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Plasma-Enhanced Atomic Layer Deposition of Nanoscale Yttria-Stabilized Zirconia Electrolyte for Solid Oxide Fuel Cells with Porous Substrate

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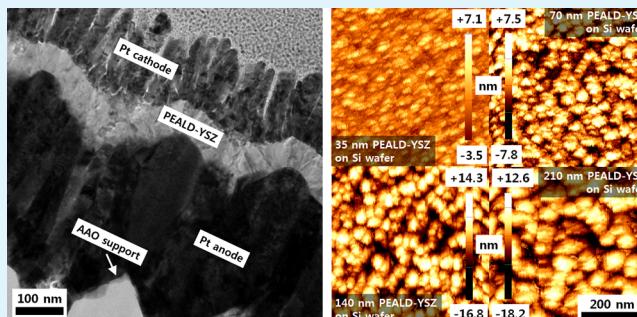
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Supporting Information

ABSTRACT: Nanoscale yttria-stabilized zirconia (YSZ) electrolyte film was deposited by plasma-enhanced atomic layer deposition (PEALD) on a porous anodic aluminum oxide supporting substrate for solid oxide fuel cells. The minimum thickness of PEALD-YSZ electrolyte required for a consistently high open circuit voltage of 1.17 V at 500 °C is 70 nm, which is much thinner than the reported thickness of 180 nm using nonplasmatic ALD and is also the thinnest attainable value reported in the literatures on a porous supporting substrate. By further reducing the electrolyte thickness, the grain size reduction resulted in high surface grain boundary density at the cathode/electrolyte interface.

KEYWORDS: plasma-enhanced atomic layer deposition, yttria-stabilized zirconia, thin film, anodic aluminum oxide, solid oxide fuel cell



Solid oxide fuel cell (SOFC) is considered as one of the promising electricity-generating devices because of its high energy conversion efficiency, high fuel flexibility, and pollution-free exhaust.¹ However, its excessively high operating temperature (above 800 °C) requires costly balance of plant and massive energy loss, narrowing its application to stationary power generators. Therefore, lowering the operating temperature is critical to expanding the applicability of SOFCs to mobile devices. On the other hand, the low-temperature operation of SOFCs incurs poor ionic conduction through the electrolyte and sluggish reaction kinetics at the electrode/electrolyte interfaces.^{1,2} Reducing the ion conducting resistance through the electrolyte can effectively reduce ohmic resistance so as to maintain competent cell performance at low temperatures.² This can be achieved by either employing electrolyte materials with higher ionic conductivity or reducing the electrolyte thickness. The latter approach has been demonstrated with functional electrolytes with the thickness of tens or hundreds of nanometers by several research groups using vacuum-based (such as sputtering, pulsed laser deposition (PLD), or atomic layer deposition (ALD)) or solution-based (such as sol–gel or chemical solution deposition) coating techniques.^{3–5} Such cells with nanothin film electrolyte have been typically implemented through a silicon-based micro-

fabrication by performing through-wafer etching to release the electrolyte.^{3,4,6} However, silicon-based freestanding thin film SOFCs have active cell areas of at most a few hundred square millimeters because of the lack of thermomechanical stability and their output power level has been limited to a few milliwatts.^{7,8} Meanwhile, as a way to increase the output power, the augmentation of the active cell area in thin film SOFCs was attempted in various ways, for which scalable substrates with nanopores showing excellent gas diffusivity were effectively utilized as the supporter.

The use of an anodic alumina oxide (AAO) for thin film SOFCs has been reported by several groups.^{9,10} One major challenge of using such a porous substrate for the fabrication of thin film SOFC is to form a gastight, pinhole-free electrolyte while maintaining the electrolyte thickness in a submicrometer scale.^{9–11} Many works have tried to deposit a very thin electrolyte on a porous substrate using vacuum deposition techniques including PLD, sputtering, ALD, or a combination of these methods.^{6,9} However, the required thickness for a

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gastight, pinhole-free electrolyte reaches micrometer-scale, which makes it economically nonviable as the deposition of such a thick film takes a significant amount of processing time and source material.

