Report Title:

**ACTIVE CATHODES FOR SUPER-HIGH POWER DENSITY
SOLID OXIDE FUEL CELLS THROUGH SPACE CHARGE EFFECTS**

Type of Report: Quarterly Technical Report

Reporting Period Start Date: January 1, 2003
Reporting Period End Date: March 31, 2003
Principal Author: Professor Anil V. Virkar
Date Report Was Issued: October 11, 2003
DOE Award Number: DE-FC26-02NT41602

Name and Address of Submitting Organization:

Department of Materials Science & Engineering
122 S. Central Campus Drive
University of Utah
Salt Lake City, UT 84112

DISCLAIMER:

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

ABSTRACT

This report summarizes the work done during the second quarter of the project. Effort is directed in two areas: (1) The use of a novel method to achieve a given porosity level with high contiguity and thus conductivity. (2) Relate the measured conductivity to porosity and contiguity. The rationale for these experiments was to develop cathodes with high ionic conductivity, so that the effective polarization resistance will be concomitantly lowered.

TABLE OF CONTENTS

	Page
INTRODUCTION	5
EXECUTIVE SUMMARY	6
EXPERIMENTAL	8
RESULTS AND DISCUSSION	8
CONCLUSION	10
REFERENCES	20
LIST OF ACRONYMS AND ABBREVIATIONS	20

INTRODUCTION

It is known that electrode transport properties and morphology have a profound effect on electrode polarization and thus on solid oxide fuel cell (SOFC) performance [1-4]. Recent work has shown that a large part of the polarization loss is associated with the cathode [5,6]. In addition to the morphological effect, it is also known that ionic conductivity of the cathode has a large effect on cathodic polarization. It is assumed that the electronic conductivity of the cathode is high enough not to be a limiting factor. This is usually a good assumption with materials such as LSM and LSC, which have electronic conductivities over the temperature of interest between ~ 200 and 1000 S/cm. By contrast, the ionic conductivity of either YSZ or ceria or LSGM is well below 1 S/cm under similar temperatures. The grain size also has a large effect on conductivity [7]. It is desired that the cathode microstructure close to the electrolyte be as fine as possible. However, when the particle size is very fine, there can be a significant effect of space charge on transport [8-13]. The effect of space charge can be potentially greater in the ionic conductor. It could either increase conductivity, or could decrease it. It is desired that the space charge be such that it enhances ionic conductivity of porous bodies. It is possible, however, that space charge effects are actually detrimental. In such a case, the approach should be to seek to lower these effects – assuming this is possible. One area in which space charge effects can be significant is the effect of grain size on conductivity. As part of this work, therefore, effect of grain size on cathode polarization will be examined in the future.

EXECUTIVE SUMMARY

Solid oxide fuel cells (SOFC) can operate over a wide temperature range, from ~600 to 1000°C, and can use a variety of hydrocarbon fuels, once appropriately processed. The current target for SOFC is about 800°C, although efforts are presently underway to lower the operating temperature below 700°C. The largest voltage loss (polarization) in SOFC is known to occur in the cathode. There are two types of cathodic polarizations: (1) Concentration polarization – that associated with gas transport. (2) Activation polarization – that associated with the occurrence of the overall electrochemical reaction of charge transfer. The former is relatively small, as long as the cathode is thin and has sufficient porosity. The latter is the dominant one, and depends upon a number of microstructural and intrinsic – fundamental parameters. This research aims to address cathodic activation polarization. Specifically, this research aims to lower the cathodic polarization. Our prior work has shown that the effective cathodic polarization resistance depends upon the following factors. (1) The particle size of the ionic conductor in a composite cathode, comprising a two phase, porous, contiguous mixture of an ionic conductor and an electrocatalyst – which is an electronic conductor. In general, the smaller the particle size of the ionic conductor, the lower is the cathodic activation polarization. (2) The ionic conductivity of the ionic conductor also has a significant effect – the higher the ionic conductivity, the lower is the cathodic polarization. (3) Intrinsic charge transfer resistance – the lower the intrinsic charge transfer resistance, the lower is the cathodic activation polarization.

