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

Christopher Muhich, Samantha Miller, Ryan Trottier, Emory Smith, Alan Weimer and Charles Musgrave (P.I.)

University of Colorado at Boulder

Project: PD120
NSF CBET-1433521

This presentation does not contain any proprietary, confidential or otherwise restricted information

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

  2014-2017: $525,371K NSF

- 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.

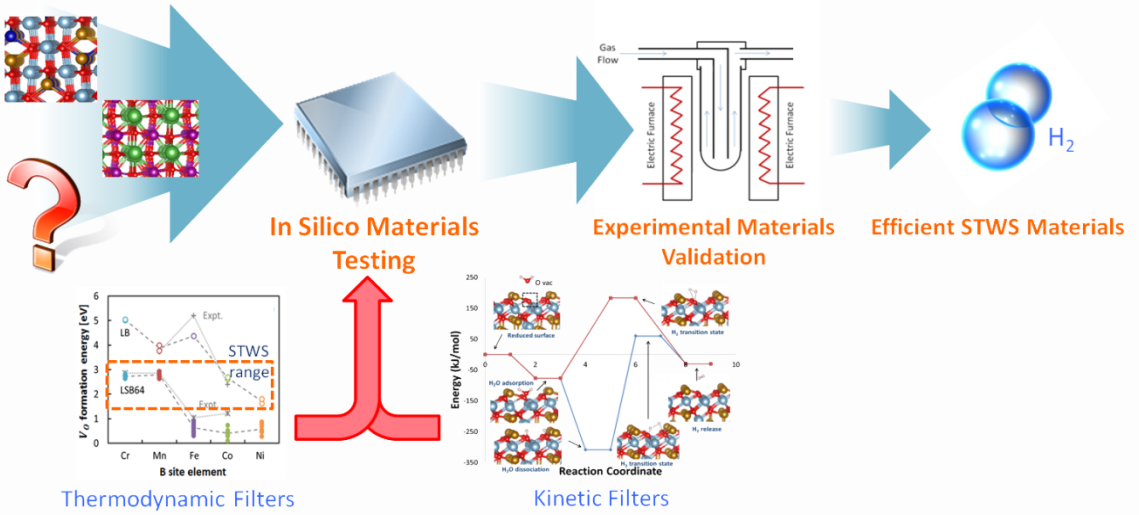
Objectives This Period:

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.

