“New Cathode Materials for Intermediate Temperature Solid Oxide Fuel Cells”
Quarterly Report for 4/1/2005 to 9/30/2005

DE-FC26-03NT41960

Nov. 17, 2005

Allan J Jacobson
Center for Materials Chemistry
University of Houston
Houston, Texas 77204-5003

“This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.”
Abstract

Operation of SOFCs at intermediate temperatures (500 – 800 °C) requires new combinations of electrolyte and electrode materials that will provide both rapid ion transport across the electrolyte and electrode - electrolyte interfaces and efficient electrocatalysis of the oxygen reduction and fuel oxidation reactions. This project concentrates on materials and issues associated with cathode performance that are known to become limiting factors as the operating temperature is reduced.

The specific objectives of the proposed research are to develop cathode materials that meet the electrode performance targets of 1.0 W/cm² at 0.7 V in combination with YSZ at 700 °C and with GDC, LSGM or bismuth oxide based electrolytes at 600 °C. The performance targets imply an area specific resistance of ~0.5 Ωcm² for the total cell. The research strategy is to investigate both established classes of materials and new candidates as cathodes, to determine fundamental performance parameters such as bulk diffusion, surface reactivity and interfacial transfer, and to couple these parameters to performance in single cell tests.

In this report, the oxygen exchange kinetics of a P2 composition are described in detail. The oxygen exchange kinetics of the oxygen deficient double perovskite LnBaCo₂O₅₋δ (Ln=Pr and Nd) have been determined by electrical conductivity relaxation. The high electronic conductivity and rapid diffusion and surface exchange kinetics of PBCO suggest its application as cathode material in intermediate temperature solid oxide fuel cells.
1. List of Graphical Materials

Figure 1. The structure of PrBaCo$_2$O$_{5.5+x}$. The purple and gray spheres represent the barium and praseodymium cations, the square pyramidal coordination of cobalt ions is shown in blue, and the partially occupied oxygen ion sites as orange spheres.

Figure 2. Rietveld refinement of PrBaCo$_2$O$_{5.7}$ with cell parameters, a = 3.9084(1) Å, b = 3.9053(1) Å, c = 7.6343(2) Å.

Figure 3. Rietveld refinement of NdBaCo$_2$O$_{5.7}$ with cell parameters, a = 3.8057(1) Å, b = 3.9045(1) Å, c = 7.7893(3) Å.

Figure 4. Thermogravimetric analysis of LnBaCo$_2$O$_{5.5+x}$ (Ln = Pr, Nd).

Figure 5. The thermodynamic factors for PrBaCo$_2$O$_{5.5+x}$

Figure 6. The thermodynamic factors for NdBaCo$_2$O$_{5.5+x}$

Figure 7. Total conductivity of PrBaCo$_2$O$_{5.5+x}$ at 0.01 (♦) and 0.21 (▲) atm and NdBaCo$_2$O$_{5.5+x}$ at 0.01 (○, ●) and 0.21 atm (□, ■). The open and closed symbols correspond to measurements on increasing and decreasing temperature.

Figure 8. (a) The temperature dependence of the diffusion ($D_{chem}$) and surface exchange coefficients ($k_{chem}$). (b) The temperature dependence of the self-diffusion ($D_{O^2-}$) and surface exchange coefficients ($k_{ex}$) for LnBaCo$_2$O$_{5.5+x}$ (Ln = Pr, Nd). Open and closed symbols are PrBaCo$_2$O$_{5.5+δ}$ and NdBaCo$_2$O$_{5.5+δ}$, respectively.
2. Introduction

The objectives of the project are to discover new oxide cathode materials that meet a performance target of 1.0 W/cm\(^2\) at 0.7 V in combination with YSZ at 700 °C and with CGO, LSGM electrolytes at 600 °C. An ancillary objective of the project is to increase fundamental understanding of the intrinsic transport properties of mixed electronic ionic conducting oxides and oxide-oxide interfaces that can be used to accelerate further progress in the development of cost effective high performance solid oxide fuel cells. In Phase I, we are measuring the surface exchange rates, diffusion coefficients and interfacial transport for an initial set of perovskite related oxide materials. In Phase II we will synthesize and characterize new cathode materials and measure their kinetic parameters. The thermal and chemical compatibility with different electrolytes will be determined. Based on the results, a subset of the best materials will be selected for single cell tests. The phase III objectives are to evaluate the performance of the best materials identified in Phase I and II. The optimum electrode composition and microstructure will be determined and the longer term performance characteristics evaluated.

