Transformative Materials for High-Efficiency Thermochemical Production of Solar Fuels

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Project Overview

Project Partners
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Project Vision
Combine high-throughput computation and experiment to discovery and design novel, improved STCH materials.

Project Impact
Will explore enormous combinatorial space of materials, to “tune in” desired STCH enthalpy and entropy of reduction. We will design materials with reduced temperatures of reduction but sufficient gas-splitting rates.

* this amount does not include cost share or support for HydroGEN resources leveraged by the project (which is provided separately by DOE)
**Approach - Summary**

**Project Motivation**
Project builds on background of PIs in STCH materials, attempt to combine high-throughput computational and experimental exploration of oxygen off-stoichiometric oxides and phase change materials for enhancing the efficiency of STC production of solar fuels.

**Key Impact**
Identify compounds which show: a) synthesizeability, b) thermodynamics favorable for <1400°C reduction and c) thermodynamics favorable for facile water splitting. State-of-the-art currently CeO$_2$ and SLMA perovskite.

**Barriers**
Risk mitigated by exploring large space of novel STCH materials, and the combined use of high-throughput calculations and experimental efforts to explore this space. Focus to date is on perovskite and double-perovskite oxide materials.

**Partnerships**
Productive collaborations with three HydroGEN nodes and other seedling projects: Ginley (NREL) – in-situ XRD and synthesis, Zakutayev (NREL) – thin-film composition gradient synthesis, McDaniel/Coker (SNL) high-T XRD, O’Hayre (CSM) – (Sr,Ce)$_2$MnO$_4$ layered perovskite.
A Design Map for Materials:

Thermodynamics very challenging for stoichiometric reactions (at moderate pressure)

Perovskites ($ABO_3$ or $AA'BB'O_6$)
- Until recently: ceria ($CeO_2$) [1]
- More recently: perovskites [2]
- Perovskites have several good qualities for TWS
  - Tolerate large oxygen off-stoichiometry
  - High Stability
  - Studied for other applications (e.g. SOFC)
- Enormous compositional space
- High-Throughput Density Functional Theory, The Open Quantum Materials Database (OQMD)
- High-Throughput screening of ~11,000 $ABO_3$ perovskites based on stability and reduction enthalpy

Summary of Year-1 Scope of Work
(a) Experimentally measure the reduction enthalpy and entropy of twelve predicted simple perovskites
(b) Validate high-throughput methodology for measuring thermodynamic property using thin film through electrochemical impedance
(c) Initiate high-throughput computational search for promising double-perovskite compounds

This project relies heavily on the computational predictions, the correct ranking of computed vacancy formation energy relative to experimental reduction enthalpy of the nine perovskites will be validated. The obtained reduction entropy will be used to establish models to predict compounds based on reduction entropy.
Relevance & Impact

• This project aims to identify promising compounds which show:
  – a) ground state stability/synthesizeability of compound,
  – b) thermodynamics favorable for <1400C reduction and
  – c) thermodynamics favorable for facile water splitting.

State-of-the-art currently CeO$_2$ and SLMA perovskite.

• Discovery of new, higher-efficiency materials is critical towards the practical use of STCH for H$_2$ production (and solar fuels, more generally). *Our combined high-throughput computation + experimental approach is greatly accelerating this materials discovery effort.*

• *Collaborations with HydroGEN nodes (NREL, SNL) and other Seedling projects (CSM) will greatly facilitate research progress*
Accomplishments – Synthesis and Reduction of Oxide Materials

Objective

Experimental measurements of redox thermodynamics of computationally predicted perovskites by TGA

Aims:

(i) Validate the enthalpy calculation

(ii) Obtain high-quality entropy data to guide/validate future entropy calculations
Accomplishments – Thermodynamic Measurements

- 17 ABO$_3$ compounds were synthesized via sol-gel method and the temperature stability range of each material was tested.

- Thermogravimetry (TG) was employed to measure oxygen nonstoichiometry at different oxygen partial pressures and temperatures (remain single phase), and the reduction enthalpy and entropy were extracted.