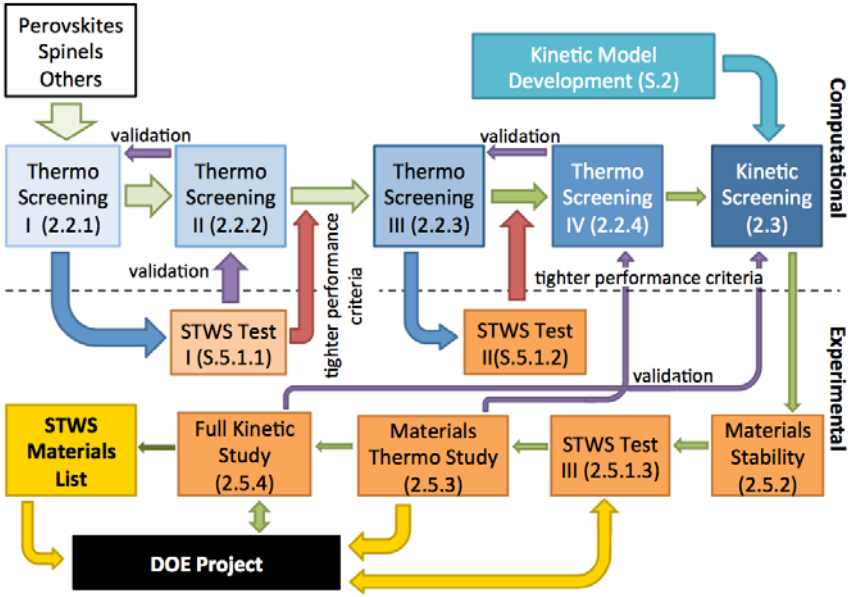
Approach

Project Technical Approach

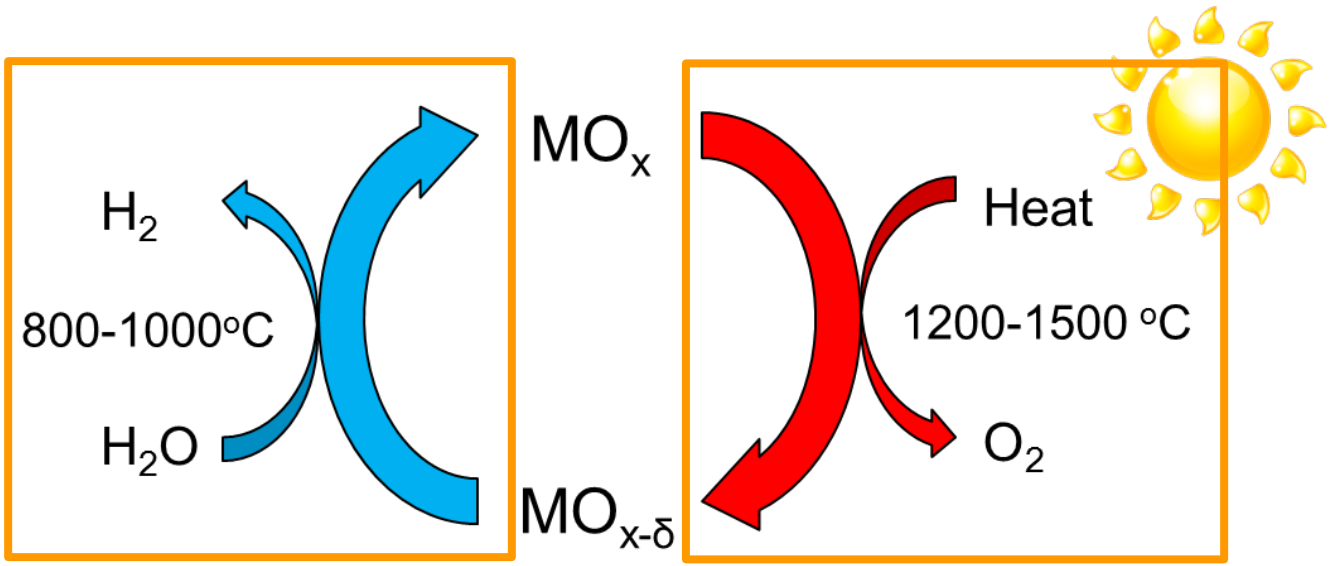
- Computational prototyping of hercynite & related materials integrating theory and experimentation
- Using both thermodynamic and kinetic filters in optimization of materials for quasi-isothermal solar water splitting



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



$\Delta H_{red} < 0$ kJ/mol

$\Delta H_{red} > 286$ kJ/mol

Overall: $H_2O \rightarrow H_2 + 1/2\ O_2$ ($\Delta H_{ws} = 286$ kJ/mol)

Oxidation: $\Delta S < 0$ therefore ΔH must be ≤ 0

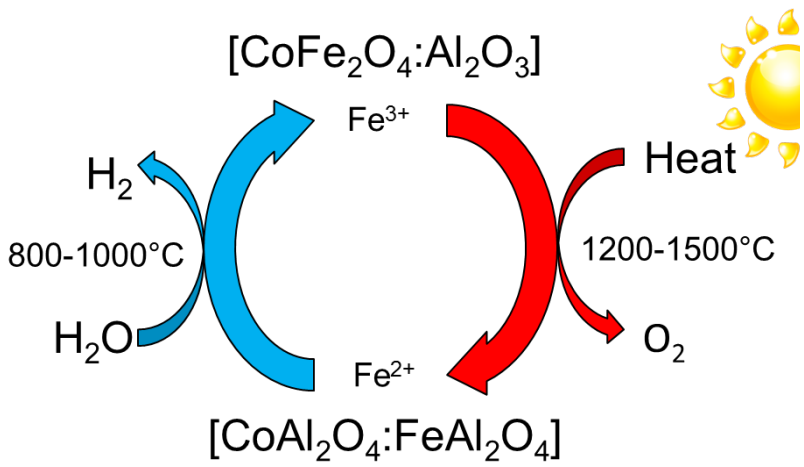
Reduction: $\Delta H_{red} + \Delta H_{ox} \geq \Delta H_{ws}$ therefore ΔH_{red} must be ≥ 286 kJ/mol

If ΔH_{red} <286 kJ/mol, the material is unlikely to drive water splitting, and can be eliminated from screen.