3. Executive Summary

The project began on October 1, 2003 and this is the seventh and eighth quarterly reports. In this report, the oxygen exchange kinetics of a P2 composition is described in detail. The oxygen exchange kinetics of the oxygen deficient double perovskite LnBaCo\(_2\)O\(_{5.5+x}\) (Ln = Pr and Nd) have been determined by electrical conductivity relaxation. LnBaCo\(_2\)O\(_{5.5+\delta}\) (Ln = Pr and Nd) were prepared by citric precursor method. The chemical oxygen diffusion coefficient (\(D_{\text{chem}}\)) and the surface exchange coefficient (\(k_{\text{chem}}\)) obtained by ECR were converted into the tracer diffusion coefficient (\(D_{\text{O}^{2-}}\)) and surface exchange coefficient (\(k_{\text{ex}}\)) with thermodynamic factors measured by TGA, in order to compare with the values obtained by isotope exchange and depth profiling. The high electronic conductivity and rapid diffusion and surface exchange kinetics of PrBaCo\(_2\)O\(_{5.5+x}\) suggest its application as cathode material in intermediate temperature solid oxide fuel cells.

4. Experimental

4.1 Synthesis of LnBaCo\(_2\)O\(_{5.5+x}\) (Ln = Pr and Nd)

LnBaCo\(_2\)O\(_{5.5+x}\) (Ln = Pr and Nd) has an oxygen-deficient double perovskite structure (Figure 1) with space group Pmmm. PrBaCo\(_2\)O\(_{5.5+x}\) (PBCO) powder was made using Pechini method.\(^1\) Stoichiometric amounts of praseodymium, barium and cobalt nitrates were dissolved in distilled water. Ethylene glycol and citric acid were added to the solution. The mixture was stirred at 150 °C until the solution began to foam and formed a dry resin. Further heating at 300 °C and then 600 °C for 24 h periods decomposed the dry foam containing residual organic components. The final mixture was pressed into a pellet in a 1-in diameter die followed by cold isostatic pressing (CIP). The pellet was sintered in air at 1100 °C for 12 h and then cooled down slowly in nitrogen. Finally, rectangular shape bars were cut for conductivity and ECR measurements. The pellet was shown to be single phase by powder X-ray diffraction and the cell parameters were determined by
Rietveld refinement using the GSAS program to be \( a = 3.9084(1) \, \text{Å}, \ b = 3.9052(1) \, \text{Å}, \) and \( c = 7.6343(1) \, \text{Å}. \)

4.2 Characterization of \( \text{LnBaCo}_2\text{O}_{5.5+x} \) (\( \text{Ln} = \text{Pr and Nd} \))

The structure of \( \text{PrBaCo}_2\text{O}_{5.5+x} \) is shown in Figure 1. X-ray powder diffraction measurements (Scintag XDS 2000) with Cu K\( \alpha \) radiation were performed to confirm the structure and its powder pattern was indexed by Rietveld refinement using GSAS program (Figure 2, 3). A scan rate of 0.125°/min was used with the range \( 5° \leq 2\theta \leq 90° \). A TA Instruments 2950 thermobalance was used to determine the equilibrium non-stoichiometry and thermodynamic factor (\( \Gamma \)) as a function of temperature and oxygen partial pressure within the range of \( 0.01 \leq p\text{O}_2 \leq 0.21 \, \text{atm} \) and \( 25 \leq T \leq 800 \, ^\circ\text{C} \).

