Effects of Morphology and Space Charge on Ionic Conductivity of Porous Bodies

Feng Zhao and Anil V.Virkar*
Department of Materials Science & Engineering
122 S Central Campus Drive, University of Utah
Salt Lake City, UT84112

Introduction

Recently porous ionic and mixed ionic/electronic conductors have become of interest in applications such as electrode materials in solid oxide fuel cells [1] and ceramic gas sensors. It is known that the apparent conductivity of porous ceramics is sensitive to their morphology, such as grain size, inter-particle neck size etc. In addition, the space charge along grain boundaries and free surfaces is also expected to have a significant effect on apparent conductivity of porous bodies. A simple mathematical model was developed to describe the effects of grain size, inter-particle neck size and space charge region on the total resistance of porous ionic conductors. The conductivities of scandia doped ceria (ScDC) with various porosity levels were measured using a four-probe DC technique. It was shown that experimental results are consistent with the predictions of the model.

Model Development

The geometry of the particle used for calculations is shown in Figure 1. It consists of a half of the grain with half of the grain boundary associated with it. The net resistance is divided into three regimes: (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 core area of grain boundary. The effective resistance, which includes the effects of space charge, grain boundary and of the neck morphology, is given by

$$R_{eff}= R_I\ (after\ integration) + R_{II}\ (after\ integration) + R_{III}$$

Experimental

ScDC powders were synthesized by combustion synthesis. Then powder compacts were formed by die-pressing. The compacts were then sintered in air over a range of temperatures to make samples of varying porosity levels. The total conductivity of the samples of varying porosity levels was measured using a four-probe DC method. The microstructures were observed via scanning electron microscopy (SEM).

Results and Discussion

Figure 2 shows the calculated total resistance as a function of grain size and the angle (which determines the neck radius) for the case with ρ_s=14520 ohm.cm, ρ_g=76 ohm.cm (8YZ at 650°C), where ρ_s is the resistivity of the space charge region and ρ_g is the resistivity of the grains [2]. The net resistance rapidly rises for small grain sizes and narrow necks. The rapid rise in the net resistance at small angles underscores the importance of good particle to particle contacts. Table 1 shows the conductivities measured at 800 °C. The conductivity of a sample with ~43% porosity is less than 1% of the value of the sample with ~3% porosity. This difference can be rationalized by the small inter-particle neck size and small grain size of the sample with high porosity level, which is consistent with the model proposed.

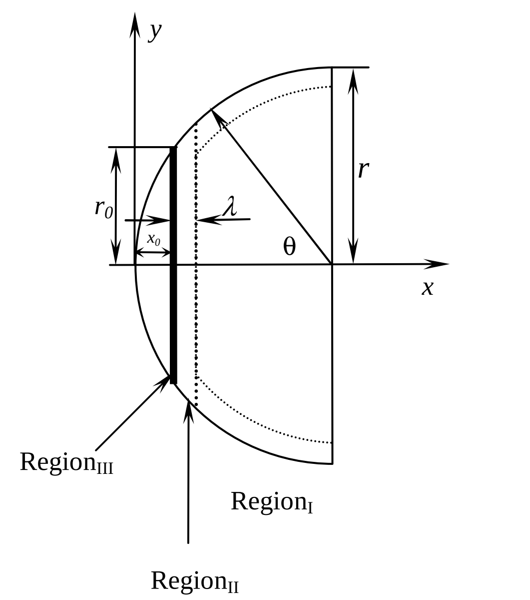

Figure 1. Geometry of the particle used for calculation

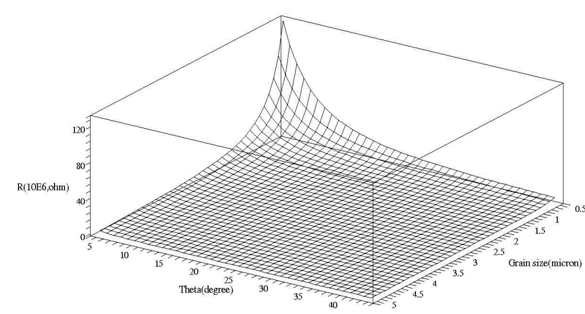

Figure 2. Total resistance as a function of grain size and the angle (which determines the neck radius) for the case with ρ_s=14520 ohm.cm, ρ_g=76 ohm.cm.

ScDC Samples (porosity)	Conductivity (s/cm)
3.3%	0.091
24.3%	0.041
43.3%	5.533E-4

Table 1. Conductivity as a function of porosity.

Reference

1. J. W. Kim, A. V. Virkar, K.-Z. Fung, K. Metha, and S. C. Singhal, *J. Electrochem. Soc.*, 146, 69 (1999).
2. X. Guo et al., *J. Electrochem. Soc.*, 148, E121 (2001).

Acknowledgements

This work is supported by the U.S. Department of Energy, under contract No: DE-FC26-02NT41602

* To whom correspondence should be addressed.