

Investigation of the Stability of SOFC Cathodes Fabricated by Impregnation Methods

Fred Bidrawn¹, Shiwoo Lee^{1,2}, John M. Vohs¹ and Raymond J. Gorte^{1*}

¹University of Pennsylvania, Philadelphia, Pennsylvania 19104 (USA)

²Korea Institute of Energy Research, Deajeon 305-343 (Korea)

*gorte@seas.upenn.edu

Introduction

Despite having a relatively high area specific resistance (ASR) at temperatures below 1023 K, the standard solid oxide fuel cell (SOFC) cathode material with yttria-stabilized zirconia (YSZ) electrolytes is still a composite of Sr-doped LaMnO₃ (LSM) with YSZ. The ASR of cathodes made from mixed-conducting perovskites, such as Sr-doped LaCoO₃ (LSCo) or Sr-doped LaFeO₃ (LSF), can be much lower; unfortunately, this high performance tends to be unstable. In the case of LSCo, deactivation is almost certainly associated with solid-state reactions that form insulating phases, such as La₂Zr₂O₇, at temperatures as low as 923 K [1]. Because electrodes based on LSF deactivate after sintering at temperatures as low as 1273 K, [2-4] it is commonly assumed that similar solid-state reactions are responsible for deactivation in these electrodes as well.

However, deactivation by formation of insulating materials may not apply to LSF. Unlike the case with LSCo where X-ray diffraction (XRD) clearly shows the formation of new phases when LSCo and YSZ are in contact at 700°C, LSF-YSZ composites only show the formation of additional phases above 1400°C, [5] a temperature higher than that necessary to form insulating phases with LSM [6]. In a study of the stability of LSF cathodes prepared by infiltration into porous YSZ from our laboratory, deactivation correlated with a loss of LSF surface area and the formation of what appeared to be a dense film of LSF covering the porous YSZ [7]. Impedance spectra also showed that the ohmic resistance of deactivated cells remained unchanged, a strong argument against the formation of insulating layers. Based on these observations, it was suggested that deactivation is either due to a decrease in O₂ adsorption rate (due to lost surface area) or to LSF forming an impenetrable barrier over the YSZ in the electrode. If LSF forms a dense layer, performance in the deactivated electrode could be limited by conduction of oxygen ions through the LSF.

Because the ionic conductivity of LaFeO₃ likely depends on the dopant, we decided to compare the performance of Ca-, Sr-, and Ba-doped LaFeO₃ [La_{0.8}Ca_{0.2}FeO₃ (LCF), LSF, and La_{0.8}Ba_{0.2}FeO₃ (LBF)]. Therefore, we set out to measure the ionic conductivities of LCF, LSF, and LBF and to determine the performance of electrodes made with these three materials.

Materials and Methods

Fuel cells were prepared by a tape casting method, with the composite cathodes formed by infiltration of stoichiometric ratios of appropriate nitrate salts into porous YSZ and calcination to desired temperatures [7]. Impedance spectra were measured using a Gamry Instruments potentiostat. Ionic conductivities were determined by measuring the rate of oxygen permeation across perovskite pellets formed by sintering pressed powder to 1773 K for 4

hours. Electrode microstructure was also characterized using scanning electron microscopy, (SEM) atomic force microscopy, (AFM) and BET isotherm measurements. Samples for AFM measurements were prepared by spraying LSF precursors onto YSZ(100) single crystals using an air brush. The crystals were then calcined in air and images were taken using a Pacific Nanotechnologies scanning probe microscope.

Results and Discussion

Electrode performance was shown to be dependent upon calcination temperature, with low temperature calcination (1123 K) showing better performance than high temperature calcination (1373 K). Structural characterization showed that calcination temperature also affected electrode microstructure. Low temperature calcination led to the formation of a small fluffy perovskite particles covering the YSZ scaffold. High temperature calcination caused the infiltrated perovskite to wet the surface of the YSZ, forming a dense film. Ionic conductivity measurements showed that the ionic conductivity of the perovskite was influenced by the dopant, with LSF showing the highest conductivity and LCF showing the lowest conductivity. The effect of different dopants and calcination temperatures on cathode performance was measured. Low temperature calcined cathodes showed identical performance, regardless of dopant. Cathodes calcined to higher temperatures showed significant degradation of performance with LSF and LCF showing the least and most severe degradation, respectively. We suggest that morphological changes that take place with high temperature calcination are similar to those that occur over thousands of hours of operation. Because of the formation of the perovskite film with high temperature calcination, the length of the three phase boundary is significantly reduced. Oxygen reduction in these electrodes must then take place on the surface of the film, requiring the oxygen ions to diffuse through the film, which increases ASR and limits performance.

Significance

Deactivation of doped LaFeO₃ cathodes is likely the result of morphological rather than chemical changes within the electrode, requiring the development of alternative strategies to improve cell stability.

References

1. Sase, M., Ueno, D., Yashiro, K., Kaimai, A., Kawada, T., and Mizusaki, J., *J. Phys & Chem. Solids*, 66, 343 (2005).
2. Simner, S.P., Bonnett, J.F., Canfield, N.L., Meinhardt, K.D., Sprenkle, V.L., and Stevenson, J.W., *Electrochemical and Solid-State Letters*, 5, A173-175 (2002).
3. Simner, S.P., Bonnett, J.F., Canfield, N.L., Meinhardt, K.D., Shelton, J.P., Sprenkle, V.L., and Stevenson, J.W., *Journal of Power Sources*, 113, 1 (2003).
4. Simner, S.P., Anderson, M.D., Bonnett, J.F., and Stevenson, J.W., *Solid State Ionics*, 175, 79 (2004).
5. Hole J., Kuseer, D., Hrovat, M., Bernik, S., and Kolar, D., *Solid State Ionics*, 95, 259 (1997).
6. Simner, S.P., Shelton, J.P., Anderson, M.D., and Stevenson, J.W., *Solid State Ionics*, 161, 11 (2003).
7. Wang, W., Gross, M.D., Vohs, J.M., and Gorte, R.J., *Journal of the Electrochemical Society*, 154, B439-45 (2007).