Enhanced Mixed Electronic-Ionic Conductors through Cation Ordering

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Final Report

This final report covers all of the previous progress reports submitted for the grant from September 1, 2009 until August 31, 2014.

Introduction

The performance of many energy conversion and storage devices depend on the properties of mixed ionic-electronic conducting (miec) materials. Mixed or ambipolar conductors simultaneously transport ions and electrons and provide the critical interface between chemical and electrical energy in devices such as fuel cells, ion transport membranes, and batteries. Enhancements in storage capacity, reversibility, power density and device lifetime all require new materials and a better understanding of the fundamentals of ambipolar conductivity and surface reactivity.

The high temperature properties of the ordered perovksites $AA'B_2O_{5+x}$, where A = rare earth ion, Y and B = Ba, Sr are being studied. The work is motivated by the high oxygen transport and surface exchange rates observed for members of this class of mixed ionic and electronic conductors.

The objectives of the work are to:

1. Understand how the cation and associated anion order lead to exceptional ionic and electronic transport properties and surface reactivity in $AA'B_2O_{5+x}$ perovskites;
2. Use this understanding to develop optimized A-site cation ordered perovskites for use in electrochemical devices;
3. Understand the effects of nanostructure and strain on structure and properties;
4. Develop fundamental understanding of defect chemistry, oxygen diffusion and surface exchange in $AA'B_2O_{5+x}$ perovskites and related defect mixed-metal oxides;
5. Investigate other promising materials, for example, $YBaMn_2O_{5+x}$.

A combined experimental and computational approach, including structural, electrochemical, and transport characterization and modeling is used. The approach attacks the problem simultaneously at global (e.g., neutron diffraction and impedance spectroscopy), local (e.g., pair distribution function, nuclear magnetic resonance) and molecular (ab initio thermokinetic modeling) length scales.

Accomplishments

1. We have extended measurements of the oxygen non-stoichiometry of $PrBaCo_2O_{5+x}$ and $NdBaCo_2O_{5+x}$ by Coulometric titration to cover more temperatures and to check reproducibility.

The details of the technique can be found elsewhere. [1] The oxygen non-stoichiometry change $\Delta\delta$ was recorded as a function of pO_2 at $10^{-6} \le pO_2 \le 0.21$ atm and at 675 to 900 °C at 25 °C intervals. The measurements have made twice for both $PrBaCo_2O_{5+x}$ and $NdBaCo_2O_{5+x}$ and have been normalized by the absolute oxygen stoichiometries determined by neutron diffraction.

The complete set of data that we have measured for $PrBaCo_2O_{5+x}$ is shown in Figure 1. Measurements were made on pumping oxygen out of the cell and then back in. As found for $NdBaCo_2O_{5+x}$, the data are characterized by a large hysteresis effect indicative of a first order phase transformation. In the intermediate regions the kinetics are extremely slow (days) and it was necessary to program the system

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[1] Yoo, J.; Jacobson, A. J., Proceedings Electrochemical Society *2002-26*(Solid-State Ionic Devices III), 354-363 (**2003**).

so that the same criterion for the attainment of equilibrium was used everywhere. As can be seen in Figure 1, the pO_2 values defining the hysteresis effect change with temperature. We now know from the neutron diffraction data on $PrBaCo_2O_{5+x}$ that the sample contains a small amount of CoO which was not detected in the X-ray diffraction pattern. The transformation between CoO and Co_3O_4 accounts for the discontinuity. From the magnitude of the change in the oxygen content, we calculate that the sample contains ~ 3% CoO. The amount present in $NdBaCo_2O_{5+x}$ is ~1.5%.

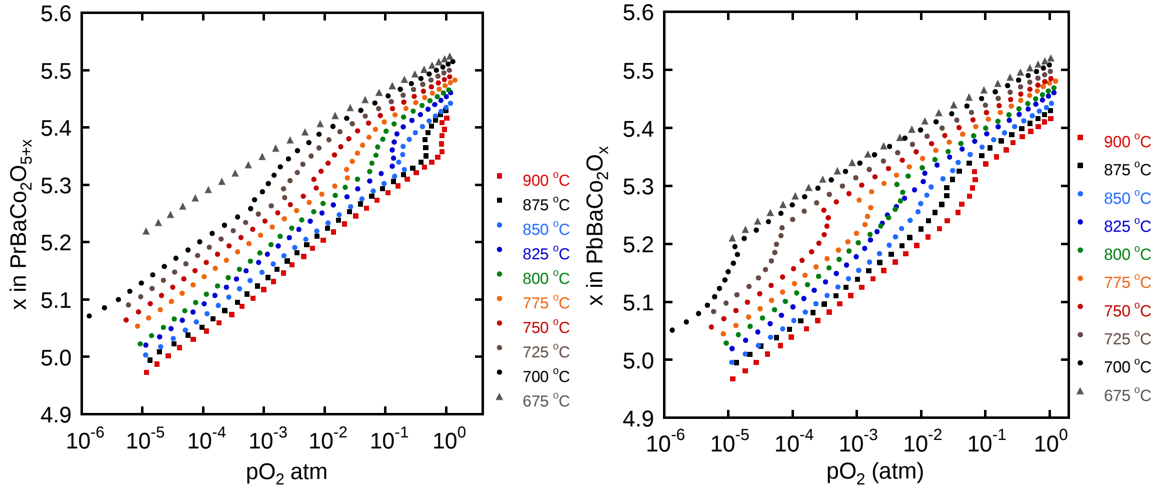

Figure 1: Absolute stoichiometry data for $PrBaCo_2O_{5+dx}$ under both oxidizing and reducing conditions.

2. **We have determined the oxygen non-stoichiometry in $PrBaCo_2O_{5+x}$ and $NdBaCo_2O_{5+x}$ as a function of temperature and oxygen partial pressure by neutron diffraction.** (in collaboration with Steven McIntosh (Lehigh), Rosemary Cox-Galhotra (Virginia Tech) Jason Hodges and Ashfia Huq (ORNL))

We made a series of neutron diffraction experiments in which patterns were obtained for $PrBaCo_2O_{5+x}$ and $NdBaCo_2O_{5+x}$ at SNS. Data were collected in flowing 0.01%, 0.1% 1% and 100% O_2 at temperatures of 550, 650, 750 and 825 °C. The data were processed by the Rietveld method using the GSAS program. Various structure models have been tested and used to determine the variations of the atom positions, the oxygen non stoichiometry and the lattice parameters.

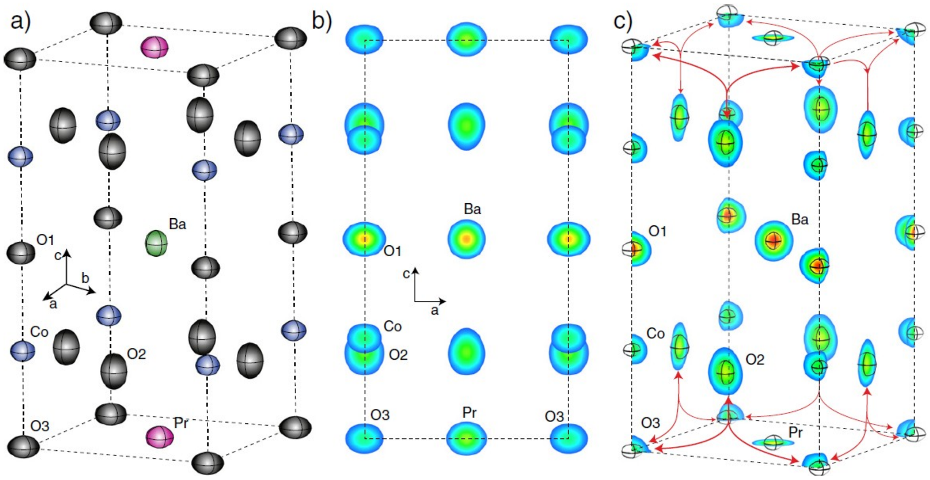

Figure 2: a) Crystal structure with thermal ellipsoids (50% probability), b) projected observed Fourier densitymap and c) composite of Fouriermap and thermal ellipsoids (20% probability) for $PrBaCo_2O_{5+x}$

(P4/mmm) at 10−1 atm oxygen and 573 °C. In b) the Co atom is in front of the O2 and red denotes high density. In c) the arrows indicating preferred oxygen transport pathways are as a guide to the eye only.

The results for $PrBaCo_2O_{5+x}$ have been published recently[2]. Representative results are shown in Figure 2.

3. **We have prepared two new series of compositions $PrBaCo_{2-x}Fe_xO_{6-\delta}$ (x = 0, 0.5, 1.0, 1.5 and 2) and $LnBaCoFeO_{6-\delta}$ (Ln = La, Pr, Nd, Sm, Eu and Gd).**

Somewhat surprisingly, the A cations are disordered in the $PrBaCoFeO_{5+\delta}$ (PBCF) system when synthesized in air at 1150 °C suggesting that the oxygen vacancy concentration is small and that system is more like $LaBaCo_2O_{5+x}$ in terms of oxygen stoichiometry. In agreement with this supposition, annealing in argon at 1150 °C leads to A site order. We have extended this work to include two new series of compounds $PrBaCo_{2-x}Fe_xO_{6-\delta}$ (x = 0, 0.5, 1.0, 1.5 and 2) and $LnBaCoFeO_{6-\delta}$ (Ln = La, Pr, Nd, Sm, Eu and Gd). The lattice constants for the $PrBaCo_{2-x}Fe_xO_{6-\delta}$ samples are shown in Table 1 showing the transition from ordered to disordered structure with increasing iron content.

Table 1: The lattice constants for the $PrBaCo_{2-x}Fe_xO_{6-\delta}$ phases

Compounds	**Crystal System**	**Space Group**	**Lattice constant (Å)**	**Volume/Z (Å^3)**
$PrBaCo_2O_{6-\delta}$	Tetragonal	P4/*mmm*	*a* = 3.9115(6), *c* = 7.683(6)	58.43
$PrBaCo_{1.5}Fe_{0.5}O_{6-\delta}$	Tetragonal	P4/*mmm*	*a* = 3.9113(4), *c* = 7.674(1)	58.70
$PrBaCoFeO_{6-\delta}$	Tetragonal	P4/*mmm*	*a* = 3.913(1), *c* = 7.720(3)	59.09
$PrBaCo_{0.5}Fe_{1.5}O_{6-\delta}$	Cubic	P*m*-3*m*	*a* = 3.9143(2)	59.97
$PrBaFe_2O_{6-\delta}$	Cubic	P*m*-3*m*	*a* = 3.9336(2)	60.86

Experimentally, it has proven very difficult to prepare samples with sufficiently high densities (>95%) for this series of samples for all except $PrBaCoFeO_{6-\delta}$. We have recently been successful and measurements continue.

In contrast we have been we have been successful at determining conditions for preparing dense samples of $LnBaCoFeO_{6-\delta}$ compounds and have made electrical conductivity relaxation (ECR) measurements on them as indicated in Table 2. We are in the process of finishing the data analysis, completing the thermogravimetric analysis measurements needed to determine the thermodynamic factor and measuring the thermal expansion coefficients. The data is complete and will be published in the near future.

Table 2: Status of the measurements for the $LnBaCoFeO_{6-\delta}$ phases

Compound	**Synthesis**	**Characterization**	**Densification**	**ECR**	**TGA**	**Dilatometry**
$LaBaCoFeO_{5+x}$	√	√	√	√	√	√
$PrBaCoFeO_{5+x}$	√	√	√	√	√	√
$SmBaCoFeO_{5+x}$	√	√	√	√	√	√
$GdBaCoFeO_{5+x}$	√	√	√	√	√	√

4. **Temperature dependence of the lattice constants of $PrBaCo_2O_{5+x}$ and $PrBaCoFeO_{5+x}$.**

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[2] Cox-Galhotra, R. A.; Huq, A.; Hodges, J. P.; Yu, C.; Wang, X.; Jacobson, A. J.; McIntosh, S. J. Solid State Ionics, 249-250), 34-40 (2013).

We discovered that, somewhat surprisingly, the A cations are disordered in the $PrBaCoFeO_{5+\delta}$ (PBCF) system when synthesized in air at 1150 °C suggesting that the oxygen vacancy concentration is small and that system is more like $LaBaCo_2O_{5+x}$ in terms of oxygen stoichiometry. In agreement with this supposition, annealing in argon at 1150 °C leads to A site order. The lattice constants for the $PrBaCo_2O_{5+x}$ and $PrBaCoFeO_{5+x}$ were determined for A site ordered samples from high temperature X-ray powder diffraction data (Fig. 3).