![Figure 1. The structure of \( \text{PrBaCo}_2\text{O}_{5.5+x} \). The purple and gray spheres represent the barium and praseodymium cations, the square pyramidal coordination of cobalt ions is shown in blue, and the partially occupied oxygen ion sites as orange spheres.](image)
Figure 2. Rietveld refinement of PrBaCo$_2$O$_{5.7}$ with cell parameters, \(a = 3.9084(1) \text{ Å}, b = 3.9053(1) \text{ Å}, c = 7.6343(2) \text{ Å}\).

Figure 3. Rietveld refinement of NdBaCo$_2$O$_{5.7}$ with cell parameters, \(a = 3.8057(1) \text{ Å}, b = 3.9045(1) \text{ Å}, c = 7.7893(3) \text{ Å}\).

Thermogravimetric analysis (TGA) was used to determine the oxygen stoichiometry as function of \(pO_2\) in the temperature range relevant to the electrical conductivity relaxation experiments. The results are shown in Figure 4.
Figure 4. Thermogravimetric analysis of LnBaCo$_2$O$_{5.5+x}$ (Ln = Pr, Nd).

Figure 5. The thermodynamic factors for PrBaCo$_2$O$_{5.5+x}$.
Figure 6. The thermodynamic factors for NdBaCo$_2$O$_{5.5+x}$

Figure 5 and Figure 6 show the thermodynamic factors for PrBaCo$_2$O$_{5.5+x}$ and NdBaCo$_2$O$_{5.5+x}$, respectively. The thermodynamic factors were derived from the thermogravimetric data according to

$$\Gamma = \frac{\partial \ln a_O}{\partial \ln c_O} = \frac{1}{2} \frac{\partial \ln pO_2}{\partial \ln c_{O^2-}}$$

(1)

Table 1 summarizes the thermodynamic factors for LnBaCo$_2$O$_{5.5+x}$ (Ln = Pr, Nd). As the temperature increases, the values of the thermodynamic factor decrease. The values of the TDFs of NdBaCo$_2$O$_{5.5+x}$ are systematically smaller than those of PrBaCo$_2$O$_{5.5+x}$ over this temperature range.

<table>
<thead>
<tr>
<th>Temperature (ºC)</th>
<th>$\Gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PrBaCo$<em>2$O$</em>{5.5+x}$</td>
<td>NdBaCo$<em>2$O$</em>{5.5+x}$</td>
</tr>
<tr>
<td>288</td>
<td>193(26)</td>
</tr>
<tr>
<td>342</td>
<td>179(22)</td>
</tr>
<tr>
<td>397</td>
<td>162(19)</td>
</tr>
<tr>
<td>452</td>
<td>150(17)</td>
</tr>
<tr>
<td>650</td>
<td>116(10)</td>
</tr>
<tr>
<td>700</td>
<td>107(9)</td>
</tr>
</tbody>
</table>

4.3 DC Conductivity of LnBaCo$_2$O$_{5.5+x}$ (Ln = Pr and Nd)

The total conductivities were measured on rectangular bars of PrBaCo$_2$O$_{5.5+x}$ (1.3×0.19×0.15 cm) and NdBaCo$_2$O$_{5.5+x}$ (1.4×0.2×0.21 cm). Near ambient temperature,
the conductivities reach 600 Scm$^{-1}$ and 1000 Scm$^{-1}$ for the Pr and Nd compounds, respectively (Figure 7). As the temperature is increased, the conductivities begin to decrease at $\sim$150 °C due to the loss of oxygen atoms from the lattices and reduction of Co(IV) to Co(III). The data indicate that the onset temperature for oxygen loss is slightly lower for the Nd compound.

Figure 7. Total conductivity of PrBaCo$_2$O$_{5.5+x}$ at 0.01 (♦) and 0.21 (▲) atm and NdBaCo$_2$O$_{5.5+x}$ at 0.01 (○, ●) and 0.21 atm (□, ■). The open and closed symbols correspond to measurements on increasing and decreasing temperature.

