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A Novel Method for Fabrication of Y_2O_3-Stabilized ZrO_2 Electrolyte Films

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Gas-tight Y_2O_3-stabilized ZrO_2 (YSZ) films were prepared on NiO–YSZ and NiO–SDC ($Sm_{0.2}Ce_{0.8}O_{1.9}$) anode substrates by a novel method. A cell, Ni–YSZ/YSZ(10 μm)/LSM–YSZ, was tested with humidified hydrogen as fuel and ambient air as oxidant. The maximum power densities of 1.64, 1.40, 1.06, and 0.60 W/cm^2 were obtained at 850°, 800°, 750°, and 700°C, respectively. With methane as fuel, a cell of Ni–SDC/YSZ (12 μm)/LSM–YSZ exhibited the maximum power densities of 1.14, 0.82, 0.49, and 0.28 W/cm^2 at 850°, 800°, 750°, and 700°C, respectively. The impedance results showed that the performance of the cell was controlled by the electrode polarization rather than the resistance of YSZ electrolyte film.

I. Introduction

Solid oxide fuel cells (SOFCs), which can convert chemical energy into electrical energy directly, are attracting more and more attention because of their high efficiency, low pollution, and fuel flexibility.[1,2] From the viewpoint of cost reduction and long-term stability, many researchers have paid attention to the fabrication of SOFCs operating at reduced temperatures (600°∼800°C). Reducing the thickness of Y_2O_3-stabilized ZrO_2 (YSZ) electrolyte is an effective approach to lower the operation temperature of SOFCs, while retaining the high performance. Chen *et al.*[3] reported a unique thin-film SOFC design based on thin-film deposition and microlithographic processes. In their experiment, 2 μm thick YSZ films were deposited onto 6 μm thick polycrystalline nickel foils by pulsed laser deposition and the single cell showed a maximum power density of 110 mW/cm^2 at 570°C. de Souza *et al.*[4] reported an anode-supported SOFC with a 10 μm thick YSZ electrolyte film and the Ni–YSZ/YSZ/LSM cell showed an extremely high power density of 1.9 W/cm^2 at 800°C. Recently, the effect of cell parameters (electrolyte thickness, cathode interlayer thickness, anode thickness, etc.) on polarization in anode-supported SOFCs has been investigated in detail by Zhao and Virkar.[5] Based on the optimized cell parameters, the corresponding maximum power density was ∼1.8 W/cm^2 at 800°C. Dollen and Barnett[6] developed anode-supported YSZ film SOFCs by screen printing technology and got a maximum power density of 1.45 W/cm^2 at 800°C. A variety of film deposition techniques have been explored for the preparation of dense ceramic films on porous electrode substrates, including chemical vapor deposition,[7] DC magnetron sputtering,[8] tape casting,[9] spray coating,[10] centrifugal casting,[11] and so on. To date, YSZ is still the most promising electrolyte material for SOFCs commercialization due to its high physical and chemical stability and high mechanical properties.[12]

In this paper, our aim is to develop a handy and cost-effective method for thin YSZ film fabrication based on a simple physical and co-firing process. Some initial experimental results are reported here.

II. Experimental Procedure

(1) Preparation of Starting Powders

NiO powder was prepared by an ammonia precipitation method from nickel nitrate solution. Ammonia (analytical reagent, A.R.) was added to $Ni(NO_3)_2 \cdot 6H_2O$ (A.R.) solution drop by drop to obtain nickel hydroxide deposition. Then, the as-prepared deposition was aged at 70°C for 40 min. After washing by alcohol and drying at 105°C, the resultant deposition was finally fired at 400°C for 2 h to get nickel oxide powder.

SDC ($Sm_{0.2}Ce_{0.8}O_{1.9}$) powder was prepared by a citric-nitrate process. Stoichiometric amounts of $Ce(NO_3)_3 \cdot 6H_2O$ (A.R.) and Sm_2O_3 (A.R.) were dissolved in diluted HNO_3 (A.R.), and citric acid (A.R.) was added as the complexant. The molar ratio of total cation to citric acid was 1/1.15. The solution was evaporated at 75°C to form a transparent gel. After drying at 100°C for 12 h, the transparent gel changed to a brown dry gel. The dry gel was subsequently fired at 750°C for 2 h to get SDC powder.