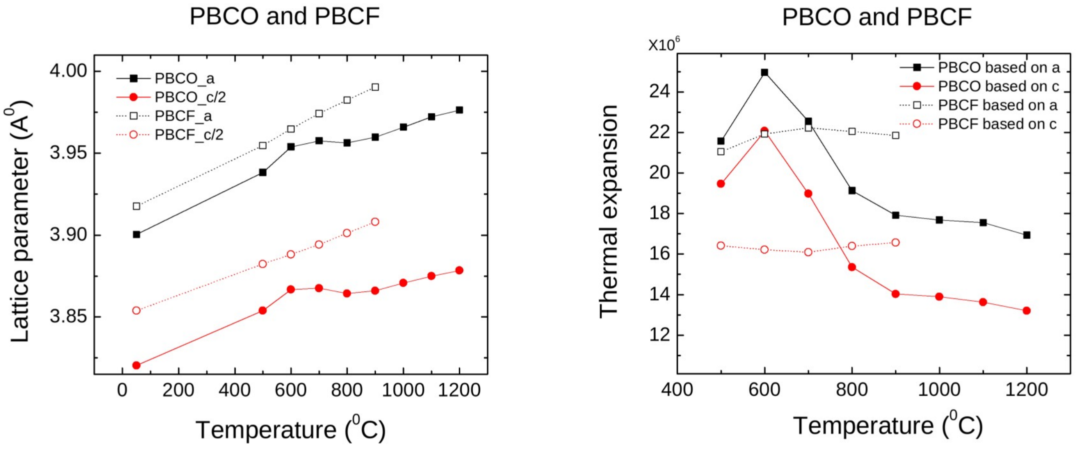

Figure 3: Temperature dependence of the lattice parameters and thermal expansion of $PrBaCo_2O_{5+x}$ and $PrBaCoFeO_{5+\delta}$ on heating in air.

For PBCO, the high temperature TEC results are consistent with the dilatometer data and we now believe that the anomaly at ~600 °C is due to the phase boundary. No such anomaly is present in the data for PBCF indicating that the introduction of Fe suppresses the phase transformation.

5. Enhanced performance of $La_{0.5}Sr_{0.5}CoO_{3-x}$ electrodes by using nanostructured inter-layers prepared by pulsed laser deposition. (in collaboration with Haiyan Wang and Qing Su (TAMU))

In earlier work, we have shown that nano-crystalline $La_{0.5}Sr_{0.5}CoO_{3-x}$ (LSCO) thin films deposited on a polycrystalline CGO substrate using pulsed laser deposition (PLD) can have very low resistances. At 600 ^oC, in air, the area specific resistance (ASR) of a LSCO thin film with a thickness of ~400 nm was ~0.06 Ω cm^2. We extended this work to bilayer structures that combine a thick screen printed layer of LSCO to provide in-plane electrical conductivity and an intermediate nanoporous LSCO layer prepared by PLD. Symmetric cells on CGO were investigated by AC impedance at 500 to 700 °C and at oxygen partial pressures of 0.01, 0.1 and 1 atm. We demonstrated that the 100 nm PLD interlayer at 750 °C and pO_2 = 1.0 atm decreases the ASR by 50% compared to the reference sample without any interlayer. Increasing the PLD interlayer thickness to 500 nm further improves the performance by an additional 40% under the same conditions. We have completed the analysis of these data and the work has been published in J. Electrochem Soc.[3]

6. We have measured the surface exchange rate and diffusion coefficient for $Sr_3YCo_4O_{10.5}$ using electrical conductivity relaxation (ECR)

The compound $Sr_3YCo_4O_{10.5}$ crystallizes in the tetragonal space group *I4/mmm* with lattice parameters *a* = 7.62389(1) Å, *c* = 15.32701(5) **Å.** The structure of $Sr_3YCo_4O_{10.5}$ (Figure 4) consists of layers of tilted CoO_6 octahedra that alternate with oxygen-deficient layers containing the Co atoms in tetrahedra. The oxygen atoms in the oxygen-deficient layers are partially disordered in the structure model with the O4 atom

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[3] Q. Su, W. Gong, D. Yoon, C. Jacob,.Q. Jia,.A. Manthiram, A J. Jacobson, and H. Wang, *J. Electrochem. Soc.*, **161** (4) F1-F8 (2014)

distributed over four closely situated sites with a site occupancy factor of 0.25. The oxygen diffusion in this compound has been determined previously by Isotope Exchange Depth Profiling combined with SIMS (IEDP/SIMS), and Molecular Dynamics calculations (MD). We have used the ECR technique for comparison.

Dense pellets of the $Sr_3YCo_4O_{10.5}$ were prepared by cold isostatically pressing at 30 kpsi with subsequent sintering at 1160 °C for 4 h. with heating and cooling rates of 1°C/min. The density of the pellets was measured by the Archimedes technique and was greater than 95%. For ECR measurements, a bar with dimensions t = 1.43 mm, w = 1.09 mm and l = 19.72 mm was cut and polished to decrease the effect of surface morphology on oxygen diffusion. Oxygen diffusion was investigated with ECR in the temperature range 650 – 900 °C by following switches of oxygen partial pressure: 2% ↔ 5%, 10% ↔ 20%, 10% ↔ 75% .Values of chemical oxygen diffusion and chemical surface exchange were obtained after the fitting of all profiles (relative conductivity vs. time).   Activation energies for D_{chem} and k_{chem} are 1.16 ± 0.01 eV and 0.76 ± 0.05 eV, respectively. Values of chemical oxygen diffusion do not depend on the initial and final oxygen partial pressures and depend only on the temperature, which is in good agreement with the model, describing oxygen diffusion in bulk material.

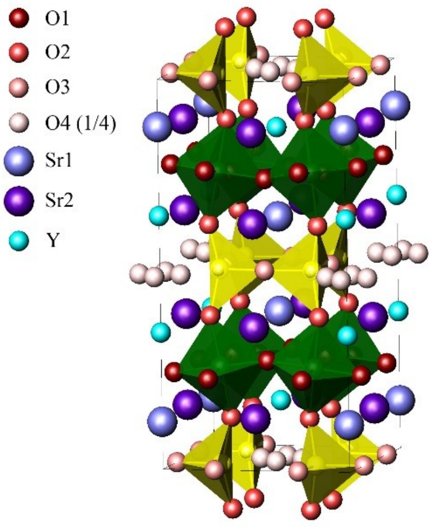

Figure 4: The crystal structure of Sr3YCo4O10.5 with alternating CoO6 and CoO4 layers.

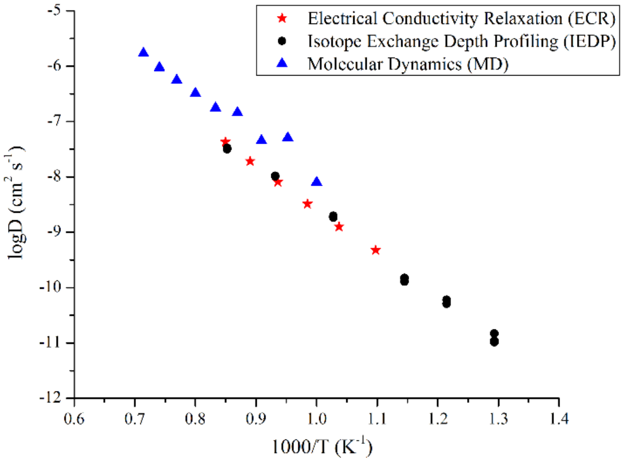

Figure 5: Comparison of oxygen diffusion in Sr3YCo4O10.5 obtained by ECR, IEDP/SIMS and MD.

To compare the results of oxygen diffusion determined by ECR technique with the results of Isotope Exchange Depth Profiling it is necessary to know how the oxygen content in the sample changes with the change of temperature and oxygen partial pressure in surroundings, the so called thermodynamic factor. Thermogravimetric analysis was performed at different oxygen partial pressures in the temperature range 25-900°C to determine this. The thermodynamic factor, ½ $d\mathit{ln}(pO_2)/d\mathit{ln}(C_O)$, 611 at 650°C to 177 at 900°C where C_O is the concentration of oxygen in $Sr_3YCo_4O_{10.5}$. The corrected data obtained by ECR is compared with the results from IEDP and MD in Figure 5. Very good agreement is observed between the different methods. The activation energy obtained from the MD experiment is 1.56 eV. The slightly higher values of oxygen diffusion predicted by the MD can be explained by the ideal conditions and some assumptions during the modelling experiment. This work has been pulished in Solid State Ionics.

7. Oxygen Uptake and Release by the Double Perovskite $YBaMn_2O_6$.

Non stoichiometric oxides which rapidly and reversibly release and take-up oxygen molecules are of interest as oxygen storage materials for use in a variety of hydrocarbon and small molecule oxidation reactions. The most well-known example is CeO_{2-x} which is used in three way catalysts in car exhausts. Recently the double perovskite oxide, $YBaMn_2O_6$, has been shown to store and release a significant amount of oxygen (~3.85%) at moderate temperatures (350 -750 °C). X-ray diffraction measurements have indicated that three phases are formed in the $YBaMn_2O_x$ system with x = 5.0, 5.5, and 6.0. The oxygen uptake and release kinetic behavior have been studied but nothing is known concerning the thermodynamics and reversibility under near equilibrium conditions. We have investigated non-stoichiometric behavior of $YBaMn_2O_x$ in sealed electrochemical cells using the technique described previously by us for other double perovskites. A representative set of data obtained on reduction at 650 °C are shown in Figure 6. The sample was prepared initially with a composition $YBaMn_2O_5$ by the method reported in the literature and then oxidized to the composition O_6 before beginning the reduction. As expected, the compound shows three well defined phases, two with narrow ranges of non-stoichiometry (5.0 and 5.5) and one with a broader range from 5.95 to 5.83 at 650 °C, separated by two phase regions. The results obtained at 850 °C are different. The experiment began with oxidation from the composition with x=5 and followed the same general pattern with the plateaus shifted to higher values of pO_2 as expected. The reduction reaction, however, which is reversible at 650 °C is not reversible at the higher temperature. We interpret this as due to the instability of the compound at high pO_2 and temperature with respect to phase separation to $BaMnO_{3-x}$ and $YMnO_3$. At lower temperature, the kinetics of this phase separation are slow compared to the measurement time and the system behaves reversibly. This is consistent with the initial synthesis of the starting materials where reducing conditions are reported to be needed to obtain a single phase. Tis work has been published in Journal of Solid State Chemistry.

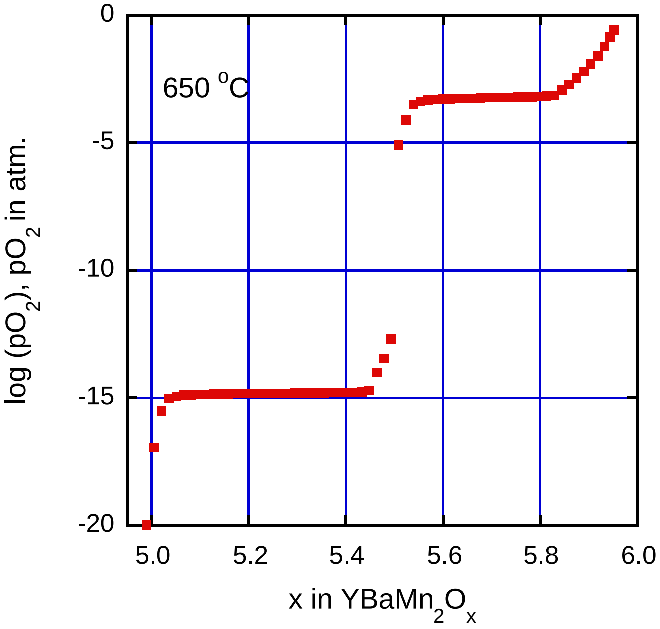

Figure 6: Non-stoichiometry data for $YBaMn_2O_{5+x}$ showing the presence of three distinct phases.