Reduction: $\frac{1}{\delta_f - \delta_i} \text{MO}_{x-\delta_i} \rightarrow \frac{1}{\delta_f - \delta_i} \text{MO}_{x-\delta_f} + \frac{1}{2} O_2(g)$

When at Equilibrium: $\Delta G = \Delta G^0 + RT \ln(K^{eq}) = 0$

$K^{eq} = pO_2^{1/2} = \exp(-\frac{\Delta G^0}{RT}) = \exp(-\frac{\Delta H^0 - T\Delta S^0}{RT})$

$\frac{R}{2} \ln(pO_2) = -\frac{\Delta H^0}{T} + \Delta S^0$

For a given $\delta$, linear relation of $\frac{R}{2} \ln(pO_2)$ vs. $\frac{1}{T}$ gives slope= $-\Delta H^0$, intercept= $\Delta S^0$

$\Delta H$ and $\Delta S$ control T, P for water splitting

Also, provides key data to validate computational methods.
Accomplishments – Measurement Procedure

Stepwise heating profile

10 °C/min ramp + 1 h hold

Example: YMnO₃

Mass change on heating

10 °C/min: 1400 → 1500 °C

Measure under 5 different $pO₂$ conditions (0.030 atm shown)

Return to reference mass at end of cycle

At end of ramp step, no mass change during isothermal hold

Sample was equilibrated throughout heating
Accomplishments – Measurement Procedure

Example:

\[ \delta = 0.018 \]

\[ \frac{R}{2} \ln(pO_2) = -\frac{\Delta H^\circ}{T} + \Delta S^\circ \]

At a given \( \delta \)

Intercept = \( 2\Delta S/R \)

Analysis inherently smoother using data from continuous profile
Accomplishments – Measurements of Two Key Thermodynamic Quantities, $\Delta H$ and $\Delta S$ of Reduction

Example: YMnO$_3$

- Enthalpy
  - Comp: 289 kJ/mol
  - $325 \pm 5$ kJ/mol
  - Corresponds to inflection at $\delta = 0.0125$

- Entropy
  - $170 \pm 3$ J/mol/K
  - Corresponds to inflection at $\delta = 0.0125$

- Data collected in *the same* experiment
- Continuous heating/cooling preferred, so long as equilibration is ensured
- Below inflection $\delta$, access oxygen interstitial sites (?), mechanistic transition (?)
Accomplishments – Are $\Delta H$ and $\Delta S$ Correlated?

**Enthalpy vs. Entropy**

Compare the enthalpy vs. entropy of reduction of twelve perovskites evaluated in Year-I:

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta H$ (kJ/mol O)</th>
<th>$\Delta S$ (J/mol O/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO$_2$</td>
<td>400</td>
<td>200</td>
</tr>
<tr>
<td>CaMnO$_3$</td>
<td>300</td>
<td>150</td>
</tr>
<tr>
<td>LaMnO$_3$ (Ref)</td>
<td>200</td>
<td>100</td>
</tr>
<tr>
<td>LaNiO$_3$</td>
<td>100</td>
<td>50</td>
</tr>
<tr>
<td>SmCoO$_3$</td>
<td>50</td>
<td>25</td>
</tr>
<tr>
<td>PrCoO$_3$</td>
<td>25</td>
<td>12.5</td>
</tr>
<tr>
<td>HoMnO$_3$</td>
<td>12.5</td>
<td>6.25</td>
</tr>
<tr>
<td>LuMnO$_3$</td>
<td>6.25</td>
<td>3.125</td>
</tr>
<tr>
<td>YMnO$_3$</td>
<td>3.125</td>
<td>1.5625</td>
</tr>
<tr>
<td>BaMnO$_3$</td>
<td>1.5625</td>
<td>0.78125</td>
</tr>
<tr>
<td>SrMnO$_3$</td>
<td>0.78125</td>
<td>0.390625</td>
</tr>
<tr>
<td>YFeO$_3$</td>
<td>0.390625</td>
<td>0.1953125</td>
</tr>
</tbody>
</table>

Generally, the higher enthalpy, the higher entropy.

