Doped-Ceria Diffusion Barriers Prepared by Infiltration for Solid Oxide Fuel Cells

Rainer Küngas  
*University of Pennsylvania*, kungas@seas.upenn.edu

Fred Bidrawn  
*University of Pennsylvania*, fbidrawn@seas.upenn.edu

John M. Vohs  
*University of Pennsylvania*, vohs@seas.upenn.edu

Raymond J. Gorte  
*University of Pennsylvania*, gorte@seas.upenn.edu

Follow this and additional works at: [http://repository.upenn.edu/cbe_papers](http://repository.upenn.edu/cbe_papers)

Part of the [Biochemical and Biomolecular Engineering Commons](http://repository.upenn.edu/cbe_papers)

**Recommended Citation**

Küngas, R., Bidrawn, F., Vohs, J. M., & Gorte, R. J. (2010). Doped-Ceria Diffusion Barriers Prepared by Infiltration for Solid Oxide Fuel Cells. Retrieved from [http://repository.upenn.edu/cbe_papers/137](http://repository.upenn.edu/cbe_papers/137)

**Suggested Citation:**


© The Electrochemical Society, Inc. 2010. All rights reserved. Except as provided under U.S. copyright law, this work may not be reproduced, resold, distributed, or modified without the express permission of The Electrochemical Society (ECS). The archival version of this work was published in *Electrochemical and Solid-State Letters*.

Publisher URL: [http://dx.doi.org/10.1149/1.3432253](http://dx.doi.org/10.1149/1.3432253)
Doped-Ceria Diffusion Barriers Prepared by Infiltration for Solid Oxide Fuel Cells

Abstract
To stabilize solid oxide fuel cells cathodes prepared by infiltration of La$_{0.8}$Sr$_{0.2}$CoO$_3$ (LSCo) into porous yttria-stabilized zirconia (YSZ), a coating of Sm-doped ceria (SDC) was first deposited onto the YSZ scaffold. The dense SDC coating was prepared by infiltration with aqueous solutions of SM(NO$_3$)$_3$ and Ce(NO$_3$)$_3$, followed by calcination to 1473 K. The SDC coating prevented ~ 20 mΩ cm$^2$, at 973 K, with acceptable degradation after heating to 1373 K.

Disciplines
Biochemical and Biomolecular Engineering | Chemical Engineering | Engineering

Comments
Suggested Citation:

© The Electrochemical Society, Inc. 2010. All rights reserved. Except as provided under U.S. copyright law, this work may not be reproduced, resold, distributed, or modified without the express permission of The Electrochemical Society (ECS). The archival version of this work was published in Electrochemical and Solid-State Letters.
Publisher URL: http://dx.doi.org/10.1149/1.3432253

This journal article is available at ScholarlyCommons: http://repository.upenn.edu/cbe_papers/137
The most commonly used material for cathodes in solid oxide fuel cells is a composite of Sr-doped LaMnO₃ (LSM) and yttria-stabilized zirconia (YSZ), with the LSM in the composite providing electronic conductivity and catalytic activity for oxygen reduction. The addition of YSZ to the electrode provides ionic conductivity to increase the length of the three-phase boundary by providing ion-conducting channels from the electrolyte to the electrode. In most cases, LSM–YSZ composites are prepared by sintering a mixture of LSM and YSZ powders onto the YSZ electrolyte. Relatively high temperatures (> 1300 K) are required to sinter the YSZ particles in the electrode to the electrolyte. Significantly improved performance can be achieved by replacing LSM with mixed conducting perovskites, such as Sr-doped LaCoO₃ or LaFeO₃,3-7 LaFeO₃ (LSF);15,16 however, it is not possible to cofire these perovskites with YSZ at the temperatures required for sintering the YSZ phase because this leads to either reaction with the YSZ or other effects that lower the electrode performance.15,16