8. Development of novel descriptors for SOFC cathode activity

We have used ab initio methods to find descriptors that can predict SOFC cathode performance. We showed that area specific resistance (ASR) and oxygen exchange rates (k*) are correlated with ab initio calculated oxygen p-band centers and oxygen vacancy energies in mixed electronic-ionic conducting perovskites. These results represent the first time it has been shown that ab initio methods can directly predict SOFC cathode performance and the first identification of a fundamental materials property descriptor for SOFC cathodes. These results open the door to practical ab initio based design of SOFC cathodes. The work has been published in *Energy and Environmental Science.* [4]

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[4] Lee, Y.-L.; Kleis, J.; Rossmeisl, J.; Shao-Horn, Y.; Morgan, D., Prediction of solid oxide fuel cell cathode activity with first-principles descriptors. *Energy & Environmental Science* **2011,** *4* (10), 3966.

9. First principle calculations of oxygen formation and migration energies in $ReBaCo_2O_{5.5}$

Erman Erdogan, Allan J. Jacobson, Yueh-Lin Lee, Guangfu Luo, Anh T. Ngo, Dane Morgan

In order to better understand how cation type influences cation-ordered perovskite performance, we have studied the formation and migrations energies of oxygen vacancies in $ReBaCo_2O_{5.5}$ (Re = La, Pr, Sm, Gd, Y) by first principles calculations based on density functional theory (see Figure 7). We have carefully treated the Hubbard U correction and used the U-ramping scheme to locate the true ground states. We have also performed cell size tests to make sure the finite size supercell interactions play only a minor role. These calculations are still underway as part of a revision to the submitted manuscript. Overall the results show a strong tendency for nearly two-dimensional diffusion and minor anisotropy within the plane, consistent with previous studies. Furthermore, the results show that oxygen vacancy and migration energies vary monotonically with the size of the Re cation. Barriers were determined by the climbing nudged elastic band method and then validated for $PrBaCo_2O_{5.5}$ with *ab-initio* molecular dynamics. Our results are in good agreement with the experimental data that have been reported in the literature and will aid in understanding the oxygen diffusion in double perovskites. The manuscript of this work is presently under peer review.

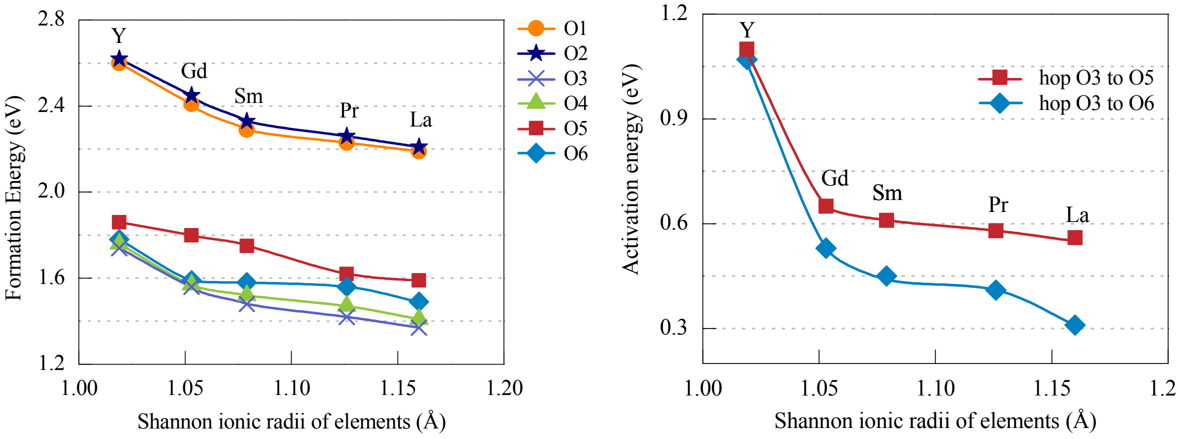

Figure 7: Oxygen vacancy formation energies (left) at six distinct sites and activation barriers (right) of two rate limiting paths for $ReBaCo_2O_{5.5}$ (Re = Y, Gd, Sm, Pr, and La).

10. Cation ordering tendencies in perovskites of type $A_{0.5}A'_{0.5}BO_3$

Milind Gadre, Anh Ngo, Tam Mayeshiba, Dane Morgan

Using High-throughput computation with density functional theory with a Hubbard U correction (DFT+U) calculations, we have investigated the role of A- and B-site cations on structural ordering tendency of A-site cations in Perovskite structures of the type $A_{0.5}A'_{0.5}BO_3$. For a range of pervoskites of the type $A_{0.5}A'_{0.5}BO_3$ (where A=Y, Sc, La, Ce, Pr, Nd, Pm, Sm; A'= Sr, Ba; and B= Fe, Co, Mn, Ni), we calculate the cohesive energy of A-site ordered and disordered structures using DFT. Various disordered structures for the A-sublattice are generated using the Special Quasi-random Structures approximation as implemented in the ATAT software[5]. We then calculate the difference between the cohesive energy of the average of three disordered structures and the layered/ordered structure as $<E_{disordered}>-E_{ordered}$, and take this to be the tendency for the material to disorder on the A-sublattice. In other words, a negative value on the plots of Figure 8 implies the material has a tendency to disorder on the A-sublattice. We observe that, for the range of materials studied, the Sr generally shows stronger ordering than Ba. This

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[5] A. van de Walle, M. Asta, and G. Ceder, The Alloy Theoretic Automated Toolkit: A user guide, Calphad-Computer Coupling of Phase Diagrams and Thermochemistry 26, p. 539-553 (2002).

result is of interest for developing cation ordered materials with enhanced transport properties for solid-state electrochemical devices, e.g. Solid Oxide Fuel cells.

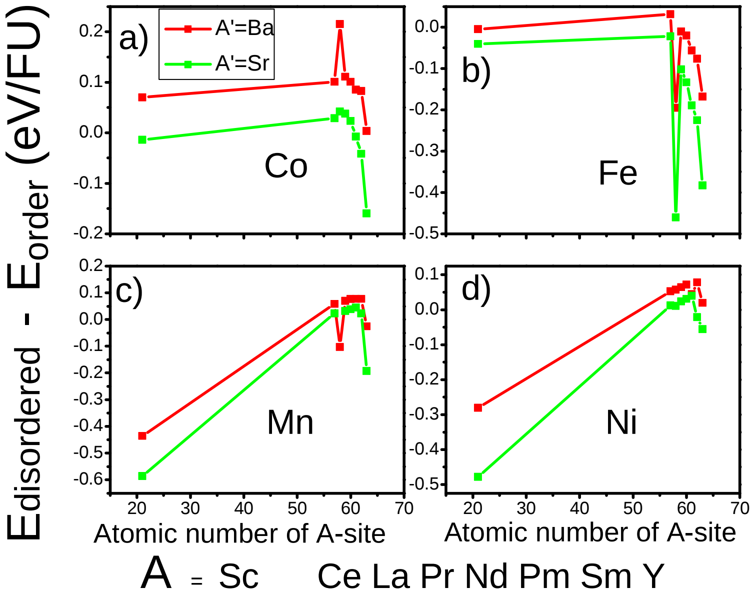

Figure 8: Energetics of $A_{0.5}A'_{0.5}BO_3$ with B= Co, Fe, Mn and Ni, as a function of A-site atomic numbers. Green data points are for A'=Sr and red for A'=Ba. We observe that the disorder on A-sublattice is significantly favored when replacing A'=Sr by A'=Ba.

11. Mechanisms for oxygen surface exchange at the solid oxide fuel cell cathodes: a case study on the surface of $La_{1-x}Sr_xCoO_{3-\delta}$

Milind Gadre, Anh Ngo, Stuart Adler, Dane Morgan

The exchange kinetics of oxygen between gas phase and solid cathode materials plays a significant role in the performance of the solid oxide fuel cells (SOFC). The relevant chemical reaction, or oxygen reduction reaction (ORR) involves a gaseous oxygen molecule (O_2) being adsorbed on the surface of the cathode that combines with 2 electrons to incorporate as an O^{2-} in the bulk cathode. In this work we use ab-initio methods to study the detailed mechanisms of ORR on the cathode material $La_{1-x}Sr_xCoO_{3-\delta}$ (LSC). We estimate the attempt frequencies, and calculate from DFT the energetics of all stable intermediates and transition-states of the oxygen reduction reaction. We comprehensively explore all possible mechanisms for ORR on CoO_2-terminated LSC materials of varying Sr concentrations to single out a possible mechanism that involves the following features: 1) physisorption of oxygen molecule at a surface Co that has a nearby oxygen divacancy, 2) dissociation into the divacancy, followed by 3) fast oxygen incorporation. We calculate the surface isotope-exchange coefficients, k_{tr}, based on the defect chemistry, electronic structure and the non-equilibrium thermodynamic quantities according to the framework developed by Adler et al.[6]. Figure 9(a) shows the calculated rates of each reaction-step of six different mechanisms (denoted M_1 through M_6). The rate coefficients k_{tr} of individual reaction steps are calculated, assuming the reaction-step under consideration is a rate-limiting step. The reaction step with the smallest rates coefficient (k_{tr}) in a given mechanism is then the true rate-limiting step of that mechanism, and would control the rate of the mechanism.

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[6] Adler, S. B.; Chen, X. Y.; Wilson, J. R., Journal of Catalysis 2007, 245, 91-109.

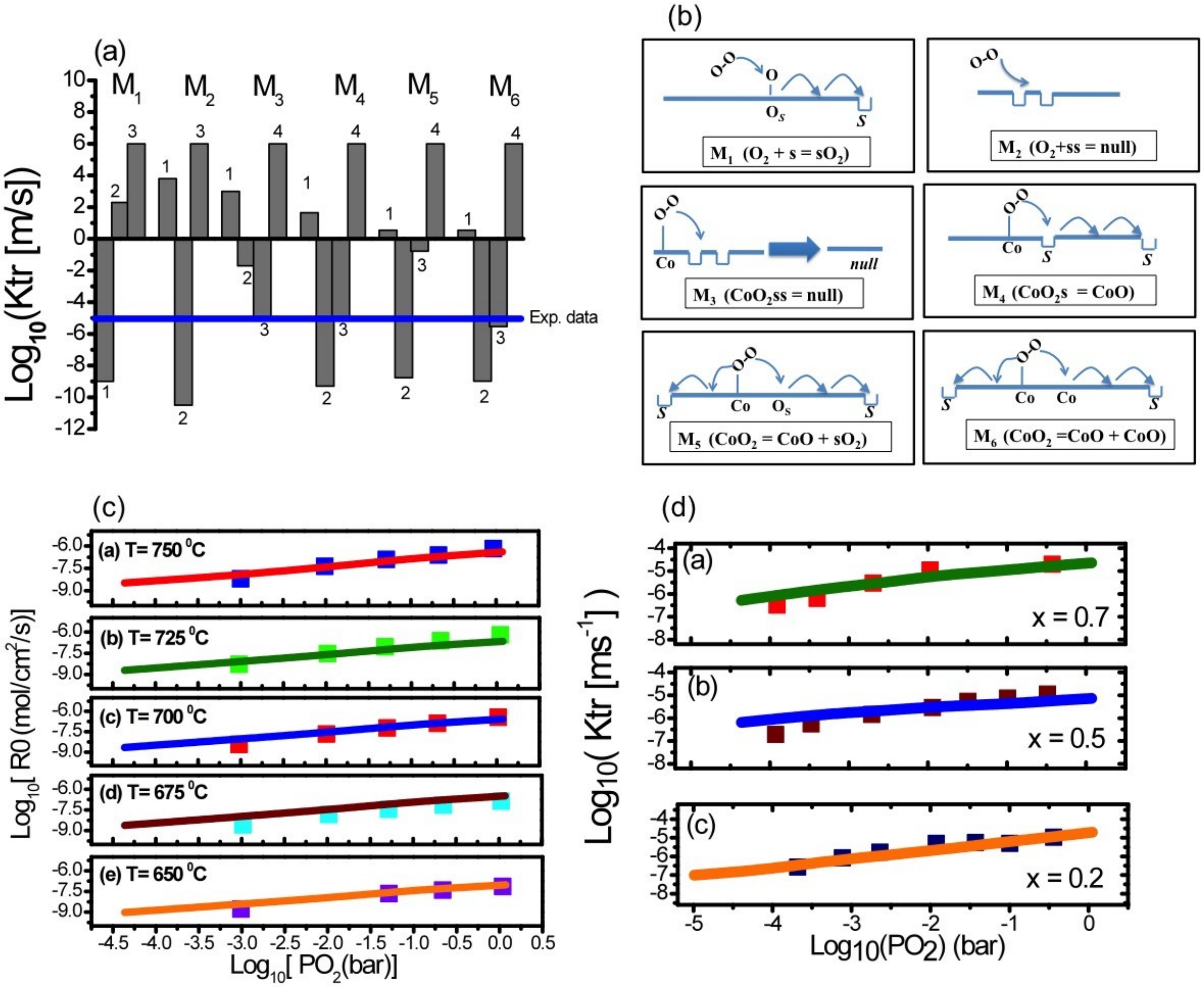

Figure 9: (a) Comparison of overall exchange rate coefficients (k_{tr}) for six different mechanisms as estimated at 1073 K and pO_2=0.2 atm. Rates of individual reaction steps of each mechanism are as denoted by the grey bars. Blue horizontal line is the experimental k_{tr} data from van der Haar et al.[7] (b) Schematic of various oxygen reduction reaction mechanisms M_1 through M_6 on the CoO_2 surface of LSC. Rate limiting steps predicted for each mechanism in this study are written in parenthesis. Symbols have the following meanings: O-O denotes gaseous O_2, Co denotes surface Co cation, *S* is a surface oxygen vacancy, *SS* is a divacancy, O_S is surface oxygen. (c) pO_2 dependence of log(R_0) for the Mechanism 3 (physisorption near oxygen divacancy followed by dissociation) at different temperatures varying from 650-750°C. R_0 is the surface exchange rate expressed in cm^2/s. Squares are experimental data from Lu et al.[8] (d) pO_2 dependence of the oxygen surface exchange coefficient (k_{tr} (ms^{-1}), in log scale) for varying x(Sr) in $La_{1-x}Sr_xCoO_{3-\delta}$ (x=0.2, 0.5, 0.7). Squares are experimental values from van der Haar et al.