Among all the deposition techniques for depositing nanothin film electrolytes on a porous substrate, ALD is currently best suited for a large area deposition while maintaining good film quality. The binary sequential reaction of precursors and reactants in ALD enables thin film deposition with atomic level thickness control, uniformity, and excellent step coverage.¹² We have reported the deposition of dense electrolytes on porous AAO substrates in the past few years.^{6,10,13} For example, Ji et al. demonstrated a 40 nm thick yttria-stabilized zirconia (YSZ) layer deposited by ALD can effectively prevent ceria-based electrolytes from being reduced under a highly reducing anodic environment. However, the allegedly insufficient density and poor quality of the blocking layer, the open circuit voltage (OCV), and peak power density were limited to 1.07 V (Nernstian potential: 1.18 V) and 35 mW/cm² at 450 °C. Recently, Ha et al. demonstrated a gastight YSZ electrolyte (390 nm) deposited via a combination of sputtering and ALD on an AAO substrate, which rendered a peak power density of 180 mW/cm² at 450 °C. Nevertheless, it necessitated an ALD YSZ blocking layer as thick as 150 nm with long deposition time, which motivated to find strategies to obtain higher quality and denser electrolyte films.

The search for deposition methods to deposit high-quality electrolytes on porous substrates is ongoing. Plasma-enhanced ALD (PEALD), a derivative of ALD, in which the reactants are excited by a plasma source to have higher reactivity during deposition. Compared to the nonplasmatic ALD, PEALD renders better films in terms of density, crystallinity, and purity, and is more economically viable because of its higher growth rate.^{14,15} However, the use of PEALD for the deposition of SOFC electrolyte has not yet been demonstrated. In this study, we present the first demonstration of an YSZ electrolyte deposition by PEALD, which enables the reduction of film thickness while warranting a gastight, pinhole free electrolyte on a porous substrate. The PEALD-YSZ electrolyte was deposited on an AAO substrate with the thickness of 35–210 nm, and their functionality was studied through electrochemical characterization.

The PEALD-YSZ film was deposited with a showerhead-type commercial ALD apparatus (Atomic Premium, CN1, South Korea) with a radio frequency plasma generator. Tetrakis-(dimethylamido)zirconium, Zr(NMe₂)₄, and tris-(methylcyclopentadienyl)yttrium, Y(MeCp)₃, were used as the precursors for zirconium and yttrium, respectively. The substrate was heated to 250 °C.^{4,16} The temperatures of canisters with charged precursors were 50 and 145 °C, and the line temperatures were 70 and 155 °C for zirconia and yttria deposition, respectively. The precursors were delivered using an electropolished stainless steel (SS) bubbler fed by 300 sccm Ar gas with 99.99% purity. 100 sccm O₂ gas with 99.99% purity was used as the oxidant. At the stage of plasma generation, a mixture of 300 sccm Ar and 100 sccm O₂ gases was supplied to the chamber. The power of plasma was selected to be 50 W for a good control of density, purity, and growth rate. Zirconia was deposited by repeating the sequence of precursor pulse (3 s), Ar gas purging (30 s), O₂ gas pulse (1 s), plasma generation (8 s), and Ar gas purging (30 s). The sequence for depositing yttria is precursor pulse (5 s), Ar gas purging (60 s), O₂ gas pulse (1 s), plasma generation (8 s), and Ar gas purging (60 s).

PEALD-YSZ was deposited by iterating the deposition processes of zirconia and yttria, and the doping concentration of YSZ was controlled by the ratio of number of cycles for zirconia and yttria depositions. When the ratio of zirconia to yttria cycle is 7:1, the atomic concentration of each element in the YSZ film, determined by an X-ray photoelectron spectroscopy analysis, was Zr 3d = 34.8%, Y 3d = 4.9%, O 1s = 58.8%, and C 1s = 1.5%. The Y₂O₃ mole fraction, *x*, in the YSZ chemical formula of (ZrO₂)_{1-x}(Y₂O₃)_x was ~0.08, which was reported to render the maximum oxygen ion conductivity.¹⁷ The growth rate of YSZ film during the initial 250 cycles was 1.4 Å/cycle and the film thickness increased proportionally with the deposition cycles.

Figure 1 shows a schematic diagram of the micro-SOFC fabrication process we employed. Commercial porous AAO

