EFFECT OF ANODE POROSITY AND PORE SIZE ON ELECTROCHEMICAL PERFORMANCE

Xiaohua Deng and Anthony Petrie
Department of Materials Science and Engineering
McMaster University
Hamilton, Ontario, Canada, L8S 4L7

ABSTRACT

Solid oxide fuel cells consisting of LSCF, YSZ and Ni-YSZ were fabricated with anodes of controlled porosity and pore size. The effects of porosity and pore size on cell performance were investigated theoretically and experimentally. A geometric simulation was used to determine the three-phase-boundary length (TPBL) which is one of main factors determining the anodic reaction and consequently the cell performance. The TPBL calculation indicated there exists an optimum porosity and pore size in the anode, depending on grain size. A porosity of 35-40% was found to be optimum for fuel cell performance in our cells. Based on the anodes tested with pore size from 1 to 10 μm, it was found that cell performance improved with increasing pore size.

INTRODUCTION

A very important aspect in the development of SOFCs is the optimization of the electrodes. Materials selection and structural design are the key factors in obtaining low polarization electrodes.

The anodes of common solid oxide fuel cells consist of three phases: gas, metal, and electrolyte. Nickel is the most practical metal because of its high electrical conductivity, good catalytic performance and low cost. An electrolyte material is incorporated with nickel to prevent grain growth, maintain porosity, and provide ionic conduction and both chemical and thermal compatibility with the electrolyte. The three-phase-boundary (TPB) provides active sites for the anode reaction. Hence, pores in the anode are one of most critical parameters determining gas diffusion, three phase boundary length (TPBL) and consequently the anode reaction rate and anodic polarization. However, little work has been reported on this subject outside of modeling (1,2).

In this paper, the porosity and pore size in the anode were varied and their effects on the cell performance were investigated. The TPBL was calculated based on geometry of the anode. The results indicated trends in optimal pore size and porosity which conform with experimental results.
MODELING

The calculation is based on a geometric analysis of all solid phases and pores. In the anode, YSZ is a pure oxygen ion conductor, Ni is an electronic conductor, and pores allow for gas transfer. The three-phase-boundary forms at the common junction line. Because the grains of YSZ and Ni are very close in size, and assuming they are spheres having same volume fraction, the two-phase-boundary number can be obtained from the following equation if the distributions of Ni and YSZ grains are uniform:

\[ N_s A_s - N_{2pb} A' = A_p^{total} \]  \[1\]

\[ N_s = V_s / [(4/3) \pi (D_s/2)^3] \]

\[ A_s = \pi D_s^2 \]

\[ A_p^{total} = \pi D_p^2 V_p / [(4/3) \pi (D_p/2)^3] \]

\[ V_s + V_p = 1 \]

\( N_s \) = number of solid grains per unit volume

\( A_s \) = surface area of one solid grain

\( N_{2pb} \) = number of two-phase-boundary per unit volume

\( A' \) = surface area disappeared due to the contact between two solid grains

\( A_p^{total} \) = total surface area of the pore phase

\( D_s \) = diameter of solid grains

\( D_p \) = diameter of pores

\( V_s \) = volume of solid per unit volume

\( V_p \) = volume of porosity per unit volume

The length of the three-phase-boundary is given by the following equation:

\[ L_{3pb} = N_{3pb} A_p^{total} = [6/D_s - (6/D_s + 6/D_p) V_p] (6 V_p) / (A' D_p) \]  \[2\]

In using this model, we apply certain reasonable assumptions. When \( D_s = 6 \mu m \) and estimating \( A' = 15 \mu m^2 \), the above equation is simplified to,

\[ L_{3pb} = [1 - (1 + 6/D_p) V_p] (6 V_p) / (15 D_p) \]  \[3\]

From Eq. 3, we obtain the relationship between the three-phase-boundary length and porosity or pore size in the anode, shown in Figs. 1 and 2. Fig. 1 shows the TPBL variation with porosity. It is obvious that too low or too high porosity will decrease the TPBL although high porosity would enhance gas transfer. The porosity corresponding to maximum TPBL increases with increasing pore size.

