Short communication

The effect of porosity gradient in a Nickel/Yttria Stabilized Zirconia anode for an anode-supported planar solid oxide fuel cell

Chung Min An [a], Jung-Hoon Song [b], Inyong Kang [c], Nigel Sammes [a],*

[a] Department of Metallurgical and Materials Engineering, Colorado School of Mines, Golden, CO, USA
[b] RIST, Pohang, Republic of Korea
[c] Department of Chemical Engineering, Colorado School of Mines, Golden, CO, USA

ARTICLE INFO

ABSTRACT

In this paper, a graded Ni/YSZ cermet anode, an 8 mol.%YSZ electrolyte, and a lanthanum strontium manganite (LSM) cathode were used to fabricate a solid oxide fuel cell (SOFC) unit. An anode-supported cell was prepared using a tape casting technique followed by hot pressing lamination and a single step co-firing process, allowing for the creation of a thin layer of dense electrolyte on a porous anode support. To reduce activation and concentration overpotential in the unit cell, a porosity gradient was developed in the anode using different percentages of pore former to a number of different tape-slurries, followed by tape casting and lamination of the tapes. The unit cell demonstrated that a concentration distribution of porosity in the anode increases the power in the unit cell from 76 mW cm^{-2} to 101 mW cm^{-2} at 600 °C in humidified hydrogen. Although the results have not been optimized for good performance, the effect of the porosity gradient is quite apparent and has potential in developing superior anode systems.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Fuel cells have been considered for many years as a possible solution for energy requirements due to their higher efficiency and low pollution, since the exhaust gases are predominantly H_2O and CO_2. Many types of fuel cells have been investigated, including proton exchange membrane fuel cells (PEMFC), molten carbon fuel cells (MCFC), alkaline (AFC), and solid oxide fuel cells (SOFC) [1,2]. A planar-SOFC, which includes active anode layers with different porosities, is the focus of this paper. The SOFC is composed of an anode (Ni/8 mol.% Y_2O_3-stabilized ZrO_2) (YSZ), electrolyte (8 mol.% Y_2O_3-stabilized ZrO_2) (YSZ) and cathode ($La_{0.8}Sr_{0.2}MnO_3$) [3,4].

Due to the operating temperature of the SOFC being approximately 800–1000 °C, many physical and chemical problems are prevalent when it is applied to electric devices [5]. The focus of research in SOFC's is, thus, on the intermediate operating temperature below 800 °C. There are a number of ways to achieve this, including using a thin electrolyte layer (below 20 μm); changing the electrolyte material in order to get good ionic conductivity in the intermediate temperature range; and finally, adding active layers to the anode site to increase the triple phase boundary (TPB), and thus potential anode reactivity.

Methods for fabricating the anode-supported SOFC include electrochemical vapor deposition (EVD), chemical vapor deposition (CVD), screen-printing, and tape casting [6,7]. Tape casting is one technique that can be used for mass production and recycling of the SOFC [8]. Furthermore, a porosity gradient can easily be introduced into the anode using tape casting techniques [9].

This research focuses on the effect of the porosity gradient in the anode, because it could provide a higher probability of collision between the TPB and the hydrogen (fuel) on the multi-active layer [10]. The process of fabricating green ceramics for the anode, electrolyte and active layer, in this work, is via tape casting, while screen-printing is used for the cathode coating. Due to the TPB and hydrogen activation being dependent on porosity and porosity shape, the performance is expected to be related to the porosity gradient, because the porosity concentration is dependent on the pore-former concentration in the slurry [11]

2. Experimental

In this study, 8 mol.% YSZ (TZ-8Y, Tosoh Co., Japan; FYT 13-010H, Unitech Ceramics, UK), NiO (Ferro Co., USA), carbon black (Ravern 430, Columbian Chemicals, USA), modifier (M1201, Ferro Co., USA), binder (B74001, Ferro Co., USA) and solvent (ethanol and toluene) were mixed together to make the tape-cast slurry for the anode via tape casting using a ball mill and 3YSZ ceramic balls [3]. For fabricating the green ceramic film of the electrolyte, using the tape casting technique, 8 mol.% YSZ (TZ-8Y, Tosoh Co., Japan), dispersant

