SYNTHESIS AND CHARACTERIZATION OF HYDROGEN SEPARATION MEMBRANES

by

Karthikeyan Lakshminarayanan

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Mechanical Engineering

MONTANA STATE UNIVERSITY
Bozeman, Montana

December, 2005
APPROVAL

of a thesis submitted by

Karthikeyan Lakshminarayanan

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

Dr. Vic A. Cundy / Dr. Hugo Schmidt

Approved for the Department of Mechanical and Industrial Engineering

Dr. Chris Jenkins

Approved for the College of Graduate Studies

Dr. Joseph J. Fedock
STATEMENT OF PERMISSION TO USE

In presenting this thesis in partial fulfillment of the requirements for a master’s degree at Montana State University – Bozeman, I agree that the library shall make it available to borrowers under rules of the Library.

If I have indicated my intention to copyright this thesis by including a copyright notice page, copying is allowable only for scholarly purposes, consistent with “fair use” as prescribed in the U.S. Copyright Law. Requests for permission for extended quotation from or reproduction of this thesis (paper) in whole or in parts may be granted only by the copyright holder.

Karthikeyan Lakshminarayanan
December, 2005
I would like to thank Dr. Hugo Schmidt for his guidance in my research and thesis work. I would like to express my appreciation to Dr. Vic Cundy and Dr. Alan George for their work as committee members.

I gratefully acknowledge the Department of Mechanical and Industrial Engineering and Dr. Hugo Schmidt for their financial assistance without which this work would not have been possible. I thank Dr. Jiaping Han for mentoring me throughout this research.

Acknowledgements are due to Dr. Phillip Himmer and Dr. Asghar Kayani for use of Magnetron and RBS apparatus respectively, and also to Dr. John Neumeier for the use of vapor deposition apparatus.

Finally, I would like to appreciate the continued support I received from the staff members of the Department of Mechanical and Industrial Engineering and the fellow graduate students.
TABLE OF CONTENTS

LIST OF TABLES.............................................................................................................vii

LIST OF FIGURES..........................................................................................................viii

NOMENCLATURE...........................................................................................................xi

ABSTRACT....................................................................................................................xiv

1. INTRODUCTION.........................................................................................................1

   Methods...................................................................................................................2

2. CONCEPT OF COMPLEX IMPEDANCE.......................................................................5

   Analysis of Impedance Spectroscopy Data...............................................................9

   Uniqueness of Models............................................................................................10

3. BRICK LAYER MODEL (BLM)-A DISCUSSION.......................................................12

4. SELECTION OF MATERIALS..................................................................................19

5. SYNTHESIS OF CGO AND CGO DOPED WITH 5 % La2O3.....................................21

   Impedance of CGO and CGO-5% La Samples without Blocking Electrodes.......33

6. SYNTHESIS OF BaCe0.65Zr0.15Y0.2O3 (BCY) BY GLYCINE NITRATE PROCESS (GNP) ......................................................... 36

7. DEPOSITION OF MgO BY MAGNETRON SPUTTERING.........................................38

8. SCANNING ELECTRON MICROSCOPY...................................................................40

9. ANALYSIS OF SURFACE CONSTITUENTS BY RBS.............................................44

   Calculations...........................................................................................................46

10. DESIGN OF APPARATUS FOR HYDROGEN PERMEATION TESTING..................48

    Stress Analysis.....................................................................................................54
TABLE OF CONTENTS – continued

11. TESTING OF SAMPLES WITH BLOCKING LAYER OF MgO
   BCY Analysis..........................................................................................................55
   CGO Analysis..........................................................................................................74

12. CONCLUSION........................................................................................................78
   Recommendations for Future Work..................................................................78

13. REFERENCES........................................................................................................80
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Common Electrical Elements</td>
<td>9</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Impedance Spectroscopy Measurement System</td>
<td>3</td>
</tr>
<tr>
<td>2. Sinusoidal Current Response in a Linear System</td>
<td>6</td>
</tr>
<tr>
<td>3. Nyquist Plot with Impedance Vector</td>
<td>8</td>
</tr>
<tr>
<td>4. Bode Plot with One Time Constant</td>
<td>8</td>
</tr>
<tr>
<td>5. Two Time Constant Spectrum</td>
<td>10</td>
</tr>
<tr>
<td>6. Equivalent Circuit Models with Two Time Constants</td>
<td>11</td>
</tr>
<tr>
<td>7. A Grain along with its Boundary in the Brick Layer Model</td>
<td>13</td>
</tr>
<tr>
<td>8. Equivalent Circuit with Two Possible Current Paths</td>
<td>13</td>
</tr>
<tr>
<td>9. Nyquist Plot for Path 1 of Fig. 8</td>
<td>15</td>
</tr>
<tr>
<td>10. Nyquist Plot Representing Path 2 of Fig. 8</td>
<td>17</td>
</tr>
<tr>
<td>11. Impedance Spectrum of CGO-La$_2$O$_3$ at 500 C</td>
<td>23</td>
</tr>
<tr>
<td>12. Impedance Spectrum of CGO at 500 C</td>
<td>24</td>
</tr>
<tr>
<td>13. Impedance Spectrum of CGO-La$_2$O$_3$ at 550 C</td>
<td>25</td>
</tr>
<tr>
<td>14. Impedance Spectrum of CGO at 550 C</td>
<td>26</td>
</tr>
<tr>
<td>15. Impedance Spectrum of CGO-La$_2$O$_3$ at 600 C</td>
<td>27</td>
</tr>
<tr>
<td>16. Impedance Spectrum of CGO at 600 C</td>
<td>28</td>
</tr>
<tr>
<td>17. Impedance Spectrum of CGO-La$_2$O$_3$ at 650 C</td>
<td>29</td>
</tr>
</tbody>
</table>
List of Figures-continued

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>18. Impedance Spectrum of CGO at 650 C</td>
<td>30</td>
</tr>
<tr>
<td>19. Impedance Spectrum of CGO-La$_2$O$_3$ at 700 C</td>
<td>31</td>
</tr>
<tr>
<td>20. Impedance Spectrum of CGO at 700 C</td>
<td>32</td>
</tr>
<tr>
<td>21. Plot of Resistance vs Temperature for Samples CGO and CGO-La$_2$O$_3$</td>
<td>35</td>
</tr>
<tr>
<td>22. Magnetron Sputtering at MMF</td>
<td>38</td>
</tr>
<tr>
<td>23. SEM at Image and Chemical Analysis Laboratory</td>
<td>40</td>
</tr>
<tr>
<td>24. SEM Image of MgO on Si Wafer at 10,000 Times Magnification</td>
<td>41</td>
</tr>
<tr>
<td>25. SEM Image of MgO on Si Wafer at 1,000 Times Magnification</td>
<td>41</td>
</tr>
<tr>
<td>26. SEM Image of MgO on Si Wafer at 40,000 Times Magnification</td>
<td>42</td>
</tr>
<tr>
<td>27. SEM Image of MgO on Si Wafer at 5,000 Times Magnification</td>
<td>42</td>
</tr>
<tr>
<td>28. SEM Image of MgO on Si Wafer at 40,000 Times Magnification</td>
<td>43</td>
</tr>
<tr>
<td>29. RBS Chamber for Materials Analysis at IBL</td>
<td>44</td>
</tr>
<tr>
<td>30. 2 MV van de Graaff Accelerator</td>
<td>45</td>
</tr>
<tr>
<td>31. SIMNRA Computer Simulation</td>
<td>46</td>
</tr>
<tr>
<td>32. Sectional View of Apparatus</td>
<td>49</td>
</tr>
<tr>
<td>33. Apparatus Drawings</td>
<td>50</td>
</tr>
<tr>
<td>Figure</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>------</td>
</tr>
<tr>
<td>34. Outer Inconel End Piece</td>
<td>51</td>
</tr>
<tr>
<td>35. Center Inconel End Piece</td>
<td>52</td>
</tr>
<tr>
<td>36. Inner Inconel End Piece</td>
<td>53</td>
</tr>
<tr>
<td>37. CGO Heating and Cooling</td>
<td>55-62</td>
</tr>
<tr>
<td>38. BCY Heating and Cooling</td>
<td>62-68</td>
</tr>
<tr>
<td>39. Resistivity vs Temperature Plots for BCY and CGO samples</td>
<td>69</td>
</tr>
<tr>
<td>40. Real Permittivity vs Imaginary Permittivity for BCY</td>
<td>70</td>
</tr>
<tr>
<td>41. Real Permittivity vs Imaginary Permittivity for CGO</td>
<td>75</td>
</tr>
</tbody>
</table>
### NOMENCLATURE

