ABSTRACT

Bar-shaped samples of porous samaria-doped ceria (SDC) with large neck sizes were fabricated using a three-step method. In the first step, two phase samples containing NiO + SDC were fabricated by sintering powder compacts. In the second step, NiO was reduced to Ni at 800°C in a hydrogen-containing atmosphere. In the third step, Ni was removed by acid leaching, leading to the formation of porous SDC samples with wide inter-particle necks. The conductivity of bar samples was measured using a DC 4-probe technique between 650 and 800°C. The samples were then annealed at 1200 and 1400°C. The conductivity of the samples was again measured between 650 and 800°C. It was observed that the lower the annealing temperature, the lower was the conductivity. Anode-supported cells were fabricated with cathode made of Sr-doped LaCoO₃ (LSC) and SDC, wherein the SDC layer was formed by the three-step method. Cell performance was measured at 800°C with the cells subjected to thermal treatments at 1200 and 1400°C prior to infiltration of LSC using aqueous salt solutions. It was observed that the lower the annealing temperature, the lower was the cell performance. The observed behavior is attributed in part to space charge effects. Thermal treatments, however, may also lead to precipitation of insulating phases at grain boundaries thereby increasing resistance and lowering cell performance.

INTRODUCTION

Recent work has shown that cathodic polarization can be substantially reduced provided the porous cathode is a mixed conductor [1-4]. For this reason, the cathode must either be made of a single-phase mixed ionic/electronic conductor (MIEC), or a composite mixture of an oxygen ion conductor (e.g. yttria-stabilized zirconia, YSZ), and an electrocatalyst (e.g. LSM) which is an electronic conductor. In terms of the intrinsic charge transfer resistance (area specific charge transfer resistance, \(R_{ct}\) in \(\Omega\text{cm}^2\)), the oxygen ion conductivity of the cathode, \(\sigma_{oi}\), the grain size of the cathode, \(d\), and the porosity of the cathode, \(\nu_p\), the polarization resistance can be given by [2]

\[
R_p \approx \sqrt{\frac{dR_{ct}}{\sigma_{oi}(1-V_p)}} \tag{1}
\]
For a given cathode material, equation (1) shows that the larger the $\sigma_{Ct}$, the lower is the $R_p$, and thus the better is the cathode. It is known that the apparent conductivity of porous ceramics is a function of porosity and morphology, such as grain size, inter-particle neck size, etc. The smaller the grain size, generally the lower is the conductivity (the higher is the resistivity). According to the analytical model on the role of connectivity on electrical conductivity of porous bodies including effects of grain boundaries and space charge, small neck size has a profoundly adverse effect on the effective conductivity [5]. Also, the space charge layer at grain boundaries and free surfaces in porous media can have a significant effect on the effective conductivity.

It has been reported that the grain-boundary resistivity is strongly influenced by thermal history [6-8]. After quenching from high temperatures, the grain-boundary resistivity is generally quite small. However, after annealing at lower temperatures, the resistivity increases significantly. The effect of heat treatment on zirconia electrolytes has been extensively studied and is closely related to the type of dopant and the dopant concentration [9-11]. Heat treatment leads to the segregation of a dopant-rich layer near grain boundaries and triple points and also the formation of a layer of space charge region, which has been attributed to the decrease in the conductivity of YSZ [12, 13]. However, very little information is available on the effect of high temperature heat treatment on conductivity of ceria-based materials, and especially for porous bodies.

In this study, the conductivity of porous SDC samples was measured using a four-probe DC technique. In order to study the effect of heat treatment on conductivity of porous bodies, porous SDC samples sintered at a high temperature were heat treated at lower temperatures. The porous SDC samples used in this study were made by the three step method involving a leaching step. Then the conductivity of the samples was measured again using a four-probe DC technique at various temperatures. The measurement temperature was always much lower than the thermal treatment temperature such that no microstructural changes were expected during the measurements.

The role of effective conductivity of porous ionic conductors on electrode polarization was examined. The effects of space charge and morphology were included in the model. A leaching process was used to fabricate porous SDC layers on anode-supported cells. Then, the cells with the porous layers were heat treated at lower temperatures. Subsequently, an infiltration process was used to fabricate composite cathodes. This involved the introduction of an aqueous solution of salts of La, Sr, and Co, followed by a low temperature (less than 1100°C) firing to form LSC in-situ. Electrochemical testing of the as-fabricated cells was conducted to determine the possible effect of space charge.