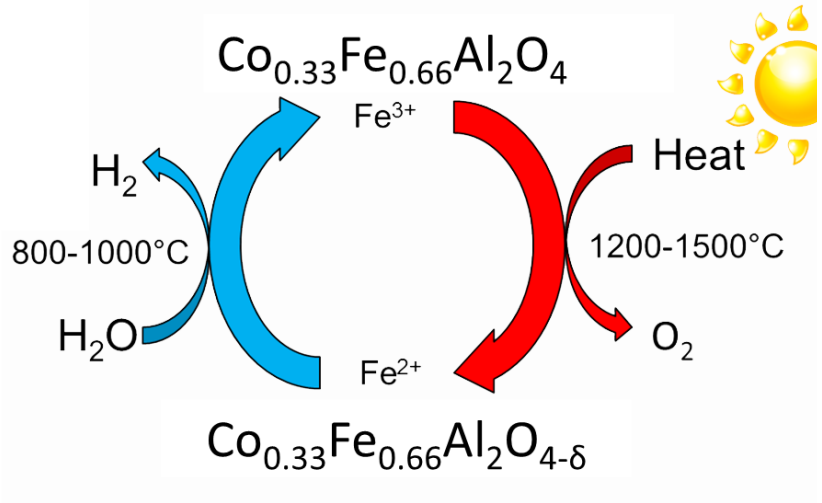
A Case Study: Metal Aluminates

Determine doped hercynite cycle mechanism

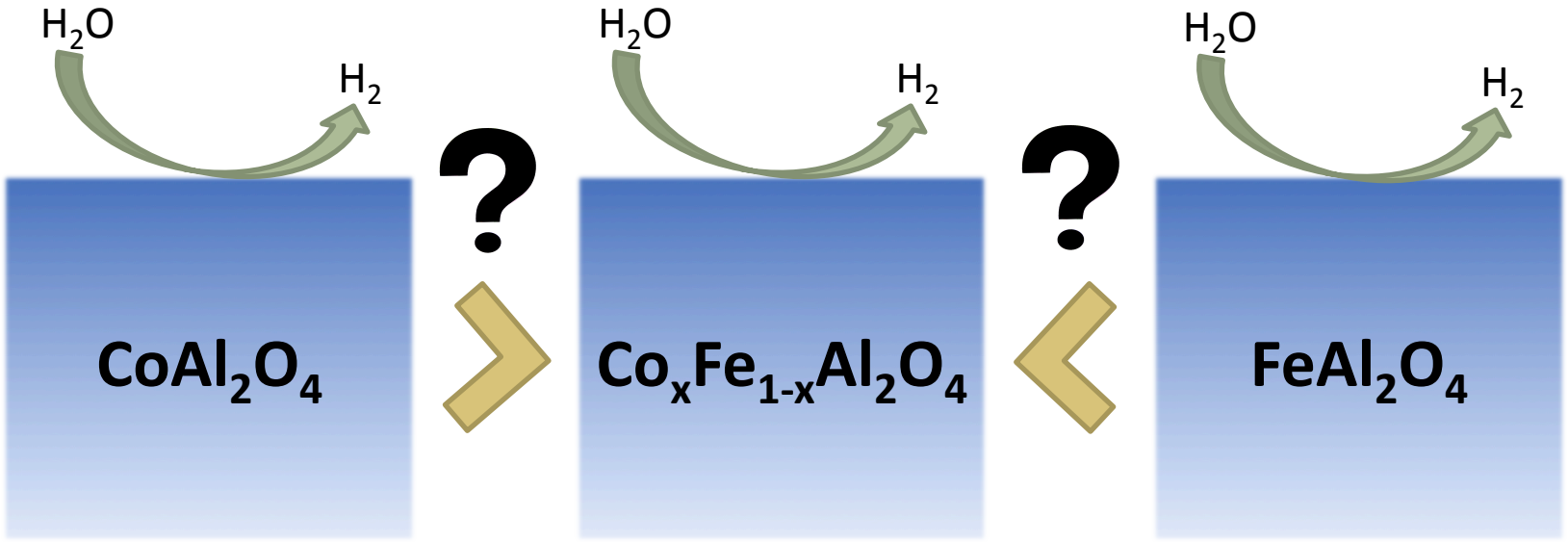
Stoichiometric Mechanism



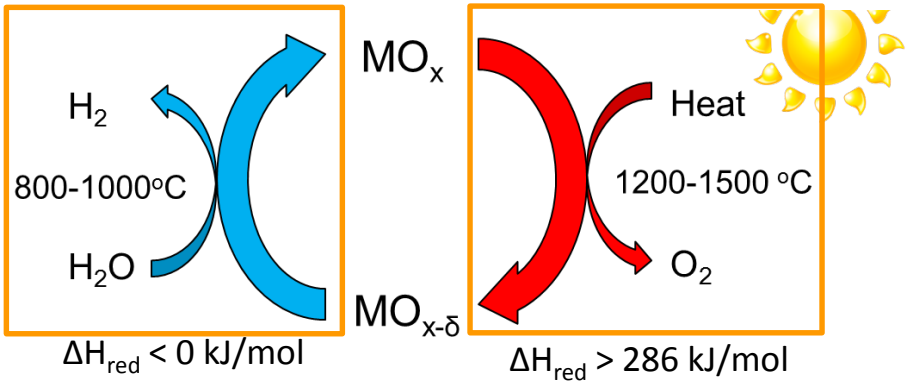
O-vacancy Formation mechanism



Determine predictive ability with novel aluminate STWS materials

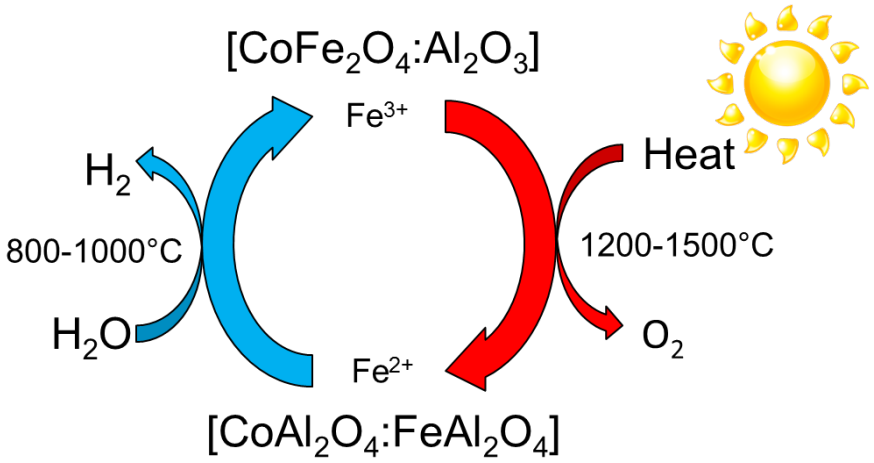


