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Fabrication of YSZ electrolyte for intermediate temperature solid oxide fuel cell using electrostatic spray deposition: II – Cell performance

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Abstract

Electrostatic spray deposition (ESD) was applied to fabricate a thin-layer of yttria-stabilized zirconia (YSZ) electrolyte on a solid oxide fuel cell (SOFC) anode substrate consisting of nickel-YSZ cermet. A colloidal solution of 8 mol% YSZ in ethanol was sprayed onto the substrate anode surface at 250–300 °C by ESD. After sintering the deposited layer at 1250–1400 °C for 1–2 h depending on temperature, the cathode layer, consisting of lanthanum strontium manganate (LSM), was sprayed or brush coated onto the electrolyte layer. Performance tests and AC impedance measurements of the complete cell were carried out at 800 °C to evaluate the density and conductance of the electrolyte layer formed by ESD. With a 97% H_2/3% H_2O mixture and air as fuel and oxidant gas, respectively, the open-circuit voltage (OCV) was close to theoretical and electrolyte impedance was about $0.23\Omega\ cm^2$. A power density of 0.45 W cm^{-2} at 0.62 V was obtained. No abnormal degradation was observed after 170 h operation. The electrolyte sintering temperature and time did not significantly affect the electrolyte impedance.

1. Introduction

An important requirement for the realization of a commercially promising intermediate-temperature SOFC (IT-SOFC), operating at 600–800 °C, is the reduction of ohmic losses in the cell. These losses occur across mixed ionic-electronic conducting electrodes as well as the ionic-conductor electrolyte, but the maximum contribution is from the electrolyte. Reduction of the electrolyte thickness to a few micrometers while maintaining 100% density is the most effective method to decrease the ohmic losses in the cell and ensure IT-SOFC power density levels comparable to, or above, those of the high-temperature SOFC [1, 2].

The Electrostatic Spray Deposition (ESD) technique originally developed for advanced-battery electrodes may be applied to thin-film deposition of yttria-stabilized zirconia (YSZ) electrolyte onto the anode substrate of an IT-SOFC, as demonstrated in earlier work [3]. By means of this technique while using a colloidal solution of YSZ, a NiO–YSZ anode-supported thin-film was manufactured with a final electrolyte thickness (after sintering) of 4–10 μm. This paper focuses on the assembly of a complete cell incorporating the electrolyte fabricated by ESD, and on the electrochemical characterization of the cell.

2. Electrostatic spray deposition (ESD)

ESD combines several attractive features of chemical-reaction-based deposition processes (e.g., chemical vapor deposition) with those of particle-based deposition processes. A complete review of ESD and other deposition processes is available elsewhere ([3–9]).

Specifically for SOFC fabrication, two methods are available to carry out ESD:

1. Using a colloidal suspension of particles consisting of pure oxides in the stoichiometric proportion required for the SOFC component in question, or of particles of the mixed oxide itself, as required for the SOFC component.
2. Using solutions of metal-organics in alcohols or other non-aqueous solvents. Metal-organic solutions are typically premixed in desired stoichiometric ratio, similarly as in the method of using colloidal particle suspensions.

3. Cell assembly

For the cell assembly it is necessary to match the thermal expansion coefficient (TEC) of the composite anode material with that of the electrolyte material. Likewise, the TEC of the electrolyte material must match that of the cathode material. The TEC matching of cathode and electrolyte is more stringent than that of anode-electrolyte, but can be satisfied by choice of materials (e.g., in the high-temperature SOFC by using YSZ8 and appropriately doped LSM).

On the other hand, the anode, usually being a cermet, must accommodate larger microscale variation of TEC but also allow a greater range of composition and structure. An important criterion of effective anode-electrolyte joining is adequate coverage of the anode pores by the electrolyte layer, especially when the latter is of micrometer-scale thickness.

In this work, a Ni/YSZ composite material was used for the anode, with porosity and pore size, designed to ensure a large enough effective surface area for electrochemical oxidation. The overall cell design was of the anode-supported type, which requires an anode thickness of at least 100–200 μm.

