REPORT TITLE:

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

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Principal Author: Professor Anil V. Virkar
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Name and Address of Submitting Organization:
Department of Materials Science & Engineering
122 S. Central Campus Drive
University of Utah
Salt Lake City, UT 84112

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ABSTRACT

This report summarizes the work done during the fifth quarter of the project. Effort was directed in two areas: (1) 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 region. (2) Fabrication of porous samaria-doped ceria (SDC) and investigation of the effect of thermal treatment on its conductivity. The model developed accounts for transport through three regions: (a) Transport through the bulk of the grain, R_I , which includes parallel transport through space charge region. (b) Transport through the space charge region adjacent to the neck (grain boundary), R_{II} . (c) Transport through the structural part of the neck (grain boundary), R_{III} . The work on the model development involves calculation R_I , R_{II} , R_{III} , and the sum of these three terms, which is the total resistance, as a function of the grain radius ranging between 0.5 and 5 microns and as a function of the relative neck size, described in terms of the angle θ , ranging between 5 and 45°. Three values of resistivity of the space charge region were chosen; space charge resistivity greater than grain resistivity, equal to grain resistivity, and lower than grain resistivity. Experimental work was conducted on samaria (Sm_2O_3)-doped ceria (SDC) samples of differing porosity levels, before and after thermal treatment at 1200°C. The conductivity in the annealed samples was lower, consistent with enhanced Debye length. This shows the important role of space charge on ionic transport, and its implications concerning cathode polarization.

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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. This is expected to be the case regardless of whether the cathode is a mixed ionic electronic conducting (MIEC) composite cathode or a MIEC single-phase cathode. The focus of this work discussed in this report is a composite cathode. 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 of the electrocatalyst. 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. 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. In this report, results are presented on the three contributions of electrode microstructure, which includes space charge region and structural part of the grain boundary, on conductivity. Experimental results are presented on the ionic conductivity of porous SDC, with emphasis on the role of thermal treatment on conductivity, which provides evidence of the role of space charge.

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 by 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 effect, 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 fourth quarterly report, results of further model development were included, wherein the effect of space charge region was explicitly included. Three cases have been considered: Space charge region having higher, equal to, and lower resistivity compared to the bulk grains. The effect of neck size on the effective resistivity has been explicitly calculated. In this report, the model was further extended to estimate the total resistance and effective resistivity of porous bodies. Experimental work is reported on SDC ceramics made by sintering NiO + SDC composites, reducing NiO to Ni, leaching away Ni to form single-phase porous SDC with large neck sizes. Conductivity was measured as a function of temperature after leaching and after subjecting to a thermal treatment at 1200°C. It was observed that the conductivity decreased after annealing, consistent with enhanced Debye length.

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 structural part of grain boundaries and the effect of space charge region on the effective resistivity.
2. Porous samples of SDC were fabricated using a process comprising sintering NiO + SDC composites, reducing NiO to Ni, and leaching away Ni. This process is hereafter referred to as the SLP process (sintering & leaching process). Conductivity of one set of samples was measured over a range of temperatures between 650 and 800°C. The other set of samples was annealed in air at 1200°C for 6 hrs. Conductivity of these samples was also measured over a range of temperatures between 650 and 800°C.
3. After testing, the fractured pieces of the samples 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).
4. The microstructures of porous samples were characterized by quantitative stereology in order to estimate the volume fraction porosity.

RESULTS AND DISCUSSION

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

Figure 1 shows the geometry used for calculations. This is the same geometry shown in the last quarterly report. Figure 2 shows the RI, RII and RIII, and the total resistance as a function of the angle for grain radii corresponding to 0.5 and 5 microns. The following parameters were used in the calculations: Grain boundary (structural) resistivity, $\rho_{gb} = 5000 \text{ } \Omega\text{cm}$. Grain boundary (structural) thickness, $\delta_{gb} = 1 \text{ nm}$. Width of the space charge region, $\lambda = 15 \text{ nm}$. Grain interior resistivity, $\rho_g = 30 \text{ } \Omega\text{cm}$. Resistivity of the space charge region, $\rho_s = 50 \text{ } \Omega\text{cm}$. The total resistance of the sample with a grain radius of 5 microns is much lower than that of the sample with 0.5 micron grain radius.

