Stability of Cobalt Infiltrated Cathodes

Craig P. Jacobson[a], Xuan Chen[b],
Lutgard C. De Jonghe[a,b], and Steven J. Visco[a]
[a]Materials Sciences Division
Lawrence Berkeley National Laboratory
1 Cyclotron Road, B62R0203
Berkeley, CA 94720, USA
and
[b]Department of Materials Science and Engineering
University of California at Berkeley
Berkeley, CA 94720, USA

Introduction

Reducing the operating temperature from 800-1000°C to 650-750°C may enable the use of low-cost metal components in a solid oxide fuel cell stack and balance of plant and therefore lower the cost of the system. The use of alternate, higher conductivity electrolytes, such as Scandia stabilized zirconia (SYSZ), should additionally improve the low temperature performance of thin-film SOFCs[1], however the cathode overpotential at the reduced temperatures is limiting further improvement. Strontium doped lanthanum manganate (LSM) is most commonly used for the cathode due to its combination of good electrocatalytic properties and chemical stability with the yttria stabilized zirconia (YSZ) electrolyte[2]. Performance of LSM cathodes is quite good in the 800-1000°C range, however the resistance of these electrodes increases rapidly below ~700°C. Alternative electrodes having improved electrocatalytic properties, such as doped $LnCoO_3$, have other properties such as high thermal expansion coefficients and high chemical reactivity, that limit their use with zirconia based electrolytes.

An alternative electrode design is to create a coarse microstructure that is well bonded to the electrolyte from a material that is chemically and thermally matched, such as the LSM, and then infiltrate a small amount of a highly catalytic materials into the electrode[3]. Recently it was demonstrated[4,5] that the LSM cathode activity can be dramatically improved by infiltrating nano-sized catalyst particles into its pores after the firing process. The purpose of this work is to investigate the stability of these infiltrated electrodes when operated between 600-800°C for 100 hour periods under various current density loads. Determining the temperature, current density window of operation for stable long-term performance of these infiltrated electrodes is the final objective.

Experimental

NiO (J. T. Baker) and SYSZ [i.e. Sc2O3)0.1(Y2O3)0.01(ZrO2)0.89] from Daiichi KigensKagakukokyo] in a weight ratio of 1:1 were attritor-milled in iso-propanol, using zirconia balls. Dried mixtures were uniaxially pressed and pre-fired at 1000°C. Thin-films were formed on the NiO-SYSZ disks by colloidal deposition[6], and co-fired at 1300°C. LSM [i.e.La0.85Sr0.15MnO3] was synthesized by a glycine-nitrate method[7], and calcined at 1200°C. The calcined LSM powder was also attritor-milled with SYSZ in a weight ratio of 1:1. Thin cathodes, 1cm^2, were formed on the co-fired disks, by the colloidal deposition and re-firing the assembly at 1150°C. Pt wire mesh and Pt paste were applied to both electrodes as current collectors. After the first electrochemical cell tests, the cathodes of the SOFCs were post-doped by applying 4 microliters per cm^2 of a cobalt nitrate solution [0.5g-Co(NO3)2.6H2O dissolved in 1 ml of water], and then retesting the same cells. The DC current-voltage (I-V) performance was recorded with a potentiostat-galvanostat (Princeton Applied Research Model 371), between 600 and 800°C; in all tests humidified hydrogen (about 3% water) and air were used. AC impedances were measured between 0.1-10 MHz with a frequency response analyzer and a potentiostat (Solartron 1260 and 1286, respectively).

Results

Performance of an anode-supported cell at 650°C was 0.19 W/cm^2 peak power and 0.13 W/cm^2 at 0.7V. The cell was cooled to room temperature and subsequently infiltrated with the cobalt nitrate solution. The performance was again measured and peak power increased to 0.34 W/cm^2 and 0.19 W/cm^2 at 0.7V. After running 1.1 A/cm^2 for 100 hours the cell was tested again. Peak power increased further to 0.37 W/cm^2 though there was little change in performance at 0.7V. A similar cell was fabricated and tested at 700°C. The cobalt infiltrated cell had a peak power of 1.07 W/cm^2 and reached 0.6 W/cm^2 at 0.7V. Durability was tested by running 2.5 A/cm^2 for 100 hours. The peak power degraded to 0.87 while the power at 0.7V was approximately the same at 0.65.

Conclusions

Encouraging short-term (100 hour) performance results have been obtained for LSM based cathodes infiltrated with cobalt nitrate solutions. When operated at 650°C and 1.1 A/cm^2 the cell performance improved over the test period. Higher currents (2.5 A/cm^2) resulted in degradation in performance at 700°C. Further work is needed to clarify the degradation mechanisms at high current and longer test periods (1000 hours) will be needed to determine the viability of this approach.

Acknowledgements

This work was supported by the U.S. Department of Energy, through the National Energy Technology Laboratory. The authors are grateful to Daiichi Kigenso Kagakukogyo for supplying SYSZ powder.

1. S. J. Visco, C. P. Jacobson, and L. C. De Jonghe, in *SOFC VI*, S.C. Singhal and M. Dokiya, Editors, **PV 99-19**, p. 861, The Electrochemical Society Proceedings Series, Pennington, NJ, (1999).
2. N. Q. Minh and T. Takahashi, *Science and Technology of Ceramic Fuel Cells*, Elsevier 1995.
3. S. A. Wallin, U.S. Pat. No. 5,670,270, September 23 (1997).
4. K. Yamahara, C. P. Jacobson, S. J. Visco, L. C. De Jonghe, submitted to Solid State Ionics.
5. R. Chiba, F. Yoshimura, Y. Sakurai, Y. Tabata, M. Arakawa, in *Extended Abstracts of 14th Int. Conf. on Solid State Ionics*, p.14 (2003).
6. S. J. Visco, C. P. Jacobson and L. C. De Jonghe, U.S. Pat. No. 6,458,170, October 1 (2002).
7. L. A. Chick, L. R. Pederson, G. D. Maupin, J. L. Bates, L. E. Thomas, and G. J. Exarhos, Mater. Lett., **10** (1-2), (1990) 6.