Electrode Optimization Studies and Cathode Surface Chemistry:

Determination of Key Correlations between Surface Features and Electrochemical Performance

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Outline for Cathode Surface Chemistry

• Overview of Program (Started May 2007)
  Background
  Goals
  Approach
  Team

• Initial Thin Film Work at CMU
  Growth Systems
  Thin Film Characteristics
  Demonstrations of Control

• Initial In-situ X-ray Characterization at ANL
  Environmental Chamber
  Initial Results

• Summary / Future
Ideal Cathode Materials

\[
\frac{1}{2} \text{O}_2(\text{g}) + 2\text{e}^- \rightarrow \text{O}^{2-}
\]

pore conductor

Actively Reduces \( \text{O}_2 \) and Transport \( \text{V}_0^{**} \) and \( \text{e}^- \)

There is no reason to believe that the ideal backbone will have the ideal surface kinetics.

There is reason to believe that the surface structure of known backbones is dynamic under load.

Can we understand / engineer highly-active and stable surfaces?
Ideal Surface Active Cathode Materials

Dynamic Surface / Promoter / Catalyst

- Actively Reduces $O_2$:
- Has high $O_2$ catalyst site density:
- Has sufficient population of $V_O^{\cdot\cdot}$:
- Has low interfacial resistance:
- Has long term surface stability:
- Actively conducts $V_O^{\cdot\cdot}$, $e^-$:

Overlays both electronic and ionic conductor

$O_2(g)$ $O_2(g)$

Electronic / Mixed Conductor Ion Conductor

Electrolyte
The basic lack of direct correlations between surface/interface chemistry/structure and performance hinders the design of optimized (active/stable) SOFC Cathodes.

- Probe the nature of atomic scale surface chemistry or interface crystallography rather than the device scale micro-structural perturbations.

- Determine key correlations between:
  solid state atomic, electronic, and chemical structure parameters and kinetic electrochemical (mass and charge transfer) performance parameters.

- Correlations will be used to develop and employ:
  a high throughput chemical screening methodology that does not require cell optimization and that will provide a sensitive measure of activity/stability in operational conditions.
**Conceptual Sample**

### General Schematic

<table>
<thead>
<tr>
<th>1 - 2 Atomic or Unit Cell Monolayers</th>
<th>≈ 20 - 50 Unit Cells of Epitaxial Perovskite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Macroscopic, Single Crystal Perovskite Substrate of specific orientation / termination</td>
<td></td>
</tr>
</tbody>
</table>

### Example

- **SrMnO$_3$**
  - (100)-terminated (La,Sr)MnO$_3$

### Concept

- Gate
- Reservoir
- Support / Electrolyte

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*Reservoir Remains the Same while the Surface layer is Varied*

*In this case:*

- $LaMnO_3$, $SrMnO_3$, $SrO$, $MnO_2$, or Metal (Pt, Ag, ...)*
Surface Activity

Guiding ideas that will lead to generation of testable hypotheses:

1. A parameter can be identified that dictates the performance of perovskite cathodes

2. This parameter is surface sensitive and is related to: cation-gas bonding, vacancy population, electronic character, etc...

3. Noble metals can be used to change landscape of oxygen surface adsorption

NEED NEW SAMPLE GEOMETRIES AND CHARACTERIZATION METHODS
REAL TIME, IN-SITU MEASUREMENTS OF SURFACE!
**Schematic Approach**

Probe the nature of atomic scale **surface chemistry** or **interface crystallography** rather than the device scale micro-structural perturbations.

Other techniques: Electrical and mass-uptake conductivity relaxation, IS ...
Experimental Values of Interest that are in Dynamic Equilibrium

1. Oxygen uptake kinetics  
   (CMU / NETL / ANL)
2. Surface reduction state / surface vacancy concentration  
   (CMU / NETL / ANL)
3. Adsorbed oxygen species  
   (CMU / NETL)
4. Cation segregation / dopant distribution  
   (CMU / ANL)
5. Nanostructural surface defects  
   step density, surface reconstruction, correlated vacancies  
   (CMU / ANL)
6. Surface band structure / electronic species  
   (ANL)
7. Surface Species  
   (NETL / CMU)
Collaborators

**Surface Engineering / Characterization / TEM**
- B. Kavaipatti, S. Wang, R. Petrova
  Carnegie Mellon
- O. Maksimov, CMU/Penn State

**Surface Stability / Interface Stability**
- L. Helmick, S. Seetharaman
  Carnegie Mellon
- R. Gemman, C. Johnson
  National Energy Technology Laboratories

**Surface Chemistry**
- J. Kitchin
  Carnegie Mellon
- C. Matranga
  National Energy Technology Laboratories

**Detailed Structure and Surface Segregation vs Oxygen Activity**
- J. Eastman, D. Fong, P. Fuoss
  APS, Argonne National Laboratories

**Detailed Structure and Surface Segregation vs Electrochemical Activity**
- K.-C. Chang, D. J. Myers, J. D. Carter, H. You
  APS, Argonne National Laboratories
- B. Yildiz, MIT