Figure 3 shows RI, RII and RIII and the total resistance as a function of grain size for the angles corresponding to 5 and 45 degrees. Figure 4 shows the total resistances as a function of degrees for the grain size ranging from 0.5 to 5 microns. For the case 0.5 micron grain radius, the resistance is much higher than that of larger grain sizes. When the grain size is larger, the effect of neck size becomes less pronounced. Figure 5 shows the total resistance as a function of grain size for the angle ranging from 5 to 45°. For small neck sizes, the grain radius has a large effect on the total resistance.

Figure 6 shows the total resistance as a function of theta for the grain radii corresponding to 0.5 and 5 microns for three specific cases, i.e. space charge region resistivity higher than, equal to, and lower than that corresponding to bulk grain resistivity. For the three cases, when the space charge region has higher resistivity compared to the bulk grain, the total resistance exhibits the largest resistance.

The effective resistivity was calculated using the following equation.

$$\rho_{eff} = \frac{4R_{eff}R^2}{R - x_0} = \frac{4R_{eff}R}{\cos \theta} \quad (1)$$

$$\text{where } R_{eff} = RI \text{ (after integration)} + RII \text{ (after integration)} + RIII \quad (2)$$

The results of calculation of effective resistivity are displayed in Figures 7, 8, and 9. Various observations can be made on the basis of these figures.

- (1) In all cases, the effective resistivity rapidly rises for small grain sizes and narrow necks. For example, the effective resistivity for $\sim 5^\circ$ (corresponding to a very small neck size), is over three times greater for a 0.5 micron grain radius as compared to that for 5 micron grain radius.
- (2) In all cases, the effective resistivity exhibits a minimum with neck size, which is the result of balance between the resistivity from the bulk of the grain, RI, the space charge region, RII, the structural part of the grain boundary, RIII, and the geometry of the grains.
- (3) The resistivity of the space charge region has a significant effect on the effective resistivity. For the case of space charge region having higher resistivity compared to the bulk, at 5° and $0.5 \mu\text{m}$, the resistivity can be as high as $4400 \Omega\cdot\text{cm}$. But for the case of space charge region having lower resistivity compared to the bulk, the resistivity at 5° and $0.5 \mu\text{m}$ is $3300 \Omega\cdot\text{cm}$.

Effect of Heat Treatment on Conductivity of Porous SDC Body:

Figures 10, 11 and 12 are SEM micrographs of porous samples fabricated using the SLP method. It is seen that these samples exhibit good connectivity. The results of conductivity measurements at various temperatures before and after heat treatment are listed in Table 1. After heat treatment, the conductivity of porous samples decreased. At 650°C , the conductivity decreased to half that of samples prior to heat treatment. At a temperature of 800°C , the conductivity decreased to $\sim 75\%$ of that of samples prior to heat treatment. Lower conductivity in heat-treated samples is attributed to the anticipated larger Debye length in annealed samples [11-13].

CONCLUSIONS

In this report, the model was developed to include the effect of space charge on transport properties of porous ionic conductors. The effective resistivity was calculated for three cases: space charge region resistivity, greater than, equal to, or smaller than grain resistivity. The results show that small neck size has profound negative effect on the effective resistivity, thereby, increasing the polarization resistance in the composite

cathode. The same effect is expected in single-phase MIEC cathodes. The heat treatment effect on the conductivity of porous bodies was also investigated. No changes in the microstructures of porous bodies were observed after heat treatment. The decrease of conductivity after heat treatment was attributed to the space charge effect.

Figure 1: A schematic of the geometry used for the estimation of the role of particle geometry and space charge on the net resistance per grain, and the effective ionic resistivity of porous bodies.

Figure 2: RI, RII and RIII, and the total resistance as a function of the angle for grain radii of 0.5 and 5 microns. ($\rho_{gb} = 5000 \text{ } \Omega\text{cm}$, $\delta_{gb} = 1 \text{ nm}$, $\lambda = 15 \text{ nm}$, $\rho_g = 30 \text{ } \Omega\text{cm}$, $\rho_s = 50 \text{ } \Omega\text{cm}$). Note that the total resistance of fine-grained sample rises sharply at small angles (small neck sizes). This occurs primarily due to the contribution from the structural part of grain boundaries.