Recently, composite electrodes have been prepared without high temperature sintering of the perovskite phase using infiltration.16-18 In this case, a porous YSZ scaffold is first sintered together with the electrolyte, and the perovskite is then added in subsequent steps by infiltrating the porous YSZ with solutions that contain either the nanoparticles of the perovskites or the appropriate cations for synthesizing the perovskites in situ.19,20 Composites prepared by infiltration have two main advantages over composites prepared by traditional approaches. First, the sintering temperature for the YSZ component of the composite can be much higher than the sintering temperature used for the perovskite. Because the YSZ scaffold can be sintered to the electrolyte at very high temperatures, the ion-conducting channels from the electrolyte into the electrode are well established and delamination of electrodes is typically not a problem. Second, because the conducting phase is added to an existing YSZ scaffold, the composites formed by infiltration are not random. One implication of the nonrandom structure is that sufficient conductivity can be achieved using perovskite loadings below the normal percolation threshold of 30 vol %.16,21 Another consequence of the nonrandom structure is that the coefficients of thermal expansion (CTE) of the composite are closer to that of YSZ scaffold than to the weighted average of the components.6 Composites of LSCO and YSZ have provided very low cathode impedances when prepared by infiltration;6,22 however, the impedance has increased dramatically with time or increased calcination temperature. Degradation with LSCO is likely due to solid-state reactions, which have occurred between YSZ and LaCoO₃ at temperatures as low as 973 K.23 The usual approach to preventing solid-state reactions between perovskites and YSZ involves incorporating a thin layer of doped ceria [e.g., CeₓSr₉₋ₓOₓ+½ (SDC)] between the electrolyte and the electrode in a manner similar to what is shown in Fig. 1a.24,25 This approach is successfully applied with cathodes based on LSCF.26 However, the incorporation of barrier layers does not prevent problems of CTE mismatch or mechanical instability. Furthermore, a recent comparison of LSM cathodes with and without doped-ceria layers indicated that doped ceria layer may alter performance in a more complicated manner.27

In the present study, we set out to test an alternative method for incorporating a barrier layer, shown schematically in Fig. 1b. The concept was to coat the porous YSZ scaffold with SDC before infiltration with the conducting perovskite. Electrodes prepared in this manner exhibit the advantages associated with infiltrated electrodes (e.g., less LSCO required for conductivity, better CTE match, and better stability toward delamination) while minimizing problems associated with solid-state reactions at the LSCO–YSZ interface.

**Experimental**

The electrode performances in this study were measured using symmetric cells. The first step in cell fabrication involved making a porous–dense–porous YSZ wafer using tape-casting methods, as described in detail elsewhere.28 After sintering the tapes at 1773 K for 4 h, the dense electrolyte layers were 88 ± 5 µm thick and 1 cm in diameter, while the two porous layers were each 55 ± 2 µm thick and 0.67 cm in diameter. Based on an earlier work, the porous layers were between 60 and 65% porous.29 To prepare an SDC barrier coating, an aqueous mixture of Ce(NO₃)₃·6H₂O (Alfa Aesar, 99.5%) and Sm(NO₃)₃·6H₂O (Alfa Aesar, 99.9%) was infiltrated into the porous YSZ layers, followed by heating in air to 723 K. Infiltration steps were repeated until the desired loading had been achieved. The cells were then fired to temperatures up to 1473 K for 4 h.

The LSCO–YSZ and LSCO–SDC–YSZ electrodes were prepared by infiltration of the porous YSZ or the SDC–YSZ scaffolds with an aqueous solution consisting of La(NO₃)₃·6H₂O (Alfa Aesar, 99.9%), Sr(NO₃)₂ (Alfa Aesar, 99%), and Co(NO₃)₃·6H₂O (Aldrich, 99.9%) at a molar ratio of La: Sr: Co = 0.8: 0.2: 1. Citric acid, in a 1:1 ratio with the metal cations, was used as a complexing agent to form the perovskite at lower temperatures. The use of a complexing agent is critical because new phases, indicative of a solid-state reaction with the YSZ, were formed at much lower temperatures when citric acid was not included. Furthermore, the reproducibility of the electrochemical test results improves significantly when a complexing agent was used. Each infiltration was followed by heat-treatment in air at 723 K. Multiple infiltration steps were needed to reach the final loading of 35 wt % (± 20 vol %). To form the desired perovskite structure, the cells were heated in air to 973 K for 4 h before applying Ag paste for current collection. The cells were then attached to an alumina rod using a ceramic adhesive (Aremco, Ceramicbond 552). Electrochemical impedance spectra were recorded us-

---

* Electrochemical Society Student Member.
** Electrochemical Society Active Member.
1 E-mail: gorte@seas.upenn.edu

Doped-Ceria Diffusion Barriers Prepared by Infiltration for Solid Oxide Fuel Cells

**R. Küngas,** F. Bidrawn, **J. M. Vohs,** and **R. J. Gorte**,z

Department of Chemical and Biomolecular Engineering, University of Pennsylvania, Philadelphia, Pennsylvania 19104, USA

The Electrochemical Society Active Member. 
E-mail: gorte@seas.upenn.edu
ing a Gamry Instruments potentiostat in the frequency range of 0.1 Hz to 100 kHz and with an ac perturbation of 5 mA, with the samples held in ambient air. All of the impedances in this paper have been divided by 2 to account for there being two electrodes.

