Project Objectives

• To identify materials with low oxygen ion conductivity but high electronic conductivity for application as coatings.
• To synthesize and characterize materials with very low oxygen ion conductivity through site-specific doping.
• To deposit coatings on stainless steels and nickel-based alloys.
• To investigate oxidation kinetics – electrical resistance.
• To develop low-cost methods for the deposition of coatings.
Approach

- Identify prospective candidates through literature search and prior work. Perovskites, spinels, TiO₂.
- **Doping** to suppress oxygen ion transport. Fabrication of sintered parts for DC conductivity measurements, Hebb-Wagner DC polarization measurements, sputtering targets.
- Measurement of **DC conductivity**, ionic conductivity by Hebb-Wagner (electron) blocking electrode method.
- Deposition of **coatings** on stainless steels and nickel-based alloy foils by sputtering; studies on oxidation kinetics.
- Estimation of kinetic parameters through ex-situ measurements; comparison with oxidation studies – comparison with an **analytical model**.
Background

• Many prospective alloys contain chromium – formation of chromia as oxidation product (or Cr-containing spinels).
• Oxidation occurs in both air and fuel atmosphere.
• Oxide scales formed exhibit relatively high electronic resistance, or spall easily, or both.
• While electronic conductivity of the oxide scale is low, it is higher than ionic conductivity – ion transport determines oxidation kinetics.
• Kinetics of oxidation is usually parabolic.
• Kinetics of oxidation is relatively rapid at 800°C and higher, so that uncoated materials are not satisfactory – 40,000 hr life is difficult with the currently available materials.

Two approaches: (a) Protective coatings, (b) Alloy development
Our Prior Work

• Investigation of oxidation kinetics (up to 10,000 hr) and ASR of Haynes 230, Inconel 718, Inconel 600 series, Hastelloy X in air and fuel (hydrogen).

• Demonstration of the role of Mn-Cr-spinels formed in-situ in suppressing oxidation kinetics.

• Investigation of oxidation kinetics of Haynes 230 coated with LSM and Mn-Cr-spinel. Both coatings found to be protective – LSM better than Mn-Cr-spinel.

• Simple parametric model for oxidation of coated materials.

• Investigation of Mn-coated interconnects in short term stack tests – coated interconnects perform better.
Some Prior Results

Stack tests with coated foils

ASR of coated foils

Kinetics of coated H230 at 800°C in air

SEM of LSM-coated H230 at 800°C in air
Observations on Oxidation of Coated Foils

• With the coatings (perovskites and spinels) investigated so far, oxide (chromia) scale forms under the coating. This means oxygen transport through the coating is faster than chromium transport through the coating.
• Electronic conductivities higher in both the oxide scale and the deposited coating, compared to respective ionic conductivities.
• Predominantly cation transport through chromia, predominantly anion transport through the deposited coating.
Oxidation of Coated and Uncoated Foils: Schematics

The coating should be such that $\text{ASR(coating)} << \text{ASR(Cr}_2\text{O}_3 \text{ scale)}$

Required properties of the coating: (1) Should not readily transport oxygen. 
(2) Should be a good ENOUGH electronic conductor.

Possible coatings: (1) Perovskites (ABO$_3$). (2) Spinels (AB$_2$O$_4$). (3) Donor-doped TiO$_2$. (4) Other.
Model

A quadratic in $x_f$

$$k_c x_f^2 + 2k_f x_c x_f = k_f k_c t$$

Base alloy rate constant

$$k_f \approx \frac{E V_M}{2F} \sigma_i^f$$

Coating permeation kinetic parameter

$$k_c \approx \frac{E V_M}{2F} \sigma_c^c$$

Two limiting cases: (a) Coating un-protective, (b) Coating protective

(a) Un-Protective coating

$$k_c x_f >> 2k_f x_c$$

$$x_f \approx \sqrt{k_f t}$$

Undesirable: Oxidation Kinetics independent of Coating: **PARABOLIC**

(b) Protective coating

$$k_c x_f << 2k_f x_c$$

$$x_f \approx \frac{k_c}{2x_c} t$$

Preferred Case: Oxidation Kinetics independent of Base alloy: **LINEAR**
Calculations Based on Model
Comparison with Experimental Results

