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Engineering of the electrode structure of thin film solid oxide fuel cells

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ABSTRACT

In this study, we systematically examined the effects of anode structures in nanoporous template-based thin film solid oxide fuel cells on the electrochemical performance. The fuel cells were fabricated by sequential sputtering of the anode, the electrolyte and the cathode on an anodic aluminum oxide substrate without pinhole problems. Systematic investigation showed the substantial impacts of the porosity and the thickness of the Pt anodes on the reactivity at the anode/electrolyte interface and the mass transport in the electrode, which are closely related to the activation and the concentration overpotentials of fuel cells, respectively. Our results provide the fundamental insights into tailoring the anode structures for improved fuel cell performance.

1. Introduction

Solid oxide fuel cells (SOFCs) have long been considered attractive power sources because of their high energy conversion efficiency and zero emission of undesirable products such as NO_x and SO_x [1–4]. However, SOFCs usually require high operating temperatures up to 1000 °C to activate the electrochemical reactivity and the ionic conductivity of their ceramic electrolyte. Such high operating temperatures cause great obstacles including limited material selection and inferior durability, which must be overcome for wider use of SOFCs [5].

Many studies to lower the electrolyte resistance of SOFCs have been conducted by exploring alternative electrolyte materials and by developing cell structures with thin film technologies [6–24]. Recently, ceria-based electrolyte materials have received attention due to their high ionic conductivity and reactivity at lower temperatures. However, their chemical instability under SOFC operation conditions imposed the practical difficulties for wider applications [6–8]. Thus, traditional zirconia-based electrolyte materials remain attractive due to their greater chemical stability and long-term reliability.

To compensate the low ionic conductivity of the zirconia-based electrolyte materials at lower temperatures, the thin film SOFCs have been developed to reduce the ohmic resistance by shortening the ionic conduction path. Some research groups have fabricated nano-scale thin film SOFCs with freestanding membranes by applying microelectromehanical system techniques [9–15]. They have also demonstrated that the electrode/electrolyte interfacial area of the freestanding thin film SOFC can be drastically increased by various nano-scale fabrications [11–13]. However, the freestanding structures with only tens of nanometer thick membranes will inevitably suffer from thermomechanical issues. Therefore, scaling-up of the freestanding thin film SOFCs to practical ranges still remains as a technical challenge [15].

In consideration of the thermomechanical stability, nanoporous templates have been suggested as substrates to support thin film fuel cells for their high reliability as well as efficient gas delivery [8,16–19]. It has been demonstrated that in cases where thin films were supported by nanoporous anodic aluminum oxide (AAO), their electrical and microstructural degradation could be significantly mitigated even at elevated temperatures [20]. However, the open circuit voltages (OCVs) were relatively low due to the pinhole defects in the thin electrolyte inherently caused by porous AAO substrates [21]. Extensive efforts, therefore, have been devoted to producing defect-free electrolyte layers with a sub-micrometer thickness on the AAO substrates. Some groups demonstrated the fabrication of the thin film SOFCs on the porous substrates without gas leakage, with the assistance of bi-layered electrolytes and modified electrolytes [8,21,22].

To date, most AAO-based thin film SOFCs have employed the dense anode structures to avoid the pinhole problems. It has been reported that formation of the porous anode structures was not required because the AAO pores were not fully clogged by thin film anodes in spite of their dense structures [18,19,21,23]. However, the porous electrode structure is known to be beneficial for mass transport, one of the main factors to determine the fuel cell performance [4,25]. In addition, in terms of the active area at the anode/electrolyte interfaces, the AAO-based thin film structures can have disadvantages compared to other types of

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anode-supported structures and freestanding structures. Therefore, the high porosity in the anode may be more favorable to the AAO-based thin film SOFCs and the properties of the anode structures require the systematic investigation to improve the fuel cell performance.

In this study, we demonstrate the AAO-based thin film SOFCs with the porous anodes. Systematic investigation shows the substantial impacts of the porosity and the thickness of the anode layer on the electrochemical performance of fabricated cells. Our results show that an optimized anode structure can lead to higher reactivity at the anode/electrolyte interface and more abundant fuel supply to the active sites in the AAO-based thin film fuel cells.

2. Experimental details

A commercial anodic aluminum oxide (AAO, Synkera Technology Inc.) with a thickness of 100 μm and a pore diameter of 80 nm was used as a template to support the thin film SOFCs with an electrolyte thickness of hundreds of nanometers. Pt thin films were sputtered on the AAO template with power of 200 W for the anode layers. During deposition, an Ar pressure was varied from 0.67 Pa to 12 Pa to control the porosity of the Pt film [19,26]. At each Ar pressure, the Pt thin films were deposited with a thickness of 150, 300 and 450 nm. An YSZ electrolyte and a porous Pt cathode were sputtered on the Pt anodes under identical sputtering conditions for all cells to investigate the effects of the anode structure on the fuel cell performance. The YSZ electrolytes with a thickness of ~500 nm were sputtered from an $Y_{16}Zr_{84}$ alloy target at 200 W. YSZ deposition was conducted at 0.67 Pa of Ar/O_2 atmosphere and at room temperature. 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.