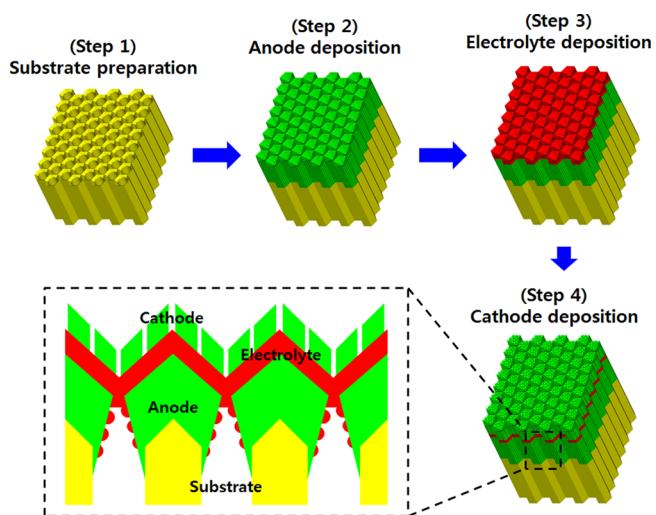


Figure 1. Schematic diagram depicting the fabrication process of anodic aluminum oxide (AAO)-supported micro-solid oxide fuel cells (SOFCs); step 1, AAO preparation; step 2, Pt anode deposition; step 3, yttria-stabilized zirconia (YSZ) plasma-enhanced atomic layer deposition (PEALD); and step 4, Pt cathode deposition.

(Synkera, USA) membranes with the thickness of 100 μm and pore size of 80 nm were used as the substrate for gas permeation and mechanical support. Figure 2a shows the images of PEALD-YSZ electrolyte surfaces with the thickness of 70 nm (left) and 210 nm (right) deposited on the Pt/AAO surface. The thin film covered the Pt/AAO surface and shows a bump array replicating the AAO pore surface; the distances between neighboring bumps are ~80 nm, which roughly corresponds to the distance between AAO pores. The grain size of PEALD-YSZ thin films deposited on silicon substrate, which gives better geometrical resolution than when deposited on AAO substrate, was scanned by atomic force microscopy (AFM) (Figure 2b). The average grain sizes for PEALD-YSZ with thicknesses of 35, 70, 140, and 210 nm are 20, 34, 41, and 52 nm, respectively. This means that the surface grain boundary density of the 35 nm film is 2.6 times higher than that of the 210 nm film.

Figure 3a shows high-resolution transmission electron microscopy (TEM) cross-sectional images of the AAO-supported micro-SOFC with 320 nm thick Pt anode, 70 nm thick PEALD-YSZ electrolyte, and 150 nm thick porous Pt cathode. The thick as-deposited Pt anode did not form a dense and gastight film as demonstrated in our previous works.^{10,16}

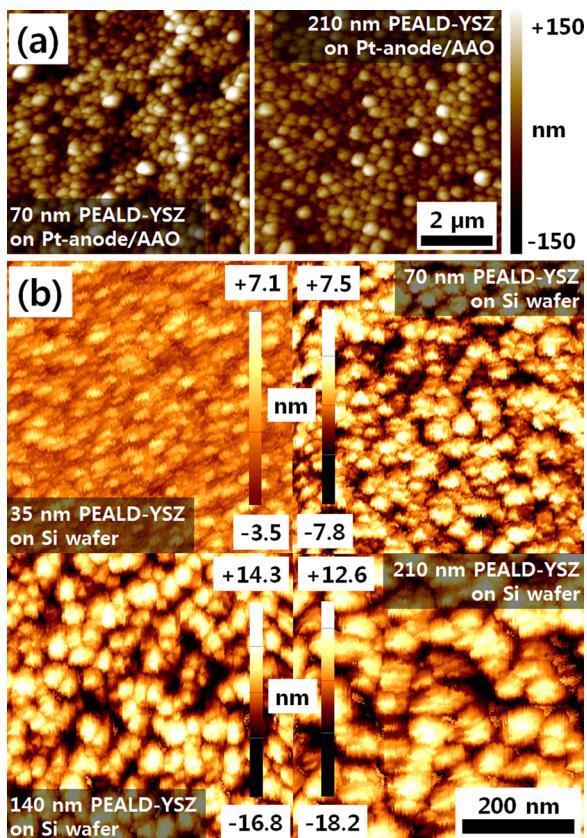


Figure 2. Atomic force microscopy topographical images of (a) 70 and 210 nm thick PEALD-YSZ films deposited on porous AAO substrates, and (b) of PEALD-YSZ films with thicknesses of 35, 70, 140, and 210 nm deposited on flat silicon substrates.