We see that except for the slowest step of M_3, all other mechanisms have at least one step that is orders of magnitude slower than the observed oxygen exchange rate (k_{tr}, from van der Haar et al.). Hence we predict that the mechanism that involves physisorption of O_2 near an oxygen divacancy, followed by

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[7] van der Haar, L. M.; den Otter, M. W.; Morskate, M.; Bouwmeester, H. J. M.; Verweij, H.Journal of The Electrochemical Society 2002, 149, J41-J46

[8] Lu, Y.; Kreller, C.; Adler, S. B. Journal of The Electrochemical Society 2009, 156, B513-B525.

dissociation, is the most likely candidate of oxygen surface exchange over CoO_2-terminated LSC cathode. Our results also show robust agreements of the exhange rates (R_0) with experimental data in terms of pO_2 dependence and temperature dependence, (Figure 9(c)). These results for k_{tr}, are also in good agreement with the experimental data from van der Haar et al.[9] for $La_{1-x}Sr_xCoO_{3-\delta}$ for a range of Sr-concentrations, as shown in Figure 9(d).

Our results demonstrate the ability to make semi-quantitative prediction of surface exchange rates for SOFC cathodes. Our approach and findings will further aid in molecular understanding of the surface exchange of oxygen for other perovskite cathode materials, crucial to the design of better cathodes. A paper on this work is in preparation.

12. Synthesis and evaluation of the conductivity of $LaBaIn_2O_{5.5}$

The objective is to study the use of $LaBaIn_2O_{5.5}$ as an electrolyte with double perovskite oxide electrodes and to determine whether the similar structures and compositions of the components will result in low interfacial resistances. The ionic conductivity of $LaBaIn_2O_{5.5}$ was first reported by Kakinuma et al. [10] and has been re-measured for a sample prepared by a conventional ceramic method and sintered at 1300 °C. The X-ray data and conductivity agree well with previous reports. The A site cations are disordered. The thermal expansion coefficient was measured in air by dilatometry and found to be 14×10^{-6} K^{-1} up to 1000 °C, a good match with high performance electrode materials. The ionic conductivity of this compound is 0.042 Scm^{-1} at 800 °C and 0.15 Scm^{-1} at 1000 °C and is higher than YSZ and only slightly lower than CGO and LSGM (see Fig. 10). We have made ac impedance measurements on symmetric cells of $PrBaCo_2O_{5+x}$/$LaBaIn_2O_{5.5}$/ $PrBaCo_2O_{5+x}$ using screen printed electrodes. In air, at 600 °C the electrode resistance was 0.5 cm higher than values obtained on CGO. Further studies of other electrode compositions are in progress.

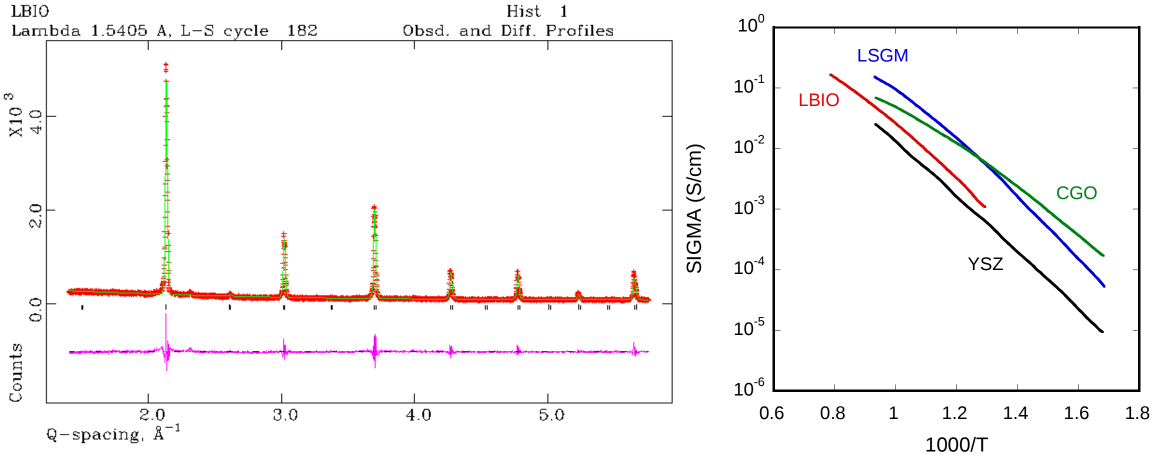

Figure 10: The cubic structure of $LaBaIn_2O_{5.5}$ (a = 4.1581(3)Å) and a comparison of its ionic conductivity with other electrolytes.

13 Combined theoretical and experimental study of the Hydrated $Ba_2In_2O_5$ fuel cell electrolyte

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[9] van der Haar, L. M.; den Otter, M. W.; Morskate, M.; Bouwmeester, H. J. M.; Verweij, H.Journal of The Electrochemical Society 2002, 149, J41-J46.

[10] Kakinuma, K.; Takahashi, N.; Yamamura, H.; Nomura, K.; Atake, T. *Solid State Ionics* **2004**, *168*, 69–74.

[1]Stony Brook University, and the [2]Universities of Cambridge and [3]Wisconsin, Madison

Work focused on an understanding of the structures formed on hydrating potential solid-state electrolytes for intermediate temperature SOFCs.

In apparent contrast to the known crystal structure where only 2 crystallographic sites are observed,[11] three distinct ^1H resonances are observed in the ^1H MAS NMR of $Ba_2In_2O_5.H_2O$, prepared by hydrating the $Ba_2In_2O_5$ at below 250 °C. On heating to above 100 °C, coalescence of the three resonances is observed, indicating the onset of proton motion with a rate that is greater than the frequency separation of the three resonances, 1KHz for the 1.7-3.3 ppm shifts and 3.3KHz for the 7.3-2.5 ppm shifts.

DFT calculations have been performed on a series of proton configurations generated from the neutron-derived crystal structure by considering the various local environments generated from the partially occupied O2 sites. The energies of the different configurations were determined, the lowest energy configurations being used as input for the CASTEP (GIPAW) code to calculate the corresponding ^1H chemical shifts.

The experimental grouping of the ^1H chemical shifts are well reproduced by the calculations, clearly assigning the O3 (strongly hydrogen bonded) sites to higher frequency. The calculated ^1H shielding distribution of the O2 layer protons indicate two groups of structures corresponding to the splitting of the 4.2ppm shift (DFT calculated value). Structures I and K (Figure 11(b), 11(e)) give rise to the 5.2ppm shift (DFT calculated value), and the J and L (Figure 11(c), 11(d)) structures are responsible for the 3.9ppm shift (DFT calculated value). The results show that the joint use of NMR spectroscopy and DFT calculations represents a powerful method for correlating local structure with properties (in this case, proton mobility).

For Figure 11 see next page

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[11] Jayaraman, V.; Magrez, A.; Caldes, M.; Joubert, O.; Taulelle, F.; Rodriguezcarvajal, J.; Piffard, Y.; Brohan, L. *Solid State Ionics 170*, 25 (2004).

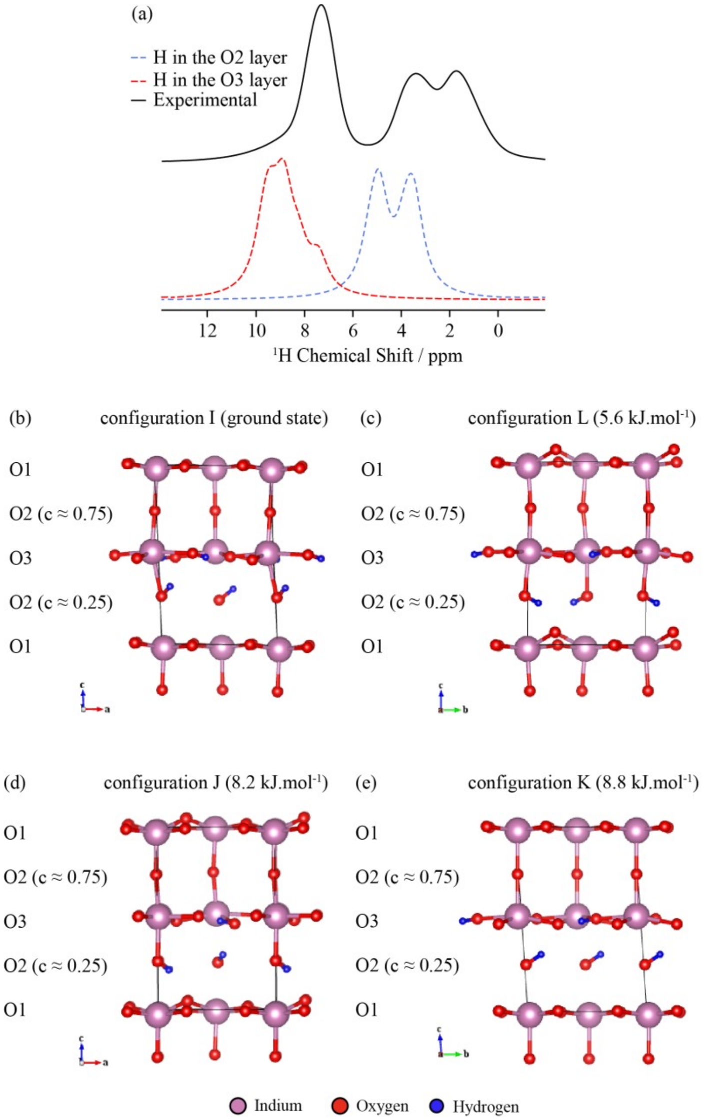

Figure 11: (a) Comparison of the experimental ^{1}H MAS NMR spectra of $Ba_2In_2O_4(OH)_2$ (full lines) at 22 °C and the simulation of the GIPAW calculated ^{1}H NMR spectra (red dashed lines, O3 layer protons and blue dashed lines, O2 layer protons in the configuration I and K at 5.6 – 5.9 ppm and in the configuration L and J at 4.0 – 4.3 ppm). Optimized geometry of (b) configuration I (ground state), (c) configuration L, (d) configuration J and (e) configuration K showing the O3 layer protons and O2 (c ≈ 0.25) layer protons. The interlayer Ba atoms have been omitted for clarity.