4. Experimental

4.1. *Electrolyte*

About 8 mol% YSZ from a commercial source (Tosoh Corporation, Japan) was ball-milled in a glass bottle for 18 h with zirconia balls of 3 mm diameter. The milled YSZ was then dispersed in ethanol and filtered (<0.8 μm). The concentration of YSZ in ethanol was about 0.1 wt.%.

4.2. *Anode*

NiO and YSZ from a commercial source (Johnson Matthey, UK) were mixed in weight ratio 1:1. The mean volume diameter of YSZ particles as received was about 60 μm. Polyethylene glycol (PEG) was added as a binder to the NiO/YSZ composite material (5 to 10 wt.%), and the pellets of NiO/YSZ composite material were formed by hot pressing. Three formulations (Types A, B and C) of anode material were tested to optimize the final composition and structure in order to maintain constant porosity during post-ESD sintering of the anode-electrolyte assembly.

Type A: NiO 47.5 wt.% + YSZ 10 wt.% + PEG 10 wt.% was mixed and ground for 18 h by ball-milling. YSZ 37.5 wt.% was added and mixed, by ball-milling for 30 min.

Type B: NiO 47.5 wt.% + YSZ 10 wt.% + PEG 10 wt.% was mixed and ground for 18 h by ball-milling. YSZ 37.5 wt.% was added and mixed, by ball-milling for 1 h.

Type C: NiO 47.5 wt.% + YSZ 10 wt.% + PEG 10 wt.% was mixed and ground for 18 h by ball-milling. YSZ 37.5 wt.% was added and mixed, by magnetic stirring for 2 h.

The optimal processing method used to fabricate the anode based on which the cell performance was tested in this work was of Type C. NiO was reduced in-situ by fuel (H_2) during the first operation of the assembled cell.

4.3. *Cathode*

$La_{0.85}Sr_{0.15}MnO_3$ (LSM) was prepared by solid-state reaction (SSR). La_2O_3, $SrCO_3$ and $MnCO_3$ (Aldrich Chemical Co., USA) were mixed in weight proportion 42:8:50 and then calcined three times at 1000 °C for 18 h. Between calcinations, the mixtures were ground by mortar and pestle. XRD measurement (Figure 1) was performed on the sample, which showed that the final product was LSM. A slurry was made from LSM (50 wt.%)/YSZ (50 wt.%) and α-terpinol, and this was coated on the electrolyte by brush-coating or precipitation.

5. Electrostatic spray deposition of YSZ

5.1. *ESD set-up*

Figure 2 shows a schematic of the ESD apparatus. It consists basically of a nozzle (hypodermic syringe and needle) with a pump delivering the colloidal suspension of YSZ to the syringe at a measured rate; furthermore, a hot plate to heat the target substrate (in this case, the pre-sintered anode), and a high voltage power supply. The distance between the nozzle and target on the hot plate is adjustable. The entire apparatus can be mounted inside a controlled-atmosphere box. The nozzle in these experiments pointed upward, and the substrate, fixed onto the hotplate, pointed downward. A high DC

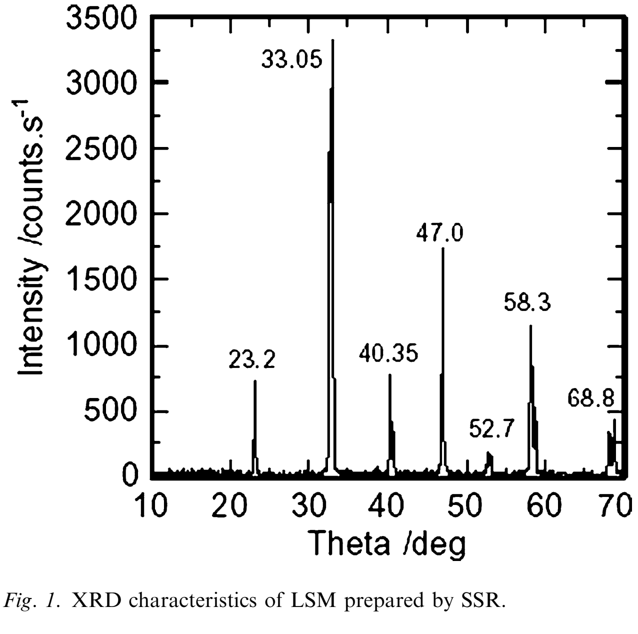

Fig. 1. XRD characteristics of LSM prepared by SSR.