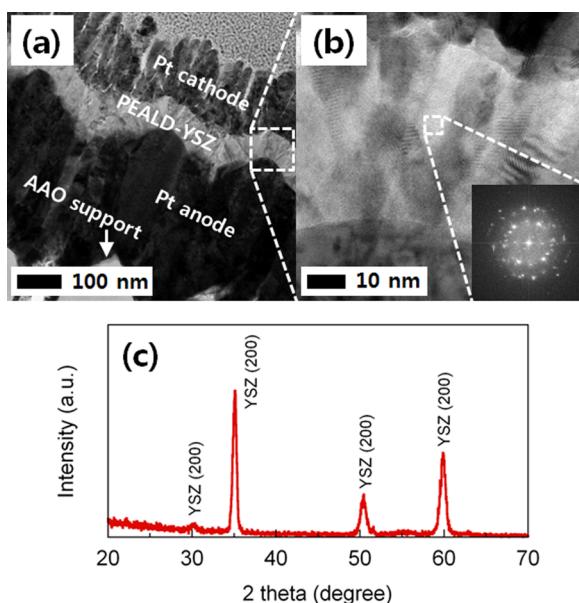


Figure 3. (a) High-resolution transmission electron microscopy cross-sectional images of an AAO-supported cell comprising 70 nm PEALD-YSZ electrolyte, 320 nm Pt anode, and 150 nm Pt cathode; (b) local diffraction pattern of the 70 nm PEALD-YSZ electrolyte (inset); (c) grazing incidence X-ray diffraction pattern of 210 nm PEALD-YSZ on a silicon (100) substrate.

The PEALD-YSZ electrolyte deposited on top of the anode showed good conformality and thickness uniformity (Figure 3b). No apparent pinholes were observed in the PEALD-YSZ on the rough surface of porous substrate. The TEM diffraction pattern (the inset of Figure 3b) indicates that the PEALD-YSZ contains both crystalline and amorphous phases. The existence of amorphous phase is likely due to the low-temperature (250 °C) during the PEALD process. The amorphous phase was also observed in YSZ films deposited with nonplasmatic ALD.⁴ However, the out-of-plane (q_z) X-ray diffraction spectrum of the 210 nm thick PEALD-YSZ film (Figure 3c) shows much sharper diffraction peaks than those deposited by nonplasmatic ALD as reported in the literature, indicating the employment of plasma during deposition has improved the crystallinity of YSZ.⁴ It was reported that the oxygen ion conductivity of crystalline YSZ is ~5 times higher than that of amorphous YSZ from both experiments and molecular dynamic simulations.^{18,19} Therefore, a higher ionic conductivity of PEALD-YSZ can be expected.

The density of the PEALD-YSZ thin film was determined to be 5.81 g/cm³ by X-ray reflectometry analysis. The value is lower than the typical bulk YSZ density of 6.1 g/cm³, possibly due to the nanosized grain that gives a higher grain boundary density within the film.⁴ Nevertheless, the density of PEALD-YSZ is higher than YSZ deposited by nonplasmatic ALD in the literatures (below 5.7 g/cm³), which is attributed to a more active rearrangement of atomic species by the oxygen plasma during deposition.¹⁴ Therefore, thinner and denser YSZ film can be obtained with PEALD with reduced amount of process time and source materials, improving both the cell integrity and charge transport.

The high OCV is one of the most direct indicators of electrolyte integrity (in terms of gas tightness and electron blockage) in a micro-SOFC. The OCVs of micro-SOFCs with different YSZ thicknesses (35, 70, 140, and 210 nm) were measured at 500 °C. Nine cells were tested for each of them. While cells with YSZ thickness of 70 nm or larger showed high OCVs of ~1.17 V, seven out of the nine cells with 35 nm thick YSZ were electrically short-circuited (Figure 4a). Therefore, we tentatively attest that 70 nm is the minimum thickness for a gastight, pinhole-free PEALD-YSZ on our platform (i.e., 320 nm thick Pt-anode deposited on an AAO substrate with 80 nm of pore diameter).

The thicknesses of PEALD-YSZ and the corresponding OCVs were compared to those other studies on porous substrate-supported low-temperature SOFCs published earlier (Figure 4b).^{5,6,9,11,13,20} It is clear that the films deposited by PEALD demonstrate a significant decrease in the electrolyte thickness required to achieve a high OCV. Unlike some of the previous works, where a combination of multiple deposition sequences was required for a dense electrolyte, the one-step deposition of dense YSZ by PEALD has also greatly reduced the process complexity.

Polarization curves were obtained at 500 °C for the micro-SOFCs with PEALD-YSZ electrolyte thickness of 70 and 210 nm. As shown in Figure 5a, the cell with a 70 nm thick electrolyte outperformed the one with a 210 nm thick electrolyte in terms of peak power density by a factor of 1.3. Although the enhancement was expected to be due to the decrease of ohmic loss, this effect was insignificant as shown in Figure 5b. It was more influenced by the significant enhancement of cathodic activity.²¹ Shim et al. previously reported that surface grain boundaries are active sites for