$La_{0.7}Sr_{0.3}MnO_3$ (LSM) was used as the cathode material in this study. The method for the preparation of LSM powder was similar to that for SDC powder, as described above. The starting materials for LSM powder preparation were all analytical reagents in this study. The LSM powder was obtained by firing the as-prepared dry gel at 1000°C for 4 h.

YSZ powder (0.2 μm) bought from Tosoh corporation (TZ-8Y, Tokyo, Japan) was used to prepare thin electrolyte films.

(2) Preparation of Anode Substrates

NiO powder and YSZ powder were used to prepare NiO–YSZ anode substrates. They were weighted and mixed in a weight ratio of 1:1. To obtain sufficient porosity in the anode substrates, 10 wt% starch was added as pore former. After being ground in an agate mortar for 1 h, the mixed powder was pressed into pellets of 13 mm in diameter and 0.5 mm in thickness under a pressure of 260 MPa. Then the pellets were subsequently sintered at 1000°C for 2 h to improve their mechanical property. After sintering, the pellets can be used as the anode substrates. NiO–SDC anode substrates were also fabricated by the same method. The NiO–SDC anode contained 50 wt% NiO powder and 50 wt% SDC powder.

(3) Preparation of YSZ Film and Cathode

A terpineol-ethylcellulose mixture was used as organic vehicle to prepare YSZ paste. The vehicle was prepared by dissolving 6

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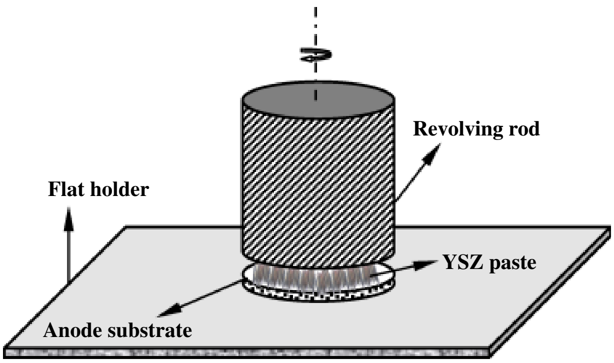

Fig. 1. Schematic diagram of Y_2O_3-stabilized ZrO_2 (YSZ) film deposition equipment.

wt% ethylcellulose (A.R., Dongfeng Chemical Reagents Plant, Wenzhou, China) into 94 wt% terpineol (A.R., Tianjin Kermel Chemical Reagents Development Centre, Tianjin, China). Figure 1 shows the schematic diagram of YSZ film deposition equipment. The equipment was composed of a revolving rod and a flat holder. The flat holder was used to support and fix the anode substrate. The revolving rod was used to spread and compact the YSZ paste onto the anode substrate. YSZ powder was firstly mixed with the organic vehicle in a weight ratio of 4:1 in an agate mortar and was ground for 1 h to obtain a stable and homogeneous YSZ paste for compacting YSZ electrolyte film. The viscosity of as-prepared YSZ paste was 263 Pa · S (25°C) as tested by an NDJ-99 rotation viscometer (Chengdu Instrument Plant, Chengdu, China). The rotation speed of the rotor was 1.5 rpm in the viscosity testing. In the next step, a certain amount of YSZ paste was dropped on the surface of the fixed anode substrate. Finally, the paste was spread and compacted onto the anode substrate by the revolving rod. The rotating rate of the rod was 60 rpm. The pressure applied to the revolving rod was 1.3 N/cm^2. After coating, the anode/film bilayer was sintered at 1400°C for 4 h at a heating rate of 5°C/min. By controlling the amount of YSZ paste, the thickness deviation for the sintered YSZ film can be controlled to be ± 2 μm. The YSZ electrolyte films were fabricated onto the NiO–YSZ anode substrates and NiO–SDC anode substrates, respectively, by the same method. For simplicity, the term "NiO–YSZ anode-supported cell" is abbreviated to "NYCELL" and the term "NiO–SDC anode-supported cell" is abbreviated to "NSCELL" hereafter.

LSM powder was mixed with YSZ powder in a weight ratio of 3:2. The mixed powder was then mixed with the terpineol-ethylcellulose vehicle in an agate mortar and was ground for 1 h to obtain a cathode printing ink. The viscosity of the ink was 70 Pa · S (25°C). LSM–YSZ composite cathode was applied onto the YSZ electrolyte by the screen printing technique. After the printing, the cathode was sintered at 1200°C for 2 h in air. The cathode-effective area was 0.25 cm^2.

