Accelerated Discovery of Advanced RedOx Materials for STWS to Produce Renewable Hydrogen

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Overview

Timeline
• Start: 9-1-2014
• End: 8-31-2017
• 25% completed as of 5/31/2015
• 2 PhD students started 1/1/2015

Budget
• Total Project Funding
• Funds received in FY15
  $58,000 (to be updated)

Partners
Prof. Alan Weimer (CU Boulder)

Barriers
X. (to be updated)
Relevance

Overall Objectives:
1. Develop a computationally accelerated and experimentally validated materials-by-design approach to discover materials with optimum STWS properties and that can be tailored for materials discovery for other technologies;
2. Use our accelerated materials discovery approach to screen metal oxide materials for STWS and the reactor developed in the DOE effort and provide a rank ordered list of promising redox materials;
3. Address fundamental and broad materials chemistry questions in accomplishing tasks 1 and 2.

Objectives This Period:
1. Develop theoretical models that predict promising STWS thermodynamics and kinetics based on fundamental materials properties (descriptors).
2. Develop a computational materials screening approach based on 1 to identify materials with promising thermodynamic and kinetic properties for STWS.
3. Apply screening approach to binary oxides and validate its predictions.
Approach

Project Technical Approach

- Computational prototyping of hercynite & related materials integrating theory and experimentation
- Using both thermodynamic and kinetic filters in optimization of materials for quasi-isothermal solar water splitting

Apply fundamental materials science, chemistry and physics to develop materials design rules and discover promising materials using state-of-the-art electronic structure theory. For this objective, quantum simulations require careful, expert application due to limits of the methods, effects of spin and complexity of detailed mechanisms.
Criteria for Materials Assessment

Overall: \( \text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2} \text{O}_2 \) (\( \Delta H_{\text{ws}} = 286 \text{ kJ/mol} \))

Oxidation: \( \Delta S < 0 \) therefore \( \Delta H \) must be \( \leq 0 \)

Reduction: \( \Delta H_{\text{red}} + \Delta H_{\text{ox}} \geq \Delta H_{\text{ws}} \) therefore \( \Delta H_{\text{red}} \) must be \( \geq 286 \text{ kJ/mol} \)

If \( \Delta H_{\text{red}} < 286 \text{ kJ/mol} \), the material is unlikely to drive water splitting, and can be eliminated from screen.
A Case Study: Metal Aluminates

Stoichiometric Mechanism

[Doped Hercynite Cycle Mechanism]

Determine doped Hercynite cycle mechanism

O-vacancy Formation mechanism

Determine predictive ability with novel aluminate STWS materials

CoAl$_2$O$_4$  Co$_x$Fe$_{1-x}$Al$_2$O$_4$  FeAl$_2$O$_4$
Hercynite Stoichiometric Rxn Has Insufficient Reduction Power, but O-vacancy Rxn Can Reduce Water

If \( \Delta H_{\text{red}} < 286 \text{ kJ/mol} \), the material is unlikely to drive water splitting, and can be eliminated from screen.

**Stoichiometric Mechanism**

\[
\begin{align*}
\text{MO}_x & \rightarrow \text{MO}_{x-\delta} \quad \text{Heat} \\
\text{H}_2 & \rightarrow \text{H}_2 \quad 800-1000^\circ\text{C} \\
\text{H}_2\text{O} & \rightarrow \text{O}_2 \quad 1200-1500^\circ\text{C} \\
\end{align*}
\]

\( \Delta H_{\text{red}} < 0 \text{ kJ/mol} \)

\( \Delta H_{\text{ox}} = 138 \text{ kJ/mol} \)

Not thermodynamically viable

**O-vacancy Formation Mechanism**

\[
\begin{align*}
\text{CO}_{0.33}\text{Fe}_{0.66}\text{Al}_2\text{O}_4 & \rightarrow \text{Fe}^{3+} \quad \text{Heat} \\
\text{H}_2 & \rightarrow \text{H}_2 \quad 800-1000^\circ\text{C} \\
\text{H}_2\text{O} & \rightarrow \text{O}_2 \quad 1200-1500^\circ\text{C} \\
\end{align*}
\]

\( \Delta H_{\text{red}} = 384 \text{ to } 621 \text{ kJ/mol} \)

\( \Delta H_{\text{ox}} = -102 \text{ to } -335 \text{ kJ/mol} \)

Thermodynamically viable
Predicted $\text{H}_2$ Generation of $\text{MAI}_2\text{O}_4$

**Predicted O-vacancy relative $\text{H}_2$ production capacity:**

Assuming full reduction of all reducible sites at 1500°C and using the relative availability of the sites, we predict the relative $\text{H}_2$ generation capacity of the aluminates operating via O-vacancy mechanism to be:

$$\text{FeAl}_2\text{O}_4 \geq \text{Co}_{0.5}\text{Fe}_{0.5}\text{Al}_2\text{O}_4 > \text{CoAl}_2\text{O}_4$$