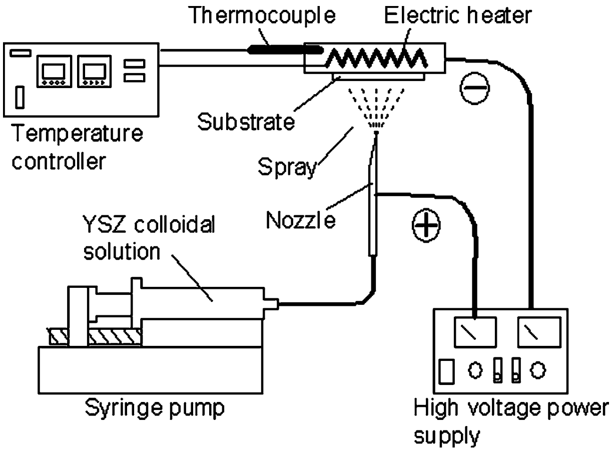

Fig. 2. Schematic of ESD apparatus.

voltage was applied between the nozzle (positive polarity) and the target substrate at ground potential.

5.2. *Sintering of YSZ layers deposited by ESD*

To assure complete densification, the YSZ layers deposited on anode substrate were sintered at 1250–1400 °C for 1–2 h depending on the temperature selected. YSZ particles start to sinter around 900 °C, but if sintering is carried out at such a low temperature, the required duration is very long. Therefore, sintering at several temperatures above 900 °C was explored.

The most important step in the sintering process is the peak sintering temperature, which is between 1250 and 1400 °C, with soak time of 1–2 h. The entire sintering profile starting from 100 °C to the peak temperature as well the cool-down programs are generated based on predetermined conditions based on long term experimental trials.

The sintered YSZ layer was transparent and its surface slightly wrinkled, which appeared to be caused by the cooling-down process. At the beginning of the cooling cycle, shrinkage occurs around discrete spots on the YSZ layer surface, and shallow cracks may be formed between the spots. If the temperature is still sufficiently high for the YSZ to flow (surface-diffusion), the cracks are filled by the electrolyte.

From systematic experiments it was found that quick heat-up and slow cool-down are necessary to generate a smooth YSZ surface. It is essential to adhere to a well-defined temperature program during sintering to obtain good results. The temperature program must be validated by post-sintering in-cell checks of gas-tightness, since micro-cracks in the sintered YSZ layer can seldom be observed with an optical microscope. Other, more obvious defects generated by sintering the ESD-generated YSZ layers on the anode substrate can be observed. These are listed below:

- Warping of the bilayer (or cell) when the shrinking force of the YSZ layer is too great for the mechanical strength of the anode.
- Growth of NiO crystals across the YSZ layer. This occurs when YSZ and NiO in the anode pellet have not been mixed sufficiently.
- Spot-peeling of the YSZ layer. This occurs if the layer thickness is not uniform.
- Large cracks occurring when the temperature program of the sintering process is seriously sub-optimal.

5.3. *Cell assembly*

After sintering of the YSZ layer deposited on the anode substrate, assembly of the test-cells was completed as follows: the cathode material was coated on the YSZ layer by brush-coating a LSM slurry, or by precipitation. This was followed by sintering of the three-layer cell, at 1200 °C for 1 h. This whole-cell heat treatment was carried out using a pre-determined sintering program.

We note here that the porous LSM cathode could have been deposited on the electrolyte equally well by ESD, following a procedure similar to that used in depositing $LiCoO_2$ or $LiMn_2O_4$ layers.

This is an area of interest and work is currently in progress by the current authors to explore it further.

After sintering the three-layer assembly, platinum-mesh current collectors were attached with platinum ink to the anode and the cathode, and the assembly was heated to ensure good bonding of the current collectors. Current and potential leads were similarly attached and bonded.