**EXPERIMENTAL**

**Fabrication of Porous Samaria Doped Ceria (SDC) Samples with Large Neck Sizes**

Powder mixtures of commercial NiO and SDC (combustion method) in various NiO:SDC weight ratios corresponding to 20:80, 30:70 and 40:60 were wet-milled, dried, and then screened. Bar-shaped powder compacts were formed by die-pressing and isostatic pressing. Bar samples were sintered in air at 1600°C for 2 hours. The samples were then
reduced in 10% hydrogen + 90% nitrogen for 2 hours at 800°C, followed by 2 hours at 800°C in 100% hydrogen. Finally the reduced bar samples were leached in dilute nitric acid for 3 hours. This led to the removal of Ni as Ni(NO₃)₂, and created additional porosity. The resulting samples were single-phase, porous SDC. Four probe DC conductivity measurements were performed on as-processed porous samples.

**Heat Treatment of Porous SDC Samples**

Some of the porous samples, of varying porosity levels and fabricated using the leaching process were heat treated at 1200°C for 20 hours and then air-quenched to room temperature at a quenching rate of ~6500°C/min. Total conductivity was measured using a four probe DC technique on samples with varying porosity levels over a range of temperatures between 650 and 800°C.

**Microstructure Characterization**

After conductivity measurements, fractured pieces of each sample were impregnated with an epoxy. After curing and hardening the epoxy, the samples were mounted in a plastic mount, and subsequently polished to a 1 micron finish. The samples were then examined under a scanning electron microscope (SEM). The microstructures of porous samples were characterized by quantitative stereology to estimate the porosity.

**Fabrication of Composite Cathodes by Infiltration and Electrochemical Testing of Single Cells**

Anode-supported cells with a Ni/YSZ anode support, a Ni/YSZ anode interlayer, and a thin film YSZ electrolyte/SDC barrier layer were green-formed by slurry coating pressed anode support discs. Subsequently, a layer of NiO + SDC powder mixture was applied on the SDC barrier layer. The resulting cells were sintered at 1600°C. Some of the cells were later annealed at 1400°C for 6 h and some at 1200°C for 20 h, followed by quenching to room temperature. The NiO + SDC layer was subjected to 10% hydrogen + 90% nitrogen for 4 hours at 800°C to reduce NiO to Ni. Nickel was leached out using dilute nitric acid for 2 hours, resulting in a highly porous framework of SDC with wide necks. An aqueous solution of La(NO₃)₃, Sr(NO₃)₂ and Co(NO₃)₂ in requisite proportions was infiltrated into the porous SDC and fired at 1100°C for 1 h to form a composite cathode containing LSC. Finally, the performance of the cells was tested at 800°C with hydrogen as fuel and air as oxidant. The ohmic contribution was measured by current interruption. After testing the microstructure was examined under SEM.

**RESULTS AND DISCUSSION**

**Microstructure of Porous SDC: Conductivity of Porous SDC Samples Before Heat Treatment**

Figure 1 shows an SEM micrograph of a typical porous SDC bar fabricated. Bars of porosity ranging between 29% and 59% were fabricated. All samples exhibited good connectivity between grains. For samples fabricated using the leaching process, the...
porosity was mainly dictated by the selected weight ratio of NiO/SDC. During sintering of the samples, NiO and SDC grains grow simultaneously and fill up the space by forming regular polyhedra (tetrakaidecahedra). The NiO skeleton in the composite keeps the SDC skeleton from collapsing and vice-a-versa. Using this process, samples of density greater than 95% of the theoretical density were made. The NiO and SDC phases in the composite form two contiguous skeletons with large neck sizes (which are grain facets). After reducing NiO to Ni and leaching it away, samples with the desired microstructures of high porosity & large neck sizes were obtained.

Table I shows porosity and conductivity of porous samples made using NiO-SDC powders, wherein the porosity was created by leaching away Ni. The total conductivity of samples with varying porosity levels was measured over a range of temperatures by a four probe DC method. It is seen that with increasing porosity from 30% to 59%, the conductivity decreases from 0.053 to 0.027 S/cm at 800°C. Figure 2 shows a plot of the relative conductivity vs. relative density. It is known that at relatively high volume fractions of insulating phases, the net conductivity can be far below that of the conductive phase corrected for porosity through a simple linear relationship, provided the inter particle contact is poor. That is, the conductivity is dependent not only on porosity, but also on other microstructural parameters, such as grain size and neck size, etc. When the neck size is large, the effective conductivity can be calculated using a simple phenomenological equation, namely

\[ \sigma_{\text{porous}} \approx \sigma_0 (1 - V_f) \]  

Effect of Heat Treatment on Conductivity of Porous SDC Samples

The results on conductivity measurements before and after heat treatment at 1200°C for 20 h are listed in Table I. After heat treatment, the conductivity of the porous bodies decreased. At 650°C, the conductivity decreased to half that of samples prior to the heat treatment. At a temperature of 800°C, the conductivity decreased to ~75% of that without heat treatment. The effect of heat treatment on the conductivity can in part be attributed to space charge, because no change in the microstructures (based on SEM micrographs) of the porous bodies was observed. However, the possibility of formation of secondary insulating phases along grain boundaries cannot be ruled out. A careful microstructural analysis using transmission electron microscopy (TEM) will be required to determine the possible existence of secondary grain boundary phases. The following discussion is based on the assumption of the existence of a space charge layer.