Compared with CeO$_2$, CaMnO$_3$ (orthorhombic), LaNiO$_3$ and SrMnO$_3$ may be promising perovskites.
Accomplishments: Data-Driven Approach

The Open Quantum Materials Database (OQMD) oqmd.org
Large-scale materials database of ~600,000 compounds

OQMD:
The Open Quantum Materials Database

Newsflash: OQMD v1.1 is out! (Download it here.)

Welcome to the Open Quantum Materials Database

The OQMD is a database of DFT-calculated thermodynamic and structural properties. This online interface is for convenient, small-scale access; for a more powerful utilization of the data, we recommend downloading the entire database and the API for interfacing with it, from the link below.

You can...

Search for materials by composition,
Create phase diagrams using the thermochemical data in OQMD,
Determine ground state compounds at any composition,
Visualize crystal structures, or
Download the entire database (and the API) for your own use!


HydroGEN: Advanced Water Splitting Materials
Accomplishments: High-throughput DFT Screening of STCH Materials

High-Throughput of ~11,000 ABO$_3$ Perovskites Screened for Stability and Reduction Enthalpy

Provides initial targeted compounds for experimental exploration

Accomplishments: Accurate DFT Vacancy Formation Energies Require Correct Crystal Structure

ABO₃ compounds can exist in many structure types:
- Perovskites, with various types of distortions
- Non-perovskites

Example: YFeO₃

Observed ground state structure is distorted perovskite
Vacancy Formation Energy in distorted vs. cubic perovskite = 4.22 eV vs. 3.20 eV

Previous High-Throughput Study (Emery et al., 2016), calculated vacancy formation energies in cubic structures only. Assumption of high-T cubic phases.

We can now compare with experimental results and find this previously-used approximation to be poor! So, we had to re-evaluate many of the vacancy formation energies with the correct ground state structures!
Accomplishments: Quantitative Validation of Approach

Comparison of Experimental and DFT Calculated Reduction Enthalpies
(Key factor for both reduction and water splitting reactions)

LuFeO₃, HoFeO₃, LuCrO₃, ErCrO₃, HoCrO₃ – mass loss in stability window too small for reliable experimental measurement of reduction enthalpy
Accomplishments: New double perovskites discovery by using high throughput (HT) screening

B-site ordered $\text{Ba}_2\text{BB'}\text{O}_6$

- HT calculations on $\sim 10^4$ double perovskite compounds.
- Our high throughput DFT screening reproduces most already known compounds and predicts $\sim 400$ new, stable double perovskite compounds.
- Several hundred new $\text{Sr}_2\text{BB'}\text{O}_6$ and $\text{Ca}_2\text{BB'}\text{O}_6$ compounds have been discovered (not shown here)

These predicted double-perovskites will serve as initial points of exploration for Year 2 experiments
Accomplishments: Computational Prediction of Double Perovskites for STCH

- Key finding: B-site Mn$^{4+}$ is much easier to reduce than other cations. Provides a chemical target for our search - double-perovskites with B-site Mn$^{4+}$. (The spread of the value is mainly from the effects of octahedral distortion.)

- Therefore, we performed DFT calculations on known Mn$^{4+}$ containing double perovskites, and found the oxygen vacancy formation energy varies from 2.2 to 3.4 eV/vacancy.