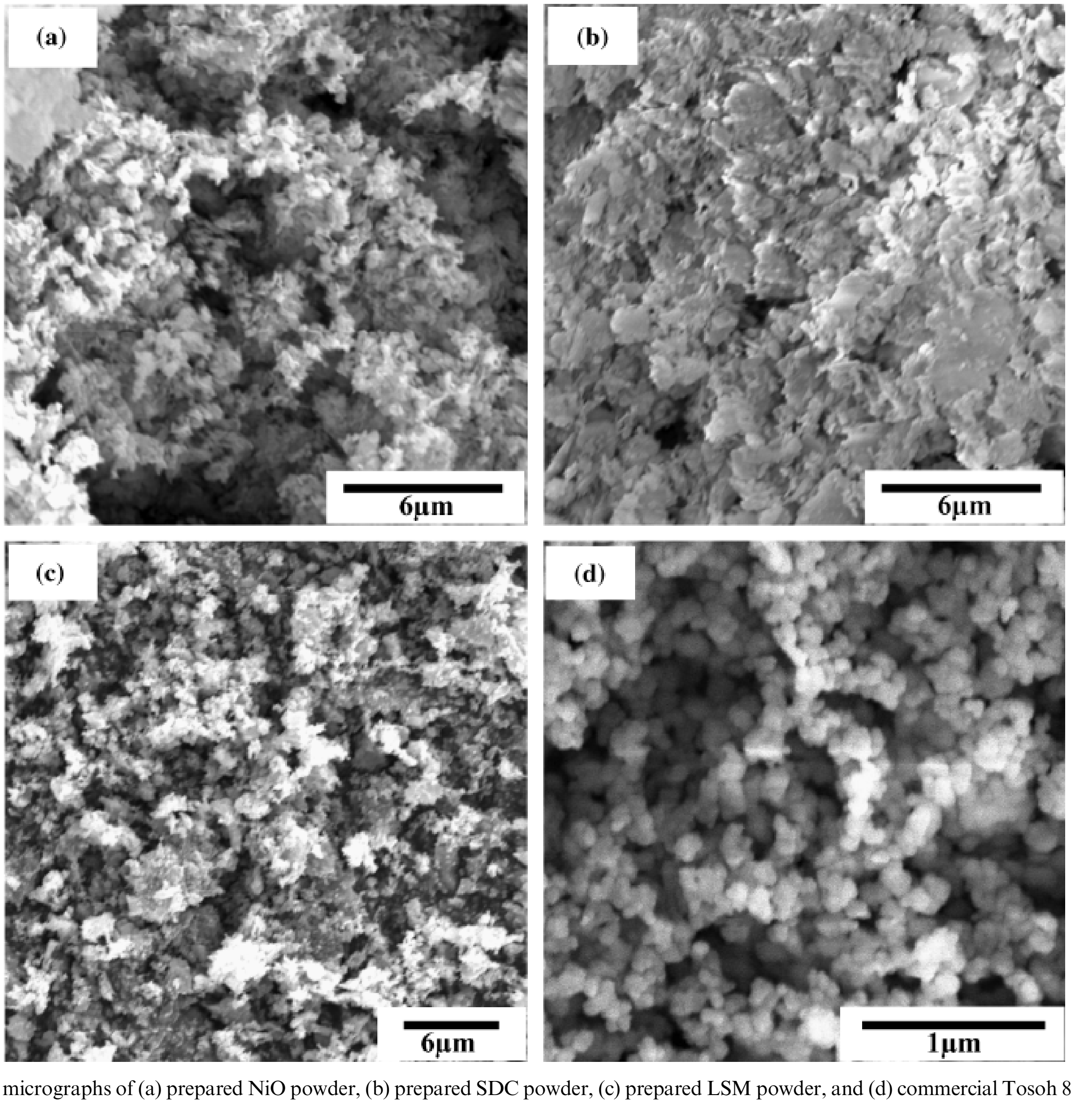

Fig. 2. SEM micrographs of (a) prepared NiO powder, (b) prepared SDC powder, (c) prepared LSM powder, and (d) commercial Tosoh 8YSZ powder.