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Area</td>
</tr>
<tr>
<td>C</td>
<td>Capacitance</td>
</tr>
<tr>
<td>$C_{gb}$</td>
<td>Capacitance of grain boundary</td>
</tr>
<tr>
<td>$C_{gr}$</td>
<td>Capacitance of grain</td>
</tr>
<tr>
<td>$d_b$</td>
<td>Thickness of MgO layer</td>
</tr>
<tr>
<td>D</td>
<td>Length of edge of grain in the brick layer model</td>
</tr>
<tr>
<td>$\langle D \rangle$</td>
<td>Apparent grain-size</td>
</tr>
<tr>
<td>$E_a$</td>
<td>Activation energy</td>
</tr>
<tr>
<td>E</td>
<td>Instantaneous voltage</td>
</tr>
<tr>
<td>$E_0$</td>
<td>Maximum voltage</td>
</tr>
<tr>
<td>I</td>
<td>Instantaneous current</td>
</tr>
<tr>
<td>$I_0$</td>
<td>Maximum current</td>
</tr>
<tr>
<td>j</td>
<td>Square root of -l</td>
</tr>
<tr>
<td>k</td>
<td>Boltzmann constant</td>
</tr>
<tr>
<td>l</td>
<td>Thickness of the sample</td>
</tr>
<tr>
<td>L</td>
<td>Inductance</td>
</tr>
<tr>
<td>$P_{O_2}$</td>
<td>Partial pressure of oxygen</td>
</tr>
<tr>
<td>r</td>
<td>Resistance of blocking layer</td>
</tr>
<tr>
<td>R</td>
<td>Resistance</td>
</tr>
<tr>
<td>$R_{ct}$</td>
<td>Resistance of contacts</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------------------------------------------</td>
</tr>
<tr>
<td>$R_p$</td>
<td>Polarization resistance</td>
</tr>
<tr>
<td>$R_{gr}$</td>
<td>Resistance of grain</td>
</tr>
<tr>
<td>$R_{gb}$</td>
<td>Resistance of grain boundary layer</td>
</tr>
<tr>
<td>$S$</td>
<td>Electrode area</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
</tr>
<tr>
<td>$t$</td>
<td>Time</td>
</tr>
<tr>
<td>$Y$</td>
<td>Admittance</td>
</tr>
<tr>
<td>$Z$</td>
<td>Impedance</td>
</tr>
<tr>
<td>$Z_0$</td>
<td>Ratio of maximum voltage and maximum current</td>
</tr>
<tr>
<td>$Z'$</td>
<td>Real part of impedance</td>
</tr>
<tr>
<td>$Z''$</td>
<td>Imaginary part of impedance</td>
</tr>
<tr>
<td>$</td>
<td>Z</td>
</tr>
<tr>
<td>$\beta$</td>
<td>Davidson-Cole exponent</td>
</tr>
<tr>
<td>$\delta_{gb}$</td>
<td>Thickness of boundary layer</td>
</tr>
<tr>
<td>$\varepsilon'$</td>
<td>Real permittivity</td>
</tr>
<tr>
<td>$\varepsilon''$</td>
<td>Imaginary permittivity</td>
</tr>
<tr>
<td>$\varepsilon_b$</td>
<td>Permittivity of MgO boundary layer</td>
</tr>
<tr>
<td>$\varepsilon_r$</td>
<td>Relative permittivity</td>
</tr>
<tr>
<td>$\varepsilon_s$</td>
<td>Static value of permittivity</td>
</tr>
<tr>
<td>$\varepsilon_o$</td>
<td>Permittivity of free space</td>
</tr>
</tbody>
</table>
NOMENCLATURE-continued

$\varepsilon_{gr}$  Permittivity of grain

$\varepsilon_{gb}$  Permittivity of grain boundary layer

$\rho$  Resistivity

$\rho_o$  Pre-exponential resistivity factor

$\sigma_{gb}$  Conductivity of grain boundary layer

$\sigma_{gr}$  Conductivity of grain

$\varphi$  Phase angle

$\omega$  Angular frequency

$\tau_0$  Maximum dielectric relaxation time

$\tau$  Dielectric relaxation time
ABSTRACT

Hydrogen can be obtained from purification of water gas by ceramic hydrogen separation membranes. These membranes need to be further improved to obtain reasonable production of hydrogen from water gas. Fuel cell materials and state of the art ceramic membranes were characterized by impedance spectroscopy and dielectric measurements.

To block the ionic and electronic conductivity, blocking layers of MgO were used. The coating thickness was analyzed by RBS and SEM techniques. Dielectric measurements with blocking layers and impedance measurements without any blocking layers were made over a wide range of temperatures. The data obtained were used to model equivalent circuits. The activation energies and conductivities of the samples were also found from data obtained and were compared with those available in the literature. MgO was found to be a suitable blocking layer material.
Solid oxide fuel cells (SOFC) are solid state energy conversion systems which are used to convert chemical energy to electrical energy directly. Fuel cells are basically similar to batteries barring the difference that where batteries run down and get depleted, fuel cells are continually replenished with fuel and thus provide a continuous supply of electric power.

SOFCs operate at high temperatures and utilize ceramics as functional elements of the cell. Each cell is composed of an anode and a cathode separated by a solid impermeable electrolyte, which during operation conducts oxygen ions from the cathode to the anode where they react chemically with the fuel. The electric charge carried by the passage of the ions is collected and conducted away from the cell. Each cell generates a limited voltage but just as with the cells of a battery, series connected stacks may be constructed to increase the voltage and hence the useful power that can be supplied. Each individual cell is connected electrically via an interconnect to its neighbor to achieve this. In some designs the interconnect is also used to isolate the fuel and air supplies for each cell.

The interest in solid oxide fuel cells (SOFC) is mainly because of the clean conversion of chemical energy to electricity, low levels of noise pollution, the flexibility to use different fuels, but most of all-high efficiency. The superior efficiency of SOFC
in comparison with other energy conversion systems is partly because of its high operating temperature, which in some designs may exceed 1000°C.

For such high operating temperatures, the potential exists to boost the overall efficiency of the SOFC system to ~70% by extracting the energy present in the high temperature exhaust gases - e.g. by using gas or steam turbines. SOFCS operate on most fuels which are composed of hydrocarbons but run best on pure hydrogen. Hence the need for hydrogen separation membranes which can filter hydrogen from water gas. Some of the electrolytes used for fuel cells can be used for this purpose as well.

**Methods**

Impedance spectroscopy is a useful tool to investigate the electrical conduction as well as electrochemical phenomena in an electrochemical system. Most of the work [Lane] on the ion transport properties of ceramic materials has been undertaken using AC impedance spectroscopy or other electrical techniques. In general, these techniques are excellent methods for measuring the ionic conductivity of materials, such as gadolinia-doped ceria (CGO, currently state of the art oxide ion conductor and also BCY). We also investigated barium cerate based hydrogen separation membranes for their conductivity indirectly by measuring their permittivity instead. Some of the samples in our case were coated with a blocking layer of MgO by magnetron sputtering. To analyze the coating of MgO on the samples, Scanning Electron Microscopy (SEM) and Rutherford Backscattering Spectroscopy (RBS) were used.
For other samples without MgO coatings, an impedance spectroscopy measurement system, shown in Fig. 1 was used. The set-up shown has a Hioki LCR Tester which was later upgraded to a Solartron Electrochemical Impedance Analyzer (Model 1260 and 1287 Interface). The impedance of SOFC materials is measured in the high temperature oven under an oxidizing atmosphere, which simulates conditions...
in a SOFC.