7 New Predictions for Stable Double-Perovskites with Favorable Water Splitting Thermodynamics

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Structure</th>
<th>$E_v^0$ (eV/vacancy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr$_2$TiMnO$_6$</td>
<td>P21/c</td>
<td>2.190</td>
</tr>
<tr>
<td>La$_2$CuMnO$_6$</td>
<td>P21/c</td>
<td>2.892</td>
</tr>
<tr>
<td>La$_2$ZnMnO$_6$</td>
<td>P21/c</td>
<td>3.031</td>
</tr>
<tr>
<td>Sr$_2$CuWO$_6$</td>
<td>Fm-3m</td>
<td>3.071</td>
</tr>
<tr>
<td>Sr$_2$CuWO$_6$</td>
<td>I4/m</td>
<td>3.111</td>
</tr>
<tr>
<td>Sr$_2$ZrMnO$_6$</td>
<td>Fm-3m</td>
<td>3.270</td>
</tr>
<tr>
<td>La$_2$NiMnO$_6$</td>
<td>P21/c</td>
<td>3.438</td>
</tr>
</tbody>
</table>
Collaboration: Discovery of Layered Perovskite STCH Compound

Collaboration with HydroGEN node (SNL) and other project (CSM)

Layered perovskite

\[ \text{Formula: } \text{Ce}_x\text{Sr}_{2-x}\text{MnO}_4 \]

<table>
<thead>
<tr>
<th>Formula</th>
<th>Stability [eV/atom]</th>
<th>Decomposition reactions</th>
<th>Oxygen vacancy formation energy [eV/O atom]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce(<em>{0.1})Sr(</em>{1.9})MnO(_4)</td>
<td>0</td>
<td>Stable</td>
<td>1.763</td>
</tr>
<tr>
<td>Ce(<em>{0.2})Sr(</em>{1.8})MnO(_4)</td>
<td>0</td>
<td>Stable</td>
<td>2.243</td>
</tr>
<tr>
<td>Ce(<em>{0.3})Sr(</em>{1.7})MnO(_4)</td>
<td>0</td>
<td>Stable</td>
<td>2.661</td>
</tr>
<tr>
<td>Ce\text{SrMnO}_4</td>
<td>0.061</td>
<td>0.500 Ce(_2)O(_3) + 0.500 Sr(_2)Mn(_2)O(_5)</td>
<td>-</td>
</tr>
</tbody>
</table>

DFT calculations suggest:
- Stability of layered perovskite for \(x\sim0.1-0.3\).
- Vacancy formation energy suitable for STCH

Experimental results corroborate stability and water-splitting ability of this compound!!

Collaboration: HydroGEN Node In-Situ XRD

Collaboration with HydroGEN, data collected at SNL

Major conclusion: Stability highly dependent on $pO_2$

Waterfall plot shows phase separation behavior

$825^\circ C$: $\text{YMnO}_3 \rightarrow \text{Y}_2\text{O}_3 + \text{MnO}$

Courtesy of Robert Bell and David Ginley, NREL
Publications (several in preparation)


Invited Presentations (partial list)

- 2019 American Chemical Society
- 2019 Materials Research Society
- 2019 Telluride Science Research Center Workshop
- 2018 TMS
Proposed Future Work

Experimental:
• The experimental work will test site-substituted versions of the most promising materials found in Year 1
• Synthesis and testing of double perovskite compounds predicted by computation in Year 1.
• Synthesizing combinatorial samples for electrochemical testing
• Continued testing of electrochemical method and comparison to TGA (e.g., thicker samples).

Computational:
• Significantly expand range of chemistries consider for potential double-perovskites; use experimental data from Year 1 to validate more refined thermodynamic models.
• Entropy calculations of reduction entropy – to compare with TGA experiments
• High throughput DFT screening of oxygen vacancy formation energy of double perovskites
• Tailoring oxygen vacancy formation energy by A- and B-site doping: alloying B-site metals with different reduction energies, e.g., BaMnxCe1-xO3; alloying A-site metals to control octahedral rotation, which also has large influence on oxygen vacancy formation energy
Project Summary

• Experimentally measured the enthalpy and entropy of predicted twelve perovskites and validated the high-throughput DFT calculation approach.

• Validated the high-throughput electrochemical impedance approach to extract redox thermodynamics by using gradient film.

• Initiated the evaluation of predicted double perovskites and doped perovskites.