14. Anomalous Interface/Surface Strontium Segregation in Heterostructure $La_{1-x}Sr_xCoO_{3-\delta}$ / $(La_{1-y}Sr_y)_2CoO_{4\pm\delta}$ Oxide Thin Films

Zhenxing Feng, Yizhak Yacob, Milind J. Gadre, Yueh-Lin Lee, Wesley T. Hong, Hua Zhou, Michael D. Biegalski, Hans M. Christen, Dane Morgan, and Yang Shao-Horn

In this work, we studied the atomic-structure and layer-by-layer strontium distribution in ~6 nm thick $LSCO_{113}$-$LSCO_{214}$ heterostructured thin films. Significant Sr segregation was found near the $LSCO_{113}$/$LSCO_{214}$ interface and surfaces, with a mean Sr concentration ~1. It has previously been reported that Sr segregation to the interface may contribute to the enhanced ORR activity in heterostructured $LSCO_{113}/LSCO_{214}$[12], and this study provides the first evidence of absolute layer-by-layer Sr atomic concentrations in such a heterostructure, illustrating the Sr redistribution to the interface, as shown in Figure 12. Annealing was not found to change the Sr distribution significantly in the film.

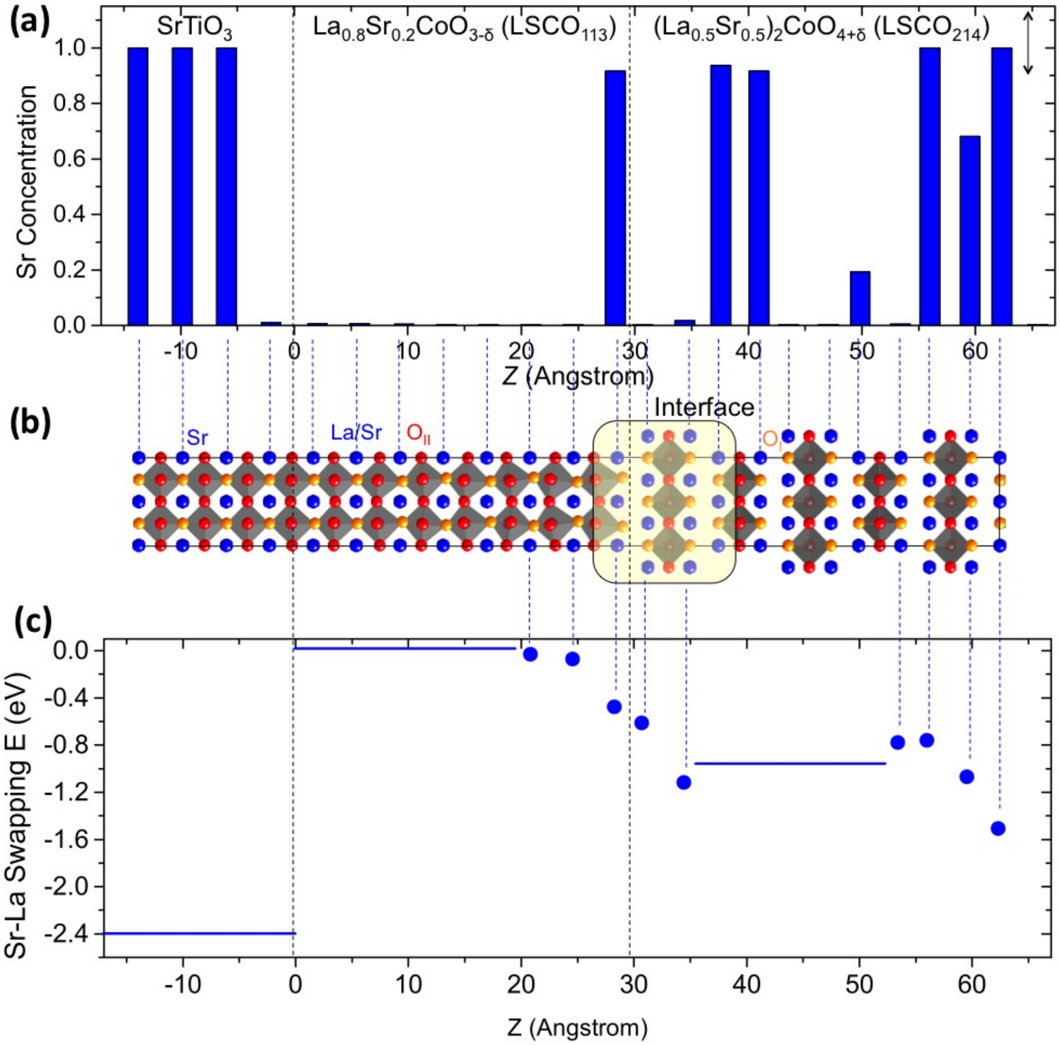

Figure 12: (a) Layer-by-layer Sr concentration vs. depth profile determined from differential COBRA method for LSCO as-deposited sample. The double arrow indicates the error bar. The dashed black lines represent the nominal substrate/LSC_{113} and LSC_{113}/LSC_{214} interfaces, respectively. (b) A schematic crystal model shows the structure of our film. (c) Calculated bulk and surface/interface La/Sr swapping energy for LSCO from *ab initio* methods. Lower swapping energy indicates the tendency of more Sr segregation, which shows the consistent depth-dependent Sr distribution trend.

To further understand the physical origin of Sr segregation in the $LSCO_{113}/LSCO_{214}$ film, we performed *ab initio* calculations to simulate the heterostructured system. The Sr-La substitution

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[12] M.J. Gadre, Y.-L. Lee, and D. Morgan, Physical Chemistry Chemical Physics, 14, (8), 2606-2616, (2012)

energies in bulk STO, $LSCO_{113}$, and $LSCO_{214}$ were used to approximate the film chemistry away from interfaces. In addition, the layer-by-layer substitution energies across the $LSCO_{113}/LSCO_{214}$ interface were also calculated (data points, Figure 12). Our DFT results show that the Sr_{La} substitutional defect is thermodynamically more stable at the $LSCO_{113}/LSCO_{214}$ interface and $LSCO_{214}$ surface than in the $LSCO_{113}$ film. This suggests a strong driving force for Sr to segregate from $LSCO_{113}$ to the $LSCO_{113}/LSCO_{214}$ interface (~ -0.8 eV/Sr) and $LSCO_{214}$ surface (~ -1.5 eV/Sr), which is qualitatively consistent with the observed Sr distribution from differential COBRA. The alternating Sr-rich and Sr-depleted layers in $LSCO_{214}$ suggest that La-Sr A-site ordering may occur in the films under the PLD condition (T=~550 °C and 50 mTorr O_2). Our preliminary DFT modeling results suggest that effects such as strain and oxygen defects can help stabilize A-site cationic ordering. Overall, the first principles modeling results demonstrate three driving forces that could lead to the observed chemical distribution of the $LSCO_{113}/LSCO_{214}$ heterointerfaces, including segregation from $LSCO_{113}$ to $LSCO_{214}$, surface segregation in $LSCO_{214}$, and ordering tendencies in $LSCO_{214}$, although a full $LSCO_{113}/LSCO_{214}$ heterointerface model is still needed for quantitative prediction of the chemical composition. The modeling portion of this work is funded in part under this grant. A paper on this work was published in J. Phys. Chem. Lett.

15. Including Magnetic Contributions in $LaMnO_3$ Defect Models

With a focus on the defect models for perovskites in solid oxide fuel cell applications, this work demonstrates how magnetic free energy terms can be incorporated into a $LaMnO_3$ defect model that was recently published in Physical Chemistry Chemical Physics 14 (1), 290-302 (2012)[13]. We found the magnetic contributions to the defect reactions energies are much smaller than the total defect reaction energetics, and are close to the accuracy range of the adopted modeling approaches. Our results suggest that the magnetic contributions are relatively minor and can often be ignored without significant loss of accuracy. This work has been published in the Transactions of the Electrochemical Society.[14]

16. Ab-initio study of Oxygen Reduction and Oxygen Evolution reactions on perovskite surfaces in alkaline aqueous conditions – case of $LaMnO_3$ and $LaCrO_3$.

Achieving faster kinetics of oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) in the aqueous alkaline conditions is vital to the development of electrochemical devices and processes such as alkaline fuel cells or water electrolysis for hydrogen production. Although this is a low temperature catalytic process, we have extended some of our modeling tools and understanding from the high-temperature applications to this new area. Transition metal-based perovskites are promising as catalysts and there is a growing interest in using simulations to help design better materials. However, modeling of ORR/OER on perovskite oxides is challenging due to the electronic structure of the transition metal, possible surface reconstructions, and potentially complex surface coverages. Previous ab-initio simulations of the ORR and OER on transition metal oxide surfaces have considered a simple approximation of pristine (001)-BO_2-terminated surfaces. Their predicted voltages from these simplified surface models often deviate by ~0.5*V*-1.5*V* compared to the experimental voltages[15]. In this study we use DFT with GGA+*U* to predict the ORR and OER voltages. We further include the (voltage-dependent)

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[13] Y.-L. Lee and D. Morgan, Physical Chemistry Chemical Physics 14 (1), 290-302 (2012).

[14] Including Magnetic Contributions in $LaMnO_3$ Defect Models Y.-L. Lee and D. Morgan, ECS Trans. 50 (27), 91-95, (2013).

thermodynamically stable surface coverage in aqueous environment in the modeling. The results, as shown in Figure 13, demonstrate that including GGA+*U* and the surface coverage effect together can play a critical role in correctly estimating the relative binding energies of reactive intermediates of ORR, OER. This leads to predicted overpotentials within ~0.3V of experimental reported voltages, a significant improvement over previous calculations at the GGA-level.

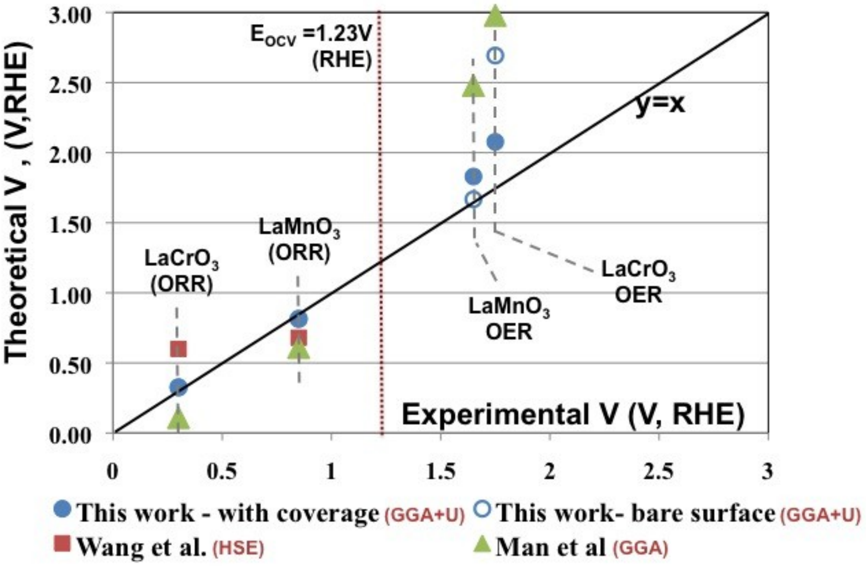

Figure 13: Theoretical (predicted) vs experimental voltages of aqueous ORR, OER (vs V/RHE). Dashed lines are guidelines to compare a set of voltages calculated with different ab-initio methods, (GGA, GGA+U, HSE, with coverage effects) for OER/ORR on a single surface. Blue circles (filled) are the coverage-consistent voltages calculated using GGA+*U* in this work. Open circles (blue) are calculated in this work with bare surfaces with GGA+*U*; and when compared with the values from Man et al.[15] (triangles) demonstrate the effect of *U* parameter. Experimental voltages are included from Suntivich, et al.[16] and Bockris, et al.[17] Previous calculations with the HSE methods are included from Wang, et al.[18]

We observe that including Hubbard-*U* makes the 3d-transition metal harder to oxidize, thereby altering the Gibb's free energy change of the crucial potential determining step of OER (*OH --> *O) and of ORR (* --> *OOH), where *X refers to X on the surface. The Hubbard-*U* may therefore correct the predicted ORR/OER voltages by up to ~0.5*V*. Further including the surface effect, even in its simplest picture of a monolayer of a single, most-stable species, may further improve the accuracy of predicted voltages by up to 0.2-0.5*V*. This work helps both understand and quantify the role of different surface effects on the catalytic activity of the promising La*B*O_3 surfaces towards oxygen reduction/evolution. Achieving more accurate activity predictions from computational methods, even at the GGA+*U* level, will enable future

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[15] Man, I. C.; Su, H.-Y.; Calle-Vallejo, F.; Hansen, H. A.; Martínez, J. I.; Inoglu, N. G.; Kitchin, J.; Jaramillo, T. F.; Nørskov, J. K.; Rossmeisl, J. ChemCatChem 2011, 3, 1159-1165.