The cell package (20.5-mm diameter and about 1-mm thick) was then seated across the top of a 19.5-mm ID, 25.4-mm OD, 50-cm long zirconia pipe, and sealed in place with several layers of ceramic cement (Figure 3). The pipe was inserted in a vertical tube furnace open to air at both ends such that the pipe end with the cell on it was far enough into the hot zone of the tube furnace to ensure the correct operating temperature, while the cathode remained practically in convective contact with bulk air. The other (cool) end of the zirconia pipe remained outside the tube furnace and could be sealed with a stopper through which a long and a short glass tube were inserted to serve as, respectively, fuel gas lead-in (extending to within a few cm from the anode) and gas exit. The fuel gas was hydrogen humidified with 3% H_2O. The operating temperature of the cell was ascertained by a thermocouple tube, with its junction within a few mm of the SOFC test cell, which was also fed through the stopper. The entire test assembly is shown schematically in Figure 4.

5.4. *Cell performance test*

The test cells were slowly heated and maintained at an operational temperature of 800 °C. Figure 5 shows the open circuit voltage over the temperature range of 600–800 °C. The values are very close to theoretical and showed that the gas-tightness of the cell assembly was satisfactory, with no electrical leaks due to inadvertent contact of electric leads. The cell performance was tested at a specific temperature of 800 °C. There is currently no data available for the cell performance at 600 and 700 °C, although ongoing work by our research group will include cell performance testing at these temperatures.

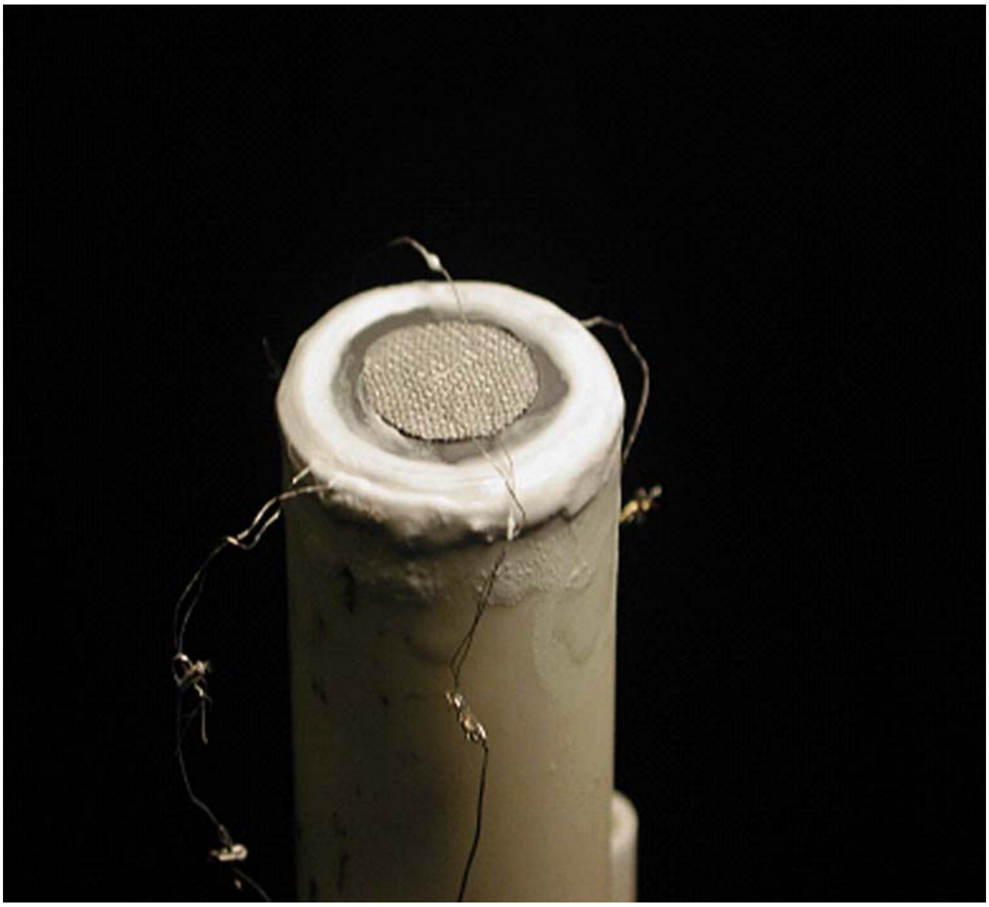

Fig. 3. Picture of single cell on test stand.