The impedance of the ceramic material was measured over a wide range of frequencies \( f = 10^3-10^5 \text{ Hz} \) and also DC, temperatures \( 20^\circ-1000^\circ \text{ C} \), and oxygen partial pressures \( P_{\text{O}_2} \). The electrical conductivities were then extracted from the data of impedance spectroscopy. The dielectric measurements for the SOFC as well as hydrogen separation membrane materials were used to obtain conductivity data. In the future, these and other data will be analyzed together with the compositional and microstructural analysis to obtain a series of important information, such as the activation energies of conductivities, the charge carrier types and their contributions to the conductivities, the electrical conduction mechanisms, and how the composition and structure of the materials affect the conductivity, etc. The obtained information will help to optimize the composition, structure, and synthesis process of SOFC and hydrogen membrane materials and to reduce the operating temperatures and fabrication cost of SOFC’s.
CHAPTER 2

CONCEPT OF COMPLEX IMPEDANCE

Impedance spectroscopy is central to this thesis, so a brief introduction to this technique is provided here. It follows the general outline of a work by [Gamry] but whereas their publication is aimed at electrochemical cells, our description deals with ceramic samples. Impedance is a generalization of the concept of resistance. The concept of electrical resistance is pretty straightforward. It is the ability of a particular circuit element (a resistor) to resist current flow. Quantitatively, Ohm's law defines resistance in terms of voltage $E$ and current $I$ as:

$$ R = \frac{E}{I} $$

(1)

In a resistor the AC current and voltage are in phase. In other circuit elements they may be out of phase, and the idea of resistance must be generalized to that of impedance. Impedance is a measure of the ability of a circuit to resist the flow of electrical current. In particular, in capacitors the current leads the voltage by 90° and in inductors it lags by 90°. Impedance is usually measured by applying an AC potential (in our case, a maximum magnitude of 10 mV) to an electrical or electrochemical system (in our case the ceramic samples) and measuring the current. If we apply a sinusoidal potential, the response in general is a nonlinear AC current, containing the excitation frequency and its harmonics. Ceramic samples like ours are quite linear, so if the contacts behave linearly also, the only source of apparent non-linearity would be sample heating.
by too high an applied potential. We use a small enough excitation signal (10 mV) so that the sample’s response is pseudo-linear. Then the current response will have no harmonics but will be a sinusoid at the same frequency but shifted in phase, as shown in Fig. 2.

![Fig. 2. Sinusoidal Current Response in a Linear System](Adapted from Ref. 2.)

The excitation voltage can be expressed as:

$$E(t) = E_o \cos(\omega t)$$

(2)

In a linear system, the response current signal, $I(t)$, is generally shifted in phase by an angle $\phi$ and can be represented by:

$$I(t) = I_o \cos(\omega t - \phi)$$

(3)

The impedance expression is analogous to Ohm's Law:
In the above form, \( Z \) has the undesirable property of being time-dependent. To eradicate the inconvenience, \( E(t) \) and \( I(t) \) are expressed in the complex plane.

Using Euler’s relationship,
\[
\exp(j\phi) = \cos\phi + j\sin\phi
\]
(5)

the potential is,
\[
E(t) = E_0 \exp(j\omega t)
\]
(6)

and the current response is,
\[
I(t) = I_0 \exp(j\omega t - j\phi)
\]
(7)

The impedance is then a complex parameter,
\[
Z = \frac{E}{I} = Z_0 \exp(j\phi) = Z_0(\cos\phi + j\sin\phi)
\]
(8)

If the real part \( Z' \) is plotted on the x axis and the imaginary part \( Z'' \) on the y axis of a graph both to the same scale, we obtain a Nyquist plot. Equivalent circuits representing our samples typically contain capacitors which have negative imaginary impedance. Accordingly, in our plot the y-axis shows \( -Z'' \) so that the points are above the x axis. Each point on the Nyquist plot is the impedance at some certain frequency. The Nyquist plot for a parallel RC circuit appears in Fig. 3.

Nyquist plots have the drawback that one cannot tell the frequency at any data point unless marked explicitly. This is overcome by the supplemental use of Bode plots.

These display log frequency on the x-axis and the magnitude of the impedance
\[ |Z| = Z_0 \] and the phase-shift \( \varphi \) on the y-axis, as shown in Fig. 4. Our Solartron system displays all three of these plots, allowing quick determination of radial frequency at any point on the Nyquist plot.

---

**Fig. 3. Nyquist Plot with Impedance Vector**  
(Adapted from Ref. 2.)

**Fig. 4. Bode Plot with One Time Constant**  
(Adapted from Ref. 2.)
Analysis of Impedance Spectroscopy Data

Impedance Spectroscopy (IS) data are usually analyzed by fitting them to an equivalent electrical circuit model which may not be unique. The circuit elements are usually resistors, capacitors, and inductors. The elements in the model should bear relevance to physical entities in the sample. In the simplest case, a ceramic sample’s dielectric response is represented by a capacitor C, in parallel with a resistor R representing its resistance to flow of ionic and/or electronic current. Knowledge of the impedance of the standard circuit components is therefore essential. Table 1 lists the common circuit elements and the equations for their current versus voltage relationship and their impedance.

<table>
<thead>
<tr>
<th>Component</th>
<th>Current Vs.Voltage</th>
<th>Impedance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistor</td>
<td>E= IR</td>
<td>Z = R</td>
</tr>
<tr>
<td>Inductor</td>
<td>E = L dI/dt</td>
<td>Z = j\omega L</td>
</tr>
<tr>
<td>Capacitor</td>
<td>I = C dE/dt</td>
<td>Z = 1/j\omega C</td>
</tr>
</tbody>
</table>

IS data are analyzed by finding an equivalent circuit model whose impedance matches the measured data. With experience, for ceramic sample systems consisting of the ceramic, its electrical contacts and any partially or completely blocking layers, one chooses RC circuits corresponding to physical models for that system. For example a simple series RC circuit fits the spectrum approximately for a resistive sample in series with a blocking layer. Then circuit components are added to successively fit finer spectral
features. When the fit is sufficiently good, one should try to correlate the circuit components (usually resistors and capacitors) to the physical parameters of the system. This correlation to physical parameters is important, because it enables the researcher to predict which physical parameters need to be changed to improve performance of the ceramic material.

**Uniqueness of Models**

The equivalent circuit may fit the data obtained very closely but yet may not be the only one that does so. Let us look at the impedance spectrum in Fig. 5 which shows two clearly defined time constants.

![Fig. 5. Two Time Constant Spectrum (Adapted from Ref. 2.)](image)

This spectrum can be modeled by any of the equivalent circuits shown in Fig. 6 below:
We see that there doesn’t exist a unique equivalent circuit that fits the spectrum. We choose a model that best fits physical parameters of the sample. Any such physical model ought to be verified before being used. One way to do so is to modify a single system component, for example, increase a blocking layer thickness, and see if the impedance spectrum changes as expected.

Fig. 6. Equivalent Circuit Models with Two Time Constants
(Adapted from Ref. 2.)
An important analysis method of impedance spectroscopy of ceramics is the brick layer model, a simple electrical model for ceramics whose grain boundaries may have different conductivity than the grains. The BLM was first proposed by [Beekmans]\(^3\) and then developed by [Dijk]\(^4\). Our outline of this model follows in general the outline by [Kleinlogel]\(^5\), in order to explicitly point out approximations made implicitly by them in Eqn. (8) and (10), and to mention errors made in their work in Fig.10 and associated text.

