Mixed Ionic Electronic Conducting Quaternary Perovskites: Materials by Design for Solar Thermochemical Hydrogen

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HydroGEN Kick-Off Meeting

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PI, Arizona State University
Co-PI, Princeton University

Project Vision
Accurate (enough) first principles calculations of the oxygen chemical potential for complex mixed ionic electronic (off-stoichiometric) doubly substituted perovskite solid solutions from which we can extract the thermodynamics

Project Impact
We aim to contribute to materials discovery for improved STCH materials. Aim to offer strategies to boost solar to hydrogen thermal efficiency, as well as to provide experimentalists with crucial input to synthesize, validate, and perform further tests on promising candidates. Aim to determine best possible depending on operating conditions to guide systems design.

Change in Entropy
\[ \partial \Delta S(\delta; T) / \partial \delta \]

Ceria (CeO₂ Fluorite structure)
Innovation and Objectives

Project history
As program manager of Sandia’s Sunshine to Petrol grand challenge LDRD, funded Chris Wolverton to develop material’s discovery capabilities.

Awareness of the Carter group capabilities on related Solid Oxide materials and on complex photovoltaic semiconductors chemical potential. Known each other for a long time, but we had not collaborated scientifically before and knew that the perfect postdoc was joining her group.

Barriers
Directly comparison experiment / theory.
Open shells and disorder.
Adapt and apply computational materials design capability to calculate and validate chemical potentials.
Relate calculated oxygen chemical potentials to materials thermodynamics, enthalpy and entropy of reduction and the equilibrium off-stoichiometry for a range of gas phase conditions.

Proposed targets

<table>
<thead>
<tr>
<th>Metric</th>
<th>State of the Art</th>
<th>Proposed</th>
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</thead>
<tbody>
<tr>
<td>Parameter 1</td>
<td>Reduction temperature &gt; 1500 °C</td>
<td>Reduction temperature &lt; 1450 °C</td>
</tr>
<tr>
<td>Parameter 2</td>
<td>Reduction Capacity $\Delta \delta &gt; 0.15$ per cation</td>
<td>Or best possible at practical partial pressures</td>
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<tr>
<td>Parameter 3</td>
<td>N/A</td>
<td>20% accurate chemical potentials over relevant operating window</td>
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Partnerships
Dean Emily Carter, Princeton University
Dr. Sai Gopalakrishnan, Princeton University

Expertise: developing new DFT capabilities, complex oxides, calculating chemical potentials in complex disordered materials

Specific capabilities: functionals (SCAN+U), transferable “U” parameters, cluster expansion
Solar thermochemical cycles with redox active metal oxides

\[ \text{MO}_x \to \text{MO}_{x-\delta} + \delta/2 \text{O}_2 \]  
1. Endothermic Reduction on Sun

\[ \text{MO}_{x-\delta} + \delta \text{H}_2\text{O} \to \text{MO}_x + \delta \text{H}_2 \]  
2. Exothermic Re-oxidation off Sun

- Two step thermochemical cycle – two temperatures, different partial pressures of oxygen, different oxygen chemical potentials - repeat over and over indefinitely
- Like charging and discharging a battery, must have a electron accepting band.

\[
\begin{align*}
\text{O}_{(s)}^{-2} & \leftrightarrow 2e_{r,(s)}^- + \frac{1}{2} \text{O}_{2,(g)} \\
2e_{r,(s)}^- + \text{H}_2\text{O}_{(g)} & \leftrightarrow \text{O}_{(s)}^{-2} + \text{H}_2_{,(g)}
\end{align*}
\]
Promising class of materials

• Mixed Ionic-Electronic Conducting (MIEC) Perovskites or Fluorite oxides
• Several properties of significance:
  – High temperature stability and phase “stable”
  – Redox-active (like charging a battery, receptive multivalent metal site, happy home in a conduction band for the reducing electrons that are left behind)
    – E.g., (A,A’)(B,B’)O_{3-x} \leftrightarrow ABO_{3-x-\delta} + \delta/2 \text{O}_2(\text{g})
    – equilibrium $\delta$ is a function of $T$ and $p_{O_2}$

• Redox activity is continuous over a range of $T$ and $p_{O_2}$
• No major crystallographic phase change occurs during redox
• Vacancies facilitate oxygen ion transport, bulk active
• Best studied is Ceria CeO$_2$

Like SrTiO$_3$ – but redox active. SrMnO$_3$

O$^{2-}$ ion can “hop” via vacancies

A cation
B cation
Oxygen anion
Vacancy on anion lattice
Technology Innovation

- Develop a capability to calculate solid state equation of state: $\delta = \delta(T, p_{O_2})$
- Extract thermodynamic properties from $(T, p_{O_2}, \delta)$ triplets
  - Derived from experimental and/or computational data with uncertainty quantification
- Validating computation with experiment
  - Current practice
    - van’t Hoff approximation with or without invoking defect models
      - Apply arbitrary or “informed” $\delta$-dependence
    - CALPHAD (very rigorous! Very time-consuming)
- Model-free approach to analyze $(T, p_{O_2}, \delta)$ data
  - $\Delta H(\delta, T)$ and $\Delta S(\delta, T)$ derived from equilibrium $(T, p_{O_2}, \delta)$ response surface
Mapping the $p_{O_2}$-T-$\delta$ space