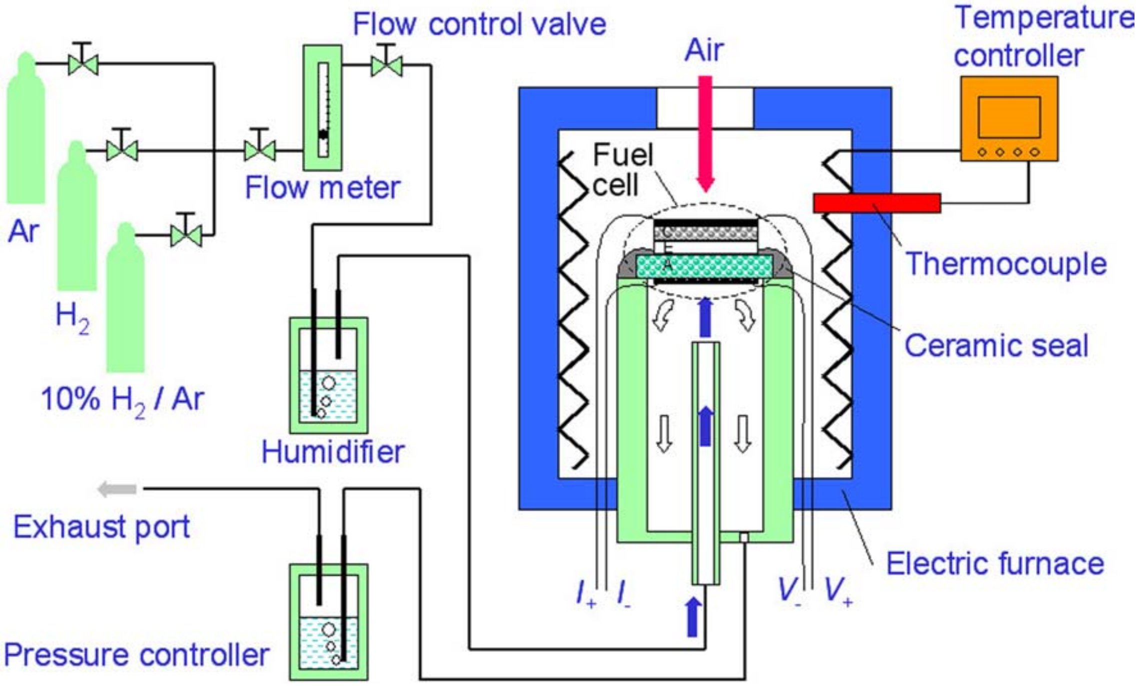

Fig. 4. Apparatus used for performance testing.

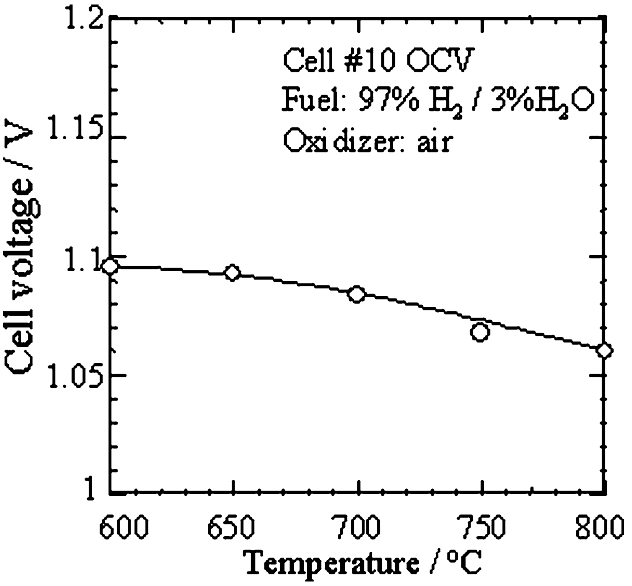

Fig. 5. Open-circuit voltage of typical cell as a function of temperature.