Brunauer, Emmett, and Teller (BET) and X-ray diffraction (XRD) characterizations were carried out on 3 × 3 × 10 mm slabs, prepared from the same slurries that were used in the tape-casting process for the porous YSZ. XRD patterns were measured using Cu Ka radiation. BET isotherms were measured using Kr adsorption at 78 K and were used to determine surface areas. Scanning electron microscopy (SEM) coupled with an energy-dispersive X-ray analyzer (FEI Quanta 600 FESEM) was used to determine the microstructure and elemental distribution of prepared cells.

**Results and Discussion**

In earlier studies of ceria incorporation into YSZ scaffolds, ceria formed a porous coating of nanoparticles over the porous YSZ following calcination at temperatures below 1123 K, with increasingly dense films being formed at calcination temperatures above 1473 K. Because the doped-ceria interlayers must be dense to effectively prevent interfacial reactions, we first investigated the effect of sintering temperature on the morphology of SDC in YSZ using SEM and BET isotherms.

The SEM results for the SDC coatings are shown in Fig. 2. Figure 2a is a micrograph of the empty YSZ scaffold. The pore structure has an appearance similar to that of a sponge, with pores ranging between 0.5 and 3 μm. After adding 20 wt % (−10 vol %) SDC with calcination to 1373 K, the YSZ scaffold is covered by well-defined particles that are much less than 0.1 μm in diameter. There appear to be gaps between the particles that would allow fluid-phase species to interact with the underlying YSZ. The SDC particles grow dramatically after heating to 1473 K (Fig. 2c), forming crystallites that are 0.2–0.3 μm and that completely cover the YSZ scaffold. An energy dispersive X-ray analysis (EDX) scan along the line A–B in Fig. 2c and d demonstrated that Ce was evenly distributed on the surface of the underlying YSZ. The peaks in the Ce concentration in this line scan correspond to the edges of the original YSZ features, where the SDC film appears thicker to the electron beam used in the EDX measurement. There were no signs of phase segregation or of large blocks of SDC anywhere in the sample.

Data from the BET isotherms, shown in Table I, confirm the above picture. In the absence of added SDC, the YSZ scaffold had a surface area of 0.27 m²/g. For a material with uniform cylindrical pores, a porosity of 65%, and walls having the bulk density of YSZ, the average pore diameter is calculated to be ∼3 μm, a value that agrees reasonably with the SEM measurements. Following the addition of 20 wt % SDC and calcination to 1123 K, the surface area increased to 1.2 m²/g due to the presence of small SDC particles. Only after calcination to 1473 K did the specific surface area of the SDC–YSZ composite decrease below that of the original YSZ, indicating the formation of a dense film of SDC over the YSZ. Further heating to 1573 K had a minimal effect on the surface area,

Because SDC can react with YSZ to form solid solutions, XRD measurements of 40 wt % (−20 vol %) SDC in YSZ were performed as a function of temperature, as shown in Fig. 3. There were no changes in the YSZ peaks at 30.17 and 35.12° as the temperature was increased from 973 to 1473 K, and features associated with SDC at 28.43 and 32.95° simply narrowed due to increasing crystallite size. At 1523 K, there was a shifting of both the SDC and the YSZ peaks because of the formation of solid solutions at the interface. At 1573 K, the extent of the solid-state reaction between SDC and YSZ is such that the XRD patterns are nearly that of a single-phase oxide.

**Table I. BET surface areas of an empty YSZ scaffold and 20 wt % SDC in YSZ composite, shown as a function of SDC calcination temperature. The measurements were conducted on 3 × 3 × 10 mm SDC/YSZ slabs.**

<table>
<thead>
<tr>
<th>SDC–YSZ calcined to</th>
<th>BET surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1123 K</td>
<td>0.27</td>
</tr>
<tr>
<td>1273 K</td>
<td>1.24</td>
</tr>
<tr>
<td>1373 K</td>
<td>0.57</td>
</tr>
<tr>
<td>1473 K</td>
<td>0.39</td>
</tr>
<tr>
<td>1573 K</td>
<td>0.24</td>
</tr>
</tbody>
</table>