A representation of a grain along with its boundary is shown in Fig. 7. Each grain is assumed to be a cube with an edge of length \(D\) with a grain boundary of thickness \(\delta_{gb}\). The apparent grain size including its half of the boundary is a cube of edge:

\[
\langle D \rangle = D + \delta_{gb}
\]  

The current is assumed to be one-dimensional for simplicity. The current flows either through grains and across grain-boundaries (Fig. 8, path 1) or along grain-boundaries (Fig. 8, path 2) depending on the relative magnitudes of the grain and grain boundary conductivities \(\sigma_{gr}\) and \(\sigma_{gb}\). Fig. 8 shows that for path 1 there is perpendicular crossing of grains and grain boundaries. In path 2, the boundaries short-circuit the grains and current flows along parallel grain boundaries. \(R_1\) represents the resistance of current leads while \(R_2\) and \(C_2\) model the partial blocking by the electrodes.
Case 1: \( \sigma_{gb} \ll \sigma_{gr} \) and \( \delta_{gb} \ll \langle D \rangle \)

If the grain boundary conductivity, \( \sigma_{gb} \), is much smaller than the conductivity of the grain, \( \sigma_{gr} \), and/or the grain boundary thickness is small compared to the grain size.
size $\delta \ll \langle D \rangle$, then current flow only through grain boundaries perpendicular to the applied field is considered. The equivalent circuit then consists of two parallel RC (resistor-capacitor) elements in series. $R_3$ and $C_3$ models the grain resistance and capacitance, while $R_4$ and $C_4$ models the grain-boundary contribution (Fig. 8, path 1). The current flow in the grain boundary parallel to the field is ignored in this case. The grain resistance, $R_{gr}$, and the total grain-boundary resistance, $R_{gb}$, can be obtained from the Nyquist plots as shown in Fig. 9. This procedure works only if the time constants $R_3C_3$ and $R_4C_4$ are considerably different, otherwise the arcs overlap. As the frequency at the peak of each semicircle is given by:

$$\omega_0 = \frac{1}{R_iC_i}$$

the capacitances, $C_i$, can be calculated. Since $R_i$ and $C_i$ are given by:

$$C_i = \frac{\varepsilon_r \varepsilon_r}{S}$$

$$R_i = \frac{l}{\sigma_i S}$$

Therefore,

$$\frac{1}{\omega_0} = R_iC_i = \frac{\varepsilon_r \varepsilon_r}{\varepsilon_i}$$

where $\sigma_i$ is the conductivity, $\varepsilon_i$ denotes the relative dielectric constant, and $\varepsilon_0$ the permittivity of free space. $S$ is the electrode area and $l$ the thickness of the sample. This expression relates the conductivity of either material to its dielectric constant. The dielectric constant in sintered materials does not vary significantly on a spatial basis.
compared to the conductivity, so it is assumed that:

\[ \varepsilon_{gr} \approx \varepsilon_{gb} \]  \hspace{1cm} (6)

The capacitance ratio of the two components is given by:

\[ \frac{C_{gb}}{C_{gr}} = \frac{\varepsilon_{gb}}{\varepsilon_{gr}} \frac{D}{\delta_{gb}} \]  \hspace{1cm} (7)

The grain capacitance, \( C_{gr} \), and the grain-boundary capacitance, \( C_{gb} \), are given by:

\[ C_{gr} = \frac{\varepsilon_{gr} \varepsilon_{0} \delta}{1 - \delta_{gb}} \approx \frac{\varepsilon_{gr} \varepsilon_{0} S}{l} \]  \hspace{1cm} (8)

\[ C_{gb} = \frac{\varepsilon_{gb} \varepsilon_{0} S}{\delta_{gb}} \]  \hspace{1cm} (9)
The above $C_{gr}$ equation, Eq. (8), provides $\varepsilon_{gr}$. If $\varepsilon_{gb}$ is assumed to equal $\varepsilon_{gr}$, then the $C_{gb}$ equation, Eq. (9), provides the grain-boundary thickness $\delta_{gb}$.

The grain conductivity, $\sigma_{gr}$, and the grain-boundary conductivity, $\sigma_{gb}$, are given by:

$$\sigma_{gr} = \frac{l - \delta_{gb}}{R_{gr}S} \approx \frac{l}{R_{gr}S}$$  \hspace{1cm} (10)

$$\sigma_{gb} = \frac{\delta_{gb}}{R_{gb}S}$$  \hspace{1cm} (11)

using for $\delta_{gb}$ the value found above.

The interpretation of the impedance spectrum (Fig. 9) discussed above is straightforward. Ignoring electrode effects, the higher frequency arc on the left is the bulk response, followed by the lower frequency arc on the right from the grain boundary response. The electrode impedance $R_\Omega$ would appear as a smaller arc or horizontal section left of the first main arc. As mentioned above, for impedance spectra which exhibit two clearly separated arcs, one can immediately deduce that

$$\sigma_{gb} \ll \sigma_{gr}$$  \hspace{1cm} (12)

since only a difference in conductivities of grain and grain boundary can give a difference in characteristic frequencies, if their permittivities are about equal. The two-arc spectrum thus provides information regarding both grain and grain boundary.

**Case 2:** $\sigma_{gb} \gg \sigma_{gr}$ and $\delta_{gb} \ll \langle D \rangle$:

In this case the grain-boundary width is small compared to the apparent grain-size $\langle D \rangle$, 

but the grain-boundary conductivity, $\sigma_{gb}$, is much higher than the grain conductivity, $\sigma_{gr}$.

The current flows mainly along grain boundaries and the above discussed BLM is then reduced to a single RC circuit (Fig. 8, path 2). The ceramic sample will show only one arc in the impedance plot (Fig. 10). The dielectric response will be mostly from the grains, as in case 1, so $\varepsilon_{gr} = C_{gr} \varepsilon_0 S$ as before, and $C_{gr} = 1/\omega_{ogr} R_{gb}$ as seen from Fig. 10. Kleinlogel\textsuperscript{5} in Fig. 10 mistakenly considered the capacitance to come only from the grain boundary and in their original figure wrote $C_{gb}$, so they did not realize that $\varepsilon_{gr}$ can be deduced from Fig. 10. They also made typographical errors, $R_{gr}$ and $\omega_{ogr}$ above, which are corrected in our Fig. 10. If data concerning grain-boundary thickness $\delta_{gb}$ are available, $\sigma_{gb}$ may be estimated and some information about the composition of the grain-boundary

![Fig. 10. Nyquist Plot Representing Path 2 of Fig. 8](image)

(Corrected version of Figure from Ref. 5.)
and its properties can be deduced.

In our experimental results we saw no double arcs corresponding to case 1 (high grain boundary resistance). This means we are either in case 2, or else $\sigma_{gb} \approx \sigma_{gr}$ and $\varepsilon_{gb} \approx \varepsilon_{gr}$, a “Case 3” not discussed by [Kleinlogel]$.^5$.
Currently, gadolinia doped ceria (CeO$_2$–Gd$_2$O$_3$) is the state of the art electrolyte material for fuel cells. A 20% GdO$_{1.5}$-doped ceria solid solution, CGO20, is the most promising electrolyte for intermediate-temperature (500 °C to 600 °C) fuel cells.

Cerium oxide has a fluorite [Chiodellia]$^6$ structure. The conduction is due to the migration of oxygen anions over vacant ion sites, which are formed to preserve charge balance when replacing Ce$^{4+}$ with Gd$^{3+}$. Transition metal oxides such as MnO$_2$, Fe$_2$O$_3$, Co$_3$O$_4$ and CuO are effective sintering aids for the densification of ceria-based powders. Of those, Co$_3$O$_4$ and CuO are most effective in promoting the densification of nanosized ceria powders. It was found [T. S. Zhang]$^7$ that Fe$_2$O$_3$ is an effective sintering aid for the densification of ceria ceramics, and lowered sintering temperature by nearly 200 °C. It can be also used as a grain boundary scavenger for SiO$_2$ impurity but the doping level and sintering temperature must be carefully controlled. It was discovered a bit late in our research that SiO$_2$ acts as a contaminant as we tried to deposit SiO$_2$ as a blocking layer on CGO samples. SiO$_2$ has been known to form siliceous layers around grain boundaries, reducing the conductivity in CGO.

