

Synthesis and Stability of a Nanoparticle-Infiltrated Solid Oxide Fuel Cell Electrode

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Abstract

Nanoparticulate catalysts infiltrated into SOFC (Solid Oxide Fuel Cell) electrodes can significantly enhance the cell performance, but the stability of these electrodes has been an open issue. An infiltration procedure is reported that leads to a stable scandia-stabilized zirconia (SSZ) cathode electrode performance.

An SSZ cathode, infiltrated with 50-150nm lanthanum -strontium manganate (LSM) electro-catalyst particles, is shown to be voltage-stable for over 500 hours of operation at 650°C, at a controlled current density of 150 mA/cm². This demonstrates the potential viability of nanoparticulate-infiltrated electrodes for commercial SOFCs, and illustrates the functional stability of nanoparticulate catalysts in the demanding environment of SOFC electrodes.

Introduction

Nanoparticulate catalysts may be infiltrated into already formed SOFC electrodes to enhance electrode performance¹⁻⁴, and new electrode designs have been devised utilizing continuous nanoparticulate networks or connected nanoparticle rafts⁴⁻⁹. In these electrode designs, the nanoparticulates not only serve as reaction sites, but also provide an electron pathway from the current collector to the individual reaction sites. Hence, persistent connectivity of the nanoparticulate networks and limited coarsening are essential to stable electrode function. Although a number of papers have been published on nanoparticle-infiltrated electrodes, little mention has been made of the

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extended stability of such structures. The difficulty is that SOFC electrodes operate under demanding operating conditions: elevated temperatures (600°C -1000°C), thermal cycling, high local current densities, and high local potential gradients. These conditions can be antagonistic to the stability of nanoparticulate networks.

Nanoparticle-infiltrated porous ZrO_2 -based electrodes were prepared in a single processing step⁵; the cells showed an adequate initial performance at 650°C, but their extended stability was not examined. Further evaluation of similar nanoparticulate-LSM infiltrated, porous SSZ (scandia-stabilized zirconia) electrodes proved, for the first time, their functional stability for over 500 hours of operation at 650°C. The microstructures produced by the infiltration method are examined, and related these to essential requirements for stability of nanoparticle-infiltrated SOFC electrodes. Additionally, a focused ion beam (FIB) method was used for producing scanning electron microscope (SEM) cross-sections and lift-out thin sections for transmission electron microscopy (TEM) with minimal artifacts.

Methods

NiO (J. T. Baker) and SSZ [i.e. $(\text{Sc}_2\text{O}_3)_{0.1}(\text{ZrO}_2)_{0.9}$; from Daiichi Kigenso Kagakukogyo] in a weight ratio of 1:1 were attritor-milled in isopropanol, using zirconia balls as the milling medium. Dried mixtures were uniaxially pressed and pre-fired at 1100 °C for 1h. SSZ electrolytes were formed on the NiO-SSZ anode supports by colloidal deposition¹⁰, and were co-sintered at 1350 °C for 4h. A suspension of SSZ and graphite was then colloiddally deposited onto the SSZ electrolyte to prepare a thin layer consisting of SSZ and graphite, with an area of 1cm. The resulting trilayer structure was sintered at 1250 °C for 4h, during which graphite was burned out, leaving a porous, well-formed SSZ network. A solution of LSM ($\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$) precursor was prepared by combining 3.144g $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Alfa Aesar), 2.452g $\text{Mn}(\text{NO}_3)_2 \cdot \text{XH}_2\text{O}$ ($\text{X}=0.6-0.4$, 5 assumed; Aldrich), 0.271g $\text{Sr}(\text{NO}_3)_2$ (Alfa Aesar), 0.3g of a commercial polymeric dispersant (Triton-X100, Union Carbide

Chemicals and Plastics Co., Inc.) and 10mL H₂O, and subsequently heating to 100°C to produce a high concentration suspension. The increasingly viscous suspension was then infiltrated into the porous SSZ network using a vacuum impregnation apparatus (Epovac; Struers), and the precursors were then converted by heating at 900 °C for 0.5 h. Platinum-paste current collectors were placed on the electrodes, and then fired on, again at 900 °C for 0.5 hour.