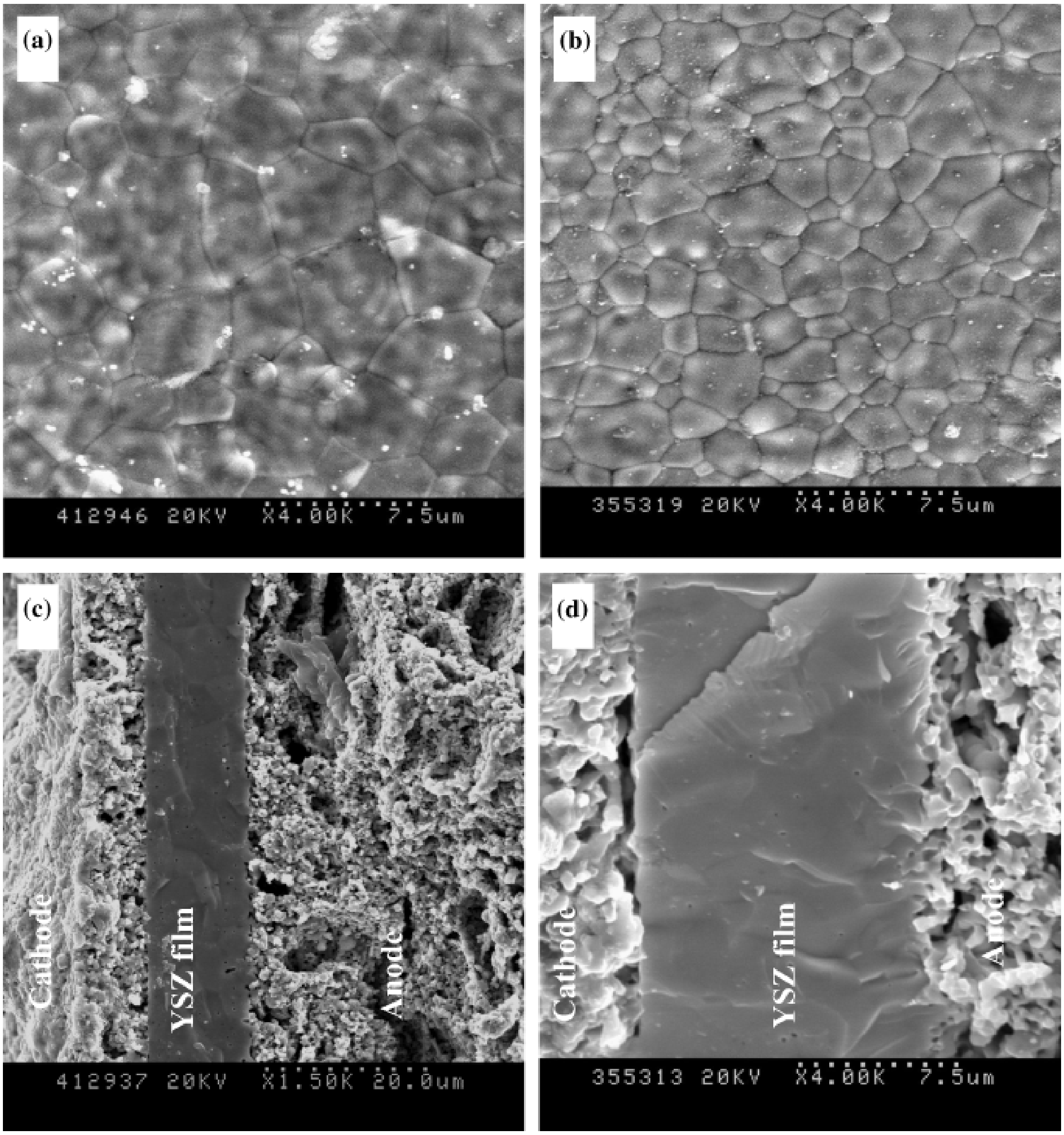

Fig. 3. SEM micrographs of the Y_2O_3-stabilized ZrO_2 (YSZ) films and cells: (a) surface of NiO–YSZ anode-supported YSZ film, (b) surface of NiO–SDC anode-supported YSZ film, (c) cross-section of NYCELL, and (d) cross-section of NSCELL.

(4) Characterizations of Prepared Powders and Anode-Supported SOFCs

The morphology of prepared powders was examined by a Hitachi S-570 (Tokyo, Japan) scanning electron microscope (SEM). X-ray diffraction (Bede D[1] X-ray diffraction meter, Bede Scientific Instruments, Ltd., Durham, UK, Cu*K*α radiation, $\lambda = 0.15418$ nm) was used to confirm the crystalline structure of the prepared powders.