We tried doping CGO20 with 5% lanthanum oxide to study the effect on conductivity. This we hoped would substitute the Ce$^{4+}$ by La$^{3+}$ and thus create more vacancies for oxygen ion conduction.

BaCe$_{0.9}$Y$_{0.1}$O$_3$ is currently the most promising proton conducting ceramic. But
CO₂ is a major constituent of water gas from which the hydrogen is separated. BaCe₀.₉Y₀.₁O₃ decomposes into barium carbonate in the presence of CO₂ at high temperatures (membrane operating temperature 600-800 °C). It has been reported [Shima]⁸ that samples with excess of barium in BaCe₀.₉Y₀.₁O₃ react with carbon dioxide to form barium carbonate, while stoichiometric and Ba-deficient compositions do not. Undoped barium cerate is unstable when barium deficiency is introduced as CeO₂ would precipitate. The doped material is stable but a large deficiency in barium resulted in a significant decrease in total conductivity.

Additional dopants can improve the chemical stability of the BCY class of materials. [Ryu and Haile]⁹ found that substitution of cerium with zirconium improved the stability of doped and undoped barium cerate but at the expense of conductivity. BaCe₀.₆₅Zr₀.₁₅Y₀.₂O₃ was therefore chosen to improve stability of the membrane in carbon dioxide environments.
CHAPTER 5

SYNTHESIS OF CGO AND CGO DOPED WITH 5 % La$_2$O$_3$

The materials were prepared by the glycine nitrate process (GNP). In this process, glycine was used as a fuel that reacts with cerium nitrate and gadolinium nitrate. The solution was then heated at 150 °C till most of the water vaporized and was then transferred to a steel container. Subsequently, the solution was heated intensely till it ignited and CGO ceramic powders were obtained.

The CGO was then analyzed by XRD to confirm the composition and was then mixed with 5% atom of La$_2$O$_3$ and mixed together with acetone in a ball rolling machine for 2 hrs at 120 rpm. The solution was then dried on by heating for 2 hours at 125 °C. These powders were then used to make pellets of 10 mm diameter and 3 mm thickness by using a pressure of 8-10 MPa for approximately 30 seconds. The samples were then sintered at 800 °C for two hours in the furnace.

The samples were then analyzed for impedance using the AC Impedance Spectroscopy setup which was upgraded with a Solartron 1260 Analyzer and a Solartron 1287 Electrochemical Interface. The frequencies swept ranged from 0.1 Hz to 100 kHz at temperatures from 500 °C to 700 °C in steps of 50 °C using ZPlot software, and impedance spectra were collected using ZView. They are displayed in Figs. 11-20. Figs. 11 and 12 show impedance spectra for CGO and CGO-La$_2$O$_3$ at 500 °C. The intercept on the real axis is about 462,000 ohms for CGO-La$_2$O$_3$ and about 150,000 ohms for CGO, which is about a third of the value obtained for CGO-La$_2$O$_3$. The rest of the spectra show
a similar trend in that the resistance of the doped CGO-La$_2$O$_3$ is higher than that of CGO. These impedance values were plotted semilogarithmically and the best fit line is used to obtain the activation energy and pre-exponential factor. There is a discrepancy in the spectrum for the CGO-La$_2$O$_3$ at 600 °C as this was taken in an earlier run from the rest but retained for its smooth characteristics. The discrepancy could have happened because of manual temperature control in this initial run where the temperature in the oven shot up above 600 °C and then cooled till 600 °C. The oven may have reached 600 °C but the sample may have still been at a higher temperature and thus the reported discrepancy. Barring this point, the rest of the data fit straight lines on the semilogarithmic plot very well.
Fig. 11. Impedance Spectrum of CGO-La$_2$O$_3$ at 500 C

(All impedances in Figs. 11-20 in ohms)
Fig. 12. Impedance Spectrum of CGO at 500 C
Fig. 13. Impedance Spectrum of CGO-La$_2$O$_3$ at 550°C
Fig. 14. Impedance Spectrum of CGO at 550 C
Fig. 15. Impedance Spectrum of CGO-La$_2$O$_3$ at 600 C
Fig. 16. Impedance Spectrum of CGO at 600°C
Fig. 17. Impedance Spectrum of CGO-La$_2$O$_3$ at 650 C
Fig. 18. Impedance Spectrum of CGO at 650 C
Fig. 19. Impedance Spectrum of CGO-La$_2$O$_3$ at 700 C
Fig. 20. Impedance Spectrum of CGO at 700 C
Impedance of CGO and CGO-5%La Samples
without Blocking Electrodes

The samples of CGO and CGO- La$_2$O$_3$ were tested without blocking electrodes. Their thickness is $d=3$ mm, and diameter is 10 mm, giving area $A=78.55$ mm$^2$. The synthesis is described in a previous section.

To interpret the impedance results, the plots in each Figure from top to bottom correspond to impedance magnitude $|Z|$ in ohms, impedance phase angle $\phi$ in degrees, and a plot of $Z''$ vs. $Z'$ (capacitive vs. resistive impedance) in ohms. Frequencies are not shown on the $Z''$ vs. $Z'$ plot, but can be found by matching $|Z|$ and $\phi$ for a given point on the bottom plot with the frequency giving the corresponding $|Z|$ and $\phi$ in the top and middle plots.

The $Z''$ vs. $Z'$ plots are not circular arcs, rather they are "skewed arcs." Their shape is similar to that of $\varepsilon''$ vs. $\varepsilon'$ plots that can be approximated by the Davidson and Cole relation

$$\varepsilon* - \varepsilon_\infty = (\varepsilon_s - \varepsilon_\infty)(1 + j \omega \tau_0)^\beta$$

where $\varepsilon_s$ is the "static" or low-frequency value and $\varepsilon_\infty$ is the "infinite-frequency" or high-frequency value. This Davidson-Cole expression results physically from a distribution $F(\tau/\tau_0)$ of dielectric relaxation times $\tau$, given by

$$F(\tau/\tau_0) = [(\sin \beta \pi)/\pi]^{\beta}$$

for $\tau < \tau_0$, and zero for $\tau > \tau_0$.

Davidson and Cole describe graphical methods for finding $\tau_0$ and $\beta$. Once these are
found, the next step in the analysis would be to try to determine the physical mechanisms responsible for the magnitudes and temperature dependences of $\tau_0$ and $\beta$.

As a first approximation, the foregoing impedance plots can be considered as being due to a parallel RC circuit, with R being the sample resistance and C its capacitance. Then R is found by reading the $Z'$ value at the right end of the curve, corresponding to the lowest frequency point, for which the capacitance has little effect in reducing the impedance from the value R. The resistivity $\rho$ is given by $\rho = RA/d$, where $A$ is sample area and $d$ is sample thickness. The resistivity as a function of temperature for both samples obeys very well the Arrhenius relation, $\rho = \rho_0 \exp(E_a/kT)$. As seen from above spectra, it was found that addition of La$_2$O$_3$ to CGO reduces conductivity. This is unfortunate, because La addition has the desirable effect of lowering the sintering temperature. Resistance R values were calculated for temperatures 500, 550, 600, 650 and 700 C for both CGO and CGO-La$_2$O$_3$. The best-fit resistivity expression for CGO-La$_2$O$_3$ found by assuming a single activation energy $E_a$ is $\rho = 8.1 \times 10^{-6} \exp(1.38 \text{ eV}/kT)$, and for CGO: $\rho = 1.13 \times 10^{-5} \exp(1.31 \text{ eV}/kT)$. The plots of the resistance of the samples as a function of temperature is shown in the following figure 21.
CGO and CGO-5% La$_2$O$_3$

![Graph showing resistance vs temperature for CGO and CGO-Lanthanum samples.]