* Corresponding author. Tel.: +1 303 960 3434; fax: +1 303 273 3795.
E-mail addresses: can@mines.edu (C.M. An), smjulie2@hanmail.net (J.-H. Song), ikang@mines.edu (I. Kang), nsammes@mines.edu (N. Sammes).
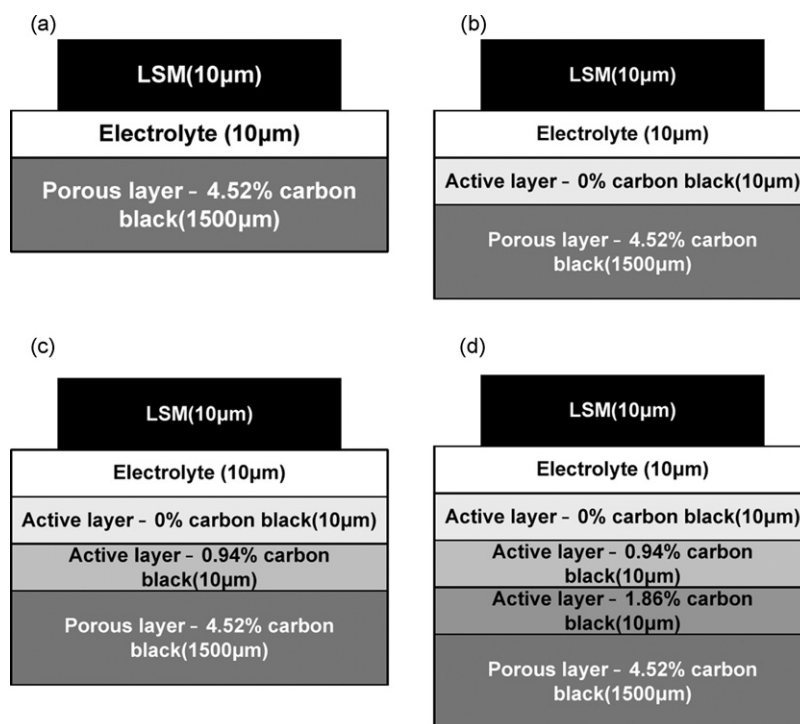
Fig. 1. Schematic of the unit cells.

(M1201, Ferro Co., USA), binder (B74001, Ferro Co., USA) and solvent (ethanol and toluene) were used. LSM-YSZ (50% LSM and 50% YSZ, Fuel Cell Materials, OH, USA) was used for the cathode and, as explained below, was screen-printed onto the electrolyte layer.

Fig. 1 represents a pictorial view on how to produce a porosity gradient in the anode. The porosity is realized by the concentration of carbon black in any particular anode layer; three kinds of active layers are synthesized, the concentration of carbon black in each layer being 0%, 0.94% and 1.86%. To make the SOFC cells, which include the active layers, every ingredient was mixed for 2 days using the ball milling process described above. The thin green ceramic films were fabricated using tape casting (HANSUNG SYSTEMS, STC-28A, South of Korea), and highly porous anode layers, in which the green ceramic thickness was 200 μm before drying, were prepared. The active layer was fabricated with a thickness of 90 μm before drying. After preparing the films, the green ceramic underwent a hot pressing lamination process. The operating temperature of the lamination step was set from 80 °C to 100 °C while the pressure was gradually raised to 300 MPa. After forming the tape cast cells by the lamination step, thus producing an anode/electrolyte couple, they were co-sintered at 1350 °C for 3 h.

The cathode was fabricated by screen-printing with a paste of a commercial LSM-YSZ product. After coating the cathode on the sintered anode/electrolyte couple, the cells were re-sintered at 1150 °C for 3 h. Finally, unit cells were fabricated with a diameter of the anode being 3 cm, and the cathode being 1.5 cm. Before testing the electrochemical-properties of the unit cells, they were heated to 800 °C for 10 h in a reducing atmosphere (4% H_2, 96% Ar). The processing steps for making the unit cell are shown in Fig. 2.

