SOFC Anodes Based on Infiltration of La$_{0.3}$Sr$_{0.7}$TiO$_3$

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Abstract
Composites formed by infiltration of 45 wt % La$_{0.3}$Sr$_{0.7}$TiO$_3$ (LST) into 65% porous yttria-stabilized zirconia (YSZ) were examined for application as solid oxide fuel cell (SOFC) anodes. Although LST does not react with YSZ, the structure of the LST deposits was strongly affected by the calcination temperature. At 1373 K, the LST formed loosely packed, 0.1 µm particles that filled the YSZ pores. The conductivity of this composite depended strongly on the pretreatment conditions but was greater than 0.4 S/cm after heating to 1173 K in humidified (3% H$_2$O) H$_2$. Following calcination at 1573 K, the LST had sintered significantly, decreasing the conductivity of the composite by a factor of approximately 5. The addition of a catalyst was critical for achieving reasonable electrochemical performance, with the addition of 0.5 wt % Pd and 5 wt % ceria increasing the power density of otherwise identical cells from less than 20 to 780 mW/cm$^2$ for operation in humidified (3% H$_2$O) H$_2$ at 1073 K. Electrodes prepared from LST deposits calcined at 1373 K were found to exhibit a much better performance than those prepared from LST deposits calcined at 1573 K, demonstrating that the structure of the composite is critical for achieving high performance.

Disciplines
Chemical Engineering | Engineering

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Composites formed by infiltration of 45 wt % La$_{0.8}$Sr$_{0.2}$TiO$_3$ (LST) into 65% porous yttria-stabilized zirconia (YSZ) were examined for application as solid oxide fuel cell (SOFC) anodes. Although LST does not react with YSZ, the structure of the LST deposits was strongly affected by the calcination temperature. At 1373 K, the LST formed loosely packed, 0.1 μm particles that filled the YSZ pores. The conductivity of this composite depended strongly on the pretreatment conditions but was greater than 0.4 S/cm after heating to 1173 K in humidified (3% H$_2$O) H$_2$. Following calcination at 1573 K, the LST had sintered significantly, decreasing the conductivity of the composite by a factor of approximately 5. The addition of a catalyst was critical for achieving reasonable electrochemical performance, with the addition of 0.5 wt % Pt and 5 wt % ceria increasing the power density of otherwise identical cells from less than 20 to 780 mW/cm$^2$ for operation in humidified (3% H$_2$O) H$_2$ at 1073 K. Electrodes prepared from LST deposits calcined at 1373 K were found to exhibit a much better performance than those prepared from LST deposits calcined at 1573 K, demonstrating that the structure of the composite is critical for achieving high performance.
ites exhibiting a lower conductivity than expected. Also, while the performance of the LST-based electrodes is reasonable, it is not comparable to that achieved with LSCM.

**Experimental**

As in the previous study with LSCM, cells were fabricated from a three-layer YSZ wafer with two porous layers separated by a 60 μm thick, dense electrolyte layer. The three-layer YSZ wafers were produced by laminating three green tapes, synthesized by tape casting, with pore formers in the two outer layers. The laminated green tapes were fired to 1773 K to produce the final structures. The porous layer on one side of the electrolyte was 200 μm thick YSZ (~65% porous) and was used as the scaffold for the cathodes, while the other porous layer was 50 μm thick YSZ (~65% porous) and was used as the scaffold for the anode. Porosity in both layers was 99.9%.

After synthesizing the three-layer YSZ wafer, LST was added to the porous anode layer by infiltration of an aqueous solution of the metal salts. For this study, the LST content was fixed at 45 wt %, or 35 vol %, of the anode. (Note: The compositions in this paper are based on the total weight and volume of the electrode.) The aqueous solution was prepared from La(NO₃)₃·6H₂O (Alfa Aesar, ACS 99.9%), Sr(NO₃)₂ (Alfa Aesar, ACS 99.0%), [CH₃CH(O·)[C₂H₄·NH₃]·Ti(OH)₃ [dihydroxy-bis-ammonium, lactate, titanium (IV), Alfa Aesar], and distilled water in the correct molar ratios. After infiltrating the porous layer with this solution, the wafer was heated in air to 723 K to decompose volatile materials. The procedure was repeated approximately 15 times until the desired weight loading of LST was achieved. Finally, the wafer was calcined in air between 1373 and 1573 K for 4 h to produce the perovskite structure.