Fig. 21. Plot of Resistance vs Temperature for Samples CGO and CGO-La$_2$O$_3$
CHAPTER 6

SYNTHESIS OF BaCe_{0.65}Zr_{0.15}Y_{0.2}O_3 (BCY) BY GLYCINE NITRATE PROCESS (GNP)

The Glycine Nitrate Process (GNP) was used to produce the ceramic powder. Nitrates of barium, cerium, zirconium and yttrium were mixed with glycine as fuel and ignited. The powders were then collected, pelletized and sintered at 1300 °C for 2 hours. The synthesis is similar to the preparation of CGO barring the sintering temperature and other intermediate processing steps like drying. It has been found [NETL]^{11} that the use of oxalic dihydrazide (ODH) instead of glycine results in the formation of ceramic powders of a better quality. Other possible fuels that could be used are urea and carbohydrazide, all of which possess N-H bonds. There is no significant difference in the size of the powder particles formed by the use of glycine and oxalic dihydrazide though higher density pellets could be obtained by use of the ODH fueled reaction.

Oxygen conduction arises from movement of oxygen ions by means of oxygen vacancy drift. These vacancies are introduced by partial substitution of Ce by Ba ions. The ceramic thus can be viewed as an extrinsic ionic semiconductor with a carrier (oxygen vacancies) concentration that is nearly independent of temperature. The activation energy for the BCY conductivity (and similarly for conductivity of the other samples) then can be attributed to the barrier encountered as a neighbouring oxygen ion hops into the vacant oxygen ion site.

Proton conduction occurs via hydroxyl [Takeuchi]^{12} ions that form when
hydrogen dissolves in the lattice. Thus fuel cell materials can also be used as hydrogen filters. The proton mobility and conductivity depend on the dopant level that controls the proton concentration, and the partial pressure of the surrounding gases.
DEPOSITION OF MgO BY MAGNETRON SPUTTERING

An insulating layer of MgO was used to block the transport of ions and electrons. To deposit the blocking layers of MgO for some of the electrical measurements, we used the magnetron sputtering apparatus in the Electrical Engineering Department with the aid of Dr. Phil Himmer. Inside the magnetron, there is a plasma created which causes the magnesium target to be sputtered on to the sample surface. The first step in this process is that electrons emitted by a hot cathode are accelerated by a large electric field. In the second step, these fast electrons collide with gas atoms (in our case, mostly argon) and ionize them. The ions then are accelerated by another electric field and strike the Mg target, knocking out Mg ions. By using an atmosphere of

Fig. 22. Magnetron Sputtering at MMF
oxygen and argon, the magnesium ions combine with the oxygen ions and thus a coating of magnesium oxide is obtained on the ceramic samples. The gas used was a mixture of 20% oxygen and 80% argon. The sputtering power was 300 W for a duration of 4 hours. Fig. 22 above shows the magnetron apparatus at the Montana Microfabrication Facility (MMF) in the Electrical Engineering Department.
The MgO coating was analyzed using a SEM. The Scanning Electron Microscope (SEM) is a microscope [MSE]\(^{13}\) that uses electrons instead of light to form images of the sample. Sample preparation is relatively easy since most SEMs only require the sample to be conductive. Our samples were dissolved in acetone and then placed on slides for examination. Fig. 23 below shows the SEM at the Image and Chemical Analysis Laboratory (ICAL).

![SEM at Image and Chemical Analysis Laboratory](image)

Fig. 23. SEM at Image and Chemical Analysis Laboratory

Fig. 24 shows the coating at 10,000 times magnification and it appears as if non-uniform and uneven. Fig. 25 is a long shot view with a magnification of 1000X and nothing much can be inferred other than that the coating looks uniform at this magnification. Fig. 26 helps us to estimate the thickness of the coating to be approximately 300 nm.
Fig. 24. SEM Image of MgO on Si Wafer at 10,000 Times Magnification

Fig. 25. SEM Image of MgO on Si Wafer at 1,000 Times Magnification
Fig. 26. SEM Image of MgO on Si Wafer at 40,000 Times Magnification

Fig. 27. SEM Image of MgO on Si Wafer at 5,000 Times Magnification
Fig. 27 at 5000 X exhibits an uneven surface which could be due to repeated attempts in slicing the wafer with the diamond cutter to make square samples. Fig. 28 is a blurred image of the same at 40000X and corroborates the thickness to be approximately 300 nm as mentioned before.

Fig. 28. SEM Image of MgO on Si Wafer at 40,000 Times Magnification
CHAPTER 9

ANALYSIS OF SURFACE CONSTITUENTS BY RBS

The constituents of the MgO coating on silicon wafers were analyzed by Rutherford Backscattering Spectroscopy (RBS) at the Ion Beams Lab (IBL) in the Physics Department with the help of Dr. Asghar Kayani. Rutherford backscattering spectroscopy of the MgO samples was performed using the RBS chamber shown in Fig. 29 and the 2 MeV van de Graaff accelerator (Fig. 30) in the IBL. Rutherford backscattering spectra were recorded with a beam of He nuclei (alpha particles) at 0° angle of incidence measured from the sample normal. Backscattered ions were collected using a silicon surface barrier detector at a scattering angle of 165°, with an exit angle of 15° from the sample normal. This geometry enhanced the depth resolution of the RBS measurements. The composition profile was determined by comparing a SIMNRA simulation with the

Fig. 29. RBS Chamber for Materials Analysis at IBL
original data.

The peaks in the spectrum shown in Fig. 31 are those of oxygen, magnesium and gold going from left to right. The data points are connected by a jagged line. The SIMNRA simulation is the smooth line, which gives an excellent fit except at the lowest energies, far from any peak.

The RBS found that there were two layers:

1. One with 50% Mg and 50% O with $240 \times 10^{15}$ atoms/cm$^2$

2. Another with 5% Au, 47.5% Mg and 47.5% O with $180 \times 10^{15}$ atoms/cm$^2$

The RBS also gives us the density of atoms per unit area. Using basic chemistry calculations and by knowledge of density, we can calculate the thickness of the layers. We neglect the contribution of gold contamination (due to gold present in the Magnetron coating apparatus from a previous run) in our calculations as it is relatively smaller in
quantity compared to other constituents, and also for the ease of calculations.

Calculations

Neglecting the small presence of gold, the thickness of the MgO layer is found as follows:
Total Thickness = Thickness of layer 1 + Thickness of layer 2

= [\{(\text{No. of atoms/cm}^2)/\text{Avogadro No.}\} \times \text{Molecular Weight}\}/ \text{Density}]

= \left\{\frac{0.5(240 + 180) \times 10^{15}}{6.023 \times 10^{15}}\right\} \times \frac{24.305 + 15.995}{3.58}

= 392 \text{ A}

Therefore, Thickness = 392 \text{ A}

The thickness of the coating found by SEM was around 300 nm which was from a sample from another run. The deposition time was 2 hours for the RBS sample and 4 hours for the SEM sample. Assuming linear deposition rates, the ratio of the coating thicknesses should have been approximately 2 but the actual ratio is nearly 8. The reason for this discrepancy is not yet known.
CHAPTER 10

DESIGN OF APPARATUS FOR HYDROGEN PERMEATION TESTING

Concurrent with our impedance spectroscopy testing of hydrogen permeation ceramics, we designed and have mostly built apparatus for testing hydrogen permeation membranes made of these ceramics under operating conditions for temperature and gas partial pressures. The original testing requirements for this apparatus stipulated a hydrogen pressure of 10 atm. but this was later relaxed to 1 atm. as sufficient data could be collected at lower pressures. The problems encountered while designing were to select an appropriate material that could be resistant to both hydrogen permeation and hydrogen embrittlement, and yet withstand high pressures. The first material proposed that could do the job was machinable aluminum nitride, trademark name Shapal-M. Most low pressure measurement apparatus uses alumina tubes. Aluminum nitride is similar to alumina, but has formula AlN instead of Al₂O₃. The form of AlN (Shapal-M) proposed for use has better thermal conductivity than alumina. AlN has been used for making hermetically sealed vacuum chambers and can be machined to very fine tolerances with standard machine tools. It is also denser than alumina and the initial cost of set up would have been higher, but this cost could have been recovered by having a durable high pressure set-up. We would have been one of the first to use this kind of apparatus.