The above factors themselves depend upon some other fundamental parameters. It is known that in the majority of the ionic conductors, the smaller the grain size, the higher is the net resistivity. This is attributed to grain boundaries, which usually offer resistance to ion transport. Part of this resistance is attributable to space charge effects, which tend to lower oxygen vacancy concentration near grain boundaries. Depending upon the dopant type and amount, it is in principle possible to actually enhance the oxygen vacancy concentration near grain boundaries. If this can be achieved, significant lowering of cathodic polarization can occur. This research aims to identify fundamental parameters, which tend to increase oxygen concentration near grain boundaries. This is expected to depend upon the chemistry of the material as well as processing.

The other factor involves the nature of inter-particle necks. If the contact between particles is poor (small), the overall resistance can be large, leading to high cathodic polarization. During the previous reporting period, the effect of inter-particle neck size on total conductivity of porous bodies was theoretically analyzed. In this reporting period, nanosize powders of Sm-doped CeO₂ were synthesized using the combustion method. The choice of Sm-doped ceria was made, as this composition has been reported to exhibit some of the highest ionic conductivity – a critical factor for lowering cathodic polarization resistance. Samples with various porosities were made using two approaches: (1) A conventional sintering process. (2) A novel process comprising first forming a two-phase dense body containing Sm-doped ceria and leachable phase. The leachable phase was removed, leaving behind Sm-doped ceria of desired porosity and improved connectivity. Using these two approaches, samples with >50% porosity, but with vastly differing connectivities were fabricated. Conductivity was measured as a function of porosity for both sets of samples. It was demonstrated that the connectivity

has a profound effect on conductivity, and thus should have large effect on cathodic polarization. This also has a direct impact on the role of space charge through the grain boundary effect, and this will be discussed at length in the next report, which will also include further modeling work on this topic.

EXPERIMENTAL

During this reporting period, efforts were directed in the following areas.

1. Two groups of samples were made with varying levels of porosity. The process for making the first group of samples is as following: SDC powder made using the process of combustion synthesis was wet-milled, dried, and then screened. Powder compacts were formed by die-pressing followed by iso-static pressing. Then the samples were sintered at various temperatures ranging from 1200°C to 1600°C to achieve various levels of porosity.
2. The process for making the second group of samples is as follows: The powder mixtures of commercial NiO and combustion-synthesized SDC in various the weight ratios, namely, 20:80, 30:70 and 40:60, were wet-milled, dried, and then screened. Powder compacts were formed by die-pressing and iso-static pressing. Bar samples were sintered in air at 1500°C for 2 hours. These bar samples were reduced in 10% hydrogen for 2 hours and 100% hydrogen for 2 hours at 800°C. Finally etching the reduced bar samples in dilute nitric acid solution for 3 hours. Since the two-phase material prior to etching has equiaxed microstructure, it is expected that the contiguity will be excellent.
3. Total conductivity of the samples with varying porosity levels was measured over a range of temperatures using a four-probe DC method.
4. After testing, the fractured pieces of each cell were impregnated with an epoxy. Upon curing and hardening the epoxy, the samples were mounted in plastic mount, and subsequently polished to a 1-micron finish. Then the samples were examined under a scanning electron microscope (SEM).
5. The microstructures of porous samples were characterized by quantitative stereology to estimate the porosity, the aggregate grain size and the neck size formed between particles.

RESULTS AND DISCUSSION

Measurement of conductivity as a function of temperature on two different groups of samples of varying porosity levels:

Figure 1 shows the measured normalized conductivity (at 800°C) as function of measured normalized density for samples of varying porosities made by the two different processes. An important point to note is at ~50% porosity, the conventionally sintered sample has a conductivity, which is orders of magnitude lower. Figure 2 shows that same data, expect that it is plotted vs. relative particle size. Figure 3 an SEM micrograph of a dense bar of

SDC sintered at 1600°C for 4 hours. Note the high density, and a relatively coarse grain size. Figure 4 is an SEM micrograph of conventionally sintered SDC (1400°C for 4 hours) with ~33.5% porosity. Figure 5 is that of a sample with ~51.2% porosity, sintered at 1200°C for 4 hours.