The resulting membranes were either held at 650 °C or electrochemically characterized, by sealing onto an alumina tube using Aremco-552 cement, and current-voltage characteristics were obtained, with 97% H₂+3% H₂O as the fuel and air as the oxidant. The cell DC current-voltage (I-V) performance was determined at 650 °C with a potentiostat-galvanostat (Princeton Applied Research Model 371). After electrochemical characterization, the cells were then fractured and further cross-sectioned using a dual focused ion and electron beam (FIB/SEM; FEI Strata 235 M) system. SEM images were taken after cross-sectioning with the FIB. Sections were also prepared for transmission electron microscope analysis (TEM; JEOL, JEM-200CX) by a lift-out technique using the above FIB/SEM system¹¹.

Results and Discussion

The microstructure that the infiltration method produces⁵, and its relation to the stability of the cathode is first characterized by scanning electron microscope. From the FIB cross-sectional SEM image, Figure 1, it is evident that the infiltration method produces a well-connected network and rafts of nanoparticulate LSM, confined nearly exclusively to the pore walls of the SSZ cathode backbone, providing a sufficient percolation path for electrons to the majority of the oxygen reduction reaction (ORR) sites.

These reaction sites are either near the SSZ/LSM pore triple junctions (TPBs) or on the surface of the dense LSM rafts. Since the LSM rafts produced by our method are generally just one nanoparticle thick, *i.e.* 50-150 nm (see inset in Fig. 1), oxygen ion conduction directly through the dense raft can contribute significantly to the overall reaction rates by enabling the ORR on the entire LSM surface.⁵ In fact, it is the tendency to form particle rafts that can greatly assist in providing stability to the infiltrated cathode performance, so long as the rafts remain in electrical contact. This requirement is much less demanding than maintaining electrical connectivity in sparse, single particle networks. Additionally, since the one-step infiltration methods leads mostly to single nanoparticle layers on the pore surfaces, effective electrodes can be obtained at much lower volume fractions than used by other workers.^{4, 6-9}

Figure 2 reveals a tendency for some orientation alignment of the nanoparticulate LSM particles with the SSZ. The significance of the orientation is so far unknown, but may affect the ORR, particularly at lower temperatures, depending on which surface orientations of the nanoparticulate LSM are presented to the gas phase.

Figure 3 shows that the contact angles of some individual LSM nanoparticles with the surface of the SSZ before and after 502 hrs at temperature have not meaningfully changed. However, in the as-formed stage contact between the LSM particles and the SSZ pore walls shows a tendency to be more sporadic than after some time at operating temperatures, Figures 4a and 4b.

The cell voltage of an anode supported SOFC with an LSM infiltrated porous SSZ cathode was recorded at a nearly constant applied current density of $\sim 150 \text{ mA/cm}^2$ for 502 hours at 650 °C, Figure 5. The cell fabricated with a porous SSZ electrode backbone showed no voltage degradation at constant current, and even shows improvement over time. Note that the applied current density was initially set at 150 mA/cm^2 , but declined somewhat after 366 hours to a low of $\sim 141 \text{ mA/cm}^2$, due to a

slight experimental instability; upon readjustment to 150 mA/cm^2 at 457 hours, the cell performance once again returned to the original voltage. These results may be contrasted to those reported by Huang *et al.*,⁹ which appear to show a significant performance decline after 100 hours at 700°C .

The improvement of the cell performance is detailed by data shown in Figure 6, which presents the I-V and power curves both before and after the long-term test. The most significant improvement is seen at current densities below 300 mA/cm^2 . This region is typically associated with ill-defined activation or reaction losses when using an LSM electrocatalyst. However, the activation is typically complete within a couple of hours in conventional composite LSM-SSZ electrodes, making it unlikely that it is of a similar origin as for the continued increase in performance of the nanoparticulate electrodes over the 502 hour test. Instead, the increase in LSM/SSZ contact, shown in Fig. 4 is viewed as the most likely cause for the gradual improvement.