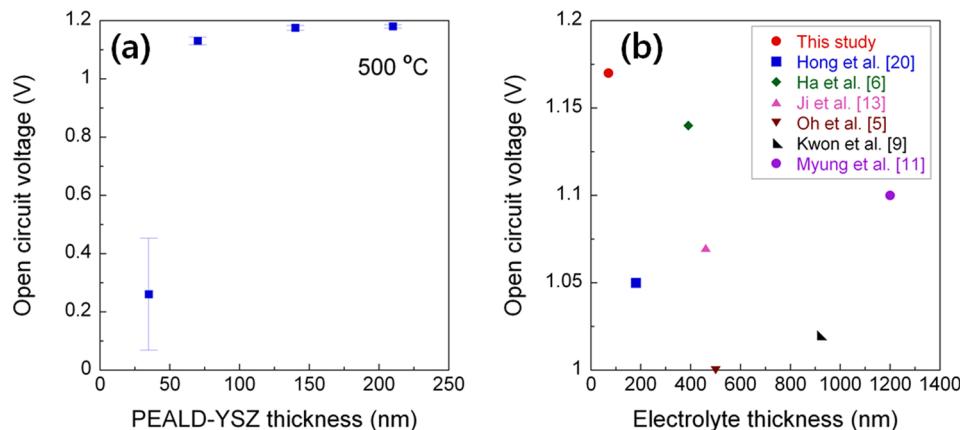


Figure 4. (a) Open circuit voltage (OCV) of cells with 35, 70, 140, and 210 nm PEALD-YSZ electrolytes measured at 500 °C; (b) comparison of OCV measured among various porous substrate-supported SOFCs, at the temperature range from 400 °C to 600 °C.

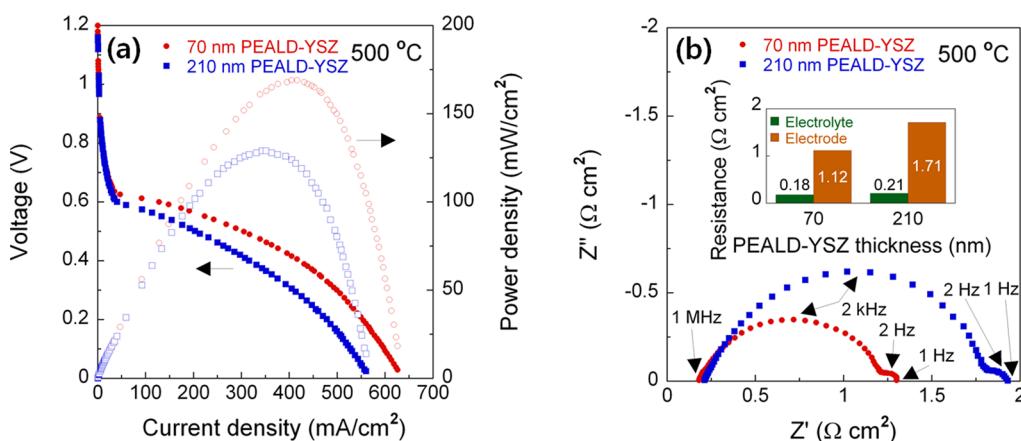


Figure 5. (a) Polarization curves and (b) alternating current impedance data for cells with 70 and 210 nm thick PEALD-YSZ electrolyte. Obtained under direct current bias voltage of 0.5 V at 500 °C.

oxygen incorporation for oxygen reduction reactions (ORRs), and our previous AFM results revealed the 70 nm PEALD-YSZ film has 1.5-fold higher grain boundary density than 210 nm PEALD-YSZ film.²² The enhancement of our cathode performance by the use of a thinner electrolyte is attributed to the higher surface grain boundary density (and thus more effective oxygen incorporation for ORR). The relatively insignificant difference in ohmic resistance between them is ascribed to the high resistivity of porous Pt cathode (101.6 $\Omega \text{ cm}$; a dense Pt film sputtered at an Ar pressure of 5 mTorr has a resistivity of 10.8 $\Omega \text{ cm}$) because the current collection in our test setup was performed through a micro-probe tip, not a planar metallic mesh.

We demonstrated that PEALD can be an ideal method for depositing thin film electrolytes on a porous AAO substrate because it enables a significant reduction of film thickness (and thus ohmic loss) while maintaining gas-tightness and electronic insulation. The OCV of the fabricated micro-SOFC using PEALD-YSZ was as high as 1.17 V with an electrolyte thickness of only 70 nm, much smaller than other to previously reported values. In addition, the decrease of electrolyte thickness resulted in an enhancement of ORR activity presumably due to a significantly increased surface grain boundary density.

ASSOCIATED CONTENT

S Supporting Information

Additional information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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