Relative $\text{H}_2$ production: $1: 0.7 : 2 \times 10^{-4}$

**Predicted Stoichiometric Reaction Relative $\text{H}_2$ Production Capacity:**

If we assume that the STWS criterion ($\Delta H > 286 \text{ kJ/mol}$) does not hold, and therefore any material can split water, we predict a relative $\text{H}_2$ generation capacity for the aluminates operating via a stoichiometric reaction mechanism to be:

$$\text{CoAl}_2\text{O}_4 > \text{Co}_{0.5}\text{Fe}_{0.5}\text{Al}_2\text{O}_4 > \text{FeAl}_2\text{O}_4$$

Relative $\text{H}_2$ production: $1: 0.13: 0.004$
Experimental Validation of Predicted STWS Behavior and Mechanism

1500/1350°C Near-isothermal Water Splitting

**Relative H₂ production capacity:**
- $\text{FeAl}_2\text{O}_4 \geq \text{Co}_{0.5}\text{Fe}_{0.5}\text{Al}_2\text{O}_4 > \text{CoAl}_2\text{O}_4$
- Relative H₂ production: 1: 0.6 : 0

**Predicted O-vacancy H₂ production capacity:**
- $\text{FeAl}_2\text{O}_4 \geq \text{Co}_{0.5}\text{Fe}_{0.5}\text{Al}_2\text{O}_4 > \text{CoAl}_2\text{O}_4$
- Relative H₂ production: 1: 0.7 : 2X10⁻⁴

**Predicted stoichiometric H₂ production capacity:**
- $\text{CoAl}_2\text{O}_4 > \text{Co}_{0.5}\text{Fe}_{0.5}\text{Al}_2\text{O}_4 > \text{FeAl}_2\text{O}_4$
- Relative H₂ production: 1: 0.13: 0.004

Experimental H₂ generation matches our predicted O-vacancy mechanism H₂ generation values. Therefore, the aluminates likely operate via an O-vacancy mechanism and the thermodynamic criteria developed for assessing STWS materials and mechanism is valid. Additionally, a new STWS material FeAl₂O₄ has been shown to be active.
Simple Descriptor Model Predicts $\Delta H_f(O \text{ vac})$

- Vacancy formation energy predicted using descriptor model.
- Errors in predicting band gap by DFT methods are systematic (as determined by $GW_0$) and scaled in model.
- Descriptor model applies to a broad range of metal oxides.

Deml, Holder, O'Hayre, Musgrave and Stevanovic, Submitted 2015.
Calculated predicted $E_{O\text{-}vac}$ for 1045 possible binary perovskites using method developed in our group by Deml et al.

- 570 materials spontaneously phase transitioned out of the perovskite structure
- 237 materials have reduction enthalpies too low to drive STWS ($E_{O\text{-}vac} < 280$ kJ/mol)
- 199 materials are potentially capable of driving STWS* ($280$ kJ/mol < $E_{O\text{-}vac} < 600$ kJ/mol)
- 39 materials have reduction enthalpies too high for practical use as STWS materials ($E_{O\text{-}vac} > 600$ kJ/mol)

*Materials were not analyzed for thermal stability or fabrication practicality
Spin Considerations

Relative energies in kJ/mol of the spin states for inverse and normal aluminate and ferrite spinels.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Co$_3$O$_4$</th>
<th>CoAl$_2$O$_4$</th>
<th>CoFe$_2$O$_4$</th>
<th>Fe$_3$O$_4$</th>
<th>FeAl$_2$O$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>All up$^c$</td>
<td>135</td>
<td>0</td>
<td>71</td>
<td>52</td>
<td>0.0</td>
</tr>
<tr>
<td>Alternating layers$^d$</td>
<td>57</td>
<td>0.7</td>
<td>19</td>
<td>0.0</td>
<td>0.3</td>
</tr>
<tr>
<td>Tetrahedral and octahedral$^e$</td>
<td>83</td>
<td>N/A</td>
<td>0.0</td>
<td>8</td>
<td>N/A</td>
</tr>
<tr>
<td>Other</td>
<td>0.0$^f$</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>All up$^c$</td>
<td>N/A</td>
<td>19</td>
<td>34</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Alternating layers$^d$</td>
<td>0</td>
<td>0</td>
<td>N/A</td>
<td>54</td>
<td></td>
</tr>
<tr>
<td>Inversion energy$^g$</td>
<td>85</td>
<td>-14</td>
<td>33</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Inversion parameter (x) at 1200 °C</td>
<td>0.02</td>
<td>0.85</td>
<td>0.23</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$Energy differences in kJ/mol
$^b$All electrons for Co and Fe atoms initially set to spin up
$^c$Electrons in every other layer of Co and/or Fe atoms initially set to alternate spin up & spin down.
$^d$Electrons of all tetrahedral atoms initially set to spin up. Electrons of all octahedral atoms initially set to spin down.
$^e$Electrons of tetrahedral Co atoms initially set to high spin states (μ=3) and octahedral Co atoms initially set to low spin states (μ=0.1).
$^f$The energy difference, in kJ/mol, between the lowest energy inverse structure and normal structure. A positive number indicates that the normal structure is energetically preferred, while a negative number indicates that the inverse structure is preferred.