Conclusion

A nanoparticulate LSM electrode was produced that was stable for over 500 hours of operation at 650°C , under a near-constant applied current density of $\sim 150 \text{ mA/cm}^2$. Furthermore, the cell showed some improvement over this period. The stability is attributed in large part to the specific nanoparticle distribution produced by our single-step infiltration method, leading to connected networks and monolayer rafts of nanoparticles that are confined to the pore walls.

The combination of FIB and TEM allowed for an unambiguous imaging of the nanoparticulate infiltrated electrodes, and of the TPB boundaries. Coarsening of the nanoparticles was minimal after more than 500 hours at 650°C ; the tendency for particle raft formation is likely to assist in suppressing coarsening. While contact angles did not appear to change measurably with time, contact between the

nanoparticulate LSM and the SSZ pore walls tended to increase with time at temperature, as a result of sintering processes, leading to a measurable improvement of the cell performance.

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References

1. K. Yamahara, C. P. Jacobson, S. J. Visco and L. C. De Jonghe, *Solid State Ionics*, **176** (3-4), 275-279 (2005).
2. C. Lu, T. Z. Sholklapper, C. P. Jacobson, S. J. Visco and L. C. De Jonghe, *Journal of the Electrochemical Society*, **153** (6), 1115-1119 (2006).
3. M. Watanabe, H. Uchida, M. Shibata, N. Mochizuki and K. Amikura, *Journal of the Electrochemical Society*, **141** (2), 342-346 (1994).
4. S. P. Jiang, *Materials Science and Engineering, A* **418** (1-2), 199-210 (2006).
5. T. Z. Sholklapper, C. Lu, C. P. Jacobson, S. J. Visco and L. C. De Jonghe, *Electrochemical and Solid-State Letters*, **9** (8), 376-378 (2006).
6. Y. Huang, J. M. Vohs and R. J. Gorte, *Journal of the Electrochemical Society*, **151** (4), 646-651 (2004).
7. S. Park, J. M. Vohs and R. J. Gorte, *Nature*, **404** (6775), 265-267 (2000).
8. Y. Huang, J. M. Vohs and R. J. Gorte, *Electrochemical and Solid-State Letters*, **9** (5), 237-240 (2006).
9. Y. Huang, J. M. Vohs and R. J. Gorte, *Journal of the Electrochemical Society*, **152** (7), 1347-1353 (2005).
10. S. de Souza, S. J. Visco, and L. C. De Jonghe, *Journal of the Electrochemical Society*, **144** (3), 35-37 (1997).
11. *Introduction to Focused Ion Beams*, L. A. Giannuzzi and F. A. Stevie, Editors, Springer, New York (2005).

Figures

Figure 1. SEM image of FIB cross-sectioned nanoparticulate LSM-infiltrated cathode. The streaking in the image is an unavoidable consequence of the presence of pores. The inset shows the size of some of the LSM nanoparticles.

Figure 2. TEM a) Bright Field, b) Dark Field Patterns and c) corresponding Diffraction Pattern taken on [110] zone axis of SSZ with circle around nanoparticulate LSM reflection used for Dark Field Imaging, showing nanoparticulate LSM grains on the SSZ porous electrode backbone.

Figure 3. TEM Dark Field Images of LSM catalyst particles a) before and b) after 502 hours operation at 650 °C under $\sim 150 \text{ mA/cm}^2$ applied current. Contact angle changes are not evident.

Figure 4. SEM images of FIB cross-sectioned nanoparticulate LSM infiltrated cathodes a) before and b) after 502 hours operation at 650 °C under $\sim 150 \text{ mA/cm}^2$ applied current. The contact between the LSM and the SSZ pore walls is more sporadic before testing, as is evident and marked where arrowed in 4a).

Figure 5. Performance of anode supported SOFC with nanoparticulate LSM infiltrated cathode over 502 hours operation at 650°C under near-constant applied current of $\sim 150 \text{ mA/cm}^2$.

Figure 6. I-V curve before and after 502 hours operation at 650 °C under $\sim 150 \text{ mA/cm}^2$ applied current.