A typical polarization curve together with the power density curve at 800 °C is shown in Figure 6. The active area considered to calculate current density was based on the approximate diameter of the wire gauze current collector. The approximate diameter therefore considered in power density calculations is between 12 to 14 mm.

The individual measurements at intervals of 50 mA cm^{-2} were taken several hours after each current step. The polarization curve shows that at low current densities, electrode-kinetic resistance seems to be significant, but from approximately 400 mA cm^{-2}, the cell polarization appears to be mainly ohmic with a fairly constant ASI (area-specific impedance) of 0.368 ohm cm^2. This ASI can be considered quite satisfactory. The highest power density achieved in the test of Figure 6 was 0.45 W cm^{-2} at 700 mA cm^{-2}. The polarization curve was voluntarily terminated around 700 mA cm^{-2} without any specific reason. The curve did not display any hysteresis.

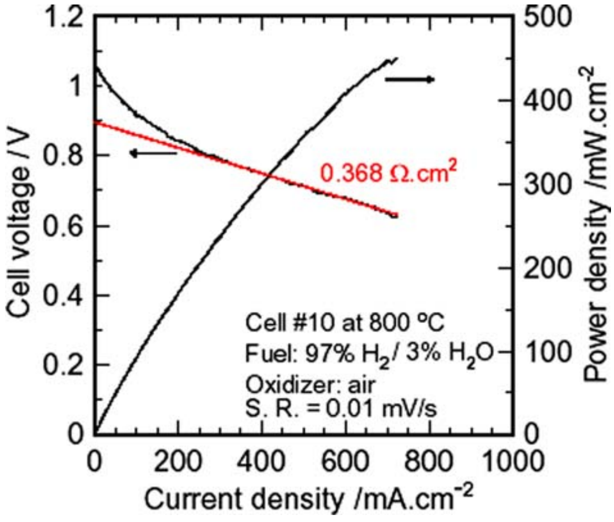

Fig. 6. Polarization and power density curves of typical cell at 800 °C.

However, this was clearly not the maximum attainable power density. From a rough extrapolation, the maximum attainable power density appears to be around 0.55 W cm^{-2} at 1.2 A cm^{-2}. These results show that the ESD deposition technique is suitable for fabricating IT-SOFC cells which exhibit a very good performance at 800 °C, and probably at lower temperatures as well.

An AC-impedance test of the cell was carried out under load (0.7 V, i.e., approximately 500 mA cm^{-2} DC current), under the conditions used in the test shown in Figure 4. The Cole–Cole impedance plot (100 kHz to 0.01 Hz) is shown in Figure 7. Apart from a high-frequency inductive effect, the plot shows three semi-circles of which the two low-frequency curves overlap. Without a detailed equivalent-circuit analysis, it appears justified to conclude that the kinetic resistance and diffusion resistance (first and second semi-circles) are approximately equal and relatively small (0.232 ohm cm^2 at 631 Hz), while the low-frequency resistance, probably due to Nernst potential response at slow gas flow rate, is slightly larger.

The performance of the cell at 0.6 V over 170 hours of operation was monitored (Figure 8). It appeared to stabilize after 80 h and remained constant for 170 h, at which point the test was voluntarily terminated. The power density at 170 h was 0.28 W cm^{-2}, which is close to the initial value of 0.3 W cm^{-2} at 400 mA cm^{-2} shown in Figure 6. Based on these results and the ASI values shown in Figure 7, power densities well above 1 W cm^{-2} should be attainable by reducing the electrolyte thickness to few microns, which generally is adequate to avoid cross-leakage by microcracks or diffusion.