Figure 6 is an SEM micrograph of sample that was made by the etching process. The two-phase material was sintered at 1600°C for 4 hours. The porosity is ~31.2%. Note the high degree of connectivity, as compared to the sample shown in Figure 4, which has the same porosity. Similarly, Figures 7 and 8 show SEM micrographs of samples made by the etching process, with respectively ~39.7% and ~54.8% porosity. Note that comparison of Figures 8 and 5 shows a vast difference in connectivities, which is reflected in their conductivities.

Data on the two sets of samples are given in Tables I and II. From Tables I & II, it is noted that in the first group of samples fabricated using the conventional method, the conductivity of the dense sample is approximately double that of the sample with 33.5% porosity. This is approximately consistent with expectations since a crude rule of thumb is that conductivity of a porous sample, σ_{porous} , containing volume fraction porosity given by V_v , is related to the conductivity of the fully dense sample, σ_{dense} , via an equation of the form

$$\sigma_{porous} \sim \sigma_{dense}(1 - V_v) \quad (1)$$

The conductivity of the more porous sample with 51.2 % porosity was far lower than can be expected purely based on total porosity. The relevant equations which describe dependence of conductivity on connectivity are given in the first quarterly report.

For the porous samples fabricated using reducing-etching method, with the porosity increase from 31.2% to 54.8%, the conductivity decreases from 0.05 to 0.0328 S/cm. The decrease of conductivity is not as large as in the samples fabricated using the conventional method.

The results show that the conductivity is related not only to porosity, but also to neck size and grain/particle size. In fact, the effect of neck size (contiguity) is rather large. This aspect is expected to have a major effect on cathode polarization.

Microstructure Characterization:

Table I shows that with porosity increase from 5.2% to 51.2%, there is significant variation in the grain/particle size varying between 6.4 and 1.1 μm , as a function of porosity. It is observed that for the second group of samples, with the porosity increase from 31.2% to 54.8%, the grain/particle size shows a moderate trend of decreasing from 3.9 to 2.1 μm .

Also of interest to note is that the connectivity (inter-particle neck size) has a large effect on conductivity of porous ionic conductor. Comparing sample 3 (Figure 5) and sample 6

(Figure 8), these two samples have similar porosities. But a large difference of conductivity, as large as one hundred times, exists between these two samples. The grain size difference is not so large. The only possible reason for the large difference in conductivities is related to the connectivity.

CONCLUSION

In the first quarterly report, a simple analytical equation was derived, which describes the conductivity as a function of connectivity. It was shown that at very low connectivity (small neck size between particles), the conductivity can be very low – orders of magnitude lower. This was shown in sintered samples of ceria containing Sc_2O_3 . In this reporting period, samples of SDC were made by two methods. (1) A conventional method, which at high porosities result in poor connectivity – and thus low conductivity. (2) A novel method involving leaching of a fugitive constituent. In this method, samples of high porosity can be made with good connectivity, and thus high conductivity. It was shown that in samples with ~50% porosity, the conductivity of the samples made by the second method was ~75 times higher than those made by the conventional method. This has profound implications concerning cathodic polarization resistance. The specific role of space charge effect and grain boundaries, as it concerns cathodic polarization, will be briefly addressed in the next report, and in much greater detail in future reports.

Table I: Porosity, particle size and conductivity as a function of sintering conditions. (The samples fabricated using conventional method)

SDC (Ce/Sm = 80/20)		Sample 1 Sintered at 1600°C 4hours	Sample 2 Sintered at 1400°C 4hours	Sample 3 Sintered at 1200°C 4hours
Porosity		4.2%	33.5%	51.2 %
Particle Size (μm)		6.4 ¹	2.5	1.1
Conductivity (S/cm)	650(°C)	0.0272	0.01152	5.18x10 ⁻⁵
	700(°C)	0.0373	0.01658	1.19x10 ⁻⁴
	750(°C)	0.0563	0.02517	2.52x10 ⁻⁴
	800(°C)	0.0706	0.03198	4.31x10 ⁻⁴

Table II: Porosity, particle size and conductivity as a function of sintering conditions (The porous samples were made of reducing-etching method).