After forming the LST in the anode layer, the LSF (La₀.₈Sr₀.₂FeO₃₋ₓ)–YSZ cathodes were synthesized by impregnating the 200 μm thick layer with an aqueous solution containing La(NO₃)₃·6H₂O, Sr(NO₃)₂, and Fe(NO₃)₃·9H₂O, to a loading of 40 wt % (~25 vol %) LSF, followed by calcination to 1123 K. Detailed procedures for forming the LSF–YSZ cathodes and a complete description of their characteristics are given elsewhere. Based on those studies, the impedance at 973 K of LSF–YSZ cathodes prepared in this way is between 0.1 and 0.15 Ω cm² and is independent of current density. Following the addition of LSF, the total volume percent of LST in the LST–YSZ composite was estimated to be 30 vol % based on the SEM results, close to the value measured as a function of temperature in humidified aqueous solutions of the nitrate salts and heating in air to 723 K.

The electronic conductivities of the LST–YSZ composites were measured as a function of temperature in humidified (3% H₂O) H₂, using four-probe measurements, on samples that were prepared by infiltrating 45 wt % (~35 vol %) LST into porous YSZ slabs that were 2.5 × 2.5 × 10 mm in size. The YSZ slabs were prepared by lamination and sintering of the same green tapes used for the preparation of the electrode layer. Because the electronic conductivity of LST in reducing environments shows hysteresis with temperature and P(O₂), the measurements in our study were first performed in humidified (3% H₂O) H₂ with increasing temperature, on a sample that had initially been calcined in air, then again with decreasing temperature.

For fuel cell testing, cells were attached to a 10 mm diameter alumina tube with a ceramic adhesive (Arencor, Ceramabond 552). Electrical connections were achieved using Ag paste and Ag wire at both the anode and cathode. The fuel to the anode was humidified (3% H₂O) H₂ with a flow rate of 50 mL/min and injected within a distance of 30 mm from the anode surface using a 3 mm diameter tube, while the cathode was exposed to air. Impedance spectra were measured at open circuit in the galvanostatic mode with a frequency range of 0.1 Hz to 100 kHz and a 1 mA root-mean-square ac perturbation using a Gamry Instruments potentiostat. The active area of the cells, equal to the anode area, was 0.35 cm², but the area of the electrolyte and cathode was approximately 1 cm².

**Results**

**Physical characterization of the LST–YSZ composites.** To determine the structure of the infiltrated LST–YSZ composites, the materials were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Figure 1 is a diffraction pattern of the composite, performed on a 50 μm thick slab that had been calcined to 1473 K. The pattern demonstrates that the composite has the proper microstructure, because the primary diffraction lines were those corresponding to the LST and YSZ phases.

**Figure 1.** XRD pattern of the 45 wt % LST–YSZ composite that had been calcined to 1473 K. YSZ (○) and LST (●).

**Figure 2a** shows the porous YSZ structure prior to the addition of LST and indicates that YSZ is made up of random pores, ranging between 1 and 10 μm in size. Previous Brunauer, Emmett, and Teller surface-area measurements indicated a specific surface area of 4.3 m²/g, demonstrating that the YSZ scaffold must be essentially dense, with no significant microporosity. Figure 2b is the micrograph obtained following the addition of 45 wt % LST and calcination to 1373 K. The figure demonstrates that the open structure of the YSZ has now been filled with small LST particles, approximately 0.1 μm in size. While the LST particles are in contact with each other, they are loosely packed, so that the porosity of LST phase within the YSZ pores is roughly 50%. Because the porosity of the YSZ prior to the addition of LST was approximately 65%, the total volume percent of LST in the LST–YSZ composite is estimated to be 30 vol % based on the SEM results, close to the value of 35 vol % calculated from the weight loading. Figure 2c shows the same LST deposits at higher magnification, with the YSZ scaffold at the bottom.

Figures 2d and e are micrographs at low and high magnification of the LST–YSZ composites after calcination to 1573 K. Although previous work has demonstrated that there are no solid state reactions between LST and YSZ at temperatures up to at least 1823 K, the LST deposits at higher temperature resulted in significant sintering of the LST within the YSZ pores. The feature size of the LST in the center of the pores has increased to approximately 0.5 μm. Even more important, a significant fraction of the LST appears to have collapsed onto the surface of the YSZ pores. This is especially observable in Fig. 2e, which suggests there is a rough coating of LST over the YSZ scaffold.