Polarization characteristics of the fabricated cells were measured by a commercial analytical interface Solatron 1260/1287 at 500 °C. The schematic configuration of the test set-up and the fabricated cells was reported in our previous publications [18,19]. A silver paste was used for the physical and electrical connections between the anode and the custom-made metal chamber in a halogen heating system. Ceramic adhesive (Aremco Products Inc.) was used for the gas sealing. The current response from the cathode was collected by a microprobe. The anode side was fed by 100 sccm of dry hydrogen through the AAO pores, while the cathode side was exposed to ambient air. Field emission secondary electron microscope (FE-SEM: Supra 40, Carl Zeiss) was used to examine the surface morphologies of the anode, the YSZ electrolyte and the cathode. Focused ion beam and scanning electron microscope (FIB-SEM: Quanta 3D FEG, FEI Company) were utilized to observe the cross-sectional images of the fabricated fuel cells.

3. Results and discussion

Fig. 1 represents cross sectional images of the fabricated thin film SOFCs on AAO substrates. In all cells, we used the identical conditions for deposition of the electrolyte and the cathode, while varied the deposition conditions for the anode to examine the effects of the anode structure on the cell performance. We controlled the porosity and the thickness of the anode by varying the Ar pressure during deposition and the deposition time. The lower Ar pressure (0.67 Pa) produced the dense Pt anode, while the higher Ar pressure (12 Pa) produced the porous Pt anode [26]. At each Ar pressure, we fabricated cells with an anode thickness of 150, 300 and 450 nm. Accordingly, a total of 6 cells were investigated to examine the correlations between the porosity and the thickness of the Pt anode and the cell performance.

The current–voltage curves of fabricated cells measured at 500 °C are depicted in Fig. 2. The open circuit voltage (OCV) values for all cells were comparable, regardless of the anode structures. The measured OCV values (1–1.1 V) were close to the theoretically expected values from the Nernst equation at given conditions (1.18 V) [25]. These high OCV values indicate that the electrolytes deposited on nanoporous substrates were dense enough to be free from pinhole defects. The serious problems with pinhole defects have been reported when the YSZ electrolytes were sputtered on nanoporous AAO substrates with a thickness of several hundred nanometers [18,21,22]. To mitigate the inherent pinhole defects, the dense anodes have been used in thin film fuel cells supported by nanoporous substrates, compensating the overall cell performance. In this study, we demonstrate the fabrication of the AAO-based thin film fuel cells with the high OCV values on the 150 nm thick and the highly porous anode. Moreover, the sequential

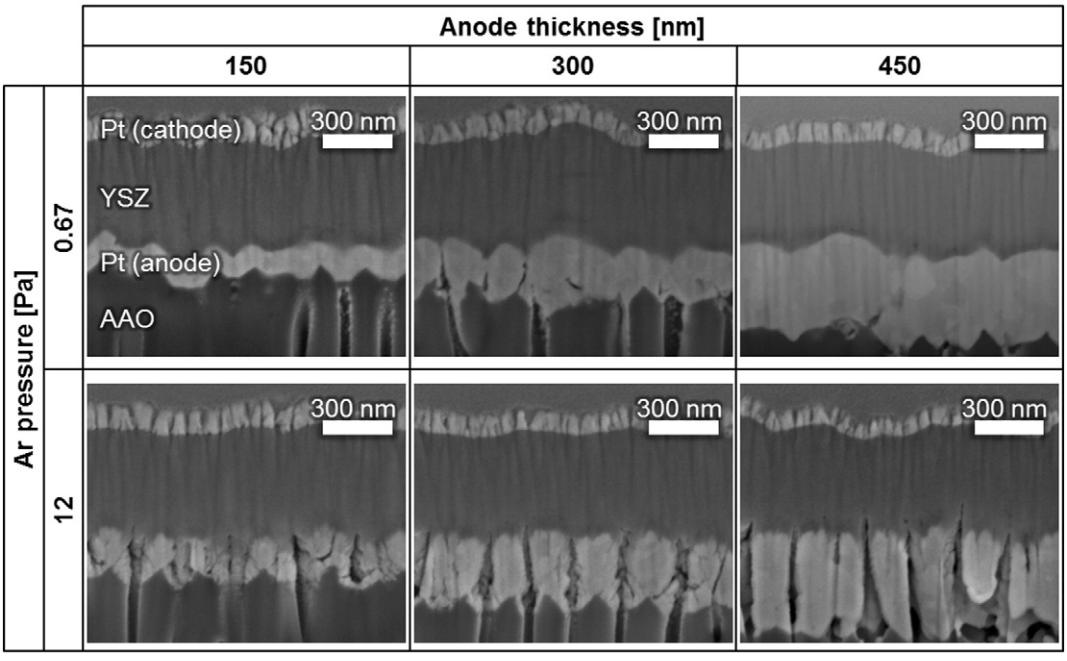

Fig. 1. Cross sectional images of the fabricated cells.