- Experimentally measure oxygen off-stoichiometry concentration ($\delta$) in non-stoichiometric oxides as a function of $p_{O_2}$ and Temperature.
  - Thermogravimetry (TGA), coulometric titration, other methods (electrochemical)?
- Calculate from first principles


CeO$_2$

La$_{0.6}$Sr$_{0.4}$MnO$_3$ (LSM40)
O₂ gas properties and functional dependence of equilibrium δ on T and p₀₂ determines the thermodynamics

• Fit a two dimensional response surface (material specific parameters, one functional form) given measured triplets {T, p₀₂, δ} ideally from computation validated by experiment so that:

\[- z(δ) \equiv f \left( \frac{T_{\text{ref}}}{T}, \frac{1}{2} \ln \frac{p_{\text{ref}}}{p₀₂} \right) \text{ and} \]

\[- \frac{1}{2} \ln \frac{p_{\text{ref}}}{p₀₂} \equiv g \left( \frac{T_{\text{ref}}}{T}, z(δ) \right) \text{ - convenient if easily invertible} \]

• Need reliable and reproducible (T, p₀₂, δ) data over a relevant range of expected conditions

- Low T, low p₀₂ for gas splitting
- Avoid extrapolating outside data envelope unless we can derive physically relevant response surfaces
Reactions measured at fixed $T$ and $p_{O_2}$

What we refer to as $\Delta H(\delta; T)$ and $\Delta S(\delta; T)$ is really:

$$\Delta H(\delta; T) = \lim_{d\delta \to 0} \frac{H_{sol}(\delta + d\delta; T) - H_{sol}(\delta; T)}{d\delta} + \frac{1}{2} H_{O_2,g}(T)$$

$$\frac{\partial H_{solid}(\delta; T)}{\partial \delta} = \frac{R T_0 \partial \ln \left( \frac{p^{ref}}{p_{O_2}} \right)}{2 \partial \left( \frac{T_{ref}}{T} \right)} - \frac{1}{2} H_{O_2,g}(T)$$

$$\frac{\partial S_{solid}(\delta; T)}{\partial \delta} = -\frac{R \partial \ln \left( \frac{p^{ref}}{p_{O_2}} \right)}{2 \partial \ln \left( \frac{T}{T_{ref}} \right)} - \frac{1}{2} S_{O_2,g} \left( T; p_{O_2}(\delta; T) \right)$$

Enthalpy and entropy of reaction (incremental change in $\delta$) are local partial derivatives of the same function.
Fitted response surfaces and derivatives determine enthalpy and entropy of incremental reaction

\( \frac{1}{2} \ln(\text{pref}/p_{O2}) \)

Contours are for constant \( z(\delta) \)

CERIA CeO\(_{2-\delta}\) using Data from CALPHAD

\( \delta \)

Slope determines \( -\frac{\partial \Delta S(\delta;T)}{\partial \delta} \)

\( \ln(T/T_{\text{ref}}) \)

\( T_{\text{ref}}/T \)

Slope determines \( \frac{\partial \Delta H(\delta;T)}{\partial \delta} \)
Derivatives determine enthalpy and entropy of incremental reaction for Ceria (or other materials).

\[
\frac{\partial \Delta S(\delta; T)}{\partial \delta}
\]

\[
\frac{\partial \Delta H(\delta; T)}{\partial \delta}
\]

Small temperature dependence as expected.
HydroGEN: Advanced Water Splitting Materials

Fitted response surface for LSM40 using data from CALPHAD

\[ \frac{1}{2} \ln \left( \frac{p_{\text{ref}}}{p_{O2}} \right) \]

Ln(T/T_{\text{ref}}) \quad \frac{\partial \Delta S(\delta; T)}{\partial \delta} \quad \frac{\partial \Delta H(\delta; T)}{\partial \delta} \quad \frac{T_{\text{ref}}}{T}

La_{1-x}Sr_xMnO_{3-\delta} \quad x=0.4
Calculate chemical potentials from first principles

Model-free approach to analyze \((T, p_{O_2}, \delta)\) comes from

\[
\frac{\partial \mu_{\text{solid}}(\delta; T)}{\partial \delta} = -\frac{1}{2} \mu_{O_2}(T, p_{O_2})
\]

- \(H(\delta, T)\) and \(S(\delta, T)\) derived from equilibrium response surface and heat capacity (of the oxidized material) by integration of the derivatives

- Calculating chemical potentials from first principles would permit a very direct comparison between theory and experiment

- Pathway to rapid data reduction to the thermodynamics across the relevant parameter space (including, e.g., \(\delta\)-dependence of the heat capacity)
Effective Leveraging of the EMN Resource Nodes

NREL:
- Materials synthesis of promising materials

SNL:
- High-temperature x-ray diffraction and complementary thermal analysis.
- Uncertainty quantification in computational (and experimental) models of physical systems.
- Virtually accessible laser heated stagnation flow reactor for characterizing redox chemistry of materials under extreme conditions.

Hope the following will become available for the consortium
- System efficiency as a function of the cycle operating conditions and material thermodynamics (and kinetics).
Thank you for your attention