



Short communication

Electrochemical characterizations of microtubular solid oxide fuel cells under a long-term testing at intermediate temperature operation

Toshiaki Yamaguchi^{a,b,*}, Kevin V. Galloway^a, Jieon Yoon^a, Nigel M. Sammes^a^a Department of Metallurgical and Materials Engineering, Colorado School of Mines, 1500 Illinois Street, Golden, CO 80401, USA^b National Institute of Advanced Industrial Science and Technology (AIST), 2266-98 Anagahora, Shimo-shidami, Moriyama-ku, Nagoya 463-8563, Japan

ARTICLE INFO

Article history:

Received 15 September 2010

Received in revised form 4 November 2010

Accepted 9 November 2010

Available online 18 November 2010

Keywords:

Anode support

Micro-SOFC

Long-term stability

ABSTRACT

We report the long-term stability of a microtubular solid oxide fuel cell (SOFC) operable at $\sim 500^\circ\text{C}$. The SOFC consists of NiO–Gd doped ceria (GDC) as the anode as well as the tubular support, GDC as an electrolyte and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF)–GDC as the cathode. A single tubular cell with a diameter of approximately 1.8 mm and an effective electrode length of approximately 20 mm generated 150 mW cm^{-2} and 340 mW cm^{-2} at 500°C and 550°C , respectively, under the operation conditions of 0.7 V and humidified H_2 fuel flow. The cell exhibited good stability with a degradation rate of 0.25%/100 h under operation conditions of 200 mA and 0.75 V.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Solid oxide fuel cells (SOFCs) have been investigated because of their high energy conversion efficiency and environmental compatibility. A decrease in the operation temperature of SOFCs can realize a widening of the range of applicable materials, such as metallic interconnects and glass sealants, and an improvement in the material degradation, which can result in cost reduction and elongation of the SOFC stack lifetime [1–3]. The use of alternative high performance electrolyte and electrode materials means that the SOFC operation temperature can be reduced [4,5]. In addition, miniaturization of the cell size and integration of multiple miniaturized cells is also considered to be one of the most effective approaches to increasing the volumetric power density [6]. Recently, technologies have been intensively studied to reduce operation temperature, reduce size, and improve start-up and shut-down operation [7–9]. Among the various proposed cell designs, a microtubular SOFC design exhibits many desirable characteristics, for example, increasing the net electrode area per unit volume, and the durability to thermal stress caused by rapid start-up operation [10–12]. In the case of tubular SOFCs, down-sizing the cell size enables an increase in the number of cells that can be accumulated in a certain volume, which leads to an increase in the net electrode area per volume. Thus, it is possible to increase the volumetric power density of SOFC modules at lower SOFC operation

temperatures by gaining a large electrode area per volume, even though the power density of the cell tends to decrease at the lower temperature range.

Very recently, various researchers reported excellent electrochemical performance and durability during heat-cycling for microtubular SOFC designs [7–9,13,14]. Most of the cells were supported by a porous anode tube. Therefore, the anode tubular support works as a current collector and gas diffusion layer as well as support medium for the SOFC. However, there are few reports on the investigation of the stability of performance of microtubular SOFCs during long-term testing, while many papers show single measurement data for a short time period. Thus, this report summarizes electrochemical performance analyzed for an anode-supported microtubular SOFC during long-term testing. The samples were prepared via co-sintering of the electrolyte and porous anode support, and then a cathode layer was also prepared on the electrolyte film. Evaluations were conducted using potentio/galvanostat and an impedance analyzer under humidified hydrogen flow.

2. Experimental

Anode-supported microtubular cells were fabricated as follows. Initially, anode tubular supports were extruded using a mixture of NiO powder (Seimi Chemical Co., Ltd., Japan), $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9-\delta}$ (GDC; Shin-Etsu Chemical Co., Ltd., Japan), pore former beads of $5\ \mu\text{m}$ in diameter (Sekisui Plastics Co., Ltd., Japan), and cellulose binder (Yuken Kogyo Co., Ltd., Japan). The tubular supports have a diameter of approximately 2 mm with a fuel gas channel

* Corresponding author at: 2266-98 Anagahora, Shimo-shidami, Moriyama-ku, Nagoya, Aichi 463-8560, Japan. Tel.: +81 52 736 7526; fax: +81 52 736 7665.

E-mail address: tosiro-yamaguchi@aist.go.jp (T. Yamaguchi).

