

“New Cathode Materials for Intermediate Temperature Solid Oxide Fuel Cells”  
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## 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/cm<sup>2</sup> 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 Ωcm<sup>2</sup> 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 LnBaCo<sub>2</sub>O<sub>5.5+δ</sub> (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.

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### 1. List of Graphical Materials

- 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.
- Figure 2. Rietveld refinement of  $\text{PrBaCo}_2\text{O}_{5.7}$  with cell parameters,  $a = 3.9084(1) \text{ \AA}$ ,  $b = 3.9053(1) \text{ \AA}$ ,  $c = 7.6343(2) \text{ \AA}$ .
- Figure 3. Rietveld refinement of  $\text{NdBaCo}_2\text{O}_{5.7}$  with cell parameters,  $a = 3.8057(1) \text{ \AA}$ ,  $b = 3.9045(1) \text{ \AA}$ ,  $c = 7.7893(3) \text{ \AA}$ .
- Figure 4. Thermogravimetric analysis of  $\text{LnBaCo}_2\text{O}_{5.5+x}$  (Ln = Pr, Nd).
- Figure 5. The thermodynamic factors for  $\text{PrBaCo}_2\text{O}_{5.5+x}$
- Figure 6. The thermodynamic factors for  $\text{NdBaCo}_2\text{O}_{5.5+x}$
- Figure 7. Total conductivity of  $\text{PrBaCo}_2\text{O}_{5.5+x}$  at 0.01 ( $\blacklozenge$ ) and 0.21 ( $\blacktriangle$ ) atm and  $\text{NdBaCo}_2\text{O}_{5.5+x}$  at 0.01 ( $\circ$ ,  $\bullet$ ) and 0.21 atm ( $\square$ ,  $\blacksquare$ ). 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  $\text{LnBaCo}_2\text{O}_{5.5+x}$  (Ln = Pr, Nd). Open and closed symbols are  $\text{PrBaCo}_2\text{O}_{5.5+\delta}$  and  $\text{NdBaCo}_2\text{O}_{5.5+\delta}$ , respectively.

## 2. Introduction

The objectives of the project are to discover new oxide cathode materials that meet a performance target of  $1.0 \text{ W/cm}^2$  at  $0.7 \text{ V}$  in combination with YSZ at  $700^\circ\text{C}$  and with CGO, LSGM electrolytes at  $600^\circ\text{C}$ . 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  $\text{LnBaCo}_2\text{O}_{5.5+x}$  ( $\text{Ln} = \text{Pr}$  and  $\text{Nd}$ ) have been determined by electrical conductivity relaxation.  $\text{LnBaCo}_2\text{O}_{5.5+\delta}$  ( $\text{Ln} = \text{Pr}$  and  $\text{Nd}$ ) were prepared by citric precursor method. The chemical oxygen diffusion coefficient ( $D_{chem}$ ) and the surface exchange coefficient ( $k_{chem}$ ) obtained by ECR were converted into the tracer diffusion coefficient ( $D_{O^{2-}}$ ) and surface exchange coefficient ( $k_{ex}$ ) 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  $\text{PrBaCo}_2\text{O}_{5.5+x}$  suggest its application as cathode material in intermediate temperature solid oxide fuel cells.

## 4. Experimental

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

$\text{LnBaCo}_2\text{O}_{5.5+x}$  ( $\text{Ln} = \text{Pr}$  and  $\text{Nd}$ ) has an oxygen-deficient double perovskite structure (Figure 1) with space group Pmmm.  $\text{PrBaCo}_2\text{O}_{5.5+x}$  (PBCO) powder was made using Pechini method.<sup>1</sup> 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  $150^\circ\text{C}$  until the solution began to foam and formed a dry resin. Further heating at  $300^\circ\text{C}$  and then  $600^\circ\text{C}$  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  $1100^\circ\text{C}$  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  $a = 3.9084(1) \text{ \AA}$ ,  $b = 3.9052(1) \text{ \AA}$ , and  $c = 7.6343(1) \text{ \AA}$ .

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

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  $\text{Cu K}\alpha$  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  $0.125^\circ/\text{min}$  was used with the range  $5^\circ \leq 2\theta \leq 90^\circ$ . 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  $25 \leq T \leq 800^\circ\text{C}$ .