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[17] Bockris, J. O. M.; Otagawa, T. Journal of The Electrochemical Society 1984, 131, 290-302.

[18] Wang, Y.; Cheng, H.-P.Oxygen Reduction Activity on Perovskite Oxide Surfaces: A Comparative First-Principles Study of LaMnO3, LaFeO3, and LaCrO3. The Journal of Physical Chemistry C 2013, 117, 2106-2112.

high-throughput computations to perform computational searches of catalytically active materials. A paper on this work is in preparation.

17. Calculation of the O^{2-}, O^{1-}, and V_O formation free energies vs. Sr composition (x) in $(La_{2-x}Sr_x)NiO_{4\pm\delta}$

In preliminary work, the O^{2-}, O^{1-}, and V_O formation free energies vs. part of the range of possible Sr composition (x) in $(La_{2-x}Sr_x)NiO_{4\pm\delta}$ were calculated using GGA+U. These calculations are done in quite small unit cells and no defect couplings or charged defect states are considered, but the results give a qualitative guide to type of energetics we expect in this system. We see that the system is O^{2-} interstitial dominated for Sr content less that about x=0.2, and then becomes peroxide O^{1-} interstitial dominated until Sr content of about x=1.0, and then will become vacancy (V_O) dominated for higher Sr content. These trends will lead to potentially complex defect thermodynamics and kinetics in this material, and determining the dominant mechanism of surface exchange and transport under these changing defect types and concentrations will be a focus of future work.

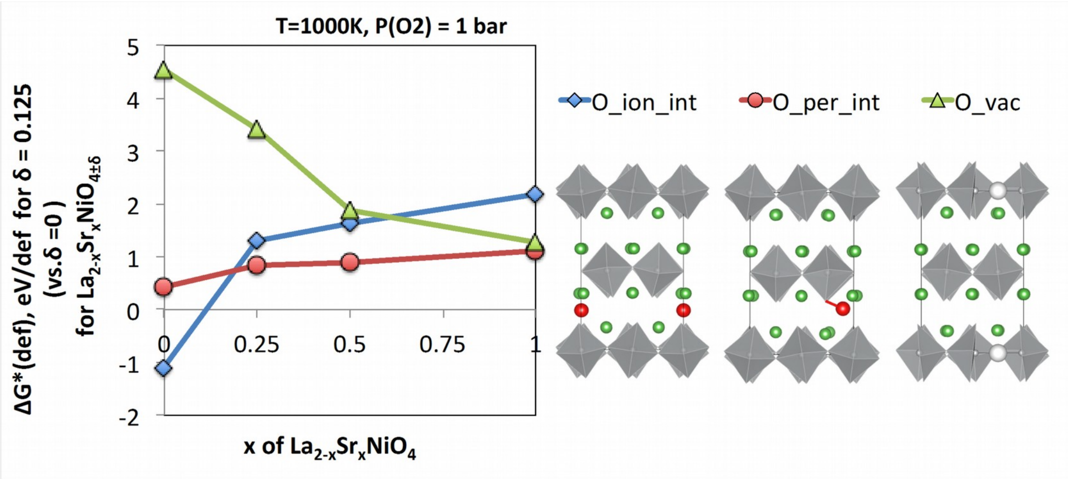

Figure 14: Predicted defect formation free energies vs. oxygen gas at 1000 K, PO_2 = 1 bar in $(La_{2-x}Sr_x)NiO_{4\pm\delta}$. The defects are the oxygen ion interstitial (O_ion_int or O^{2-}), oxygen peroxide interstitial (O_per_int or O^{1-}), and oxygen vacancy (O_vac or V_O).

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12. **Ab initio -based calculations of A-site migration in $La_{1-x}Sr_xMnO_3$,** B. Puchala, Y.-L. Lee and D. Morgan, *ECS Transactions* **50**, 97-110 (2012).

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15. **Including Magnetic Contributions in $LaMnO_3$ Defect Models** Y.-L. Lee and D. Morgan, *ECS Trans.* **50** (27), 91-95, (2013).

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18. **Interlayer Effects on Oxygen Reduction Kinetics in Porous Electrodes of $La_{0.5}Sr_{0.5}CoO_{3-\delta}$** Q. Su, W. Gong, D. Yoon, C. Jacob, Q. Jia, A. Manthiram, A. J. Jacobson, and H. Wang, J. Electrochem. Soc., **161**(4) F1-F8 (2014)

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    E. Erdogan gratefully acknowledges financial support from Republic of Turkey, Ministry of National Education. The other authors gratefully acknowledge financial support from the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under award number DESC0001284. We also gratefully acknowledge computing support from a NERSC allocation of the Center for Nanophase Materials Sciences (CNMS) at Oak Ridge National Laboratory under grant number CNMS2011-292.

20. **Anomalous Interface and Surface Strontium Segregation in $(La_{1-y}Sr_y)_2CoO_{4\pm\delta}/La_{1-x}Sr_xCoO_{3-\delta}$ Heterostructured Thin Films**, Z. Feng, Y. Yacob, M. J. Gadre, Y.-L. Lee, W. T. Hong, H. Zhou, M. D. Biegalski, H. M. Christen, S. B. Adler, D. Morgan, and Y. Shao-Horn, Journal of Physical Chemistry Letters (2014), 5(6), 1027-1034.

    This work was partially supported by DOE (SISGR DESC0002633) and King Abdullah University of Science and Technology. We thank the King Fahd University of Petroleum and Minerals in Dharam, Saudi Arabia for funding the research reported in this paper through the Center for Clean Water and Clean Energy at MIT and KFUPM. This research was supported by the Israel Science Foundation under grant no. 1005/11. Support for Y.-L.L. was provided by Department of Energy (DOE), National Energy Technology Laboratory (NETL), Solid State Energy Conversion Alliance (SECA) Core Technology Program, Funding Opportunity Number DEFE0009435, and that for M.J.G. was provided by U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under award number DESC0001284. Use of the Advanced Photon Source, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science by Argonne National Laboratory was supported by the U.S. DOE under Contract No. DE-AC02-06CH11357. We acknowledge the support from the beamline scientists including Zhan Zhang, Christian M. Schlepuetz, and Lynette Jirik at ID-33 of APS. Samples were synthesized at the Center for Nanophase Materials Sciences, which is sponsored at Oak Ridge National Laboratory by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. DOE under Contract No. CNMS2012-284.

21. **Strontium Influence on the Oxygen Electrocatalysis of epitaxial $La_{2-x}Sr_xNiO_{4\pm\delta}$ ($0 \leq Sr \leq 1.0$) Thin Films at Elevated Temperatures,** D. Lee, Y.-L. Lee, A. Grimaud, W. T. Hong, M. D. Biegalski, D. Morgan, and Y. Shao-Horn, Journal of Materials Chemistry A: Materials for Energy and Sustainability (2014), 2(18), 6480-6487.

    This work was supported in part by DOE (SISGR DESC0002633) and King Abdullah University of Science and Technology. The authors would like to thank the King Fahd University of Petroleum and Minerals in Dharam, Saudi Arabia, for funding the research reported in this paper through the Center for Clean Water and Clean Energy at MIT and KFUPM. Funding for D. Morgan and partial support for Y.-L. Lee provided by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under award number DESC0001284. This work also benefitted from the use of the Extreme Science and Engineering Discovery Environment (XSEDE), which is supported by National Science Foundation grant number OCI-1053575. PLD was conducted at the Center for Nanophase Materials Sciences, which is sponsored at Oak Ridge National Laboratory by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy.

22. **Oxygen diffusion in $Sr_3YCo_4O_{10.5}$: An electrical conductivity relaxation and thermogravimetric analysis approach**, D. Rupasov, T. Makarenko and A. J. Jacobson, Solid State Ionics **265**, 68-72 (2014).

    The work was supported by the Robert A Welch Foundation (grant no. E-0024, TM; TGA measurements) and the U.S. Department of Energy (U.S. DOE), Office of Basic Energy Sciences, Division of Materials Sciences and Engineering (under award no. DE-SC0001284, DR, AJJ; experiments and analysis).

23. **A Determination of the Oxygen Non-stoichiometry of the Oxygen Storage Material $YBaMn_2O_{5+\delta}$** K. Jeamjumnunja, W. Gong, T. Makarenko, and A. J. Jacobson, *J. Solid State Chem.* 230, 397-403, (2015).

    The work was supported by the Robert A. Welch Foundation (Grant No. E-0024, TM; TGA measurements) and the U.S. Department of Energy (U.S. DOE), Office of Basic Energy Sciences Division of Materials Sciences and Engineering (under Award No. DE-SC0001284, KJ, WG, AJJ; experiments and analysis).

Current and Pending Support (as of 8/14)

Allan J. Jacobson

Current

1. **Project/Proposal Title: "Enhanced Mixed Electronic-Ionic Conductors Through Cation Ordering"**
   Source of Support: Department of Energy (DOE), Basic Energy Sciences, DE-PS02-09ER46571
   Project Location: University of Houston
   Total Award Amount: $1,400,000 (3 PIs)
   Starting – Ending Date (MM/DD/YY): 07/01/09 –06/30/12– NCE until 08/31/14
   PIs List: PI(s): Allan Jacobson, Co-PI(s): Dane Morgan, Clare Grey.

2. **Project/Proposal Title:** “Applied Research Hub at The Texas Center for Superconductivity”
   Source of Support State of Texas Emerging Technology Fund
   Total Award Amount: $3,500,000 Period 1/10 - 12/14
   PIs List: PI(s): Allan Jacobson, Co-PI(s): Venkat Selvamanickam.
   Not related to the DoE project

Pending

1. **Project/Proposal Title: DMREF/Collaborative Research: Synthesis and Characterization of Oxygen-Deficient Cobalt Perovskite Thin Films Exhibiting Ultrafast Redox Reactions.**
   Source of Support: National Science Foundation
   Project Location: University of Houston;
   Total Award Amount: $303,679 (AJJ part)
   Starting – Ending Date (MM/DD/YY): 1/8/14 – 30/6/17
   PIs List: PI(s) C. Chen, Co-PI(s): Allan Jacobson, M. Whangbo, M. Yacaman.
   Somewhat related to the DoE project but concerned with thin films rather than the bulk materials that are the focus of the DoE project

2. **Project/Proposal Title: SusChEM: Reactions of Rare Earth Oxides with Organic Amides: A Green Chemical Approach to Recycling Rare Earth Elements.**
   Source of Support: National Science Foundation
   Project Location: University of Houston
   Total Award Amount: $362,556
   Starting – Ending Date: 08/14 - 07/17
   PIs List: Allan Jacobson
   Not related to the DoE project

3. **Project/Proposal Title:** EFRC: High Thermal Conductivity Materials Center**.**
   Source of Support: Dept of Energy
   Project Location: University of Houston
   Total Award Amount: $17,500,000
   Starting – Ending Date: 08/14 - 07/19
   PIs List: Zhifeng Ren is PI, Allan Jacobson is one of 10 co-PIs.
   Not related to the DoE project

4. **Project/Proposal Title: “**Oxygen Redox for Oxygen Conductors: A Case Study on (La,Sr)2NiO4+/-d**”**

   Source of Support: Department of Energy (DOE), Basic Energy Sciences.
   Project Location: University of Houston and University of Wisconsin
   Total Award Amount: $894,174 (2 PIs)
   Starting – Ending Date (MM/DD/YY): 09/01/14 –08/31/17
   PIs List: PI(s): Allan Jacobson, Co-PI(s): Dane Morgan
   Renewal proposal

Current and Pending Support – Dane Morgan

Current

1. **Project/Proposal Title: “High Fidelity Ion Beam Simulation of High Dose Neutron Irradiation”**
   Source of Support: DOE NE IRP
   Project Location: University of Michigan - lead, University of Wisconsin – Madison; Multiple other sites
   Total Award Amount: $5,000,000 (19 PI’s)
   Morgan Award Amount: $264,180
   Morgan person months committed (per year): 1

Starting – Ending Date (MM/DD/YY): 01/01/14–12/31/16
PIs List: PI(s): Gary Was. Co-PI(s): Dane Morgan, 17 other PIs.
Not related to the current DoE project or to the renewal proposal.