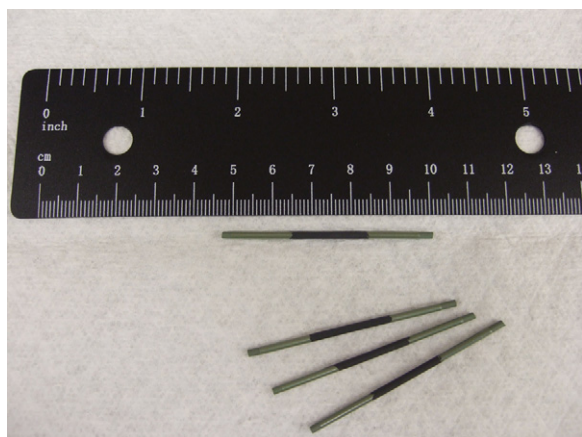


Fig. 1. Photograph of the microtubular cells.

of approximately 1 mm in diameter. The electrolyte and cathode layers were prepared by dip-coating and heating at each temperature, described below. The GDC electrolyte coating slurry was prepared by ball-milling the ceramic powder, methyl ethyl ketone and ethanol mixture solvent, poly vinyl butyral binder, amine-based dispersant, and plasticizer (dioctyl phthalate) for 24 h. The anode green extruded tubes were dipped into the GDC electrolyte slurry with a pulling rate of 1.5 mm s^{-1} , followed by co-sintering at 1400°C for 1 h in air. The GDC-coated tubes were applied with a $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) and GDC mixed cathode ink (Fuel Cell materials), then the tubes were heated at 1000°C for 2 h in air. The completed tubular cells have a diameter of approximately 1.8 mm and a cathode length of approximately 20 mm, that is, the effective electrode area is approximately 1.1 cm^2 . Fig. 1 shows a photograph of the microtubular cell used in this research.

The performance of the cells was measured at 500°C and 550°C using a Chroma 6310 series for current–voltage characterization, and a Gamry 600 for impedance analyses under humidified H_2 (3% H_2O) gas flow at a flow rate of $25 \text{ cm}^3 \text{ min}^{-1}$ and open air. Ag wire was used for current collection from the anode and cathode sides, and the wires on both sides were fixed using Ag paste (903-B; ESL ElectroScience). Current collection from the anode was conducted by winding a Ag wire around the edge of the anode support. The detailed experimental apparatus of the single cell measurement was reported elsewhere [15]. The impedance measurements were conducted in a frequency range from 0.1 Hz to 100 kHz with a signal amplitude of 5 mV under open-circuit condition.

Before the measurements, the cell was reduced at 500°C for approximately 12 h. Long-term stability testing was performed on the microtubular SOFC. The cell was held under a loading condition of 126 mW cm^{-2} (operation: 200 mA and 0.75 V) at 500°C for 100 h. All measurements were also conducted under a humidified H_2 (3% H_2O) gas flow in a flow rate of $25 \text{ cm}^3 \text{ min}^{-1}$ and open air.

3. Results and discussion

Fig. 2 shows the voltage and power density of the microtubular SOFC as a function of current density at 500°C and 550°C after an initial 12 h anode-reduction at 500°C . The open circuit voltages (OCVs) are 0.950 V and 0.934 V at 500°C and 550°C , respectively. As described in other papers, the OCV values below 1 V are due to a current leakage caused by an increase in electronic conductivity in the GDC electrolyte in a reducing atmosphere. The power densities at 0.7 V were 150 mW cm^{-2} and 340 mW cm^{-2} at 500°C and 550°C , respectively. These values are very promising when compared to other reports on anode-supported microtubular SOFCs [16,17].

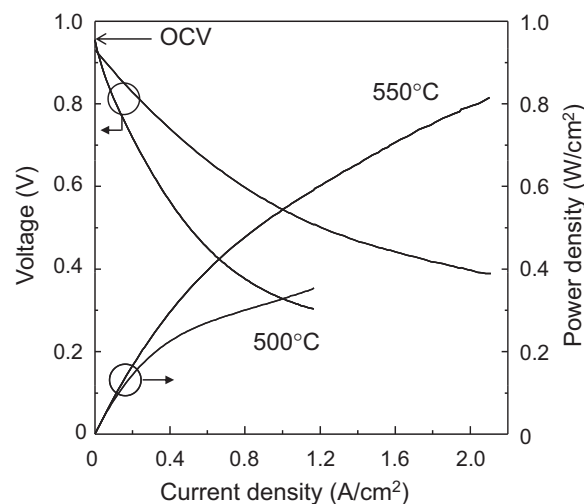


Fig. 2. Single cell performances at 500°C and 550°C .