**Electrochemical Activity and Cr-Poisoning**
- B. Ingram, T. Cruse, M. Krumpelt
  Argonne National Laboratories
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Thin film approach

Characteristics of thin film growth that affect the oxygen uptake kinetics:

- Film thickness
- Film Morphology
- Orientation/Epitaxy
- Strain
- Dislocation networks
- Growth on electrolytic substrates
- Grain/Variant boundary
- Interdiffusion

Gate Materials:
- \( \text{LaMnO}_3 \)
- \( \text{SrMnO}_3 \)

Reservoir Materials:
- \( (\text{La},\text{Sr})\text{MnO}_3 \)
- \( \text{NdNiO}_3 \)

Substrate Materials
- \( \text{SrTiO}_3 \)
- \( \text{NdGaO}_3 \)
- YSZ
Pulsed Laser Deposition
Laser MBE / MBE

Advantages of PLD

• Targets made via standard methods.
• Stoichiometric transfer from target to film
• High-quality epitaxial films for complex oxides
• High-Quality Metal Films
• Simple, versatile, and relatively inexpensive
• House 6 targets at once

Pulsed Laser Deposition

Deposition Parameters

PRESSURE: 0.00001 - 0.2 Torr
TEMPERATURE: RT - 950 °C
FLUENCE: 1-8 J/cm²
FREQUENCY: 1-10 Hz
COOLING: 0.00001-300 Torr

Depositions:
1 - 4 hrs Max
3 - 4 deps / day
3 - 4 samples / dep

• KrF Excimer Laser:
  \( \lambda = 248 \text{ nm} \)
  • Energy: \(~2 \text{ J/cm}^2\)
  • Frequency: 3 Hz
Growth rate / Surface Morphology

Oscillations in the X-ray reflectivity scan measure thickness

Determine growth rate of Reservoir and Gate

\[(La,Sr)MnO_3 - 0.11 \text{ Å/pulse}\]

\[LaMnO_3 - 0.10 \text{ Å/pulse}\]

PLD Produces High Quality Surface Engineered Films with Controlled Thickness / Roughness
Surface Morphology

LaMnO$_3$ and (La,Sr)MnO$_3$ films (~ 54 nm thick) with low roughnesses obtained on SrTiO$_3$(100) substrates

PLD Produces High Quality Surface Engineered Films with Controlled Thickness / Roughness

rms = 5.5 Å  
Peak-to-Valley = 50 Å

rms = 4.41 Å  
Peak-to-Valley = 30 Å
**$(La, Sr)MnO_3$ thin films on $SrTiO_3(100)$**

Standard X-ray Diffraction Scans of Films 54 nm thick

![Graph showing X-ray diffraction peaks for STO(200), LSMO(200), STO(300), and LSMO(300)]

$(100)_p$-oriented

Out-of-plane compression

In-plane tension

Below critical thickness

All films routinely characterized for XRD
In-plane orientation / Epitaxy

Phi Scan of in-plane X-ray Diffraction Scans of Films 54 nm thick

(402) Peak

Peaks are well aligned

Films is strained to substrate

Orientation relationship is:

\[
\{100\}_p^{Film} \parallel \{100\}_p^{Substrate}; \langle001\rangle_p^{Film} \parallel \langle001\rangle_p^{Substrate}
\]

Standard Characterization Method to Ensure Quality Prior to Other Characterization
Epitaxy along various Orientations
Orientation Mapping / Surface Sensitivity

Electron Back-Scattered Diffraction used to Identify Local Orientations
$La_{0.7}Sr_{0.3}MnO_3$ (50 nm) deposited on $SrTiO_3$
All scan areas $> 20 \times 20$ micron$^2$

(100) $SrTiO_3$
(110) $SrTiO_3$
(111) $SrTiO_3$

All three low-index surfaces are obtained as epitaxial films
(La,Sr)MnO$_3$ thin films on High Quality Insulators

Control Strain State
$La_{0.7}Sr_{0.3}MnO_3$ (54 nm) deposited on NdGaO$_3$(100)$_p$
Minimize Dislocations

Need Reasonable Perovskite Electrolyte(s) for Electrochemistry
(La,Sr)MnO$_3$ thin films on YSZ(100)

Film prefers to grow in a polycrystalline fashion on YSZ(100)

Can obtain textured (110) films

Good for comparison to real SOFC

Poor for Surface Engineering

Will study both Fluorite and Perovskite Electrolytes using Electrochemical Methods

Includes Synchrotron In-situ experiments
SrMnO$_3$ thin films on SrTiO$_3$(100)
Alternate “native perovskite” gate for LSM

Highly-oriented (h00) perovskite-like films attained on the perovskite SrTiO$_3$(100) substrates

Have made surface engineered samples with different gates: starting to measure Intermixing?
Artificial \((\text{LaMnO}_3)_{15.5}(\text{SrMnO}_3)_{5.5}\) structures

- Artificial Structures Stable
- Mixing driving force small
- Inner / Outer Layers Same
- Surface can be engineered
- Samples can be measured
- Long term stability???