6. Conclusion

This, and previous work [3] has demonstrated that ESD can be a cost-effective method for manufacturing thin

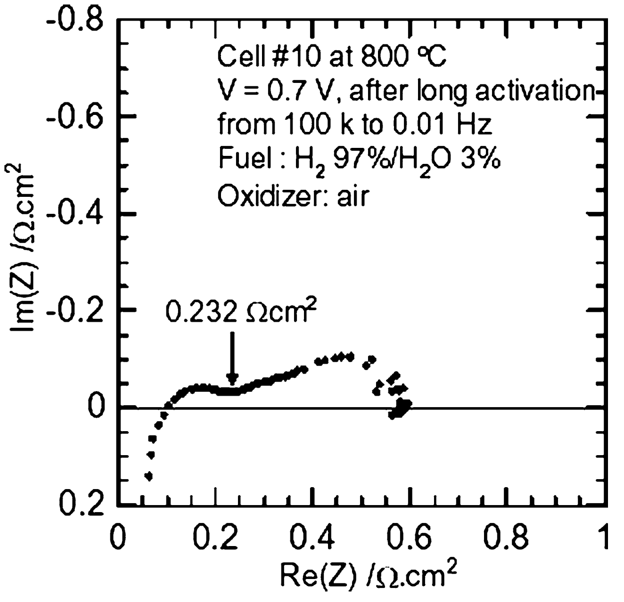

Fig. 7. AC impedance characteristics of typical cell under load, at 800 °C.

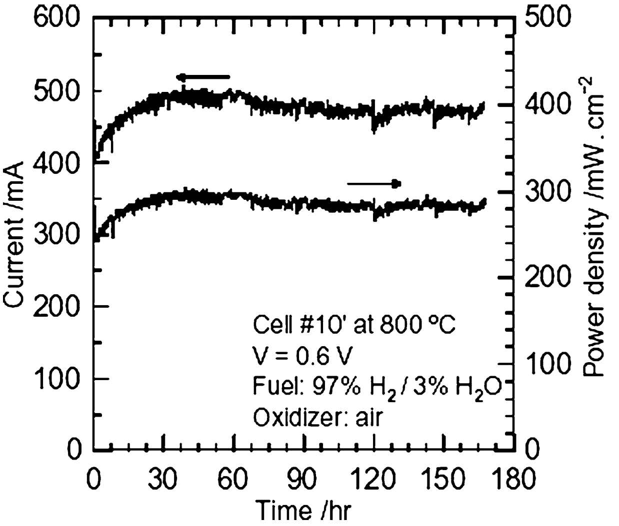

Fig. 8. Life-time (170-h) performance test of typical cell.

and dense YSZ films for IT-SOFC applications. Thin and dense YSZ layers were obtained on a thick NiO–YSZ anode substrate. The cell showed an OCV of approximately 1.06 V and a power density of approximately 0.45 W cm^{-2} at 800 °C. This suggests a probable maximum power density of 0.55 W cm^{-2} at 1.2 A cm^{-2} which is quite encouraging. Further work using ESD with alternate electrolyte material and cathode materials is being carried out to investigate cell performance at lower temperatures.

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References

1. S. de Souza, S.J. Visco and L.C. De Jonghe, *Solid State Ionics* **98** (1997) 57.
2. W. Huebner and H.U. Anderson, 'Solid Oxide Fuel Cell Performance Studies: Anode Development', Department of Ceramic Engineering University of Missouri – Rolla DOE Award No. DE-FG26-98FT0487, November 1999.
3. Hiroshi Nomura, Sandeep Parekh, J. Robert Selman, and Said Al-Hallaj, *J. Appl. Electrochem.* **35** (2005) 61.
4. K. Kordesch and G. Simader, *Fuel Cells and their Applications* (VCH Weinheim, 1996).
5. A.A. van Zomeren, 'Thin Films of Lithium Intercalation Compounds', PhD. Dissertation Technical University Delft (1995).
6. Roland Diethelm (Coordinator), 'Swiss Federal Office of Energy Program: Fuel cells and Accumulators', Institut für Nichtmetallische Werkstoffe Eidgenössische Technische Hochschule Zürich; Consortium: Low Cost SOFC; Annual Report 1999.
7. J. Schoonman, *Solid State Ionics* **135** (2000) 5.
8. J. Will, A. Mitterdorf, C. Kleinlogel, D. Perednis and L.J. Gauckler, *Solid State Ionics* **131** (2000) 79.
9. T. Nguyen and E. Djurado, *Solid State Ionics* **138** (2001) 191.