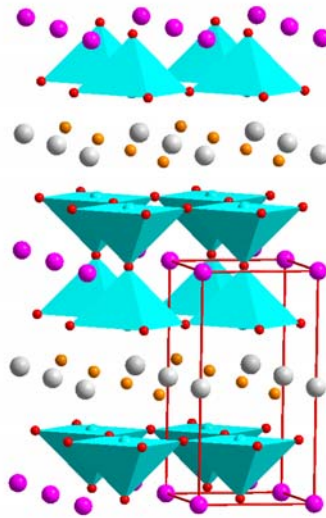


Figure 1. The structure of  $\text{PrBaCo}_2\text{O}_{5+x}$ . The purple and gray spheres represent the barium and praseodymium cations, the square pyramidal coordination of cobalt ions is shown in blue, and the partially occupied oxygen ion sites as orange spheres.

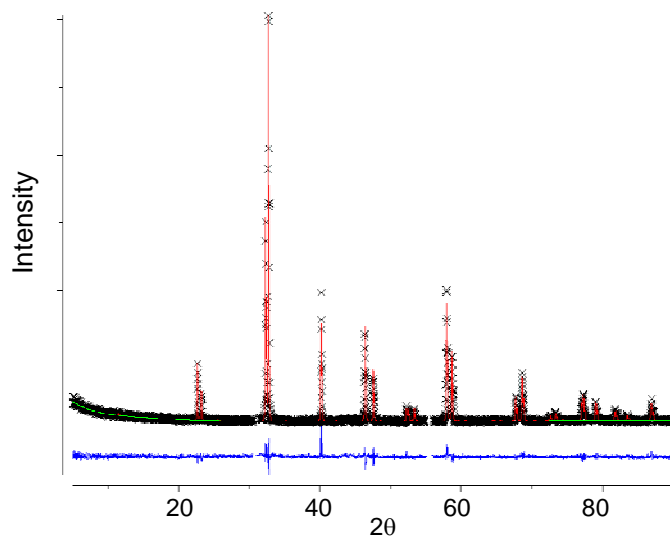


Figure 2. Rietveld refinement of  $\text{PrBaCo}_2\text{O}_{5.7}$  with cell parameters,  $a = 3.9084(1) \text{ \AA}$ ,  $b = 3.9053(1) \text{ \AA}$ ,  $c = 7.6343(2) \text{ \AA}$ .

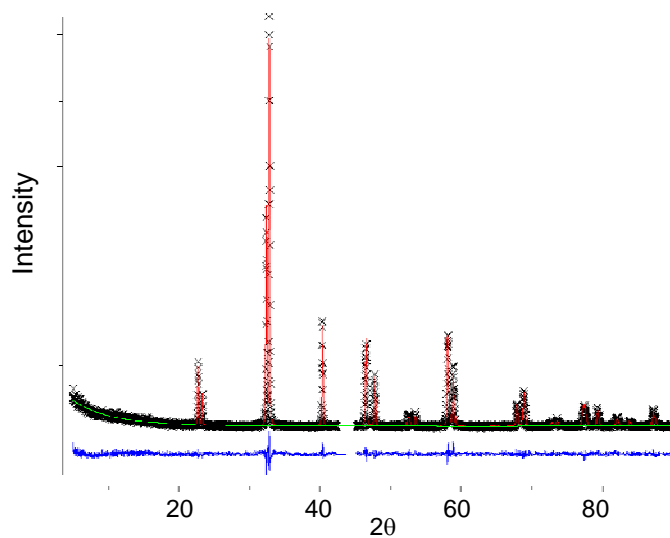


Figure 3. Rietveld refinement of  $\text{NdBaCo}_2\text{O}_{5.7}$  with cell parameters,  $a = 3.8057(1) \text{ \AA}$ ,  $b = 3.9045(1) \text{ \AA}$ ,  $c = 7.7893(3) \text{ \AA}$ .

Thermogravimetric analysis (TGA) was used to determine the oxygen stoichiometry as function of  $p\text{O}_2$  in the temperature range relevant to the electrical conductivity relaxation experiments. The results are shown in Figure 4.