2. **Project/Proposal Title: "DMREF: A Combined Experiment and Simulation Approach to the Design of New Bulk Metallic Glasses"**
Source of Support: National Science Foundation (NSF), DMREF
Project Location: University of Wisconsin, Madison
Total Award Amount: $1,665,652 (4 PI's)
Morgan Award Amount: ~$320,000
Morgan person months committed (per year): 0.25m sum yr 1,2; 0.5m sum yr 3,4
Starting – Ending Date (MM/DD/YY): 9/1/13 – 8/31/17
PIs List: PI(s): John Perepezko (UW); Co-PI(s): Dane Morgan (UW), Izabela Szlufarska (UW), Paul Voyles (UW)
Not related to the current DoE project or to the renewal proposal.

3. **Project/Proposal Title: "Collaborative Research: Helium Diffusion in Lower Mantle Minerals"**
Source of Support: National Science Foundation (NSF), Cooperative Studies Of The Earth's Deep Interior (CSEDI), EAR-1265283
Project Location: Case Western Reserve - lead, University of Wisconsin, Madison, Harvard University
Total Award Amount: $567,845 (3 PI's)
Morgan Award Amount: $221,492
Morgan person months committed (per year): 0.12, 0.5, 0.5
Starting – Ending Date (MM/DD/YY): 05/01/13–04/30/16
PIs List: PI(s): James Van Orman. Co-PI(s): Dane Morgan, Sujoy Mukhopadhyay.
Not related to the current DoE project or to the renewal proposal.

4. **Project/Proposal Title: "Modeling Strategy to Assess Radiation Induced Segregation and Phase Stability in Austenitic Steels in Light Water Reactors during extended service"**
Source of Support: Department of Energy (DOE), Oak Ridge National Laboratory, Solicitation # 640011862 and Subcontract # 400119154
Project Location: University of Tennessee - lead, University of Wisconsin, Madison
Total Award Amount: $~500,000 (2 PI's)
Morgan Award Amount: $~249,443
Morgan person months committed (per year): 0.5
Starting – Ending Date (MM/DD/YY): 10/01/12–12/31/14
PIs List: PI(s): Brian Wirth. Co-PI(s): Dane Morgan.
Not related to the current DoE project or to the renewal proposal.

5. **Project/Proposal Title: "SI2-SSI Collaborative Research: A Computational Materials Data and Design Environment"**
Source of Support: National Science Foundation (NSF), Software Infrastructure for Sustained Innovation (SI2), Award 1147892
Project Location: University of Wisconsin, Madison – Lead, Massachusetts Institute of Technology (MIT), Lawrence Berkeley National Laboratory (LBNL), University of Kentucky
Total Award Amount: $2,050,000 (5 PI's)
Morgan Award Amount: $1,050,000
Morgan person months committed (per year): 1
Starting – Ending Date (MM/DD/YY): 10/01/12–09/30/17
PIs List: PI(s): Dane Morgan. Co-PI(s): Gerbrand Ceder, Kristin Persson, Alan Dozier, Raphael Finkel
Not related to the current DoE project or to the renewal proposal.

6. **Project/Proposal Title: "Enhancement of SOFC Cathode Electrochemical Performance Using Multi-Phase**

Interfaces"
Source of Support: Department of Energy (DOE), National Energy Technology Laboratory (NETL), Solid State Energy Conversion Alliance (SECA) Core Technology Program, Funding Opportunity Number: DE-FOA-0000677
Project Location: University of Wisconsin, Madison; Massachusetts Institute of Technology, University of Washington (Seattle).
Total Award Amount: 625,162 (20% cost share) (3 PI's)
Morgan person months committed (per year): 0.0
Morgan Award Amount: $159,926
Starting – Ending Date (MM/DD/YY): 11/01/12 –10/30/15
PIs List: PI(s): Dane Morgan, Co-PI(s): Stuart Adler, Yang Shao-Horn.

This project is focused on $(La,Sr)_2CoO_4$ / $(La,Sr)CoO_3$ *interfaces and therefore also includes aspects of both phases separately. The* $(La,Sr)_2CoO_4$ *phase has the same structure as the* $(La,Sr)_2NiO_4$ *compound being proposed for study in the revewal proposal. Therefore, there will be significant synergy between the two projects. However,* $(La,Sr)_2CoO_4$ *will not be studied in the SECA project if the present project is awarded, thereby creating a clear distinction between the projects.*

7. **Project/Proposal Title:** "**Imaging Points Defect with Quantitative STEM"**
Source of Support: Department of Energy (DOE), Basic Energy Sciences (BES), DE-FG02-08ER46547
Project Location: University of Wisconsin, Madison (UW)
Total Award Amount: $663,489 (2 PI's)
Morgan Award Amount: $222,716
Morgan person months committed (per year): 0.5 (yr 3)
Starting – Ending Date (MM/DD/YY): 05/01/12 –08/30/15
PIs List: PI(s): Paul Voyles. Co-PI(s): Dane Morgan.
Not related to the current DoE project or to the renewal proposal except that some characterization of the $(La,Sr)_2CoO_4$ / $(La,Sr)CoO_3$ *interface described above may be undertaken. No study of* $(La,Sr)_2NiO_4$*, which is the focus of the renewal proposal, is planned in this work.*

8. **Project/Proposal Title: "Stabilization of high-voltage cathodes for lithium-ion batteries"**
Source of Support: DOW Chemical
Project Location: University of Wisconsin, Madison.
Total Award Amount: $2,973,919 (4 PI's)
Morgan Award Amount: ~$500,000
Morgan person months committed (per year): 0.25 (Year 1), 0.5 (Years 2-5)
Starting – Ending Date (MM/DD/YY): 01/01/12–12/31/16
PIs List: PI(s): Robert Hamers. Co-PI(s): Dane Morga, Tom Kuech, Mahesh Mahanthappa
Not related to the current DoE project or to the renewal proposal.

9. **Project/Proposal Title: "UW CEMRI on Structured Interfaces"**
Source of Support: National Science Foundation, CEMRI (MRSEC)
Project Location: University of Wisconsin, Madison
Total Award Amount: Large collaborative center
Morgan person months committed (per year): 0
Morgan Award Amount: $60,000
Starting – Ending Date (MM/DD/YY): 06/01/11 - 5/31/16
PIs List: PI(s): Nicholas Abbott. Co-PI(s): Dane Morgan and many others.
Not related to the current DoE project or to the renewal proposal.

10. **Project/Proposal Title: "Fundamental Materials Studies for Advanced High Power Microwave and Terahertz Vacuum Electronic Radiation Sources"**
Source of Support: Air Force Office of Scientific Research (AFOSR), grant No. FA9550-11-1-0299
Project Location: University of Wisconsin, Madison

Total Award Amount: $986,025 (4 PI's)
Morgan Award Amount: ~$150,000
Morgan person months committed (per year): 1
Starting – Ending Date (MM/DD/YY): 08/01/11–07/31/14
PIs List: PI(s): John H. Booske. Co-PI(s): Susan C. Hagness, Irena Knezevic, Dane Morgan.
Not related to the current DoE project or to the renewal proposal.

11. **Project/Proposal Title: "Ag transport through non-irradiated and irradiated SiC"**
Source of Support: Department of Energy (DOE), Nuclear Energy University Program (NEUP), 12-2988
Project Location: University of Wisconsin, Madison
Total Award Amount: $1,055,456 (3 PI's)
Morgan person months committed (per year): 1
Morgan Award Amount: $265,929
Starting – Ending Date (MM/DD/YY): 06/15/11 –06/14/14, extended to 9/30/15
PIs List: PI(s): Izabela Szlufarska. Co-PI(s): Dane Morgan, Todd Allen.
Not related to the current DoE project or to the renewal proposal.

12. **Project/Proposal Title: "Radiation Effects in Nanocrystalline Ceramics: Multi-Scale Model and Experiment"**
Source of Support: Department of Energy (DOE), Basic Energy Sciences (BES), DE-PS02-07ER07-04, Basic Research for Advanced Nuclear Energy Systems
Project Location: University of Wisconsin, Madison
Total Award Amount: $678,000 (3 PI's)
Morgan person months committed (per year): 0.25, 0.5, 0.5
Morgan Award Amount: $236,206
Starting – Ending Date (MM/DD/YY): 06/15/11 –06/14/14
PIs List: PI(s): Izabela Szlufarska. Co-PI(s): Dane Morgan, Todd Allen.
Not related to the current DoE project or to the renewal proposal.

13. **Project/Proposal Title: "Collaborative Research: Determination of Ni-Fe-Cr Species Dependent Transport Through Control of Temperature, Irradiation, and Grain Size"**
Source of Support: National Science Foundation (NSF), Metals and Metallic Nanostructures (MMN), grant No. 1105640
Project Location: University of Wisconsin, Madison – Lead, Drexel University
Total Award Amount: $597,441 (4 PI's)
Morgan Award Amount: $93,837
Morgan person months committed (per year): about 0.1
Starting – Ending Date (MM/DD/YY): 05/01/11–04/31/14
PIs List: PI(s): Dane Morgan. Co-PI(s): Izabela Szlufarska, Todd Allen, Mitra Taheri
Not related to the current DoE project or to the renewal proposal.

14. **Project/Proposal Title: "CSEDI Collaborative Research: Valence State of Iron in the Lower Mantle"**
Source of Support: National Science Foundation (NSF), Cooperative Studies Of The Earth's Deep Interior (CSEDI), EAR-0968685
Project Location: Massachusetts Institute of Technology - lead, University of Wisconsin, Madison
Total Award Amount: $503,588 (2 PI's)
Morgan Award Amount: $172,647
Morgan person months committed (per year): 0.0
Starting – Ending Date (MM/DD/YY): 06/01/10–05/31/14
PIs List: PI(s): Sang-Heom Shim. Co-PI(s): Dane Morgan.
Not related to the current DoE project or to the renewal proposal.

15. **Project/Proposal Title: "CASL: Consortium for Advanced Simulation of LWRs"**
Source of Support: Department of Energy (DOE), Funding Opportunity Number: DE-FOA-0000170

Project Location: Oak Ridge National Laboratory (Lead), University of Wisconsin – Madison, Many other sites
Total Award Amount: ~$100m
Morgan Award Amount: $90,000
Morgan person months committed (per year): 0.0
Starting – Ending Date (MM/DD/YY): 10/01/10–09/30/15
PIs List: PI(s): Izabela Szlufarska, CO-PI(s): Dane Morgan
Not related to the current DoE project or to the renewal proposal.

16. **Project/Proposal Title: "Enhanced Mixed Electronic-Ionic Conductors Through Cation Ordering"**
Source of Support: Department of Energy (DOE), Basic Energy Sciences, DE-PS02-09ER09-01
Project Location: Lead - University of Houston; University of Wisconsin – Madison; Stony Brook University.
Total Award Amount: $1,400,000 (3 PIs)
Morgan Award Amount: $490,000
Morgan person months committed (per year): 0.0
Starting – Ending Date (MM/DD/YY): 09/01/09 –08/28/14– NCE until 08/31/14
PIs List: PI(s): Allan Jacobson, Co-PI(s): Dane Morgan, Clare Grey.

Current Computing

1. **Project/Proposal Title: "*Ab initio* Based Modeling of Multi-Component Alloy Thermokinetics"**
Source of Support: National Science Foundation (NSF), XSEDE, MCA09X001
Project Location: University of Wisconsin – Madison (UW)
Total Award Amount: 3.53×10^6 SUs (~CPU hours) (1 PI's)
Morgan Award Amount: 3.53×10^6 SUs (~CPU hours) (100%)
Starting – Ending Date (MM/DD/YY): 10/01/13 –09/30/14
PIs list: PI(s): Dane Morgan, Co-PI(s): None.

Not related to the current DoE project or to the renewal proposal.

2. **Project/Proposal Title: "Factors governing oxygen reduction on epitaxial thin films for low temperature and surface decorated epitaxial thin films for high temperature electrocatalysis"**
Source of Support: User grant from Oak Ridge National Laboratory (ORNL) Center for Nanophase Materials Sciences (CNMS), CNMS2013-292
Project Location: Massachusetts Institute of Technology (MIT) – lead
Total Award Amount: 500,00 CPU hours (1 PI's)
Morgan Award Amount: 500,00 CPU hours (100%)
Morgan person months committed (per year): 0.0
Starting – Ending Date (MM/DD/YY): 08/01/13-07/31/14
PIs List: PI(s): Yang Shao Horn, Co-PI(s): Dane Morgan, Stuart Adler, Hans Christen.

Not related to the current DoE project or to the renewal proposal.