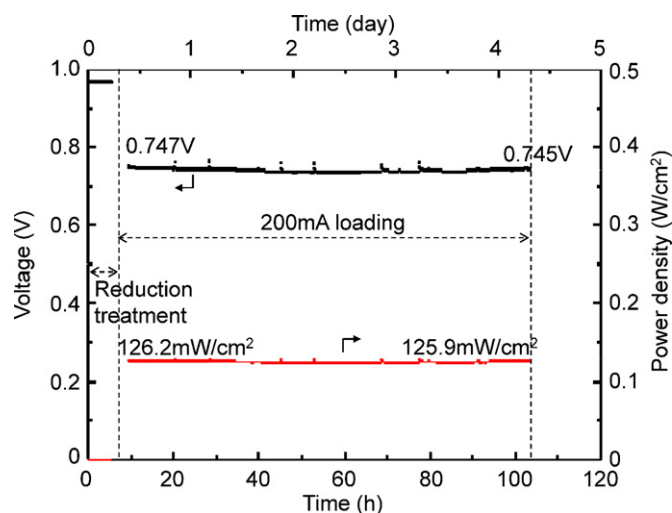


Fig. 3. Long-term stability data of the single cell operated at 500°C .

Fig. 3 shows the change in the operation voltage and the power density as a function of time, at a loading of 200 mA (current density: 169 mA cm^{-2}). The fabricated microtubular SOFC exhibited excellent long term stability, and the 100 h operation brought about a voltage drop of approximately 2 mV, which led to a power density drop of approximately 0.3 mW cm^{-2} . The initial working voltage and power density are 0.747 V and 126.2 mW cm^{-2} , respectively, therefore the degradation rate is calculated to be 0.25%/100 h. A commercial ceramic bond is used as the gas sealant for the single-cell measurements. In view of gas leakage through the ceramic bond layer with partial gas tightness, it is considered that the cell shows an incredibly stable performance. This behavior is quite different from that previously reported [17] using a similar microtubular SOFC (degradation rate: 50%/24 h). The Ref. [17] and this report selected different ways to collect the anode current, even though the material components were similar (Fig. 4 shows the cell setup in this report). Thus, further detailed experiments on the relations between the anode current collection method and long-term characterization are necessary.

Fig. 5 summarizes the change of the impedance spectra over a period of 4 days. Electrode polarization includes both the cathode and anode polarization for gas diffusion and reaction. The “0 day” spectrum (initial datum) has a larger arc in the low frequency region, which belongs to electrode polarization. This indicates that

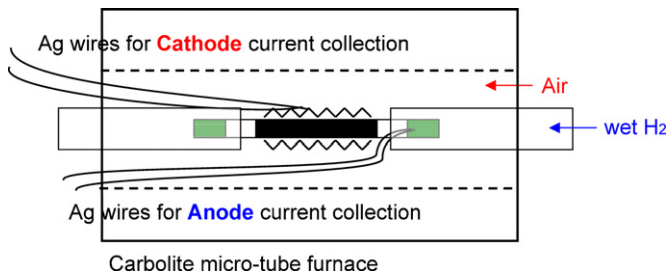


Fig. 4. Cell setup in this report.

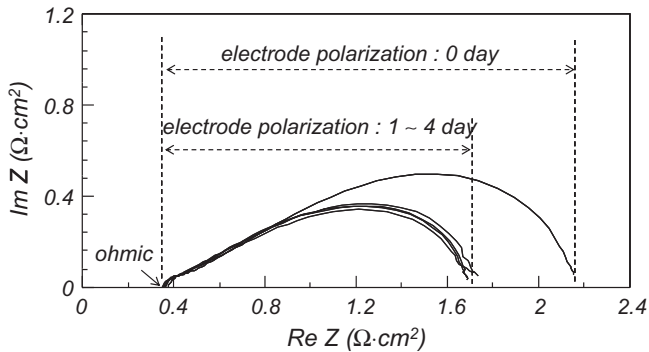


Fig. 5. Impedance spectra of the single cell during a long-term stability testing at 500 °C.

the reduction of NiO to Ni in the anode structure was not complete, and H₂ gas diffusion towards the three phase boundary (TPB) anode reaction sites, and/or the amount of anode TPB reaction sites, were not enough, even after a reduction time of 12 h.