The test cell apparatus to measure the electrical performance is shown in Fig. 3. Current–voltage characteristics were measured using an electric load (Chroma System Solutions Inc. DC electronic load) at 600 °C, in humidified hydrogen ($50\,cc\,min^{-1}$, 3% water) for the anode, and in dry air ($100\,cc\,min^{-1}$) for the cathode, using silver mesh as the current collector. Impedance spectra of the unit cells were measured at 600 °C using AC impedance spectroscope (Gamry Instruments, reference 600) in the frequency range
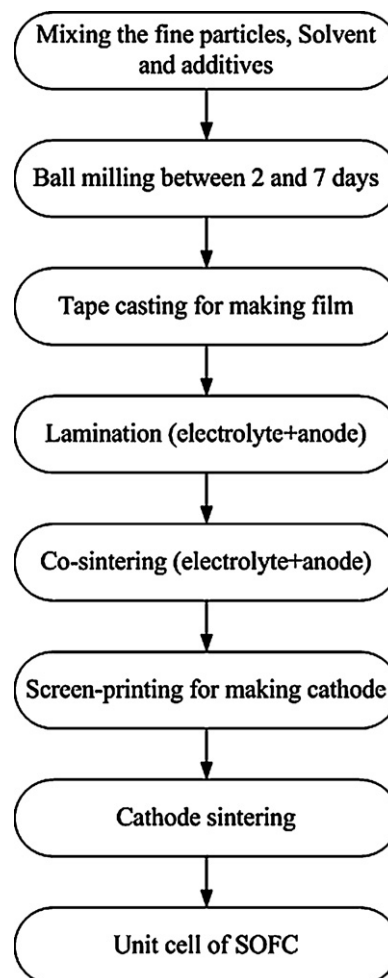

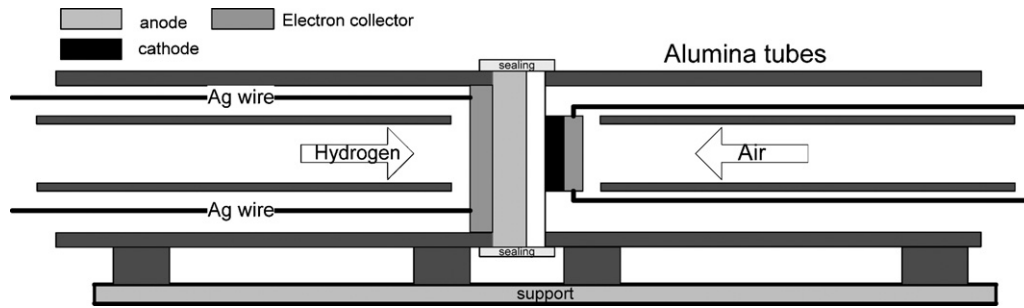**Fig. 2.** Overall flow chart for fabrication of the SOFC unit cell.

Fig. 3. Test cell for the unit cells.

of 100 KHz to 0.02 Hz with signal amplitude of 5 mV under open cir-cuit conditions. The microstructure of the unit cells, formed on the Si-coated polyethylene terephthalate film (PET) by the tape casting process, and the sintered anode-supported electrolyte, were stud-ied using SEM (FEI Quanta 600 Environmental Scanning Electron Microscope). The porosity of each active layer was measured by studying the SEM micrograph using an ImageJ program.

3. Results and discussion

Fig. 4 shows cross-sectional micrographs of the unit cells after reduction in the hydrogen-environment at 800 °C for 10 h. It was found that the electrolyte layer was crack free, and the anode layer had high porosity. As shown in Fig. 1, the thickness of each active layer was observed to be approximately 20 μm. Each active layer thickness was between 20 μm and 30 μm after co-sintering, how-ever, as shown in Fig. 4. The thickness of each active layer in the unit cells, after sintering, increased due to increasing porosity in the active layer, as a function of the increased pore former in the slurry. The porosity was 20%, 24%, 26% and 35% for the 1st-, 2nd- and 3rd-active layers and the porous layer, respectively, Fig. 1. The change in porosity implies that the unit cells have porosity gradients.