**Figure 2a** shows the porous YSZ structure prior to the addition of LST and indicates that YSZ is made up of random pores, ranging between 1 and 10 μm in size. Previous Brunauer, Emmett, and Teller surface-area measurements indicated a specific surface area of 4.3 m²/g, demonstrating that the YSZ scaffold must be essentially dense, with no significant microporosity. Figure 2b is the micrograph obtained following the addition of 45 wt % LST and calcination to 1373 K. The figure demonstrates that the open structure of the YSZ has now been filled with small LST particles, approximately 0.1 μm in size. While the LST particles are in contact with each other, they are loosely packed, so that the porosity of LST phase within the YSZ pores is roughly 50%. Because the porosity of the YSZ prior to the addition of LST was approximately 65%, the total volume percent of LST in the LST–YSZ composite is estimated to be 30 vol % based on the SEM results, close to the value of 35 vol % calculated from the weight loading. Figure 2c shows the same LST deposits at higher magnification, with the YSZ scaffold at the bottom.

The electronic conductivities of the 45 wt % LST–YSZ composite in humidified (3% H₂O) H₂, determined using four-probe measurements, are shown as a function of temperature in Fig. 3. Because the conductivity of the porous YSZ was very low compared to any of the values shown in Fig. 3,23 the conductivities are due to the LST

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calcined to only 1373 K for the first set, then 1473 K, and finally 1573 K. The conductivities were measured while increasing the temperature of the sample and again while decreasing the temperature. As reported by others,25 the conductivities increased significantly with increasing reduction temperatures but remained relatively constant when cooling in a reducing environment.

Two observations are made from the data in Fig. 3. First, the conductivities of the composite decreased substantially with increasing calcination temperature, with the 1573 K composite exhibiting conductivities that were approximately 5 times lower than that of the 1373 K composite. Second, the conductivity of the composite calcined at 1373 K and reduced at 1173 K was greater than 0.4 S/cm, a value higher than was achieved by more traditional LST–YSZ composites having higher volume fractions of LST.26 The obvious conclusion is that the structure of the composite is important in determining the conductivity, and that the structural changes that occur with increasing calcination temperature cause a decrease in the conductivity.

Electrochemical characterization of LST–YSZ composites.—Figure 4 shows the polarization curves for two fuel cells, operating in humidified (3% H\textsubscript{2}O) H\textsubscript{2} at 1073 K, for which the anode was made from the 45 wt % LST–YSZ composite that had been calcined to 1373 K. Both cells had identical LSF–YSZ cathodes and 60 μm thick electrolytes, and differed only in that 5 wt % ceria and 0.5 wt % Pd had been added to one of the cells for catalytic activity. While the open-circuit voltages (OCVs) were approximately 1.1 V for both cells, in good agreement with the Nernst potential, the addition of the catalyst had a dramatic effect on fuel cell performance. The maximum power density increased from less than 20 to approximately 780 mW/cm\textsuperscript{2} upon the addition of Pd/ceria, demonstrating that LST itself has minimal electrochemical activity for oxidation of H\textsubscript{2}.

Additional characteristics of the 1373 K, LST–YSZ anode, with the Pd/ceria catalyst, are demonstrated in Fig. 5 and 6, which show the V–i polarization and Cole–Cole impedance plots as a function of temperature in humidified H\textsubscript{2}. The V–i polarization curves in Fig. 5 indicate that the cell potentials decrease linearly with the current density. As expected, the maximum power densities increased with temperature, from 400 mW/cm\textsuperscript{2} at 973 K to 1100 mW/cm\textsuperscript{2} at 1173 K.

The sources of the losses in the fuel cell were investigated using the open-circuit impedance plots in Fig. 6. The ohmic losses, determined by the high-frequency intercept with the abscissa, decrease...
The conductivity of the LST–YSZ composite is sufficient to make the ohmic losses negligible at higher temperatures. As determined from the data in Fig. 6, the ohmic losses at 973 K are estimated to be 0.06 S/cm, very close to what is observed in Fig. 8. The ohmic losses for the 1373 and 1473 K cells were much closer to the value expected for the electrolyte.