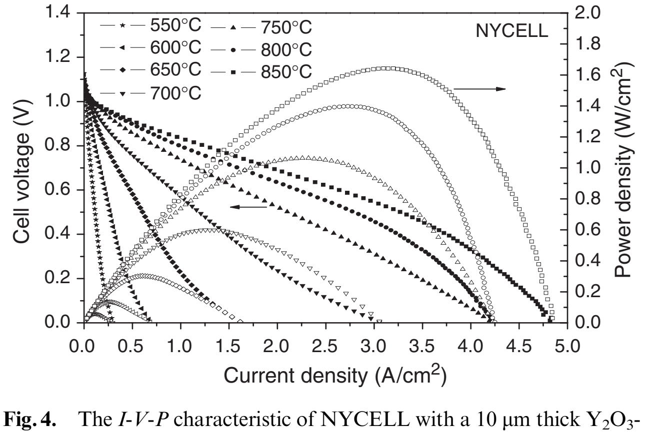

Fig. 4. The *I-V-P* characteristic of NYCELL with a 10 μm thick Y_2O_3-stabilized ZrO_2 (YSZ) film. Humidified H_2 was used as fuel and ambient air as oxidant.

The NYCELL was tested from 650° to 850°C with humidified H_2 as fuel and ambient air as oxidant, while the NSCELL was tested from 700° to 850°C using methane as fuel and ambient air as oxidant. The cell performance and electrochemical impedance spectroscopy were measured using SI-1260 impedance/gain-phase analyzer in combination with SI-1287 electrochemical interface (Solartron Instruments, Hampshire, UK). A four probe set up was used to eliminate the resistive loss in the lead wires. Silver paste was used as the current collector for both anode and cathode. The microstructures of the cell after testing were examined by SEM.

III. Results and Discussion

(1) Prepared Powders

XRD results suggested that all the prepared powders of NiO, SDC, and LSM exhibited the expected phase structure. Figure 2 shows the SEM micrographs of starting powders for the preparation of anode-supported cells. As can be seen from Figs. 2(a)–(c), the prepared powders of NiO, SDC, and LSM were foam-like. The commercial Tosoh 8YSZ powder, as shown in

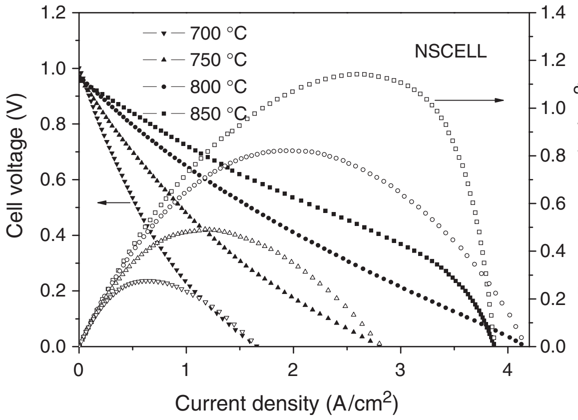

Fig. 5. The *I-V-P* characteristic of NSCELL with a 12 μm thick Y_2O_3-stabilized ZrO_2 (YSZ) film. Methane was used as fuel and ambient air as oxidant.

Fig. 2(d), was composed of spherical-shaped particles with an average particle size of 0.2 μm.

(2) Microstructure of YSZ Film and Electrode

Figures 3(a) and (b) show the surface micrographs of the NiO–YSZ anode-supported YSZ film and the NiO–SDC anode-supported YSZ film, respectively. It can be seen that the YSZ films were composed of irregular grains without cracks or pinholes. The green YSZ film possessed a relative density of 46% before sintering. After sintering at 1400°C for 4 h, the relative density increased to 97%. The shrinkage of the NiO–YSZ anode and the NiO–SDC anode was 21.64% and 21.70%, respectively. The "*z*-direction" shrinkage of the YSZ electrolyte film was calculated by comparing the thickness of the green film with the sintered film. The results showed that the "*z*-direction" shrinkage for the NiO–YSZ anode-supported film was 21.8%, while this ratio for the NiO–SDC anode-supported film was 22.4%. Figure 3(c) shows the cross-sectional SEM micrograph of the NYCELL with a 10 μm thick YSZ film. Figure 3(d) exhibits the cross-sectional view of the NSCELL with a 12 μm thick YSZ film. As can be seen from Figs. 3(c) and (d), the YSZ films were almost fully dense, and both the anode and the cathode exhibited a porous structure. The anode porosity was about 63% as tested using the standard Archimedes method. The porosity for cathode was estimated from the SEM photos to be about 45%.