**Figure 2.** The microstructure of (a) the YSZ matrix and YSZ–SDC composites with 20 wt % SDC fired to (b) 1373 and (c) 1473 K. The result of an EDX scan along the path A–B is shown in (d).
The XRD data in Fig. 4d and e implies that LSCo–YSZ electrodes are not stable. Therefore, to prevent a solid-state reaction between LSCo and YSZ, we first incorporated 20 vol % SDC into the YSZ scaffold before adding LSCo. The pattern in Fig. 4f was obtained from this composite after calcination at 1373 K for 4 h. While overlap of features associated with SDC and La$_2$Zr$_2$O$_7$ near 28.5° 2θ prevents us from seeing whether La$_2$Zr$_2$O$_7$ is formed, there is no evidence in the XRD pattern for features corresponding to SrZrO$_3$, suggesting that the SDC layer has prevented the solid-state reactions. Slight broadening of the YSZ peaks at 30.17 and 35.12° 2θ is evident from the peak at 28.5° 2θ. After calcining at 1373 K, the peak corresponding to La$_2$Zr$_2$O$_7$ has grown larger, and an additional feature at 30.86° 2θ due to SrZrO$_3$ is observed.

In a previous study of the stability of cathodes formed by infiltration of LSF into porous YSZ, calcination to 1373 K caused similar changes to the cathode as those observed after fuel cell operation at 973 K for several thousands of hours. Assuming that a similar correlation exists between operating time and calcination temperature for the LSCo–YSZ composites, the observation of new phases in the XRD data in Fig. 4d and e implies that LSCo–YSZ electrodes are not stable. Therefore, to prevent a solid-state reaction between LSCo and YSZ, we first incorporated 20 vol % SDC into the YSZ, followed by calcination to 1373 K, before again adding 20 vol % LSCo. The diffraction pattern in Fig. 4f was obtained from this composite after calcination to 1373 K for 4 h. While overlap of features associated with SDC and La$_2$Zr$_2$O$_7$ near 28.5° 2θ prevents us from seeing whether La$_2$Zr$_2$O$_7$ is formed, there is no evidence in the XRD pattern for features corresponding to SrZrO$_3$, suggesting that the SDC layer has prevented the solid-state reactions. Slight broadening of the YSZ peaks at 30.17 and 35.12° 2θ is evident from the peak at 28.5° 2θ. After calcining at 1373 K, the peak corresponding to La$_2$Zr$_2$O$_7$ has grown larger, and an additional feature at 30.86° 2θ due to SrZrO$_3$ is observed.
The impedances for the cells that had been calcined to 1373 K overestimate the losses that would be observed during fuel cell operation. As shown in Fig. 5d, when a current of 600 mA/cm² was applied to the symmetric cells, the nonohmic losses decreased to 0.15 Ω·cm² for the cell with SDC and 0.43 Ω·cm² for cell without. Although application of a current makes the cells asymmetric, the cathodic impedances of the two electrodes cannot be larger than the sum of the impedances of the two electrodes. Therefore, the electrode impedances for the two cells decrease with current density. This was also observed with LSF–YSZ electrodes calcined to higher temperatures and, again, appears to be due to the coarsening of the perovskite nanoparticles.

Although the impedances of the electrode prepared by infiltration of LSCo into a YSZ scaffold with an SDC barrier in this study was good, this can almost certainly be improved. For example, a previous work showed that the pore structure of the YSZ scaffold can have a large impact on electrode impedance. We made no attempt to optimize this pore structure in the present investigation. We also did not investigate whether there is an optimal thickness for the SDC layer.

The additional steps required for fabricating electrodes by infiltration are a barrier to adopting this procedure, particularly when an SDC film must first be added into the YSZ scaffold to prevent solid-state reactions between the YSZ and the perovskite. However, the present results show that one can use this method to make high performance electrodes, with good stability, from materials that are not well matched for CTE. The fact that the YSZ scaffold is heated together with the electrolyte to very high temperatures also ensures that these electrodes adhere well to the electrolyte. Therefore, this approach is worth considering as a method for producing high performance cathodes.

**Conclusion**

The possibility of preparing a samaria-doped ceria diffusion barrier layer by infiltration methods was investigated. The best results were observed when the SDC was calcined to 1473 K. Both electrode impedances measured on symmetric cells and XRD data suggest that such layers are effective in reducing the extent of the solid-state reaction between LSCo and YSZ.

**Acknowledgment**

This work was funded by the U.S. Department of Energy's Hydrogen Fuel Initiative (grant DE-FG02-05ER15721).

University of Pennsylvania assisted in meeting the publication costs of this article.

**References**