Journal of Power Sources 274 (2015) 611–618

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Low-temperature performance of yttria-stabilized zirconia prepared by atomic layer deposition

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HIGHLIGHTS

- Conductivity of ALD YSZ is greater than reference YSZ by several orders below 100 °C.
- Y_2O_3 concentration of ALD YSZ and humidity are important in electrolyte performance.
- SOFCs with ALD YSZ mark OCVs close to 1 V and decent power below 100 °C.

ARTICLE INFO

Article history:
Received 28 August 2014
Received in revised form
27 September 2014
Accepted 3 October 2014
Available online 16 October 2014

Keywords:
Atomic layer deposition
Yttria-stabilized zirconia
Ion conduction
Solid oxide fuel cells

ABSTRACT

We report on the performance of thin-film yttria-stabilized zirconia (YSZ) synthesized by atomic layer deposition (ALD) at temperatures of 50–525 °C. Electrochemical impedance spectroscopy (EIS) was used for conductivity measurements. Relatively high conductivity values were observed in the low-temperature region when compared to reference values of YSZ synthesized by other methods. To investigate the conduction mechanism, various experimental variables were modified during the electrical measurements, including the ratio of yttria to zirconia in the ALD YSZ films and the atmospheric conditions. To relate the electrical properties to the structural characteristics, the crystallinity and microstructure were investigated using transmission electron microscopy (TEM) and X-ray diffraction (XRD). Finally, the suitability of an ALD YSZ membrane as the electrolyte of micro solid oxide fuel cells was evaluated. An open circuit voltage of almost 1 V and decent power output were successfully measured below 100 °C.

1. Introduction

Yttria-stabilized zirconia (YSZ) films have been widely used as ceramic electrolytes for various high-temperature electrochemical systems, including solid oxide fuel cells (SOFCs), solid oxide electrolyzers (SOECs), and gas sensors. The main reason for their widespread use is that YSZ films exhibit reasonably high conductivity of oxide ions (O^{2-}) at elevated temperatures, as well as excellent thermal, chemical, and mechanical stability. There have been recent efforts to use atomic layer deposition (ALD) to produce YSZ electrolytes in order to develop high-performance SOFCs [1–6]. ALD is a modified chemical vapor deposition (CVD) technique for the surface-limited, cycle-by-cycle, chemical deposition of nano-scale films. Using this method, the substrate surface is alternately exposed to different vaporized source chemicals or precursors. With each exposure cycle, the film grows until the chemisorbed precursors occupy the full surface area of the substrate in the form of a single layer; even with an excessive precursor supply, the growth will not continue beyond a single layer. For this reason, both the thickness and the composition of ALD films can be precisely controlled at the atomic (layer-by-layer) scale [7–11].

ALD-prepared YSZ (hereafter referred to as ALD YSZ) films can be synthesized by alternating the ALD cycles between the host material, ZrO_2, and the dopant, Y_2O_3. It is noteworthy that SOFCs with ALD YSZ electrolytes outperform similar SOFCs using YSZ films prepared by other thin-film techniques [1,6,12,13]. This enhanced performance has been attributed to two properties: the reduced ohmic loss across the ultrathin membrane when used as a

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http://dx.doi.org/10.1016/j.jpowsour.2014.10.022
0378-7753/

freestanding electrolyte in micro-SOFCs, and the greatly improved surface kinetics of nanocrystalline ALD YSZ films [1,6,12].

Since the activation energy for the migration of O^{2-} ions is relatively high (0.9–1.0 eV), the ionic conductivity of YSZ tends to decrease quickly with decreasing temperature [14]. However, no significant drop in the electrical conductivity has been reported for YSZ at temperatures below 100 °C [15–23]. It has been claimed that these phenomena are due to either the fast diffusion of protons (H^+) through physical pores, or the presence of grain boundaries in which H^+ seems to reside in the form of hydroxyl ions OH^- [3,15,17,18,21–28]. An abundance of H^+ ions and their effect on conduction during fuel-cell operation have been identified in ALD YSZ films. These properties are suspected to be a consequence of sample synthesis using vaporized water as the oxidizing source for the ALD cation precursors [3,28]. However, to the best of our knowledge, there are no reports on the electrical properties and fuel cell performance of ALD YSZ films at temperatures below 100 °C, where proton diffusion is dominant.

In this work, we prepared nanoscale YSZ thin films by ALD and measured the conductivity across the films at temperatures as low as 50 °C. The properties of the ALD films were evaluated in relation to the concentration of Y_2O_3. Our results were compared with reference data for similarly thick YSZ thin films, fabricated by other techniques, including spray-pyrolysis (SP) and aerosol-assisted CVD (AA-CVD). Finally, we tested the applicability of ALD YSZ membranes as freestanding electrolytes in dry hydrogen micro-SOFCs. The fuel-cell performance was evaluated in terms of voltage and current.

2. Experimental

Tetrakis(ethylmethylamido) zirconium(IV) (UP Chem.) and tris(methyl-cyclopentadienyl) yttrium(III) (Strem Chem.) were used as cation precursors for the ALD of ZrO_2 and Y_2O_3, respectively, and distilled water was used as the oxidant. The temperature of deposition was 250 °C, and dry nitrogen was used as the purge and carrier gas (flow rate of 0.5 sccm). The precursor and oxidant pulsing times were both 0.5 s, followed by 30 s of N_2 purging. The ALD cycle ratios of ZrO_2 to Y_2O_3 were 2:1, 4:1, and 10:1, resulting in about 15–16, 8–9, and 2–3 mol% of Y_2O_3, respectively [4,16,17]. This was confirmed by X-ray photoelectron spectroscopy (XPS, SSI S-Probe, monochromatic Al Kα radiation). For comparison, pure ALD ZrO_2 films were also prepared.