Fig. 2 shows the relationship between TPBL and pore size. The TPBL increases sharply with pore size when the pore size is small, and attains a maximum value as a function of pore size for different levels of porosity. The TPBL is reduced when the pore size increases further. It is understandable that the optimal pore size shifts to higher value when porosity increases. The trend of TPBL with pore size is in agreement with Maggio’s model (2). It maybe noted that the maximum TPBL is higher for small pore size, which implies that a fine structure would benefit the TPBL (1). On the other hand,
a fine structure needs low porosity for maximum TPBL, but such low porosity would hinder the gas transfer and limit the cell performance.

Figure 1. Three-phase-boundary length as a function of anode porosity and pore size.

Figure 2. Three-phase-boundary length vs. pore size in anode at different porosities.
EXPERIMENTAL

Cell Fabrication

Yttria stabilized zirconia (YSZ, 8 mol% Y₂O₃, Tosoh) electrolyte based fuel cells were fabricated in two steps. A laminate of electrolyte and anode (Ni/YSZ, 50 vol%) was cofired at 1400°C for 2 hours in air. In order to focus on the changes in the anode, the influence of the cathode should be minimized as much as possible. The LSCF cathode was deposited on the electrolyte by spin-coating and sintered at 600°C. A buffer layer of Ce₀.₈Sm₀.₂O₂ was sandwiched between the cathode and electrolyte by spin-coating to avoid reaction between YSZ and the cathode (3). To produce a precursor solution for the spin-coating, a stoichiometric ratio of metal nitrates was dissolved in water. After the solution became totally clear, ethylene glycol (40 ml) and citric acid (1 g) were added in a defined molar ratio to yield 0.02 mole of the final oxide. The solution was then heated at 80°C to expel the water and other volatile matter and became a gelatinous liquid. The liquid was spun onto the surface of the sintered sample and dried at 320°C. Crystallization and grain growth of the as-deposited films resulted from subsequent heat treatment at 600°C. The resulting cathode was 1 micron thick with nano-size grains. A porous Pt layer was applied on the cathode as a current collector.

Fugitive phase

One way to create porosity in a ceramic sample is to mix a fugitive phase with the ceramic powder. The fugitive phase should be burnt-out before the sintering range of the ceramic to leave residual porosity. Certain organic compounds can be used as the fugitive phase. Special precaution must be taken in this case because of their narrow burnt-out temperature range. Carbon burnt-out is more gradual and occurs at a higher temperature than the organics. This may be seen by a comparison of polyvinyl butyral (PVB) and carbon in Fig. 3. Carbon has also negligible solubility in tape-casting slurry.

![Figure 3. Carbon and PVB burn-out profile.](image-url)
solvents and is more effective, practical and controllable as a fugitive agent for this purpose.

Three-types of carbon were used as the fugitive phase in this experiment to control the pore size: spherical carbon black (C-b) with a diameter of 75 nm, graphite flakes (C-g), and carbon fiber (C-f) approximately 10 μm diameter and 20 μm long.

**Characterization of Fuel Cells**

Porosity of samples was measured by means of the Archimedes method. The sample was heated to 500°C to remove materials adsorbed on the surface and placed in a desiccator during cooling from 200°C to room temperature. Kerosene was the medium for this measurement. Three or more samples were measured to obtain an average for each point. Scanning electron microscopy (SEM) was used to analyze pore size in the anode as well as the approximate porosity. The cell performance was measured in the procedure described in our previous work (4).

**RESULTS AND DISCUSSION**

**Porosity**

Porosity was controlled by varying the loading of the fugitive phase in the anode. The anode in samples 1 to 5 contained 0, 10, 20, 25, and 30 wt% carbon black respectively. Up to 35% open porosity was obtained in the sintered anode. The porosities after reduction of NiO to Ni in the anode increased to 27-44% as shown in Fig. 4, depending on the nickel content. Maximum power density output from these cells at 800°C is also shown in Fig. 4.

![Figure 4. Open porosity in anode vs. cell performance.](image-url)
The low power density of samples 1 and 2 indicates that the porosity in the anode is insufficient for proper fuel supply. As the porosity increases, the cell performance improves until porosity is too high (45% in sample 5). Excess porosity reduces both the solid phase content, which reduces the amount of anode reaction sites, and the mechanical strength. Hence, a porosity of 35-40% appears to be optimum for the anode application. Due to the difficulty of dispersing all phases uniformly in the anode and the grain and pore size fluctuations, e.g., due to agglomeration, it is reasonable to expect deviation between experimental curves and the calculation. Still the strong correlation between cell performance and porosity shown in Fig. 4 is consistent with the trend of the calculation in Fig. 1. The TPBL is one of the factors that affect cell performance. When porosity is too low, not only the TPBL is low but also gas transfer in the anode will be hindered.