Fig. 5 represents the I–V curves of the unit cells. The electro-chemical tests for the I–V curves and the impedance of the unit cells were measured at 600 °C. From the I–V curves in Fig. 5, the power output of the cells was 76 (for non-active layer), 86 (for 1-active layer), 97 (for 2-active layers) and 101 (for 3-active layers) mW cm^{-2}. The 3-active layer cell was found to have the high-est power output of 101 mW cm^{-2}. Although the power output in this research is not as high as other work, and other sys-tems, it is apparent that a porosity gradient can be fabricated across an anode by tape casting different porous anode layers, and then laminating them together. It should also be noted that Zhao and Virkar [12] observed a value of approximately 0.4 W cm^{-2} at 600 °C for an optimized anode-supported SOFC on hydrogen, as compared to approximately 0.2 W cm^{-2} at 600 °C for a standard
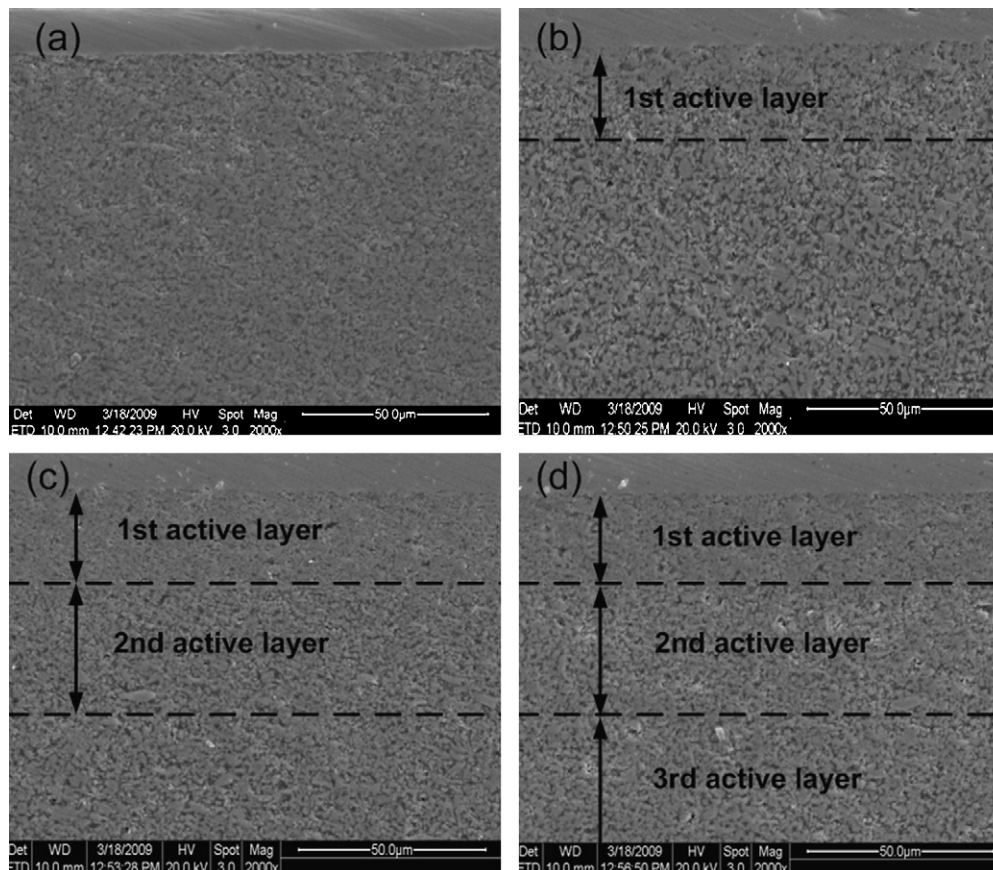

Fig. 4. SEM images of (a) non-active layer cell, (b) 1-active layer cell, (c) 2-active layers cell, (d) 3-active layers cell.
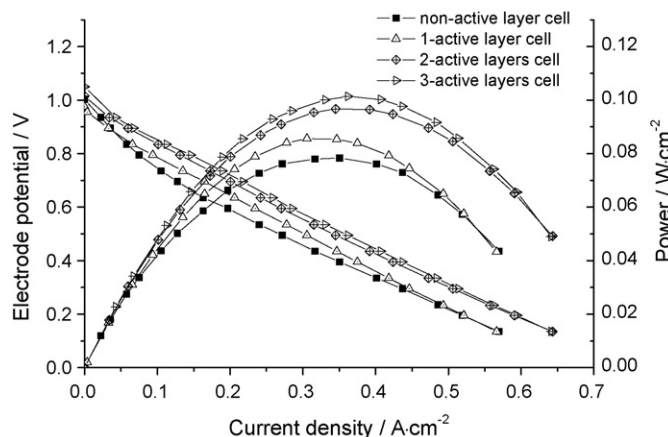
Fig. 5. *I–V* and power curve for characterization of the unit cells at 600 °C.
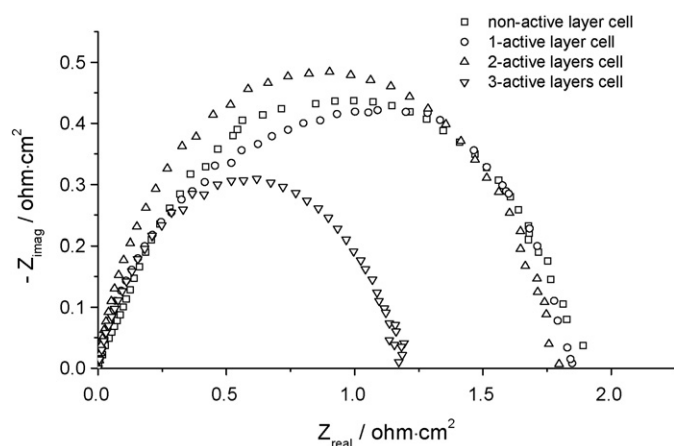