The ohmic and electrode polarizations are re-plotted as a function of the elapsed time in Fig. 6. The ohmic polarizations were extremely stable and the values were approximately 350 mΩ cm² (300 mΩ), which were composed of resistances due to the anode current collection of approximately 100 mΩ and the GDC electrolyte film (approximately 15 μm thick) of approximately 200 mΩ [18]. Further, the electrode polarizations were also highly stable at approximately 1.33 Ω cm² (1.12 Ω), except for the “0 day” spectrum (1.75 Ω cm² (1.48 Ω)). The semicircles for the electrode polarizations are about 4 times higher than those for the ohmic ones, which indicate that the cells can be optimized by optimizing their electrode reaction activity and their electrode porosity (gas diffusivity) [9].

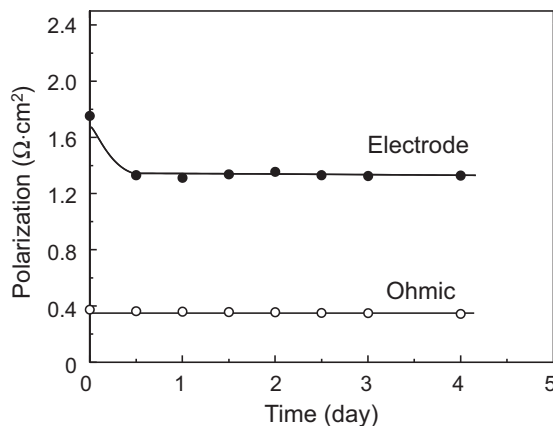


Fig. 6. Ohmic and electrode polarizations of the single cell during a long-term stability testing at 500 °C.

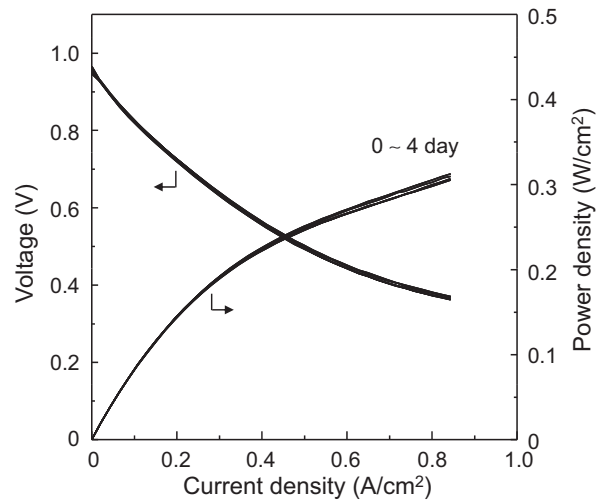


Fig. 7. Single cell performances of the single cell during a long-term stability testing at 500 °C.

Fig. 7 shows the voltage and power densities of the microtubular SOFC on each day, as a function of the current density. All five curves follow approximately the same line, and the power density at 0.7 V remained at approximately 150 mW cm⁻² through the 100 h stability test, which agrees with the description in Fig. 3. In addition, all these data follow the following Tafel Eq. (1), as shown in Fig. 8:

$$\log j = a\eta + \log j_0 \tag{1}$$

where j is the current density, a is a coefficient, η is the electrode polarization, and j_0 is the exchange current density. In addition to following the Tafel equation, an anode porosity above 50%, which was previously reported [19], results in gas diffusion in both of the anode and cathode layers are not affected even by an application of a large overpotential. There were also no deviations in the exchange current density (j_0 : 0.061 A cm⁻²), except for the “0 day” curve (j_0 : 0.050 A cm⁻²). j_0 increases by approximately 20%, which implies that the number of TPB reaction sites on “0 day” was slightly lower when compared to those after the “1 day” operation, while the anode has enough porosity for H₂ gas diffusion even on “0 day”. This corresponds with the results and discussion of the impedance analyses (Fig. 5). The j_0 value of 0.061 A cm⁻² is comparable to that of YSZ-based cells operated at 800 °C [20,21], resulting in the demonstration of our GDC-based cell’s high performance.