Due to budget constraints, the planned material was later changed to a nickel superalloy, Inconel 600, which is already being used by other research organizations for hydrogen permeation testing. Figs. 32-36 show the engineering drawings of the
components of the proposed Inconel apparatus. Another student, Sam Friesen, was assigned simultaneously to design an apparatus based on different materials which was finally chosen for construction and is nearing completion.

Fig. 32. Sectional View of Apparatus
Fig. 33. Sectional View of Apparatus (Dimensions in mm in Figs. 33-36)
Fig. 34. Outer Inconel End Piece
Fig. 35. Center Inconel End Piece
INNER INCONEL END PIECE

Fig. 36. Inner Inconel End Piece
Stress Analysis

The set-up shown in Figs. 32-36 when made of Inconel has a life depending on the temperature range being used. The pressure that it can withstand also affects the life. For safety reasons owing to hydrogen embrittlement and permeation, we recommend disposing of the pieces after running its useful rated life. From literature and basic shell analysis, we estimated the life of the set up with Inconel 600 as shown below.

HOOP STRESS: MAX. PRESSURE = 20 ATM. @ 982 C 1000 HRS LIFE

65 ATM. @ 816 C, 1000 HRS LIFE
CHAPTER 11

TESTING OF SAMPLES WITH BLOCKING LAYER OF MgO

Samples of KTP, copper, CGO and BCY, all coated with MgO were tested by the low temperature impedance spectroscopy apparatus from 300 K to 500 K. The KTP sample broke and copper did not display any useful data. The permittivity measurements were used to calculate the conductivity of the samples at various temperatures. The plots of the real part of the system conductivity vs. temperature are given in Fig. 37 for CGO and in Fig. 38 for BCY. Due to the MgO blocking layer and the sample capacitance, the true conductivity of the sample approaches the reported conductivity in these figures only at low frequency. True resistivities are plotted in Fig. 39.
Fig. 39. Resistivity vs. Temperature Plots for BCY and CGO Samples
BCY Analysis

The dielectric permittivity measurements for BCY and CGO ceramic samples with MgO blocking layers were done on the QuadTech 7600 Precision RLC Meter with its associated temperature control apparatus, with the aid of Chih-Long Tsai. The BCY sample has composition $\text{BaCe}_{0.65}\text{Zr}_{0.15}\text{Y}_{0.20}\text{O}_3$. Its thickness is $d=1.51$ mm, and its diameter is 16.76 mm, giving area $A=221$ mm$^2$. Its synthesis is described in a previous section. The dielectric results for all frequencies and temperatures, when plotted as $\varepsilon''$ vs. $\varepsilon'$, fit on a complete Debye-model half-circle that begins very near the origin and ends at $\varepsilon'=35,200$, $\varepsilon''=0$ (Fig. 40). Such a plot is most easily modeled as resulting from a series RC circuit. This implies that the resistance $R$ comes from the sample and the capacitance $C$ from the blocking MgO layers.

Fig.40 Imaginary Permittivity vs. Real Permittivity for BCY
In the low frequency limit, only the MgO capacitance \( C = \varepsilon_0 \varepsilon' A/d_b \) determines the admittance, where \( d_b \) is the combined thickness of the two MgO blocking layers. However, in this limit the apparatus interprets \( C \) as \( C = \varepsilon_0 \varepsilon' A/d \), where \( d \) is the ceramic sample thickness. By equating the above two expressions for \( C \), we find \( \varepsilon'_b = \varepsilon' d_b/d \). The accepted value of \( \varepsilon'_b \) for MgO is 10, so this implies an overall MgO thickness of 430 nm, or 215 nm for a single layer. The single layer MgO thickness obtained from RBS was 392 Å, whereas the thickness obtained from the SEM was 300 nm. The RBS and SEM measurements were made for MgO layers from the same sputtering run, of duration 2 hours, so the origin of this discrepancy is not yet understood. The BCY dielectric sample was coated with MgO from a sputtering run of 4 hours duration under nominally the same conditions. We can say that the above three values for MgO layer thickness agree within an order of magnitude. We can also say that there is no indication of variation of MgO permittivity over the experimental \( f \) and \( T \) ranges, \( 100 \text{ Hz} \leq f \leq 1 \text{ MHz} \) and \( 300 \text{ K} \leq T \leq 500 \text{ K} \). Such constancy of \( \varepsilon' \) and its extremely high resistivity make MgO a good material for blocking layers.

To find resistance \( R \) and resistivity \( \rho \) for the BCY sample, and capacitance \( C \) for the two MgO layers that are in series with the sample, we examine the results for frequencies \( f = \omega/2\pi \) of 0.1, 0.5, 1, 10, 100, 500, and 1000 kHz and temperatures \( T \) from 300 to 500 K. These results are presented by the apparatus in terms of permittivity \( \varepsilon = \varepsilon' - j \varepsilon'' \), where \( j = \sqrt{-1} \). The apparatus considers the (sample + MgO) as being a capacitor \( C_x \) of the thickness \( d \) of the sample, and the area \( A \) of the electrodes. For such a capacitor, the admittance \( Y \) (\( Y = 1/Z \) where \( Z \) is impedance) is
\[ Y = j\omega C = j\omega\varepsilon_0(\varepsilon' - j\varepsilon'')A/d = \omega\varepsilon_0(\varepsilon'' + j\varepsilon')A/d, \quad (1) \]

where \(\varepsilon_0\) is the MKS system constant \(8.85 \times 10^{-12} \, \text{C}^2/\text{Nm}^2\). The admittance for a series RC circuit is

\[ Y = \omega C(\omega RC + j)/(1 + \omega^2R^2C^2). \quad (2) \]

The ratios of real/imaginary parts of Eqs. (1) and (2) must be the same, so

\[ \varepsilon''/\varepsilon' = \omega RC. \quad (3) \]

Substituting the Eq. (3) result into Eq. (2) yields

\[ Y = R^{-1}(\varepsilon''/\varepsilon')[(\varepsilon''/\varepsilon')' + j][1 + (\varepsilon''/\varepsilon')^2] = R^{-1}(1 + j\varepsilon'/\varepsilon'')/[1 + (\varepsilon'/\varepsilon'')^2]. \quad (4) \]

Equating the real parts of Eqs. (1) and (4) yields the sample resistivity \(\rho\):

\[ \rho = RA/d = 1/\omega\varepsilon_0\varepsilon'[1 + (\varepsilon'/\varepsilon'')^2]. \quad (5) \]

The capacitance \(C\) is then found by substituting \(R = \rho d/A\) from Eq. (5) into Eq. (3):

\[ C = \varepsilon_0\varepsilon'A/d[1 + (\varepsilon''/\varepsilon')^2]. \quad (6) \]

But \(C = \varepsilon_0\varepsilon_bA/d_b\), where \(\varepsilon_b\) and \(d_b\) are the permittivity and combined thickness of the MgO blocking layers. Accordingly, \(d_b\) is given by

\[ d_b = d\varepsilon_b/\varepsilon'[1 + (\varepsilon''/\varepsilon')^2], \quad (7) \]

where for MgO the accepted value for \(\varepsilon_b\) is 10. Accordingly, for every data pair \((\varepsilon', \varepsilon'')\) reported by the apparatus, we obtain values for \(\rho\), \(C\), and \(d_b\). The effect of any conductivity of the MgO layers will be most evident at high temperature and low frequency, so the most reliable values for these parameters are the ones at low temperature and high frequency, near the lower left corner of the \(\varepsilon''\) vs. \(\varepsilon'\) plot. Values for the MgO layer thickness, \(d_b/2\), were obtained using Eq. (7) for data from most parts of
the $\varepsilon''$ vs. $\varepsilon'$ plot. Most of these values were in 213 to 250 nm range, which compares well with the value 215 nm found by the method described earlier.