4.4 ECR Studies of LnBaCo$_2$O$_{5+δ}$ (Ln = Pr and Nd)

The diffusion coefficients and surface exchange coefficients were measured for LnBaCo$_2$O$_{5.5+x}$ (Ln = Pr, Nd) by electrical conductivity relaxation (ECR). ECR was performed on the same sample as used for the DC conductivity measurements. The self-diffusion coefficients and surface exchange coefficients are shown in Figure 8. The values obtained for the chemical diffusion coefficient ($D_{chem}$) and surface exchange coefficient ($k_{chem}$) can be directly compared with those for the tracer diffusion and surface exchange coefficient, $D_O^{-1}$ and $k_{ex}$, obtained from $^{16}$O/$^{18}$O isotope exchange at the same temperature with $D_{chem} \approx D_O^{-1} \cdot \Gamma$ and $k_{chem} \approx k_{ex} \cdot \Gamma$, respectively.

The measured values are $D_0 = 3.7 \times 10^{-8}$ cm$^2$/s and $k_{ex} = 1.27 \times 10^{-6}$ cm/s in 1 % O$_2$ at 283 °C for PrBaCo$_2$O$_{5.5+δ}$. Both values of the self diffusion coefficient and the surface exchange coefficient of PrBaCo$_2$O$_{5.5+δ}$ are 2 times bigger than those of NdBaCo$_2$O$_{5.5+δ}$. 
5. Conclusions

The oxygen transport kinetics of the oxygen deficient double perovskite PrBaCo$_2$O$_{5.5+x}$ and NdBaCo$_2$O$_{5.5+x}$ dense ceramic bar were studied with the electrical conductivity relaxation (ECR) technique at lower temperature (300 ~ 500 °C). The
measured chemical diffusion coefficient \( (D_{chem}) \) and surface exchange coefficient \( (k_{ex}) \) are converted into the tracer diffusion and surface exchange coefficient, \( D_{O^2-} \) and \( k_{ex} \) with the thermodynamic factor obtained by thermogravimetric analysis. Both the values of self diffusion coefficient and surface exchange coefficient are remarkably high at such low temperature in comparison with other materials. Isotope exchange measurements are in progress to confirm the ECR results and a second set of samples have been sent to PNNL for electrode tests.

6. References


7. List of Acronyms and Abbreviations

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>CGO</td>
<td>Cerium Gadolinium Oxide</td>
</tr>
<tr>
<td>ECR</td>
<td>Electrical Conductivity Relaxation</td>
</tr>
<tr>
<td>EPMA</td>
<td>Electron Probe MicroAnalysis</td>
</tr>
<tr>
<td>GDC</td>
<td>Gadolinia Doped Ceria (see CGO)</td>
</tr>
<tr>
<td>LSGM</td>
<td>Lanthanum Strontium Magnesium Gallate</td>
</tr>
<tr>
<td>PLD</td>
<td>Pulsed Laser Deposition</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric Analysis</td>
</tr>
<tr>
<td>YSZ</td>
<td>Yttria Stabilized Zirconia</td>
</tr>
<tr>
<td>IEDP</td>
<td>Isotope Exchange and Depth Profiling</td>
</tr>
<tr>
<td>PBCO</td>
<td>Praesodymium Barium Cobalt Oxide</td>
</tr>
<tr>
<td>STO</td>
<td>Strontium Titanate</td>
</tr>
<tr>
<td>LAO</td>
<td>Lanthanum Aluminate</td>
</tr>
</tbody>
</table>

8. Milestones and Scope of Work

The project is divided into three phases that will overlap as shown in the timelines below

<table>
<thead>
<tr>
<th>Months</th>
<th>1-3</th>
<th>4-6</th>
<th>7-9</th>
<th>10-12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Year 1</td>
<td></td>
<td>Phase I</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Year 2</td>
<td></td>
<td>Phase II</td>
<td>Phase II</td>
<td></td>
</tr>
<tr>
<td>Year 3</td>
<td></td>
<td>Phase II</td>
<td>Phase III</td>
<td></td>
</tr>
</tbody>
</table>

Phase I: The Phase I objectives are to complete the characterization of a set of perovskite materials for which performance data already exists at PNNL. We will then measure the relevant kinetic parameters. The comparison the real performance data with the fundamental kinetic parameters will be used to guide materials selection in Phase II.