Figure 3: RI, RII and RIII, and the total resistance as a function of grain size for the angles of 5 and 45 degrees. ($\rho_{gb} = 5000 \text{ } \Omega\text{cm}$, $\delta_{gb} = 1 \text{ nm}$, $\lambda = 15 \text{ nm}$, $\rho_g = 30 \text{ } \Omega\text{cm}$, $\rho_s = 50 \text{ } \Omega\text{cm}$). Note that the resistance sharply increases at small grain sizes and small neck sizes.

Figure 4: Plots of the total resistance as a function of angle for grain radii corresponding to 0.5, 1, 3, and 5 microns. Grain boundary (structural) resistivity, $\rho_{gb} = 5000 \text{ } \Omega\text{cm}$. Grain boundary (structural) thickness, $\delta_{gb} = 1 \text{ nm}$. Width of the space charge region, $\lambda = 15 \text{ nm}$. Grain interior resistivity, $\rho_g = 30 \text{ } \Omega\text{cm}$. Resistivity of the space charge region, $\rho_s = 50 \text{ } \Omega\text{cm}$.

Figure 5: Total resistance as a function of grain size corresponding to angles 5, 15, 30, and 45 degrees. Grain boundary (structural) resistivity, $\rho_{gb} = 5000 \text{ } \Omega\text{cm}$. Grain boundary (structural) thickness, $\delta_{gb} = 1 \text{ nm}$. Width of the space charge region, $\lambda = 15 \text{ nm}$. Grain interior resistivity, $\rho_g = 30 \text{ } \Omega\text{cm}$. Resistivity of the space charge region, $\rho_s = 50 \text{ } \Omega\text{cm}$.

Figure 6: Total resistance as a function of angle for grain radii corresponding to 0.5 and 5 microns for three values of the resistivity of the space charge regions, namely, 50 Ωcm , 30 Ωcm , and 10 Ωcm . ($\rho_{gb} = 5000 \Omega\text{cm}$, $\delta_{gb} = 1 \text{ nm}$, $\lambda = 15 \text{ nm}$).

Figure 7: Effective resistivity as a function of grain radius and angle theta (which is a measure of the relative neck size). ($\rho_{\text{gb}} = 5000 \Omega\text{cm}$, $\delta_{\text{gb}} = 1 \text{ nm}$, $\lambda = 15 \text{ nm}$, $\rho_{\text{g}} = 30 \Omega\text{cm}$, $\rho_{\text{s}} = 50 \Omega\text{cm}$).

Figure 8: Effective resistivity as a function of grain radius and angle theta (which is a measure of the relative neck size). ($\rho_{\text{gb}} = 5000 \, \Omega\text{cm}$, $\delta_{\text{gb}} = 1 \, \text{nm}$, $\lambda = 15 \, \text{nm}$, $\rho_{\text{g}} = 30 \, \Omega\text{cm}$, $\rho_{\text{s}} = 30 \, \Omega\text{cm}$).

Figure 9: Effective resistivity as a function of grain radius and angle theta (which is a measure of the relative neck size). ($\rho_{gb} = 5000 \text{ } \Omega\text{cm}$, $\delta_{gb} = 1 \text{ nm}$, $\lambda = 15 \text{ nm}$, $\rho_g = 30 \text{ } \Omega\text{cm}$, $\rho_s = 10 \text{ } \Omega\text{cm}$).

Figure 10: Sm_2O_3 -doped ceria porous sample (porosity $\sim 29.8\%$) made by the SLP process. Sintered at 1600°C /4 hours.

Figure 11: Sm₂O₃-doped ceria porous sample (porosity ~38%) made by the SLP process: Sintered at 1600 °C /4 hours.

Figure 12: Sm₂O₃-doped ceria porous sample (porosity ~59%) made by the SLP process. Sintered at 1600°C /4 hours.

Table 1: Conductivity as a function of temperature for samples with three different porosity levels. **Red** numbers represent values of conductivity after the thermal treatment at 1200°C.

T(°C)	650	700	750	800
σ (s/cm)	0.018	0.028	0.035	0.053
SLP (29.8%)	0.007	0.012	0.022	0.042
σ (s/cm)	0.011	0.019	0.029	0.044
SLP (38%)	0.055	0.011	0.018	0.038
σ (s/cm)	0.008	0.012	0.019	0.027
SLP (59%)	0.005	0.009	0.014	0.024

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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
SLP:	Sintering and leaching process
SOFC:	Solid oxide fuel cell
YSZ:	Yttria-stabilized zirconia