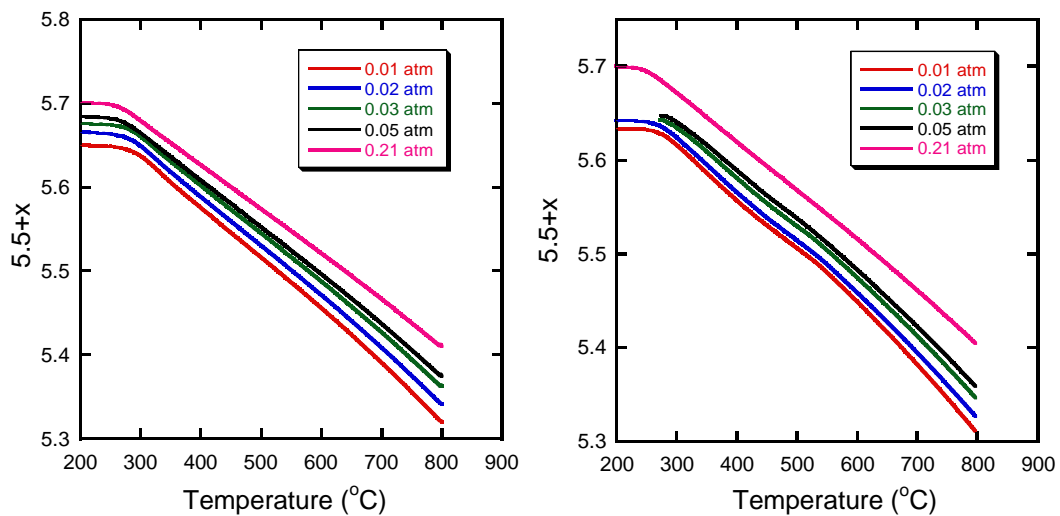


Figure 4. Thermogravimetric analysis of  $\text{LnBaCo}_2\text{O}_{5.5+x}$  ( $\text{Ln} = \text{Pr}, \text{Nd}$ ).

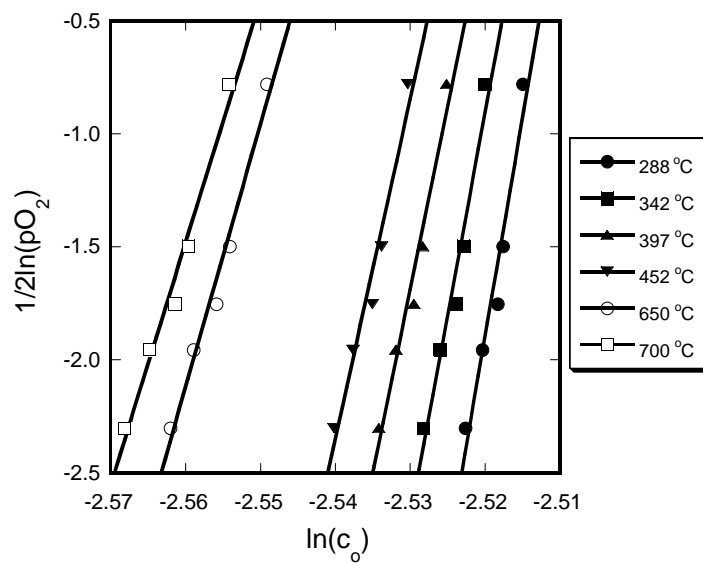


Figure 5. The thermodynamic factors for  $\text{PrBaCo}_2\text{O}_{5.5+x}$

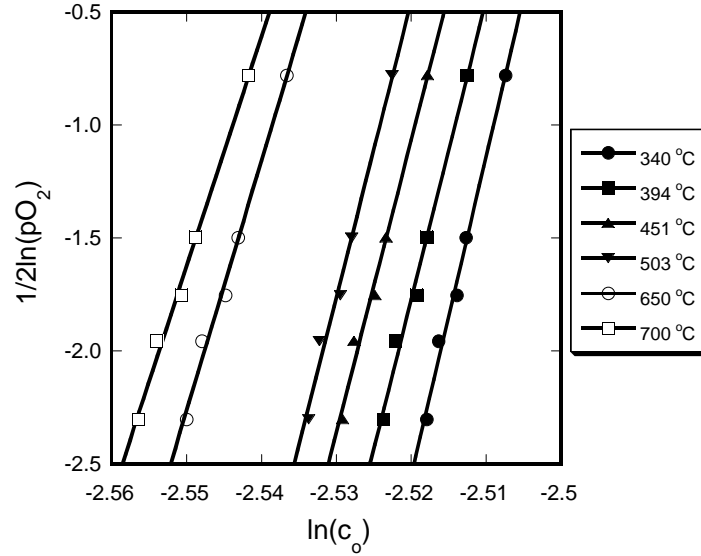


Figure 6. The thermodynamic factors for  $\text{NdBaCo}_2\text{O}_{5.5+x}$

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

$$\Gamma_O = \frac{\partial \ln a_O}{\partial \ln c_O} = \frac{1}{2} \frac{\partial \ln pO_2}{\partial \ln c_{O^{2-}}} \quad (1)$$

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

Table 1. Summary of the thermodynamic factors for  $\text{LnBaCo}_2\text{O}_{5.5+x}$  ( $\text{Ln} = \text{Pr}, \text{Nd}$ )