The resistance $R$ and resistivity $\rho$ found from Eq. (5) decrease rapidly with increasing temperature. A good fit is obtained to the Arrhenius expression that applies for thermally activated carrier creation and/or hopping, $\rho = \rho_0 \exp(E_a/kT)$. The results were slightly different for the heating and subsequent cooling run. The heating run gave activation $E_a$ of 0.573 eV and pre-exponential factor $\rho_0$ of $2.40\times10^{-3}$ ohm-m whereas the cooling run gave 0.520 eV and $6.75\times10^{-3}$ ohm-m. Such Arrhenius-law behavior is typical for ionic and electronic semiconductors, so it seems reasonable for this sample. The activation energy agrees with that found by Coors and Readey for "BCY10" which is BaCe$_{0.9}$Y$_{0.1}$O$_3$. They obtained in their lower-temperature region of 370 to 520 K a resistivity of $2.62\times10^{-5} \exp(0.56 \text{ eV/kT})$ ohm-m, compared to our heating/cooling average value of $4.6\times10^{-3} \exp(0.55 \text{ eV/kT})$. They obtained 18.0 ohm-m at 500 K, compared to our value of 1250 ohm-m at 500 K. We do not know the reason for our much higher resistivity, except that our sample had less Ce, more Y, and contained Zr also, and our sample was not protonated (exposed to hydrogen gas and water vapor). Kreuer\textsuperscript{14} \textit{et al}. for a BCY20 single crystal found about 58% as high a conductivity for a 58% protonated crystal as for a 100% protonated crystal. This implies that an unprotonated crystal could be expected to have much higher resistivity. From this BCY work and comparison with results of others, we conclude that BCY has a thermally activated conductivity, for which the activation energy is independent of hydrogen concentration in the 300-500 K
temperature range, but the magnitude of the conductivity depends on hydrogen concentration. We also conclude that good conductivity data can be obtained by using MgO blocking layers in this temperature range. Without the blocking layers, one would have to be sure that any electrode resistance could be distinguished from sample resistance, perhaps by having a different activation energy, or by showing up in different portions of a plot of -Im(Z) vs. Re(Z) plot, as was found by Coors and Readey. We recommend further work to determine the effect of protonation on our sample, when the protonation apparatus has been constructed.

**CGO Analysis**

A CGO sample prepared by Dr. Jiaping Han was examined by dielectric spectroscopy with the QuadTech system. This sample has nominal composition Ce$_{0.8}$Gd$_{0.2}$O$_2$, and was coated with MgO in the same sputtering run as the BCY sample. Identical results were obtained in heating and cooling runs that covered the 300 to 500 K range, using frequencies from 100 Hz to 1 MHz. Some of the results at higher frequency, presented as an $\varepsilon''$ vs. $\varepsilon'$ plot (Fig. 41), could be fit by a Debye half-circle with center at ($\varepsilon'$=11,000, $\varepsilon''$=0). More of the results could be fitted (but not quite as accurately) by a Cole-Cole circular arc with center below the abscissa at ($\varepsilon'$=19,000, $\varepsilon''$=-3,000). Lower-frequency/higher-temperature points such as 500 K, 100 Hz did not fit close to either circular arc. Accordingly, the analysis and interpretation of these results are more difficult than for BCY. Some preliminary but fairly accurate results and conclusions can be reported at this time.
The analysis is similar to that for BCY except that to fit the 500 K, 100 Hz region data, it seems necessary to attribute a finite conductivity to the MgO blocking layers. This requires that the series RC circuit used to represent the BCY/MgO system must be supplemented by a resistor $r$ in parallel with the capacitor $C$. This is nothing but a Randles cell. This cell is a common cell model, and is also often the starting point for more complex cell models. This $rC$ parallel circuit represents the MgO layers, while $R$ represents the CGO sample. Both $r$ and $R$ are presumed to have thermally activated conduction, while $C$ is assumed to have no temperature dependence. None of the elements are assumed to have frequency dependence.
In this analysis, the admittance $Y$ in terms of the measurement results for $\varepsilon'$ and $\varepsilon''$ is still given by Eq. (1), but Eq. (2) for $Y$ in terms of circuit elements is replaced by

$$Y = \omega C [(\frac{R+r}{r^2} \omega C+\omega RC+j)/((1+R/r)^2+(\omega RC)^2)].$$

Eq. (3) for $\varepsilon''/\varepsilon'$ must be modified accordingly. From this analysis, the capacitance $C$ is $5.23 \times 10^{-9}$ F, corresponding to each MgO layer being 186 nm thick, compared to the 215 nm calculated from the BCY results. The resistance $r$ at 500 K is calculated to be 590,000 ohms. Multiplying this by the area $A=2.20 \times 10^{-5}$ m$^2$ and dividing by an assumed overall MgO thickness of 2 x 186 nm gives MgO resistivity of $3.50 \times 10^7$ ohm-m at 500 K.

It is not known why these layers had finite conductivity, whereas the MgO layers on the BCY had negligible conductivity. We suspect local flaws in the MgO layers, and not a difference in MgO bulk properties.

Resistance $R$ and resistivity $\rho$ values were calculated using Eqs. (1) and (8) for temperatures 425, 450, 475, and 500 K. The best-fit resistivity expression for these values found by assuming a single activation energy $E_a$ is $\rho = 3.3 \times 10^{-5} \exp(0.76 \text{ eV}/kT)$. This is a higher activation energy and lower pre-exponential value than found for BCY. However, the semilogarithmic plot of $R$ vs. $1/T$ could be interpreted as having a lower activation energy above 450 K, and a higher one below that temperature. Such a kink in the resistivity was found near 500 K by Coors and Readey for BCY, and can indicate a change in the dominant conduction mechanism.

An alternate method for calculating $\rho$ was also employed, consisting in using Eq. (5) but only in the high-frequency region for which the MgO impedance is low and its finite resistivity has little effect. The points for 400, 425, 450, 475, and 500 K fit a very
straight line on an Arrhenius plot, yielding $\rho = 2.8 \times 10^{-6} \exp(0.87 \text{ eV/kT})$ ohm-m. This $E_a$ is significantly higher than calculated for this sample by the previous method, but much lower than the 1.31 eV value found from the Solartron impedance measurement on a CGO sample with lower density. It is encouraging that all the CGO and CGO:La samples have pre-exponential factors in the same range.

More measurements on CGO extending to higher temperatures and lower frequencies are recommended, to determine whether there really is a change in activation energy as temperature changes. Such measurements would also shed more light on the conduction behavior of the MgO blocking layers.
Samples of CGO and BCY were synthesized, coated with MgO by Magnetron sputtering and gold layers deposited by vapor deposition. Under normal circumstances, the impedance spectroscopy would have measured the conductivity of the samples directly but in this case we tried modeling by constructing an equivalent circuit and substituting for dielectric permittivity in the capacitance. The activation energies and the pre-exponential factor were found using the Arrhenius expression. MgO has been found to be a good blocking layer for our samples. The set-up shown previously was designed for high pressure measurements but we settled for an ambient pressure design for cost and safety reasons. The low pressure set up has almost been completed barring the gold seals. We went about to synthesize SCY but ended up with traces of Cu and Fe. We would like to test these samples too as the metal element contribute to electronic conductivity.

Recommendations for Future Work

The samples need to be tested for permeation and impedance in actual conditions viz. at high temperature and in an atmosphere of hydrogen. The BCY synthesized is known to be the state of the art material in terms of conductivity but the problem associated with it is that it starts conducting oxide ions at higher temperatures, and electronic conductivity is made comparable with ionic conductivity by adding Ni. Ni
gets oxidized to form NiO, so we suggest that we run tests with Ag-SCY for two reasons. One is that SCY is more selective than BCY towards proton conduction at high temperatures. Second, Ag forms an oxide AgO which decomposes back to Ag and oxygen so there is no presence of oxide at operating conditions. To the best of our knowledge, Ag-SCY has not been evaluated in the literature.
REFERENCES