Considerations:
- Lowest energy spin state may vary between normal and inverse structure
- Lowest energy spin states may vary between host structure and O-vacancy defect structure
- Finding spin states currently requires manually testing of multiple configurations followed by multiple runs near minimum for verification

Possible Opportunities:
- Develop script for ‘smart’ testing of spin states
- Incorporate spin effects into O-vacancy model

Both spin and inversion can significantly affect the predicted STWS behavior of candidate materials - requires added complexity in O-vacancy formation energy models
Hydrogen formation appears unfavorable without the oxygen vacancies. The activation barriers along this pathway will not be calculated.

On ceria, the formation of hydrogen is the rate limiting process in the water splitting reaction.* We expect that it will be the most important activation barrier for other materials as well.

Preliminary Kinetics Results

NEB method is being used to identify the transition state of the hydrogen evolution reaction on hercynite (in progress)

Iron hydrogen interactions appear to stabilize points around the transition state
Collaborators

Prof. Alan Weimer (Univ. of Colorado Boulder)
Prof. Ryan O’Hayre (Colorado School of Mines)
Dr. Ann Deml (NREL)
Dr. Aaron Holder (NREL)
Dr. Vladan Stevanovic (NREL)
Technology Transfer Activities

None to date
Future Work

1. Determine whether our approach for predicting the H₂ production capacities extends to a broader set of metal oxides.

2. Applied our STWS approach for predicting water splitting abilities to additional binary perovskites and then to ternary perovskites and other metal oxides.

3. Extend our descriptor model of oxygen vacancy formation energy to systems with various spin and oxygen vacancy configurations, including “smart” scripts for automated searches.

4. Continue to develop a model to predict H₂ formation kinetics (which are rate-limiting) based on fundamental materials descriptors and validate it with direct transition state calculations and kinetics experiments.

5. Develop automated processes for analyzing the materials data calculated to determine correlations between STWS redox abilities and fundamental materials properties.
Summary

1. Identified a simple criteria and approach for assessing the redox capabilities of metal oxides.
2. Developed and experimentally validated an approach to predict the H₂ production capacities and redox mechanisms in metal oxides. Extending approach to other systems.
3. Applied our previously developed model to predict the water splitting abilities of over 1000 binary perovskites (as of 4/10/2015) and identified ~200 materials with redox thermodynamics capable of splitting water.
4. Extended descriptor model of oxygen vacancy formation energy. Model applies well to systems with limited numbers of low energy spin configurations.
5. Calculated Developing automated approaches to examine the effects of local atomic and spin arrangements on oxygen vacancy formation energy and redox thermodynamics.
6. Developing a model to predict H₂ formation kinetics (which are rate-limiting) based on fundamental materials descriptors.
Acknowledgements

Amanda Hoskins (Univ. of Colorado Boulder)
Brian Ehrhart (Univ. of Colorado Boulder)
Aaron Holder (NREL)
National Science Foundation - CBET
Back-up slides
Spinel structure

- Normal:
  - Tetrahedral
  - Octahedral
  - Tetrahedral
  - Octahedral
  - Tetrahedral

- Inverse:
  - Tetrahedral
  - Octahedral
  - Tetrahedral
  - Octahedral
  - Tetrahedral

Examples:
- FeAl$_2$O$_4$
- CoFe$_2$O$_4$
High temperature XRD also suggests an O-vacancy mechanism for the hercynite cycle.
EDS analysis of phase segregation in the hercynite material

Reduced

Oxidized in CO₂
EDS analysis of phase segregation in the hercynite material
STWS phase separation or no separation

Unreacted Fe$_3$O$_4$/ZrO$_2$

Reduced Fe$_3$O$_4$/ZrO$_2$

Reduced Hercynite

Oxidized Hercynite

Scheffe et al. E&ES, 2013, 6, 963
Stagnation Flow Reactor

Gas Flow

To Mass Spectrometer

Desiccant

To Pump

Electric Furnace

Electric Furnace

Sample crucible sits here

O$_2$ analyzer
Water Splitting Reactor Set-up

O₂ Analyzer

Steam Generator

Furnace 25 – 1700 °C

In-Situ Mass Spec
Highly Porous Scaffolding

- Cavilink™ Porous Polymer
- Maximum internal volume > 90%
- Density (typical) < 0.1 g/cc
- Cavity diameter up to 30 μm
- Composition – many polymer formulations possible
Particle Coating

- SEM and TEM of Al$_2$O$_3$ coatings on polymer Scaffolding