$k_c = 10^{-11}$ cm$^2$/s
~Parabolic
Un-protective

$k_c = 10^{-15}$ cm$^2$/s
~Linear
Protective

Parabolic rate constant of the alloy, $k_f = 10^{-12}$ cm$^2$/s

$k_c$ for LSM at 800$^\circ$C is estimated to be $\sim 2.86 \times 10^{-14}$ cm$^2$/s
Calculation of Oxide Scale Thickness

Alloy rate constant: \( k_f = 10^{-12} \text{ cm}^2/\text{s} \)

Coating thickness: \( x_c = 5 \mu\text{m} \)

<table>
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<th>Time (Sec)</th>
<th>Time (hrs)</th>
<th>( x_f ) in µm</th>
<th>( x_f ) in µm</th>
<th>( x_f ) in µm</th>
<th>( x_f ) in µm</th>
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<td>No Coating</td>
<td>( k_c = 10^{-11} \text{ cm}^2/\text{s} )</td>
<td>( k_c = 10^{-12} \text{ cm}^2/\text{s} )</td>
<td>( k_c = 10^{-13} \text{ cm}^2/\text{s} )</td>
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Site-Specific Doping

• Doping on specific sites to alter point defects.
• Strategy used in the past in BaTiO$_3$ (perovskites), LiAl$_5$O$_8$ (spinels).
• Objective is to suppress oxygen ion transport – without drastically lowering the electronic conductivity.

What is the minimum electronic conductivity that the coating must have?
Suppose the coating 5 microns in thickness.
If $\sigma_{el} \sim 1$ S/cm, ASR due to coating will be $0.0005 \ \Omega cm^2$
If $\sigma_{el} \sim 0.1$ S/cm, ASR due to coating will be $\sim0.005 \ \Omega cm^2$
Site Specific Doping in Perovskites & Spinels

Approach to Materials Selection

- Perovskites, Spinels, TiO₂.
- Perovskites – LaMnO₃ with donor doping on the B-site.
- TiO₂ – donor doping.

LaMnO₃ (LM)
La₀.₉₅Sr₀.₀₅MnO₃ (LSM) Higher ionic and electronic conductivities than LM
LaMn₀.₉₅Ti₀.₀₅O₃ (LT₀.₀₅M) Lower ionic and electronic conductivities than LM
LaMn₀.₉₅Ti₀.₀₅O₃ (LT₀.₁M) Lower ionic and electronic conductivities than LT₀.₀₅M
Ti₀.₉₈Ta₀.₀₂O₂
Ti₀.₉₈Nb₀.₀₂O₂

In all of the above materials, electronic conductivity >> ionic conductivity
Fabrication of Prospective Coating Materials in Bulk Form

- Ball milling: For 24 hrs with zirconia media and ethanol.
- Calcination: At 1100°C for 2 hrs.
- Binder: Polyethylene glycol
- Pressing: 10000 lb.
- Isostatic pressing: 2000psi
- Sintering: At 1400°C for 2 hr
  - TiO₂ at 1500°C
- Density: Archimedes Measurement

Weighing powder
  - Ball milling
  - Drying
  - Calcination
  - Ball milling
  - Drying
  - Binder addition
    - Pressing
    - Isostatic pressing
  - Sintering
  - Density measurement
  - Electrical characterization
  - Microscopy
Electrical Characterization of Prospective Coating Materials

- Four Probe DC conductivity measurement (0.04 A): Total conductivity, which is mainly $\sigma_{el}$.
- Two probe, Hebb-Wagner DC polarization measurement (50 $\mu$A): Ionic conductivity, $\sigma_i$.

![Diagram showing measurement setups for $\sigma_{el}$ and $\sigma_i$]
Four Probe DC Conductivity

Even at 500°C, the $\sigma_{el}$ of doped TiO$_2$ is greater than 1 S/cm.
Sandwich Samples for Hebb-Wagner Measurements: LSM-YSZ Interface
Blocking Electrode Measurements

YSZ/LaMnO$_3$/YSZ
Without a bond (platinum paste)
Stabilizes rapidly
Incorrect measurement

YSZ/LaMnO$_3$/YSZ
Co-sintered – Good bond
Does not readily stabilize
Reliable measurement – only when stabilized
Stabilization time could be days or longer

Stabilizes rapidly
800°C

Not stabilized even
After 25 hours at 800°C
Additional Examples of Blocking Electrode Measurements

YSZ/Ti-doped LaMnO$_3$/YSZ
At 800°C: Slower kinetics of Equilibration, because of lower Ionic conductivity.