However, the effect of LST–YSZ calcination temperature on the nonohmic losses was much larger. Not only was there a significant increase in the OCV impedance in Fig. 8, but the V-i polarization curves for the cells prepared from the 1473 and 1573 K LST–YSZ composites show an increased slope at higher current densities. This kind of behavior is often associated with gas-phase diffusion limitations, but this is not likely the cause in the present case. The pore volumes for the 1473 and 1573 K LST–YSZ composites are more open for gas-phase diffusion than that for the 1373 K composite, so that diffusion should be less limiting on the cells with the poorest performance. Based on the SEM micrographs in Fig. 2, we suggest that increased nonohmic losses are associated with the LST covering the YSZ pores, as observed in Fig. 2e. Because LST has a low ionic conductivity, the electrochemical reactions can only occur on the surface of the LST-covered YSZ.
uncovered YSZ regions, decreasing the area where the three-phase boundary sites exist. Why this would cause the impedance to change with current density is uncertain.

Discussion

As pointed out earlier, LST and YSZ are completely unreactive following calcination to temperatures as high as 1823 K. In addition to the fact that LST and YSZ remain as separate phases in cofired powders, the surface interactions between these two phases are very weak, to the point that it is difficult to form ceramic structures with a sharp LST–YSZ interface because of the tendency of the two layers to delaminate.14 This is in sharp contrast to what is observed with La0.8Sr0.2MnO3 (LSM) and YSZ, where LSM particles have been shown to spread out over YSZ surfaces under some conditions, at temperatures below that at which solid state reactions between LSM and YSZ begin to occur.15 These surface interactions are related to the “wetting” and “dewetting” phenomena observed with liquid–solid interfaces.

Surface interactions appear to have an important influence on the nature of composites formed by infiltration processes. In a recent study of LSCM–YSZ composites,12 it was reported that the LSCM forms an even coating over the YSZ pores following calcination at 1473 K. Assuming that LSCM interacts with YSZ in a similar way as LSM interacts, it would appear that the tendency of the LSCM to “wet” the YSZ surface leads to a composite in which the LSCM coats the YSZ. By contrast, the tendency of LST to avoid wetting the YSZ surface leads to a composite in which the LSCM forms an even coating over the YSZ pores following calcination at 1373 K. Assuming that LSCM interacts with YSZ in a similar way as LSM interacts, the electrochemical performance of the LSCM–YSZ composite, at least after high-temperature reduction. However, the electrochemical performance of the LSCM–YSZ electrode was significantly better than any of the LST–YSZ electrodes. Using the same cathode material (i.e., 40 wt % LSF infiltrated into YSZ) and a similar electrolyte thickness, the cells with LSCM gave maximum power densities in humidified H2 of 520 mW/cm2 at 973 K and 1100 mW/cm2 at 1073 K, compared to values of 400 and 780 mW/cm2 on the best LST cell. At 973 K, the large nonohmic loss of the LSCM cell, including cathode losses, was 0.2 Ω cm2, while the anode impedance for the best 1373 K LST cell was estimated to be 0.6 Ω cm2.

There are several possible reasons for why the LSCM-based electrode showed better performance. While the ionic conductivity of LSCM is very low under oxidizing conditions,5 its ionic conductivity under reducing conditions is significantly better and much higher than that of LST. Another important factor is the morphology of the LSCM deposits. While the LSCM film that forms over the YSZ pore structure is not likely to be ideal, it has been observed that the LSCM film develops pores under reducing conditions, much like what is observed with LSM.16 Under anode conditions, it is likely that the LSCM exists as a film with pores, forming an almost ideal anode structure.

Finally, it was possible in the present study to examine the properties of LST–YSZ composites while varying the morphology of the LST within the YSZ pores, simply by changing the calcination temperature. The data showed that the morphology had a significant effect on both the conductivity of the composite and on the electrochemical properties of electrodes made from this composite. The fact that morphology has such an important influence on properties is not surprising, but it does point out the critical importance that structure, separate from composition, has on the development of electrodes. This is a critical factor in reproducing results between laboratories, because the preparation methods and calcination temperatures can be just as important as the composition in determining the performance of electrodes.

Conclusions

The properties of LST–YSZ composites depend strongly on the structure of these composites. When the composites are prepared by infiltration of LST into porous YSZ, the structure of the LST phase is influenced by the surface interactions between LST and YSZ and depends on the calcination temperature. LST–YSZ composites have insufficient catalytic activity for SOFC anodes but can provide the electronic conductivity required for the functional layer.

Acknowledgments

This work was funded by the U.S. Department of Energy’s Hydrogen Fuel Initiative (grant no. DE-FG02-05ER15721). S. L. acknowledges support from the Korea Research Foundation Grant, funded by the Korean Government (MOEHRD) (KRF-2007-611-D00014).

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

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