Phase II: The Phase II objectives of the project are to synthesize and characterize new cathode materials and to measure their kinetic parameters. The thermal and chemical compatibility with different electrolytes will be determined. Based on these results, a
subset of the best materials will be selected for single cell tests. Some additional compositions will be synthesized if indicated by the single cell test data.

Phase III: The phase three objectives are to evaluate the performance of the best materials identified in Phase I and II. The optimum electrode composition and microstructure will be determined and longer term performance characteristics evaluated.

**Updated Milestones for Years 1&2**

The updated milestones reflect two program adjustments since the original submission. The first is that we have started work on the K1 compositions ahead of the P1 compositions. The latter have been moved into the second half of the first year. The second is that in order to accelerate the thin film materials selection work we have decided to adopt a combinatorial approach which will permit the simultaneous synthesis of many compositions.

**PHASE I**

**Task 1.0**

Four modified perovskite oxide compositions (P1) selected by UH and PNNL will be synthesized and characterized by X-ray diffraction (XRD) and electron microprobe analysis (EMPA) (Months 6-9) **completed**

**Task 2.0**

The chemical compatibility with YSZ and CGO electrolytes will be determined (Months 6-9) **completed**

**Task 3.0**

The temperature dependence of the dc conductivity and stoichiometry will be determined in air for the P1 compositions. (Months 6-9) **in progress**

**Task 4.0**

The diffusion coefficients and surface exchange rates will be measured by electrical conductivity relaxation (Months 6-12) **in progress**

**Task 5.1**

Thin films of perovskite compositions will be synthesized by PLD using a combinatorial approach. (Months 3-9) **completed**

**Task 5.2**

Electrode-electrolyte interfaces will be characterized for thin films of cathode materials by AC impedance spectroscopy (Months 9-12) **in progress**

**Task 6.0**

Electrode-electrolyte interfaces will be characterized for thin films of cathode materials by IEDP (9-12) **in progress**

**PHASE II**

**Task 1.0**

Four modified perovskite oxide compositions (P2) will be synthesized and characterized by XRD and EMPA (Months 9-12) **completed**

**Task 1.1**

Two A$_2$BO$_4$ compositions (K1) will be synthesized and characterized by XRD and EMPA. (Months 1-4) **completed**

**Task 1.2**

Three additional A$_2$BO$_4$ compositions (K2) will be synthesized and characterized by XRD and EMPA. (Months 6-9) **completed**

**Task 2.0**

The chemical compatibility with YSZ, CGO and LSGM electrolytes will be determined for P2 (Month 12) **in progress**

**Task 2.1**

The chemical compatibility with YSZ, CGO and LSGM electrolytes will be determined for K1 (Month 7) **completed for YSZ and CGO**

**Task 2.2**

The chemical compatibility with YSZ, CGO and LSGM electrolytes will be determined for K2 (Month 9) **completed for YSZ and CGO**

**Task 3.0**

The dc conductivity and stoichiometry will be determined in air for the K1 compositions that have chemical compatibility. (Months 4-6) **completed**
<table>
<thead>
<tr>
<th>Task 4.0</th>
<th>The diffusion coefficients and surface exchange rates will be measured by electrical conductivity relaxation for the <strong>KI</strong> materials evaluated in Task 3 (Months 6-12). <strong>completed</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Task 4.1</td>
<td>K1 samples will be characterized in symmetric cells by AC impedance spectroscopy (Months 6-9) to confirm the measured values of $k_{ex}$. <strong>completed</strong></td>
</tr>
<tr>
<td>Task 5.0</td>
<td>Electrode-electrolyte interfaces will be characterized for thin films of cathode materials selected from Task 4.0 by AC impedance spectroscopy (Months 10-33).</td>
</tr>
<tr>
<td>Task 6.0</td>
<td>Electrode-electrolyte interfaces will be characterized for thin films of cathode materials selected from Task 4.0 by IEDP (Months 10-33) <strong>in progress</strong></td>
</tr>
<tr>
<td>Task 7.0</td>
<td>Results from Tasks 4.0, 5.0, and 6.0 will be used as they become available to select cathode electrolyte combinations for single cell tests (Months 10-33). <strong>in progress</strong></td>
</tr>
</tbody>
</table>