SDC (Ce/Sm = 80/20)		Sample 4 Sintered at 1500°C 2 hours	Sample 5 Sintered at 1500°C 2 hours	Sample 6 Sintered at 1500°C 2 hours
Porosity		31.2%	39.7%	54.8%
Particle Size (μm)		3.9	3.1	2.1
Conductivity (S/cm)	650(°C)	0.016	0.01523	0.01033
	700(°C)	0.02484	0.02395	0.01556
	750(°C)	0.03609	0.03476	0.02301
	800(°C)	0.05057	0.04901	0.03283

¹ Only for the fully dense size, the measured particle size is the grain size. In all other samples, the measured particle size may include an agglomerate of grains.

Figure 1: Relative conductivity vs. relative density. Here, relative conductivity is defined as the ratio of the conductivity of the sample with a given porosity to that of the fully sintered (negligible porosity) sample. Similarly, the relative density is the ratio of density of a sample with given porosity to that of the fully sintered sample.

Figure 2: Relative conductivity vs. relative particle size. The relative particle size is the ratio of the measured ‘particle’ size in a sample of given porosity to that of the ‘grain’ size of the fully sintered sample.

Figure 3: Sm₂O₃-doped ceria (SDC) Dense bar (porosity = 4.2%) sintered at 1600°C/4 hours. Note relatively coarse grain size. Conductivity and grain size data are given in Table I.

Figure 4: Sm₂O₃-doped ceria (SDC) bar (porosity = 33.5%) sintered at 1400°C/4 hours. Conductivity and particle size data are given in Table I.

Figure 5: Sm₂O₃-doped ceria (SDC) (porosity = 51.2%) sintered at 1200°C/4 hours. Note relatively fine particle size. The connectivity is poor. Conductivity and particle size data are given in Table I.

Figure 6: Sm₂O₃-doped ceria (SDC) bar (porosity = 31.2% - made by the leaching process) sintered at 1600°C/4 hours. Conductivity and particle size data are given in Table II.

Figure 7: Sm₂O₃-doped ceria (SDC) bar (porosity = 39.7% - made by the leaching process) sintered at 1600°C/4 hours. Conductivity and particle size data are given in Table II.

Figure 8: Sm₂O₃-doped ceria (SDC) bar (porosity = 54.8% - made by the leaching process) sintered at 1600°C/4 hours. Conductivity and particle size data are given in Table I.

REFERENCES

- 1) T. Kenjo, S. Osawa, and K. Fujikawa, *J. Electrochem. Soc.*, **138** 349 (1991).
- 2) C. W. Tanner, K-Z. Fung, and A. V. Virkar, *J. Electrochem. Soc.*, **144** 21-30 (1997).
- 3) H. Deng, M. Zhou, and B. Abeles, *Solid State Ionics*, **74** 75 (1994).
- 4) I. V. Murygin, *Elektrokhimiya*, **23** [6] 740 (1987).
- 5) A. V. Virkar, J. Chen, C. W. Tanner, and J-W. Kim, *Solid State Ionics*, **131** 189 (2000).
- 6) F. Zhao, Y. Jiang, G-Y. Lin, and A. V. Virkar, pp. 501 in SOFC VII, edited by H. Yokokawa and S. C. Singhal, Electrochemical Society Publication, Pennington, NJ, (2001).
- 7) M. J. Verkerk, B. J. Middlehuis, and A. J. Burggraaf, *Solid State Ionics*, **6** 159 (1982).
- 8) X. Guo, *Solid State Ionics*, **81** 235-242 (1995).
- 9) X. Guo, *Solid State Ionics*, **99** 137-142 (1997).
- 10) J. Frenkel, p. 37 in 'Kinetic Theory of Liquids', Dover, NY (1946).
- 11) K. Lohvece, *J. Chem. Phys.*, **21** [7] 1123-1128 (1953).
- 12) K. L. Kliewer and J. S. Koehler, *Phys. Rev.*, **140** [4A], A1226-A1240 (1965).
- 13) K. L. Kliewer, *Phys. Rev.*, **140** [4A], A1241-A1246 (1965).

LIST OF ACRONYMS AND ABBREVIATIONS

DC:	Direct current
LSM:	Sr-doped LaMnO ₃
LSGM:	Sr and Mg-doped LaGaO ₃
SDC:	Samaria-doped ceria
SEM:	Scanning electron microscopy
SOFC:	Solid oxide fuel cell
XRD:	X-ray diffraction