snu.ac.kr (I. Chang), sepril02@snu.ac.kr (G.Y. Cho), raul888@snu.ac.kr (S. Ji), leewy@skku.edu (W. Lee), swcha@snu.ac.kr (S.W. Cha).

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any gas leakage. Moreover, in tightly controlled atmosphere, deposition processes by these techniques guarantee high purity and repeatability. Thus, vacuum-assisted deposition techniques such as sputtering, pulsed laser deposition (PLD) and atomic layer deposition (ALD) have been widely used to fabricate thin-film SOFCs. Unlike PLD, which is less appropriate for scale-up processes, sputtering and ALD are suitable for industrial applications due to their high potential for mass production and uniform deposition over large areas. In addition, ALD, a modified CVD technique, can achieve isotropic deposition with conformal covering over three-dimensional substrates [20]. Therefore, ALD has been considered as a key technique to obtain high-performance thin-film SOFCs supported by nanoporous substrates [14,15,21,22].

Electrochemical reactions at interfaces often critically affect fuel cell performance levels overall, especially at low temperatures [23]. This type of electrochemical reactivity in thin-film SOFCs, however, is mainly affected by properties such as the microstructure and the chemical composition of the film. Moreover, the film properties are significantly affected by the deposition process used [21]. As a result, the performance levels of thin-film SOFCs are closely related to the thin-film deposition techniques by which they are deposited [24]. For thin-film SOFCs with freestanding membranes, it has been reported that YSZ electrolytes deposited by ALD show electrochemical characteristics superior to those deposited by sputtering [20]. However, for thin-film SOFCs with nanoporous templates, the effects of the deposition process on the electrochemical characteristics have not yet been elucidated. Thus, systematic investigations of the film properties and fuel cell performance levels are important for further improvements in the electrochemical performance of thin-film SOFCs with nanoporous templates.

In this study, we report the effects of different deposition techniques of YSZ electrolyte on the cathodic reactivity and thermal stability of AAO-based thin-film SOFCs. We fabricated and characterized fuel cells with electrolytes produced by sputtering and ALD processes. We undertook current-voltage measurements, electrochemical impedance spectroscopy, and galvanostatic measurements in order to evaluate the electrochemical properties of the cells. As a result, the cells fabricated by ALD showed a substantial enhancement of their stability in extended lifetime and their electrochemical reactivity. The microstructures and chemical compositions of the fabricated cells were systematically examined by various characterization techniques in order to find a correlation with the electrochemical performance levels of the fabricated fuel cells.

2. Material and methods

2.1. Thin-film deposition

We deposited YSZ thin films with two different deposition techniques: DC sputtering and ALD. Sputtered YSZ films were produced using an $Y_{16}Zr_{84}$ alloy target (Advantec) at 200 W. The sputtering atmosphere was O_2:Ar = 2:8 at a pressure of 0.67 Pa at room temperature. ALD YSZ films were produced by the co-deposition of zirconia (ZrO_2) and yttria (Y_2O_3) using a custom-made ALD system. Commercial tetrakis (dimethylamido) zirconium ($Zr(NMe_2)_4$) and tris (methylcyclopentadienyl) yttrium ($Y(MeCp)_3$) were used as precursors for ZrO_2 and Y_2O_3. The zirconium and yttrium precursors were heated to 70 °C and 140 °C, respectively, while the substrate was heated at 250 °C. Both oxides were deposited by repeating a sequence of the pulsing of the precursor, the purging of ligands and unreacted precursor, the pulsing of an oxidant, and the purging of byproducts. The deposition process of the YSZ monolayer consisted of seven cycles of zirconia deposition and one cycle of yttria deposition to obtain the desired YSZ composition of 7–10 mol % [1,16].

2.2. Fuel cell fabrication

Commercial anodic alumina oxide (AAO, Synkera Technology Inc.) templates with an area of 1 cm^2, a thickness of 100 μm, and a pore diameter of 80 nm were used as substrates to support the thin-film SOFCs [16–18]. A dense Pt anode with a thickness of 300 nm was deposited on the AAO substrate by DC sputtering at 200 W at room temperature with an Ar pressure of 0.67 Pa. YSZ films were deposited onto an anode layer with a total thickness of 500–550 nm by two deposition techniques. A porous Pt cathode with a thickness of 150 nm was deposited by DC sputtering at 100 W at room temperature with an Ar pressure of 12 Pa. A shadow mask was used to produce the active area of 1 mm^2 [17].

2.3. Characterization methods

A focused ion beam and a scanning electron microscope (FIB-SEM: Quanta 3D FEG, FEI Company) were utilized to observe cross-sectional images of the fabricated fuel cell samples. The surface topography and roughness of the electrolyte layer were investigated with a scanning probe microscope (SPM: SPA-400, Seiko Instruments) using a tapping mode. Symmetric $\theta/2\theta$ diffraction measurements were taken of YSZ thin films by means of an X-ray diffractometer (XRD: X'pert Pro, PANalytical) with a Cu Kα radiation source. The compositions of the films were analyzed by X-ray photoelectron spectroscopy (XPS: AXIS-His, KRATOS). Prior to the XPS analysis, the surfaces of the samples were etched with Ar ions at 150 eV to eliminate any possible surface contamination. The morphology of each porous Pt cathode was examined by a field-emission secondary electron microscope (FE-SEM: Supra 40, Carl Zeiss). For the fuel cell test, the polarization and impedance characteristics were assessed by a commercial electrochemical impedance spectroscope (Solatron Analytical, 1260/1287) at 450 °C with VAC = 30 mV and VDC = 0.5 V. The anode side of the fuel cell was fed with dry hydrogen at 20 sccm, while the patterned cathode electrode was exposed to ambient air.

3. Results and discussion

To investigate the reactivity and the stability of thin-film SOFCs with YSZ electrolyte deposited by sputtering and ALD, we fabricated three types of fuel cell structures: YSZ electrolyte deposited by sputtering (sputter cell), YSZ electrolyte deposited by ALD (ALD cell), and YSZ electrolyte deposited by sputtering with an additional layer on the cathode side deposited by ALD (multilayer cell), as shown in Fig. 1. The first two structures were fabricated for a comparison of the film quality with the same electrolyte materials but deposited by different deposition techniques. The third structure was created to identify the origin of the different reactivity levels with different structures. Anodes and cathodes were fabricated by DC sputtering with the same conditions for all samples.

To assess the effects of the electrolyte structure on the reactivity of the fuel cells, we examined the electrochemical characteristics of the cells. Fig. 2 shows the current-voltage curve of cells measured at 450 °C. The open-circuit voltages (OCVs) of all cells were comparable, at approximately 1–1.1 V. The measured OCV values were close to the theoretically predicted values under given conditions according to the Nernst equation, at 1.18 V, regardless of the electrolyte structure used [1]. These OCV values from all samples substantiate that the thin-film electrolytes were dense enough to prevent gas leakages or electrical shortages, both of which are problems inherent to thin-film fuel cells supported by porous substrates [14]. The peak power densities were 66.2, 154.6 and