By Schottky approximation and solving Possion’s equation, the maximum space charge potential for the case of no externally applied voltage can be calculated and is given by [14-19]:

\[ \Delta \phi(0) = \frac{Q_{GB}^2}{2\varepsilon\varepsilon_0 \varepsilon_r [A]_b} \]

where \( \varepsilon_r \) is the static dielectric constant of the material, \( \varepsilon_0 \) is the permittivity of free space, \( Q_{GB} \) is the charge in the grain boundary core, and \( [A]_b \) is the dopant concentration in the bulk.
Space charge layer thickness can be given by [16, 17]

\[
\lambda = \frac{Q_{GB}}{\epsilon[A]} \approx \sqrt{\frac{\epsilon_0 \epsilon_r \Delta \phi(0)}{\epsilon[A]}}
\]  (4)

From equation (3), it is apparent that the temperature dependence of \( \Delta \phi(0) \) may be due to the temperature dependence of: (a) the effective charge in grain boundary core, \( Q_{GB} \), (b) the relative static dielectric constant \( \epsilon_r \), and (c) the effective bulk acceptor concentration \( [A']_b \). The effective bulk acceptor concentration \( [A']_b \) and relative static dielectric constant \( \epsilon_r \), however, are nearly independent of temperature. Thus, the temperature-dependent behavior of grain boundary barrier height, \( \Delta \phi(0) \), must be caused by the temperature dependence of \( Q_{GB} \).

During the process of heat treatment, the dopant is expected to segregate along the grain boundary and free surfaces, i.e., annealing at intermediate temperatures should favor the creation of positively charged interfaces by enhancing dopant segregation. After quenching from the annealing temperature, the dopant segregation at the grain boundaries is almost frozen. Thus, in the annealed and quenched samples, it is expected that the grain boundary structure at the annealing temperature can be preserved at lower temperatures, e.g. with a more inhomogeneous point-defect distribution. Thus, the grain boundary barrier height should be higher in samples annealed at lower temperatures. This means, the variation in the grain boundary blocking effect can be related to the different levels of dopant segregation achieved by changing the thermal history. Higher segregation should result in both a large space charge thickness and greater depletion of oxygen vacancies leading to greater grain boundary resistivity.

**Application of Space Charge Model to Composite Cathode**

Using model developed earlier [5], equation (1) and values of various parameters from the literature [20-22], the electrode polarization resistance can be calculated. Figure 3 shows the calculated polarization resistance as a function of grain size and neck size at 800°C for an electrode using YSZ as the ionic conductor in the composite cathode, and the following parameters: \( \rho_g \) (YSZ grain resistivity) = 14 \( \Omega \).cm, \( \rho_{sc} \) (resistivity of the space charge layer) = 2,250 \( \Omega \).cm, \( \rho_{gb} \) (grain boundary core resistivity) = 10 \( \Omega \).cm, \( \lambda \) (space charge layer thickness) = 2 nm, \( \delta_{gb} \) (grain boundary core thickness) = 0.4 nm, and \( R_{ct} = 2 \Omega.cm^2 \). Figure 4 shows the calculated polarization resistance as a function of grain size and neck size at 650°C using the following parameters: \( \rho_g = 76 \Omega.cm, \rho_{sc} = 14,520 \Omega.cm, \rho_{gb} = 50 \Omega.cm, \lambda = 2 \text{ nm}, \delta_{gb} = 0.4 \text{ nm}, \text{ and } R_{ct} = 4.15 \Omega.cm^2 \). It is seen that the polarization resistance rises sharply for small necks and large grains. Over the range of particle sizes and neck sizes (angle) that the calculations were performed, the polarization resistance varies between ~0.15 and ~0.8 \( \Omega cm^2 \) at 800°C, and between ~0.5 and ~2.8 \( \Omega cm^2 \) at 650°C. This result has significant implications concerning the role of grain boundaries and grain size on the polarization resistance of composite and single
phase MIEC cathodes. The results show that a low polarization resistance is realized if the particle size is small and the neck size is large.