The ALD YSZ films were deposited onto dense Pt-coated Si(001) wafers with a titanium interlayer for Pt–Si binding. This underlying Pt/Ti layer was fabricated with a 200 W Hitachi E-1030 DC sputterer. The underlying Pt/Ti layer acted as the bottom electrode for the cross-plane conductivity measurements. The sputtering was conducted in an Ar environment at a pressure of 1 Pa, and the thickness of the layer was approximately 150 nm. The top electrodes were sputtered onto the ALD YSZ films using shadow masks to form circular patterns of dense, 250 nm thick Pt layers. The diameter of the top electrodes varied from 0.5 to 2 mm, as shown in Fig. 1(a). The variation of electrode size was used to confirm the origin of the measured impedance (*i.e.*, that it originates across the electrolyte membrane between electrodes).

The thickness and microstructure of the films were evaluated using transmission electron microscopy (TEM, JEOL JEM 2100F) in high-resolution (HR) and high-angle annular dark-field (HAADF) scanning modes. The crystal structures of the ALD YSZ samples were obtained by X-ray diffraction (XRD, TTK 450). The samples were heated in ambient air (relative humidity (RH) of 50%) or dry air to between 50 and 525 °C, and analyzed with electrochemical impedance spectroscopy (EIS, Gamry Reference 3000 Potentiostat/Galvanostat/ZRA). Before the electrical measurements, the sample temperatures were monitored using a separate temperature probe attached to the surface of a blank substrate for temperature calibration. Data analysis and fitting were performed using commercial circuit-fitting software (Gamry PHE200).

For the fabrication of micro-SOFCs with freestanding ALD YSZ electrolytes, micro-patterned Si_3N_4/Si wafers were prepared with a process similar to that reported previously in the literature [1,3,6]. The area of the freestanding Si_3N_4 window was 180 μm × 180 μm, which represents the working area of the micro-SOFCs. A 100-nm thick ALD YSZ layer was deposited on top of the Si_3N_4 side. For comparison, a 100-nm thick YSZ layer was produced by pulsed laser deposition (PLD). A KrF excimer laser (λ = 238 nm, Compex Pro 201F, Coherent) with a laser fluence of ~2.5 J cm^{-2} was used for target ablation. During PLD, the substrate temperature and ambient O_2 pressure were maintained at 700 °C and 6.67 Pa, respectively. After the preparation of YSZ films by ALD and PLD, reactive-ion etching (RIE, CF_4 etching gas) was performed to remove the backside Si_3N_4 membrane. A 100-nm thick, porous Pt layer was deposited on both sides of the wafer with DC sputtering; these layers acted as the catalytic electrodes of the micro-SOFCs. The measured sputtering growth rate was 0.02 nm s^{-1} at 350 W and an Ar environment pressure of 12 Pa. A TEM cross-sectional image of the resulting membrane-electrode assembly (MEA) is shown in Fig. 1(b). The performance of the micro-SOFCs was evaluated using the setup described in our previous report [32]. Dry H_2 gas passed through water at a constant temperature in a thermostat bath, resulting in 3%P_{H2O}. The humidified H_2 was fed into the anode-side compartment while the cathode side was exposed to ambient air during the measurements. The open circuit voltage (OCV) was monitored from 25 °C to 100 °C with constant temperature increments over time (0.125 °C s^{-1}). Current–voltage (I–V) plots were recorded from the micro-SOFCs at 100, 200, 300, and 400 °C.

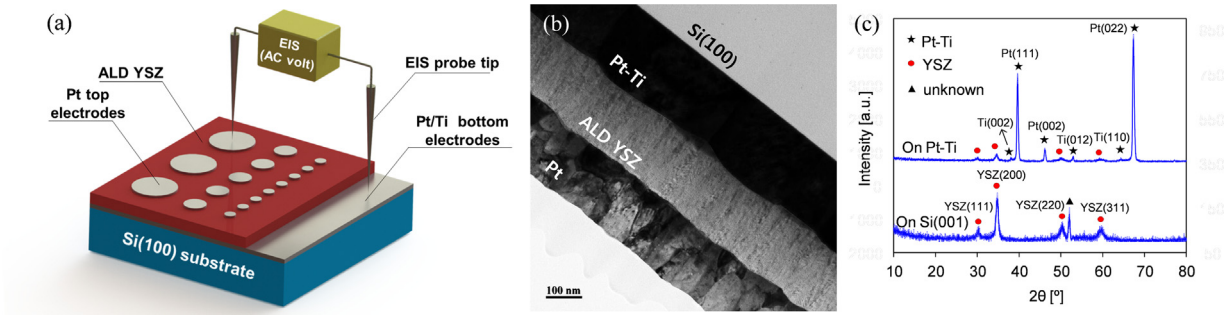

Fig. 1. (a) Experimental setup for cross-plane impedance measurements of the ALD YSZ films. (b) HRTEM image of 180 nm thick ALD YSZ (4:1) film, fabricated between sputtered Pt electrodes. (c) XRD patterns of 200 nm thick ALD YSZ (4:1) films, fabricated on bare-Si(001) and Pt/Ti-coated Si(001) wafers.