**Pore size**

By using different morphologies of carbon at a constant 20 wt% loading in the Ni/YSZ anode, the pore size was varied while porosity remained constant. As expected, different types of carbon did not produce a significant difference in porosity when the same amount of carbon was added. The porosities were approximately 35% after reduction.

Fig. 5 shows SEM micrographs of anodes made from different carbon morphologies and sintered at 1400°C. The pore sizes in the anode were different although the shapes are not perfect spheres. Cylindrical pores were formed from carbon fibers with a diameter of 10 μm (Fig. 5a). These cylinders were oriented parallel to the tape-casting direction. Fig. 5c shows an estimated average pore size of 1 μm created from the carbon black fugitive phase. The three types of fugitive phases were used to change the pore sizes in the Ni/YSZ anode while the amount of the fugitive phase remained constant. A 10 μm-thick dense layer of YSZ electrolyte was intimately bonded with the different anodes. The performance of these cells is shown in Fig. 6. The cell performance improved with increasing pore size up to the maximum 10 μm pore size in our study.

We may recall that YSZ has only ionic conduction and Ni only electronic conduction. The three-phase-boundary, i.e., between the YSZ phase, Ni metal and hydrogen gas, is the active site for the anode reaction. Hence the three-phase-boundary length (TPBL) determines the rate of the anode reaction. However, the TPBL is dependent on the geometry of the three-phases (Ni metal, YSZ, and pore) in the anode, such as phase ratio and grain or pore size. It is quite evident that very large pores in the model will reduce the TPBL. Although very small pores enhance the degree of exposure of solid phase to the fuel gas, small pores separate the contact between Ni and YSZ phases and consequently reduce the TPBL. In other words, there is an optimum pore size in the anode for maximum cell performance, as indicated by the calculation above.

Fig. 7 shows the power densities of cells at 600, 700 and 800°C. The maximum power density with 7% H₂ fuel and air at 800°C was 780 mW/cm².
Figure 5. SEM micrographs of cross-sections of cells with different pore sizes in the anodes.
Figure 6. Voltage and power density of the cells with different pore sizes in the anodes versus current at 600°C. Air and 7% hydrogen were fed onto the cathode and anode respectively.

Figure 7. Voltage and power density of the cell with 10 μm pores in the anode at 600, 700, and 800°C.
CONCLUSIONS

The TPBL calculation indicated that the TPBL depended on porosity and pore size in the anode of a cell. Controlling the pore size and porosity properly would maximize the TPBL and optimize the cell performance accordingly.

Cell performance with various porosities and pore sizes was evaluated. An anode porosity of 35-40% is optimum for SOFC operation.

For the Ni/YSZ anode, a larger pore size (near 10 μm diameter in this study) yielded the best cell performance. The power density reached 780 mW/cm² at 800°C for a cell operating on air and 7% H₂.

ACKNOWLEDGEMENT

We wish to thank Prof. H. U. Anderson of the University of Missouri-Rolla and C.C. Chen of Praxair for helpful advice and discussions. We also acknowledge the financial support of Fuel Cell Technologies Corp. and the Natural Sciences and Engineering Research Council of Canada.

REFERENCES

1. C. W. Tanner, K. Z. Fung, and A. V. Virkar, J. Electrochem. Soc., 144[1], 21-30 (1997).
2. G. Maggio, I. Ielo, V. Antonucci and N. Giordano, in SOFC-II, F. Grosz, P. Zegers, S. C. Singhal, and O. Yamamoto, Editors, Commission of the European Communities, Brussels, Belgium, pp. 611-20 (1991).
3. C. C. Chen, J. Electrochem. Soc., 140[12], 3555-60 (1993).
4. X. Deng and A. Petric, Proc. Symp. Processing and Characterization of Electrochemical Materials and Devices, Editors, P. N. Kumta, R. Manthiram, S. K. Sundaram, and Y. M. Chiang, American Ceramic Society, Westerville, OH, pp. 87-94 (1999).