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:	July 1, 2003
Reporting Period End Date:	September 30, 2003
Principal Author:	Professor Anil V. Virkar
Date Report was Issued:	December 12, 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 fourth quarter of the project. Effort was directed in two areas, namely, continued further development of the model on the role of connectivity on ionic conductivity of porous bodies, including the role of grain boundaries and space charge, and its relationship to cathode polarization; and fabrication of samaria-doped ceria porous (SDC). The work on the model development involves calculation of the effect of space charge on transport through porous bodies. Three specific cases have been examined: (1) Space charge resistivity greater than the grain resistivity, (2) Space charge resistivity equal to the grain resistivity, and (3) Space charge resistivity lower than the grain resistivity. The model accounts for transport through three regions: the bulk of the grain, the space charge region, and the structural part of the grain boundary. The effect of neck size has been explicitly incorporated. In future work, the effective resistivity will be incorporated into the effective cathode polarization resistance. The results will then be compared with experiments.

TABLE OF CONTENTS

	Page
INTRODUCTION	5
EXECUTIVE SUMMARY	6
EXPERIMENTAL	8
RESULTS AND DISCUSSION	8
CONCLUSION	10
REFERENCES	15
LIST OF ACRONYMS AND ABBREVIATIONS	15

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 the ionic conductivity of 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 at similar temperatures. Even with the possible use of bismuth oxide for the cathode, the ionic conductivity is still much lower than the electronic conductivity. 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. 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 quite large in ionic conductors. 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 many oxygen ion conductors. 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. Another one of great importance is the morphology of the cathode, and especially that of the ionic conductor in composite cathodes. When ionic current has to flow from one grain to the adjacent grain, it is necessary that narrowing in the neck region be accounted for. In the past reports, preliminary results on both theoretical analysis and experimental aspects were reported. In this report, further development of the model is described, along with the results of calculations.

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 at 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 cathodic reaction of charge transfer. The former is relatively small, as long as the cathode is thin and has sufficient porosity [14]. 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 through cathode modification through space charge effects. 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 – the latter being 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 in the cathode 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 additional 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 in some materials (e.g. YSZ) tends 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 vacancy 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 periods, the effect of inter-particle neck size on total conductivity of porous bodies was theoretically analyzed, and experimental results were presented. The results showed that the neck size between particles has a profound effect on ionic conductivity. Specifically, it was shown that for highly porous samples of identical porosities (~50%), the absolute value of conductivity was ~75 times higher in samples with sufficiently large neck sizes (good connectivity) as compared to samples with small neck sizes (poor connectivity). It is to be noted that this has profound influence on cathode polarization. In the subsequent report (Third quarterly), the effect of grain boundaries was also included. However, the effect included was only that of the structural part of the grain boundary. It is known that the effect of space charge can extend far beyond the structural part of the grain

boundary. In this report, results of further model development are included, wherein the effect of space charge region are explicitly included. There cases have been considered: Space charge region have higher, equal to, and lower resistivity compared to the bulk grain. The effect of neck size on the effective resistivity has been explicitly calculated. Experimental work is currently underway on a number of systems.

EXPERIMENTAL

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

1. Extension of the theoretical analysis of ionic conduction in porous bodies, including the role of grain boundaries and the effect of space charge region on the effective resistivity.
2. Fabrication of porous SDC samples. The approach is similar to that used for Scandia-doped ceria (ScDC), described in the first quarterly report. The fabrication procedure is as follows. Powder mixtures of NiO and SDC (made by combustion synthesis) were made in the following NiO:SDC weight proportions: 20:80, 30:70, and 40:60. The mixtures were wet-milled, dried and sieved through a screen. Bar sample were made by die-pressing followed by sintering in air at 1500°C for 2 hours. Subsequently, the samples were heated in 10% H₂ + 90% N₂ gas mixture at 800°C for 2 hours. Finally, the samples were etched in dilute nitric acid to remove the nickel. This led to the formation of porous SDC samples with good neck formation between adjacent grains. The samples were subsequently heated in air at 1200°C for 4 hours. Total conductivity of the samples will soon be measured.

RESULTS AND DISCUSSION

The Effect of Grain Boundaries on Ionic Conductivity of Porous Bodies: The Effect of Space Charge: Further Model Development:

The objective is to include the space charge effects in conduction through porous bodies. In the present case, the following nomenclature will be used.

R : Radius of the particle, which is assumed to be a grain.

r_0 : Radius of the inter-particle neck.

λ : Width of the space charge region. For simplicity, it is assumed here that in this region, the conductivity is uniform.

ρ_g : Grain resistivity without the space charge effect (Ωcm).

ρ_s : Resistivity in the space charge region (Ωcm). This may be higher or lower than the grain resistivity.

$\rho_{gb}\delta_{gb}$: Grain boundary area specific resistance(Ωcm). This is only the one associated with the structural disorder part of transport across a grain boundary. In general, the grain boundary resistivity is not amenable to a separate, unequivocal determination, and neither is the thickness. Hence, this is given as a product, which is the common practice.

In general, the particle size, R , is in the micron range, the grain boundary thickness is in angstroms, and the space charge width, λ is assumed to be in tens or hundreds of nanometers. Thus, we expect that $R > \lambda > \delta_{gb}$.

R_{eff} : The net resistance of half a grain with half the grain boundary associated with it. A schematic is shown in Figure 1.

The net resistance will be divided into three regimes, consistent with the schematic in the figure shown. (1) Region I corresponds to the net resistance for the range between $x = x_0 + \lambda$ to $x = R$. The corresponding resistance is R_I . (2) Region II corresponds to the net resistance for the range $x = x_0$ to $x = x_0 + \lambda$. The corresponding resistance is R_{II} . (3) Region III corresponds to the transport across the grain boundary (structural) at her neck, the corresponding resistance is R_{III} .