$\text{PrBaCo}_2\text{O}_{5.5+x}$		$\text{NdBaCo}_2\text{O}_{5.5+x}$	
Temperature (°C)	$\Gamma$	Temperature (°C)	$\Gamma$
288	193(26)	340	141(8)
342	179(22)	394	132(8)
397	162(19)	451	129(8)
452	150(17)	503	131(9)
650	116(10)	650	110(6)
700	107(9)	700	102(5)

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

The total conductivities were measured on rectangular bars of  $\text{PrBaCo}_2\text{O}_{5.5+x}$  ( $1.3 \times 0.19 \times 0.15$  cm) and  $\text{NdBaCo}_2\text{O}_{5.5+x}$  ( $1.4 \times 0.2 \times 0.21$  cm). Near ambient temperature,



the conductivities reach  $600 \text{ Scm}^{-1}$  and  $1000 \text{ Scm}^{-1}$  for the Pr and Nd compounds, respectively (Figure 7). As the temperature is increased, the conductivities begin to decrease at  $\sim 150^\circ\text{C}$  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.

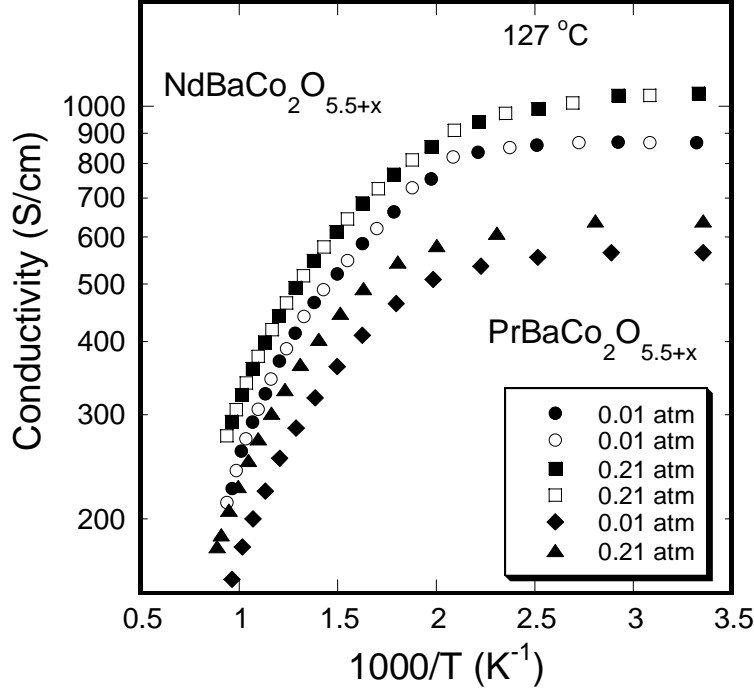


Figure 7. Total conductivity of  $\text{PrBaCo}_2\text{O}_{5.5+x}$  at 0.01 ( $\blacklozenge$ ) and 0.21 ( $\blacktriangle$ ) atm and  $\text{NdBaCo}_2\text{O}_{5.5+x}$  at 0.01 ( $\circ$ ,  $\bullet$ ) and 0.21 atm ( $\square$ ,  $\blacksquare$ ). The open and closed symbols correspond to measurements on increasing and decreasing temperature.

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

The diffusion coefficients and surface exchange coefficients were measured for  $\text{LnBaCo}_2\text{O}_{5.5+x}$  ( $\text{Ln} = \text{Pr}, \text{Nd}$ ) 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 ( $D_{\text{chem}}$ ) and surface exchange coefficient ( $k_{\text{chem}}$ ) can be directly compared with those for the tracer diffusion and surface exchange coefficient,  $D_{\text{O}^{2-}}$  and  $k_{\text{ex}}$ , obtained from  $^{16}\text{O}/^{18}\text{O}$  isotope exchange at the same temperature with  $D_{\text{chem}} \approx D_{\text{O}^{2-}} \cdot \Gamma_{\text{O}}$  and  $k_{\text{chem}} \approx k_{\text{ex}} \cdot \Gamma_{\text{O}}$ , respectively.