Fig. 6. Impedance spectra of the unit cells at 600 °C.

anode-supported cell. Thus, the authors showed that the effect of anode thickness and anode porosity greatly affected the output performance of the anode-supported cell due to improved overpotential losses.

To examine the polarization resistance as a function of the porosity gradient within the anode in more detail, impedance spectra were conducted under the same conditions as those for the electrochemical testing. Fig. 6 shows the results of the test, in which the polarization resistances were $1.92\,\Omega\,cm^2$, $1.86\,\Omega\,cm^2$, $1.8\,\Omega\,cm^2$, and $1.2\,\Omega\,cm^2$, for the non-, 1-, 2- and 3-active layer-systems, respectively. As a result of polarization losses, the resistance of the 3-active layer cell is observed to be the lowest.

Because of the porosity gradient, the TPB site would be increased and thus the hydrogen could get to the reaction sites through the porosity gradient.

The possibility of collision between the TPB and the hydrogen is increased by the porosity gradient [9,10]. Increasing the probability of collision allows for the hydrogen to react more readily within the TPB, and thus the system with a porosity gradient has the lowest activation overpotential. Because of faster consumption of hydrogen, the unit cells which have the porosity gradient within the anode, have a large partial pressure difference of hydrogen, so the concentration overpotential would be lower. Thus, it was concluded that the introduction of a porosity gradient in the unit cell could increase the performance of the IT-SOFC.

4. Conclusion

Tape casting is an excellent method for easily fabricating a unit SOFC cell, with an anode having a porosity gradient. The cells which have a porosity concentration distribution in the anode showed reasonable performance although further work is being undertaken to optimize this. The maximum power was found to be $101\,mW\,cm^{-2}$ in the 3-active layer cell at 600 °C, indicating that the concentration distribution of porosity in the anode improved the electrical performance in the unit cell. The impedance spectra of the cells indicated that the porosity gradient in the anode could reduce polarization resistance, because it generates a good contact geometry and effective TPB between the electrolyte and the anode. This study is a promising one, in that the performance increased by having a concentration distribution of porosity in the anode.

Acknowledgement

References

[1] S.P.S. Badwal, K. Foger, Ceramics Int. 22 (1996) 257–265.
[2] S.C. Singhal, K. Kendall, High Temperature Solid Oxide Fuel Cells: Fundamentals, Design, and Applications, Elsevier, Oxford; New York, 2003.
[3] H. Moon, S.D. Kim, S.H. Hyun, H.S. Kim, Int. J. Hydrogen Energy 33 (2008) 1758–1768.
[4] J. Song, S. Park, J. Lee, H. Kim, J. Mater. Processing Technol. 198 (2008) 414–418.
[5] S.D. Kim, S.H. Hyun, J. Moon, J. Kim, R.H. Song, J. Power Sources 139 (2005) 67–72.
[6] M. Inaba, A. Mineshige, T. Maeda, S. Nakanishi, T. Iomi, T. Takahashi, A. Tasaka, K. Kikuchi, Z. Ogumi, Solid State Ionics 104 (1997) 303–310.
[7] X. Ge, X. Huang, Y. Zhang, Z. Lu, J. Xu, K. Chen, D. Dong, Z. Liu, J. Miao, W. Su, J. Power Sources 159 (2006) 1048–1050.
[8] D. Simwonis, H. Thulen, F.J. Dias, A. Naoumidis, D. Stover, J. Mater. Processing Technol. 92–93 (1999) 107–111.
[9] A. Sanson, P. Pinasco, E. Roncari, J. Eur. Ceramic Soc. 28 (2008) 1221–1226.
[10] M.E.J. Newman, Phys. Rev. E 64 (2001) 016132.
[11] V. Hugo Schmidt, Chih-Long Tsai, J. Power Sources 180 (2008) 253–264.
[12] F. Zhao, A.V. Virkar, J. Power Sources 141 (2005) 79–95.