The net resistance is then given by

$$R_{eff} = R_I + R_{II} + R_{III}$$

The results of analysis for the three regions are given in what follows.

R_I calculation:

$$R_I = \int_{\cos^{-1}(\frac{R-x_0-\lambda}{R})}^{\frac{\pi}{2}} \frac{\rho_g \rho_s R \sin^3 \theta d\theta}{\pi(2R\lambda \sin^2 \theta - \lambda^2) \rho_g + \pi(R^2 \sin^4 \theta - 2R\lambda \sin^2 \theta + \lambda^2) \rho_s} \quad (1)$$

The above equation (1) gives the resistance of half a grain with a neck size of r_o and grain radius of R .

R_{II} calculation:

$$R_{II} = \int_{\cos^{-1}(\frac{R-x_0}{R})}^{\cos^{-1}(\frac{R-x_0-\lambda}{R})} \frac{\rho_s d\theta}{\pi R \sin \theta} \quad (2)$$

The above equation (2) gives the resistance associated with the transport through the space charge region adjacent to the grain boundary (neck).

R_{III} calculation:

$$R_{III} = R_{gb} = \frac{\rho_{gb} \delta_{gb}}{2\pi r_0^2} = \frac{\rho_{gb} \delta_{gb}}{2\pi (R \sin \theta)^2} \quad (3)$$

$$\theta = \cos^{-1}\left(\frac{R-x_0}{R}\right)$$

The above equation (3) gives the resistance associated with transport across the structural part of the grain boundary.

The net resistance:

The net resistance is the sum of the three contributions. From Eqns (1), (2) and (3), it is seen that if x_0 and λ are known, all three contributions can be calculated, namely, R_I , R_{II}

and R_{III} . The effective resistance, which includes the effects of space charge and grain boundary, and also of the neck morphology, is given by

$$R_{eff} = R_I + R_{II} + R_{III} \quad (4)$$

Results of Calculations: The following parameters were used in the calculations. $\rho_g = 30 \text{ } \Omega\text{cm}$, $\rho_{gb} = 5000 \text{ } \Omega\text{cm}$, $\delta_{gb} = 1 \text{ nm}$. Three values of the resistivity in the space charge region were selected: $\rho_s = 30 \text{ } \Omega\text{cm}$, $\rho_s = 50 \text{ } \Omega\text{cm}$, and $\rho_s = 10 \text{ } \Omega\text{cm}$. The width of the space charge region λ was chosen to be 15 nm. The results of calculations are displayed in Figures 2, 3, and 4. Various observations can be made on the basis of these figures.

- (1) In all cases, the net resistance rapidly rises for small grain sizes and narrow necks. Note, for example that the net resistance for $\sim 5^\circ$ angle (consistent with a very small neck – typical of a poorly sintered cathode), the effective resistance is over six times greater for a 0.5 micron grain radius as compared to 5 micron grain radius. Thus, minimizing the cathode grain size may not be necessarily advisable, especially in poorly sintered cathodes.
- (2) The rapid rise in the net resistance at small angles (narrow neck sizes) underscores the importance of good particle to particle contacts.
- (3) Comparison of figures 2 and 4 shows that the space charge layer has a significant effect on the total resistance of the porous ionic conductor, and thus the effective resistivity of the porous ionic conductor. Previous work has shown that the polarization resistance is given by

$$R_p \approx \sqrt{\frac{dR_{ct}\rho_{eff}}{(1-V_v)}} \quad (5)$$

it is imperative that the space charge and neck morphology will substantially influence cathode polarization.

CONCLUSION

In the first quarterly report, a simple analytical equation was derived, which describes the conductivity as a function of connectivity. In the second quarterly report, experimental evidence was presented on the role of connectivity on ionic conductivity. It was observed that the connectivity has a large effect on conductivity of porous bodies. In the third quarter, the model was extended to include the effect of structural part of the grain boundary on the transport properties of porous ionic conductors. In this report, the model was extended to include the effect of space charge on transport properties of porous ionic conductors. Three cases were examined: space charge region resistivity, either greater than, equal to, or smaller than the grain resistivity. For assumed values of parameters, the effect of grain size and neck size on transport properties of porous ionic conductors was evaluated. The results show that very fine particle size in the cathode may actually be detrimental, provided the cathode sintering is poor. That is, one cannot automatically assume that nanosize electrodes will necessarily give improved performance. Experimental work is underway on rare earth oxide-doped ceria as well as on zirconia. The results will be described in future reports.

Figure 2: Total resistance as a function of the angle (which determines the neck radius) and grain size for the case with $\rho_s = 50 \, \Omega\text{cm}$.

Figure 3: Total resistance as a function of the angle (which determines the neck radius) and grain size for the case with $\rho_s = 30 \, \Omega\text{cm}$.

Figure 4: Total resistance as a function of the angle (which determines the neck radius) and grain size for the case with $\rho_s = 10 \Omega\text{cm}$.

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. Lehovec, *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).
- 14) F. Zhao, T. Armstrong, and A. V. Virkar, *J. Electrochem. Soc.*, **150** [3] A249-A256 (2003).

LIST OF ACRONYMS AND ABBREVIATIONS

LSC:	Sr-doped LaCoO ₃
LSGM:	Sr- and Mg-doped LaGaO ₃
LSM:	Sr-doped LaMnO ₃
SDC:	Samaria-Doped Ceria
ScDC:	Scandia-Doped Ceria
SOFC:	Solid oxide fuel cell
YSZ:	Yttria-stabilized zirconia