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

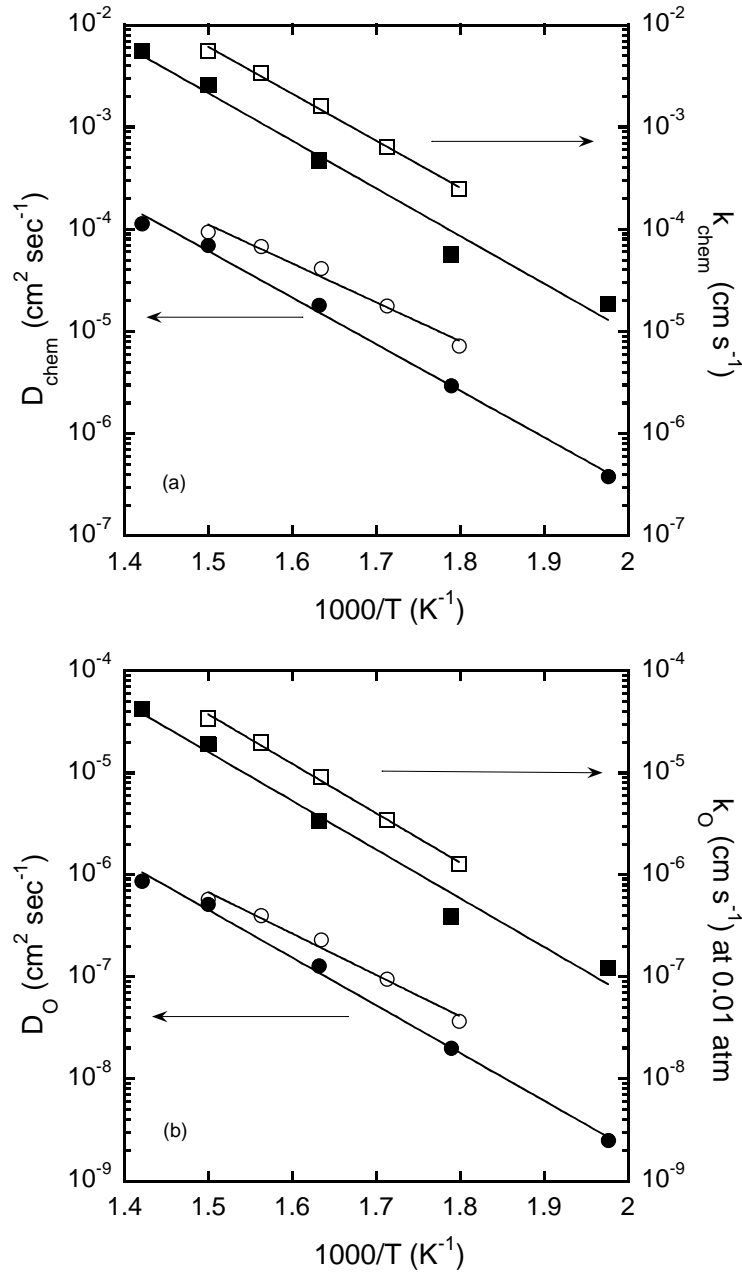


Figure 8 (a) The temperature dependence of the diffusion ( $D_{chem}$ ) and surface exchange coefficients ( $k_{chem}$ ). (b) The temperature dependence of the self-diffusion ( $D_O^{2-}$ ) and surface exchange coefficients ( $k_{ex}$ ) for  $LnBaCo_2O_{5.5+x}$  ( $Ln = Pr, Nd$ ). Open and closed symbols are  $PrBaCo_2O_{5.5+\delta}$  and  $NdBaCo_2O_{5.5+\delta}$ , respectively.

## 5. Conclusions

The oxygen transport kinetics of the oxygen deficient double perovskite  $PrBaCo_2O_{5.5+x}$  and  $NdBaCo_2O_{5.5+x}$  dense ceramic bar were studied with the electrical conductivity relaxation (ECR) technique at lower temperature ( $300 \sim 500$  °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

1. M. P. Pechini, US. Patent/3.330.697 (1967)

## 7. List of Acronyms and Abbreviations

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

## 8. Milestones and Scope of Work

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

Months	1-3	4-6	7-9	10-12
Year 1		Phase I		
Year 2		Phase II	Phase II	
Year 3		Phase II	Phase III	
		Phase III		

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  $A_2BO_4$  compositions (**K1**) will be synthesized and characterized by XRD and EMPA. (Months 1-4) **completed**
- Task 1.2 Three additional  $A_2BO_4$  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**

- Task 4.0 The diffusion coefficients and surface exchange rates will be measured by electrical conductivity relaxation for the **K1** materials evaluated in Task 3 (Months 6-12). **completed**
- Task 4.1 K1 samples will be characterized in symmetric cells by AC impedance spectroscopy (Months 6-9) to confirm the measured values of  $k_{ex}$ . **completed**
- Task 5.0 Electrode-electrolyte interfaces will be characterized for thin films of cathode materials selected from Task 4.0 by AC impedance spectroscopy (Months 10-33).
- Task 6.0 Electrode-electrolyte interfaces will be characterized for thin films of cathode materials selected from Task 4.0 by IEDP (Months 10-33) **in progress**
- Task 7.0 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). **in progress**