Samples are easy to grow once calibrated; several can be grown simultaneously.
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**Synchrotron Glancing Angle X-Ray**

**GOAL:** Understand HOW (La,Sr)MnO$_3$ and (La,Sr)(Co,Fe)O$_3$ Behave

**APPROACH:** Use IDEAL Samples and Sensitive *In-Situ* Probe

- Environmental Cell
- Good Samples
- Surface Morphology
- Grain/Variant boundary
- Segregation / Interdiffusion
- Beam Line / Time
- Structure
- Strain
- Temperature (Quenching?)
- Electrochemistry
Preliminary Investigation Using Synchrotron XRD

Environmental Chamber
Allows to Investigate
in appropriate cathode conditions

Temperature: RT - 800°C
Pressure: 10^{-3} - 7 \times 10^2 \text{ Torr}
Process Gas: O_2 - Argon
Flow Rate: 1 - 10^3 \text{ sccm}

Grazing Incidence X-ray
Provides Surface Sensitivity

Spectroscopy

Ideal thin film samples:
atomically FLAT
no wafer curvature
Low dislocation content
La$_{0.7}$Sr$_{0.3}$MnO$_3$ on SrTiO$_3$(100)

Glancing Angle Measurements on thick “Capping Layers” (14 Unit Cells)

\[ 20^\circ, 700^\circ, \text{thickness} = 54\text{Å}, pO_2 = 0.26\text{ Torr} \]

- Films Ultrathin and Ultraflat at temperature
- Thickness = 54 Å from fringes
- Film lattice-matched to the substrate in-plane scan (not shown) 0.77% tensile strain

PLD Produces High Quality Surface Engineered Films that are Flat, Stable, and Measurable
Oxygen Pressure Effects
In-situ Surface Morphology

Glancing Angle Measurements on Roughness of Thick Capping Layer

Low $pO_2$
0.26 Torr to 0.024 Torr
no measurable effect

High $pO_2$
0.26 Torr to 100 Torr
roughness increased

Real-time measure on affect of $P / pO_2$ on surface structure
**Effects of Increasing Thickness**

*Glancing Angle Measurements on thin “Reservoirs” (200 Unit Cells)*

- Thickness fringes with two characteristic lengths are observed (~68 nm and ~7.5 nm)
- Consistent with previous TEM observations of partially relaxed films
  → Wiedenhurst et al. (J. Mag. Mag. Mater., 211, 16, 2000)
  misfit dislocations localized to ~60 nm from the (La$_{7}$Sr$_{3}$)MnO$_{3}$/STO interface

*Can observe relaxations in films / Determine Strain State In-situ*
Bulk Structure of Strained La$_{0.7}$Sr$_{0.3}$MnO$_3$

Scattering Measurements on thin “Reservoirs” (200 Unit Cells)

- Observe 1/2-order reflections; likely related to octahedral tilts
- Not typical for films at 700°C (not typical to observe this)
- Observed in polycrystalline LSMO; Martin et al. (*PRB*, 53, 14285, 1996) antiferrodistortive structure
- Need to Determine Origin

Bulk Reservoir Structure Determination In-situ
Temperature Dependent Structure Investigations

Scattering Measurements on thin “Reservoirs” (200 Unit Cells)

Superstructure Persists from Room-Temperature to 700°C

Can determine structure that is “quenched”
1. Careful analysis is required to correct for absorption:
PRELIMINARY OBSERVATIONS

2. Sr-signal increases on decrease of $pO_2$, while Mn and La(+Ti) decreases

3. Consistent with few literature reports that surface segregation occurs
Surface Structure

Surface Sensitive Scattering Measurements on thin “Reservoirs” (200 Unit Cells)

Pressure Changed (at *) from 100 Torr to 0.01 Torr

1/2-order reflections Persist
Only weak drop in intensity

Surface STRUCTURE weakly changed
implies no clear phase separation

Need to combine fluorescence and XRD…

Both Structure and Composition of Surface Have been measured: being analyzed
Summary / Future Directions

• **Kicked Off Large-Scale Effort to Understand / Engineer Cathodes Surfaces for Improved Performance**
  Assembled Large Group with Appropriate Expertise
  All Groups Have Launched Initial Studies

• **Effort focused on Thin Film / Engineered Surfaces**
  CMU Generating Samples for Wide Ranging Efforts
  Characterize In-House Samples Prior to Sending
  Implement ECR / XPS / Auger In-House
  Develop / Implement High-T Crystal Microbalance
  Develop HIGH-THROUGHPUT Method to identify KEY CORRELATIONS

• **Initial In-situ X-ray Characterization at ANL**
  Environmental Chamber Analyze Results
  Investigate Surface Engineered Samples
  Use other Beams: Surface Electronic Structure / Electrochemical