3. **Project/Proposal Title: "First-principles simulations on the growth of SrTiO3 and Sr2TiO4 films by Molecular Beam Epitaxy"**
Source of Support: User grant from Argonne National Laboratory (ANL), Center for Nanoscale Materials, proposal CNM 35702
Project Location: University of Wisconsin
Total Award Amount: 420,00 CPU hours (3 PI's)
Morgan Award Amount: 420,00 CPU hours (100%)
Morgan person months committed (per year): 0.0
Starting – Ending Date (MM/DD/YY): 09/03/13-09/02/14
PIs List: PI(s): Dane Morgan, Co-PI(s): John Freeland, Dillon Fong.

Not related to the current DoE project or to the renewal proposal.

Pending

1. **Project/Proposal Title: "Basic Research on Carbon Nanotube Fiber Field Emission Cathodes"**
Source of Support: Air Force Office of Scientific Research (AFOSR)
Project Location: University of Wisconsin - Madison
Total Award Amount: $515,486 (4 PI's)
Morgan Award Amount: $~165,000
Morgan person months committed (per year): 0.25
Starting – Ending Date (MM/DD/YY): 05/01/13–07/31/16
PIs List: PI(s): John Booske. Co-PI(s): Dane Morgan, Nader Behdad, Irena Knezevic.

   Not related to the current DoE project or to the renewal proposal.

2. **Project/Proposal Title: "Water Energy Nexus Center"**
Source of Support: Department of Energy, Energy Frontier Research Center (EFRC)
Project Location: University of Wisconsin – Madison, and many others.
Total Award Amount: NA
Morgan Award Amount: $~1,200,000
Morgan person months committed (per year): 2
Starting – Ending Date (MM/DD/YY): 07/01/14–06/30/19
PIs List: PI(s): Marc Anderson. Co-PI(s): Dane Morgan and many others.

   Not related to the current DoE project or to the renewal proposal.

3. **Project/Proposal Title: "EFRC - Center For Rate-phenomena in Mesoscale Systems (RiMeS)"**
Source of Support: Department of Energy, Energy Frontier Research Center (EFRC)
Project Location: University of Washington – Seattle, University of Wisconsin – Madison, and many others.
Total Award Amount: NA
Morgan Award Amount: $~1,057,000
Morgan person months committed (per year): 1
Starting – Ending Date (MM/DD/YY): 07/01/14–06/30/19
PIs List: PI(s): Jihui Yang. Co-PI(s): Dane Morgan, and many others

   Not related to the current DoE project or to the renewal proposal.

4. **Project/Proposal Title: "Center for Mesoscale Hierarchical 3D Nanostructured Materials"**
Source of Support: Department of Energy, Energy Frontier Research Center (EFRC)
Project Location: University of Wisconsin – Madison, and many others.
Total Award Amount: NA
Morgan Award Amount: $~500,000
Morgan person months committed (per year): 1
Starting – Ending Date (MM/DD/YY): 07/01/14–06/30/19
PIs List: PI(s): Jihui Yang. Co-PI(s): Dane Morgan, and many others
This proposal will focus on catalytic processes in perovskite cathode materials and therefore has strong synergy with the proposed work. However, no study of $(La,Sr)_2NiO_4$*, which is the focus of the renewal proposal, is planned in this work.*
5. **Project/Proposal Title: "Oxygen Redox for Oxygen Conductors: A Case Study on (La,Sr)2NiO4+/-d"**
Source of Support: Department of Energy (DOE), Basic Energy Sciences
Project Location: University of Houston, University of Wisconsin
Total Award Amount: $894,174 (2 PIs)

Morgan Award Amount: ~$439,314
Morgan person months committed (per year): 0.5m sum yr 1-3
Starting – Ending Date (MM/DD/YY): 09/01/14 – 08/31/17
PIs List: PI(s): Allan Jacobson, Co-PI(s): Dane Morgan

Renewal proposal

Clare P. Grey was not actively involved in the final six month no cost extension and her Current and Pending Support is not updated from the previous report

Current Support: Stony Brook University

1. **Project/Proposal Title: Collaboration Research: New Characterization Approaches for Developing Structure-Sorption Relationships in Disordered Iron-oxyhydroxides.**
   Source of Support: National Science Foundation (CHE 0714183)
   Project Location: Stony Brook
   Total Award Amount: $1,705,000
   Starting – Ending Date (MM/DD/YY): 01/23/12 –01/22/13
   PIs List: C. P. Grey, J. Parise, B. Phillips, R. Reeder, SBU, D. Strongin, Temple U., D. Morgan, U. Wisconsin; J. Kubicki, Penn State U.
   No Overlap

2. **Project/Proposal Title:** Northeastern Chemical Energy Storage Center – NOCESC
   Source of Support: DOE Energy Frontier Research Ctr. (EFRC)
   Project Location: Stony Brook
   Total Award Amount: $4,465,996 – 5 year total to SBU
   Starting – Ending Date (MM/DD/YY): 01/06/09 – 31/05/14
   PIs List: M. Stanley Whittingham, Director, Stony Brook and Binghamton Universities Rutgers (Glenn Amatucci, Associate Director),Clare P. Grey, (Associate Director) Robert Kostecki, Lawrence Berkeley National Laboratory, Gerbrand Ceder, MIT; Anton Van Der Ven and Katsuyo Thornton (U. Michigan); Peter Chupas (Argonne National Laboratory); Jason Graetz and Xiao-Qing Yang (Brookhaven National Laboratory); Stephen Garofalini, Frederick Cosandey, Robert Bartynski (Rutgers); Y. Shirley Meng (U. Florida); and Peter Khalifah (SBU)
   No Overlap

3. **Project/Proposal Title: Enhanced Mixed Electronic-Ionic Conductors Through Cation Ordering**
   Source of Support: Department of Energy (DOE), Basic Energy Sciences, DE-PS02-09ER09-01
   Project Location: University of Houston
   Total Award Amount: $1,400,000 (3 PIs) ($369,00, C. P. Grey)
   Starting – Ending Date (MM/DD/YY): 07/01/09 –06/30/12
   PIs List: PI(s): Allan Jacobson, Co-PI(s): Dane Morgan, Clare Grey.

   University of Cambridge: Current Support

4. **Project/Proposal Title: First Principles Calculations and NMR Spectroscopy of Electrode Materials**
   Source of Support: DOE, Office of Freedom CAR, Sub-Contract from Lawrence Berkeley National Laboratory to Cambridge
   Project Location: University of Cambridge
   Total Award Amount: $375,000 per year to CPG (2012 funding approved)
   Starting – Ending Date (MM/DD/YY): 1001/01/11 – 12/31/11
   PIs List: PI(s): C. P. Grey and G. Ceder
   Funds more applied work on the characterization of battery materials, and also collaborations within the DOE "Battery program".

5. **Project/Proposal Title: Nanoionics**
   Source of Support: EPSRC Programme Grant

Project Location: University of Cambridge
Total Award Amount: £464,650 total
Starting – Ending Date (MM/DD/YY): /01/09 –07/31/13
PIs List: PI(s): PI: Peter Bruce (St. Andrews), Co-PI's: C.P. Grey, P. A. Madden (Oxford), S. Islam (Bath)

6. **Project/Proposal Title: EPSRC SUPERGEN - The Energy Storage Consortium: CORE Proposal**

   Source of Support: EPSRC

   Project Location: University of Cambridge

   Total Award Amount: £324,431 total to CPG

   Starting – Ending Date (MM/DD/YY): 02/15/10 –02/14/14

   PIs List: PI(s) MS Islam, CP Grey, University of Cambridge, P Bruce, University of St Andrews, Dr RW Dunn, University of Bath, PJ Hall, University of Strathclyde, K Scott, Newcastle University RCT Slade, University of Surrey, P Grant, University of Oxford, A. Cruden, University of Strathclyde.

7. **Project/Proposal Title: Structure and Function: The Development and Application of Novel Ex- and In-situ NMR Approaches to Study Lithium Ion Batteries and Fuel Cell Membranes**
   Source of Support: EU ERC Advanced Grant
   Project Location: University of Cambridge
   Total Award Amount: £1,781,720 total
   Starting – Ending Date (MM/DD/YY): 01/04/10 – 31/03/15
   PIs List: PI(s): C. P. Grey

8. **Project/Proposal Title: New Experimental Methods for Investigating Lithium Ion Batteries and Fuel Cells**
   Source of Support: Royal Society
   Project Location: University of Cambridge
   Total Award Amount: £75,000 total
   Starting – Ending Date (MM/DD/YY): 01/9/09 - 31/08/14
   PIs List: PI(s): C. P. Grey

9. **Project/Proposal Title: EuroLiion-High Energy Density Li-ion Cells for Traction**
   Source of Support: EC
   Project Location: University of Cambridge
   Total Award Amount: £148,76
   Starting – Ending Date (MM/DD/YY): 01/02/11 - 31/01/15
   PIs List: PI(s): C.P. Grey

10. **Project/Proposal Title: In Operando Solid State Nuclear Magnetic Resonance Spectroscopy Studies of Anionic Conductors for Solid Oxide Fuel Cells**
    Source of Support: EC NMRSOFC
    Project Location: University of Cambridge
    Total Award Amount: £178,044.74 total
    Starting – Ending Date (MM/DD/YY): 01/03/11 - 28/02/13
    PIs List: PI(s): C. P. Grey

11. **Project/Proposal Title: NMR Studies of Nanomaterials and the Role of Oxygen in Catalytic Processes**
    Source of Support: Royal Society
    Project Location: University of Cambridge
    Total Award Amount: £12,000 total to CPG
    Starting – Ending Date (MM/DD/YY): 15/03/11 - 14/03/13
    PIs List: PI(s): C. P. Grey, Co-PI: L. Peng, Nanjing University

12. **Project/Proposal Title: NMR and Pulse Field Gradient Studies of SEI and Electrode Structure**

    Source of Support: US Dept of Energy Diagnostics

Project Location: University of Cambridge
Total Award Amount: $275,000.00 per year
Starting – Ending Date (MM/DD/YY): 01/01/11 – 31/01/13
PIs List: PI(s): C. P. Grey

13. Proposal/Project Title: **Study of Electrode Materials and Battery Chemistry by Nuclear Magnetic Resonance**
Source of Support: Royal Society (Newton International Fellowship for Dr Yan-Yan Hu)
Project Location: University of Cambridge
Total Award Amount: £99,000.00
Starting – Ending Date (MM/DD/YY): 02/01/12 – 01/01/14
PIs List: PI(s): C. P. Grey

14 **Proposal/Project Title: In-Situ NMR Studies on Porous Electrodes**
Source of Support: Johnson Matthey (Industrial CASE Studentship for Amy Moore)
Project Location: University of Cambridge
Total Award Amount: £23,040.00
Starting – Ending Date (MM/DD/YY): 01/10/11 – 31/03/15
PIs List: PI(s): C. P. Grey

15 **Proposal/Project Title: Solid State Nuclear Magnetic Resonance Studies of High-Performance Battery Electrode Materials**
Source of Support: EC NMRHIPBAT (Marie Curie IIF for Dr Yan-Yan Hu)
Project Location: University of Cambridge
Total Award Amount: £166,976.00 / 200,371.80 Euros
Starting – Ending Date (MM/DD/YY): 01/01/13 – 31/12/14
PIs List: PI(s): C. P. Grey

16 **Proposal/Project Title: Energy Storage Grand Challenge**
Source of Support: EPSRC
Project Location: University of Cambridge
Total Award Amount: £308,342.16
Starting – Ending Date (MM/DD/YY): 01/10/12 – 30/09/17
PIs List: PI(s): C. P. Grey

17 **Proposal/Project Title: Solid State Nuclear Magnetic Resonance Spectroscopy Studies of Silicon Anodes for Lithium-ion Batteries**
Source of Support: EC NMRSiLion: (Marie Curie IEF for Dr Elodie Salager)
Project Location: University of Cambridge
Total Award Amount: **£177,146.96 / 209033.40 Euros**
Starting – Ending Date (MM/DD/YY): 01/03/12 – 28/02/14
PIs List: PI(s): C. P. Grey

18 **Proposal/Project Title: Insight into the Chemistry of the Lithium-Air Battery by Novel Solid State Nuclear Magnetic Resonance Techniques**
Source of Support: EC LANMR: (Marie Curie IEF for Dr Michal Leskes)
Project Location: University of Cambridge
Total Award Amount: £174,194.00 / 209,033.00 Euros
Starting – Ending Date (MM/DD/YY): 01/03/11– 28/02/14
PIs List: PI(s): C. P. Grey