Figure 4 shows the *I-V-P* characteristic of NYCELL with a 10 μm thick YSZ film. The maximum power densities are 1.64, 1.40, 1.06, 0.60, and 0.30 W/cm^2 at 850°, 800°, 750°, 700°, and 650°C, respectively. It was seen that the open circuit voltage (OCV) was close to the theoretical value and the cell provided a good output beyond 1 W/cm^2 even at an intermediate temperature of 750°C. The tested OCV of the cell was 1.13 V at 600°C. The OCV predicted using Nernst equation was about 1.135 V. The difference between the experimental value and the theoretical one was 5 mV only, which suggested that the gas leakage across the YSZ thin film was insignificant.

Figure 5 exhibits the performance of NSCELL with a 12 μm thick YSZ film using methane as fuel. The maximum power densities are 1.14, 0.82, 0.49, and 0.28 W/cm^2 at 850°, 800°, 750°, and 700°C, respectively.

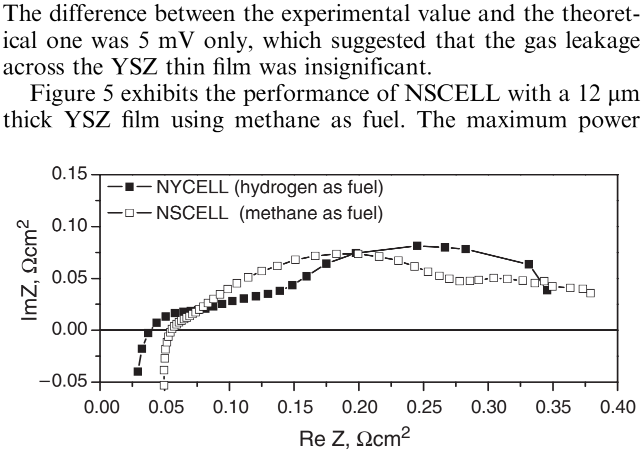

Fig. 6. Impedance spectra of cells measured under the open-circuit condition.

Table I. Characteristics of Cells and their Y_2O_3-Stabilized ZrO_2 (YSZ) Electrolyte Films

	NYCELLA	NYCELLB	NYCELLC
Thickness of YSZ film (μm)	28	8	10
Activation energy of YSZ film (kJ/mol)	66.1	68.6	67.1
Open circuit voltage of cells at 800°C (V)	1.02	1.02	1.01
Maximum power density at 800°C (W/cm^2)	1.12	1.35	1.13

Figure 6 shows two typical impedance spectra under the open-circuit condition at 800°C for both NYCELL and NSCELL. The NYCELL was tested using humidified hydrogen as fuel, and the NSCELL was operated using methane as fuel. The total area specific resistance of the NYCELL at 800°C was 0.35 $\Omega \cdot cm^2$, of which 0.04 $\Omega \cdot cm^2$ came from the YSZ electrolyte film and 0.31 $\Omega \cdot cm^2$ from the interfacial polarization resistance. So, for the NYCELL, the resistance of YSZ film was only about 11.4% of the total cell resistance. For the NSCELL, the resistance of YSZ film was 12.5% of the total cell resistance when methane was used as fuel. So, the cell performance was basically limited by the electrode polarization rather than the YSZ film resistance.

Several NYCELLs were fabricated and tested with humidified H_2 as fuel and ambient air as oxidant. Table I summarizes the characteristics of these cells including the thickness of YSZ films, values of the activation energy of YSZ films, OCV of cells, and maximum power densities.

IV. Conclusions

In conclusion, high-quality YSZ electrolyte films were successfully fabricated on porous NiO–YSZ and NiO–SDC anode substrates by a handy film fabrication technique. The cells exhibited excellent performance in the intermediate temperature range of 600°–800°C. The impedance results showed that the performance of the cell was controlled by the electrode polarization rather than the resistance of YSZ electrolyte films.

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