**The Possible Effect of Space Charge on Cell Performance**

Figure 5 shows voltage and power density vs. current density plots at 800°C for cells with cathode fabricated by the infiltration method. In each case, cell with the SDC ionic conductor skeleton in the composite cathode was annealed and then quenched to room temperature prior to cathode precursor infiltration. The as-fabricated cell without heat treatment exhibits the highest performance. By contrast, the cell annealed at 1200°C for 20 hours exhibits the lowest performance. A possible explanation is that the lower the annealing temperature, the greater is the space charge width, the higher is the ionic resistivity in the cathode interlayer, and thus the higher is the activation polarization (Equation (1)). Since the anode interlayer was subjected to the same thermal treatment, it is expected that a similar effect likely exists in the anode interlayer (higher ionic resistivity in YSZ annealed at a lower temperature). Figure 6 shows the ohmic overpotential determined by current interruption as a function of current density for cells with various thermal histories. It is seen that the cell annealed at 1200°C has a slightly higher ohmic resistance. This is also consistent with expectations since the ionic resistivity of the YSZ/SDC bi-layer electrolyte is expected to increase by annealing at a lower temperature (1200°C) due to the space charge effect. The observation, that the effect is small is also consistent with the fact that the overall ohmic contribution is generally small in cells with a thin film electrolyte. Figure 7 shows electrode polarization, which was obtained by subtracting the ohmic contribution, as a function of current density for cells with various thermal histories. Figure 7 shows that the variation in total electrode polarization with annealing temperature is substantial, with the cell annealed at 1200°C exhibiting the highest polarization and the as-fabricated cell exhibiting the lowest polarization. Higher polarization in the cell annealed at 1200°C is again consistent with a larger space charge effect. While the results are consistent with space charge effect, the possibility of secondary, insulating phases precipitating along grain boundaries in samples annealed at a lower temperature, thus raising the net resistivity cannot be ruled out. A careful characterization of grain boundary regions will be required to answer this question.

**SUMMARY**

The present work shows that samples fabricated using the leaching method exhibits the desired microstructure comprising a wide neck size and high effective conductivity in porous SDC. The present results also show that annealing at lower temperatures increases the resistivity, consistent with the existence of a space charge effect which leads to a high resistivity region near grain boundaries due to the depletion of oxygen vacancy concentration. Measurements on anode-supported cells show that cells annealed at a lower temperature (prior to the introduction of cathode precursor by infiltration) exhibit lower performance, which can be attributed to greater electrode polarization. This higher polarization can be attributed to the expected greater space charge effect in samples annealed at a lower temperature. However, even though the results are consistent with the possible existence of a space charge effect, the formation of insulating phases along grain boundaries in annealed samples as a possible reason for higher resistivity and higher
polarization resistance in annealed cells cannot be ruled out. This will require careful characterization of grain boundary regions.

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Table I. Conductivity of porous SDC before and after thermal treatments.

| T(°C) | 650  | 700  | 750  | 800  |
|-------|------|------|------|------|
| Conductivity (S/cm)  |      |      |      |      |
| Before heat treatment | 30%  | 38%  | 59%  |      |
| 650  | 0.018| 0.011| 0.008|      |
| 700  | 0.028| 0.019| 0.012|      |
| 750  | 0.035| 0.029| 0.019|      |
| 800  | 0.053| 0.044| 0.027|      |

Figure 1. An SEM micrograph of a SDC bar (porosity = 30%) sintered at 1600°C/2 hours (method comprising the fabrication of SDC + NiO composite, reduction of NiO to Ni, and removal of Ni by leaching). Conductivity data are given in Table I.
Figure 2. Relative conductivity vs. relative density. The relative conductivity is defined as the ratio of the conductivity of a 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 a given porosity to that of a fully dense sample.

Figure 3. Calculated area specific electrode polarization resistance, using YSZ as the ionic conductor in a composite cathode, as a function of angle (relative neck size) and grain size at 800°C. Note that the polarization resistance rises sharply at small angles (narrow necks).
Figure 4. Calculated area specific electrode polarization resistance, using YSZ as the ionic conductor in a composite cathode, as a function of angle (relative neck size) and grain size at 650°C. Note that the polarization resistance rises sharply at small angles (narrow necks).

Figure 5. Voltage and power density vs. current density plots at 800°C for cells with cathode fabricated using the infiltration method, wherein the cell with the ionic conductor skeleton in the composite cathode was annealed and then quenched to room temperature prior to cathode infiltration.
Figure 6. Ohmic overpotential (by current interruption) as a function of current density for cells with various thermal histories.

Figure 7. Electrode polarization as a function of current density for cells with various thermal histories.