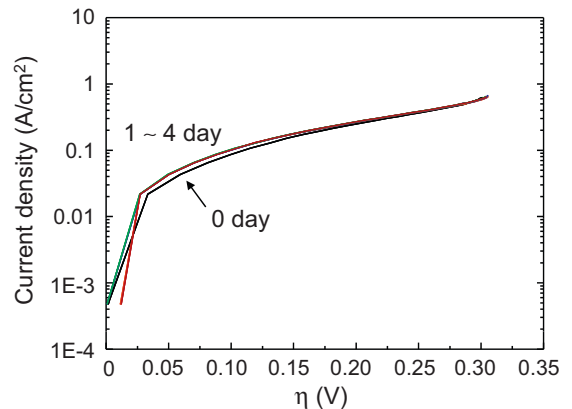


Fig. 8. Tafel plots of the single cell during a long-term stability testing at 500 °C.

4. Conclusion

Here we reported a high performance microtubular SOFC with 1.8 mm diameter operable at under 550 °C, which consists of previously reported materials and an anode microstructure with a high porosity above 50% after reduction. The results showed that the cell performance at 0.7 V was 150 mW cm⁻² and 340 mW cm⁻² and at 500 °C and 550 °C, respectively, with a humidified H₂ fuel flow. This result shows that the weighted power at 0.7 V was 0.4 W g⁻¹ (0.165 W/0.38 g) and 1.0 W g⁻¹ (0.474 W/0.38 g) at 500 °C and 550 °C, respectively. In addition, the microtubular cell possessed good stability with a degradation rate of 0.25%/100 h under an operation conditions of 200 mA at 0.75 V.

Acknowledgements

This study was supported by the Japan Society for the Promotion of Science (JSPS); Excellent Young Researcher Overseas Visit Program. We gratefully acknowledge Dr. Funahashi and NGK Spark Plug Co., Ltd. for supporting to prepare the microtubular SOFCs.

References

- [1] M. Dokiya, *Solid State Ionics* 152–153 (2002) 383.
- [2] T. Hibino, A. Hashimoto, M. Yano, M. Suzuki, S. Yoshida, M. Sano, *J. Electrochem. Soc.* 149 (2002) A133.
- [3] T. Ishihara, J. Tabuchi, S. Ishikawa, J. Yan, M. Enoki, H. Matsumoto, *Solid State Ionics* 177 (2006) 1949.
- [4] B.C.H. Steele, A. Heinzl, *Nature* 414 (2001) 345.
- [5] J.W. Fergus, *J. Power Sources* 162 (2006) 30.
- [6] N.M. Sammes, Y. Du, R. Bove, *J. Power Sources* 145 (2005) 428.
- [7] Y. Funahashi, T. Shimamori, T. Suzuki, Y. Fujishiro, M. Awano, *ECS Trans.* 7 (2007) 643.
- [8] T. Yamaguchi, S. Shimizu, T. Suzuki, Y. Fujishiro, M. Awano, *Electrochem. Commun.* 10 (2008) 1381.
- [9] T. Suzuki, Z. Hasan, Y. Funahashi, T. Yamaguchi, Y. Fujishiro, M. Awano, *Science* 325 (2009) 852.
- [10] I.P. Kilbride, *J. Power Sources* 61 (1996) 167.
- [11] K. Kendall, M. Palin, *J. Power Sources* 71 (1998) 268.
- [12] K. Yashiro, N. Yamada, T. Kawada, J. Hong, A. Kaimai, Y. Nigara, J. Mizusaki, *Electrochemistry* 70 (2002) 958.
- [13] T. Suzuki, Y. Funahashi, Z. Hasan, T. Yamaguchi, Y. Fujishiro, M. Awano, *Electrochem. Commun.* 10 (2008) 1563.
- [14] S. Lee, T. Lim, R. Song, D. Shin, S. Dong, *Int. J. Hydrogen Energy* 33 (2008) 2330.
- [15] T. Yamaguchi, T. Suzuki, S. Shimizu, Y. Fujishiro, M. Awano, *J. Membr. Sci.* 300 (2007) 45.
- [16] T. Suzuki, Y. Funahashi, T. Yamaguchi, Y. Fujishiro, M. Awano, *Electrochem. Solid State Lett.* 10 (2007) A177.
- [17] K. Galloway, N. Sammes, *J. Electrochem. Soc.* 156 (2009) B526.
- [18] B.C.H. Steele, *Solid State Ionics* 129 (2000) 95.
- [19] Y. Funahashi, T. Shimamori, T. Suzuki, Y. Fujishiro, M. Awano, *J. Power Sources* 163 (2007) 731.
- [20] W. Gong, S. Gopalan, U.B. Pal, *J. Power Sources* 160 (2006) 305.
- [21] K. Chen, X. Chen, Z. Lü, N. Ai, X. Huang, W. Su, *Electrochem. Acta* 53 (2008) 7825.