YSZ/Sr-doped LaMnO$_3$/YSZ
At 800°C: Faster kinetics of Equilibration, because of higher Ionic conductivity.
Kinetics of Stabilization: Hebb-Wagner Polarization Method

1) Kinetics of stabilization (voltage or current, depending upon constant current or constant voltage experiment) depends on:
   (a) Ionic and electronic conductivities of the three layers; namely the two YSZ layers, and the sample.
   (b) Lengths of the three individual layers. The larger the lengths (thicknesses) the longer the time required – dependence is exponential\textsuperscript{a,b}.

2) Four probe measurement is more difficult due to the longer sample lengths.
3) Kinetics is not describable by first order kinetics (not one time constant).
4) For typical transport parameters and sample dimensions, the time required for stabilization can be hours, days, months?

Preliminary Results on Ionic Conductivity Measurements (Hebb-Wagner) at 800°C

Range: \(~5 \times 10^{-5}\) to \(~7 \times 10^{-4}\) S/cm

All are overestimates (may be by orders of magnitude): Not equilibrated

Hebb-Wagner measurements will need to be done on thin sandwich structures.
Preliminary Oxidation Studies

- Oxidation studies initiated on uncoated and coated samples.
- Alloy foils selected include SS430, Inconel 718, Haynes 230.
- Ceramic coatings of thicknesses 1, 2, 3, and 5 \( \mu \text{m} \) deposited by PVD
Oxidation Studies on Uncoated Foils:
Air, 800°C, 4days
Oxidation Studies on Ti$_{0.98}$Ta$_{0.02}$O$_2$-coated (1 µm) Foils
Oxidation Studies on LaMn$_{0.9}$Ti$_{0.1}$O$_3$-coated (2 µm) Foils
Composition profile across Inc718-oxide layer- LaMn$_{0.9}$Ti$_{0.1}$O$_3$ coating: 800ºC, 8 days

- Composition profiles of elements La, Cr, Ni across metal-oxide layer-coating interface. Metal on left side, coating on right side and oxide layer in the center.
- **Sample:** 8 days oxidized Inc718 with 2µm LaMn$_{0.9}$Ti$_{0.1}$O$_3$ coating, at 800ºC

Estimated $k_c \sim 4 \times 10^{-14}$ cm$^2$/s
Composition profile across Haynes 230-oxide layer - LaMn$_{0.9}$Ti$_{0.1}$O$_3$ coating

- Composition profiles of elements La, Cr, Ni across metal-oxide layer-coating interface. Metal on left side, coating on right side and oxide layer in the center.
- Sample: 8 days oxidized Haynes 230 with 2 µm LaMn$_{0.9}$Ti$_{0.1}$O$_3$ coating, at 800°C

Estimated $k_c \sim 3 \times 10^{-14}$ cm$^2$/s
Composition profile across SS430-oxide layer-LaMn$_{0.9}$Ti$_{0.1}$O$_3$ coating

- Composition profiles of elements La, Cr, Ni across metal-oxide layer-coating interface. Metal on left side, coating on right side and oxide layer in the center.

- Sample: 8 days oxidized SS430 with 2µm LaMn$_{0.9}$Ti$_{0.1}$O$_3$ coating, at 800ºC

Estimated $k_c \sim 3 \times 10^{-14}$ cm$^2$/s
Summary

1) A few prospective coating materials were identified.
2) Some doped coating materials were made.
3) Electrical characterization (electronic and ionic conductivities) was initiated.
4) Oxidation studies on coated foils of stainless steels and nickel-based alloys was initiated.
5) Ex-situ measurements and oxidation studies are used to estimate oxidation kinetics – to design superior coating materials through defect chemistry.
6) ASR measurements will be initiated shortly.
7) For accurate measurements of ionic conductivity, thinner sandwich structures are planned.