Hercynite Stoichiometric Rxn Has Insufficient Reduction Power, but O-vacancy Rxn Can Reduce Water



If ΔH_{red} <286 kJ/mol, the material is unlikely to drive water splitting, and can be eliminated from screen.

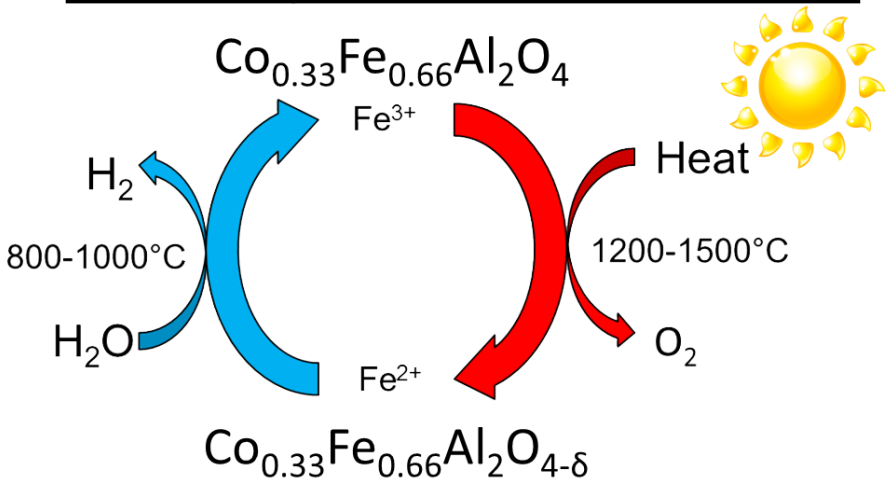
Stoichiometric Mechanism



ΔH_{red} = 150 kJ/mol
ΔH_{ox} = 138 kJ/mol

Not thermodynamically viable

O-vacancy Formation Mechanism



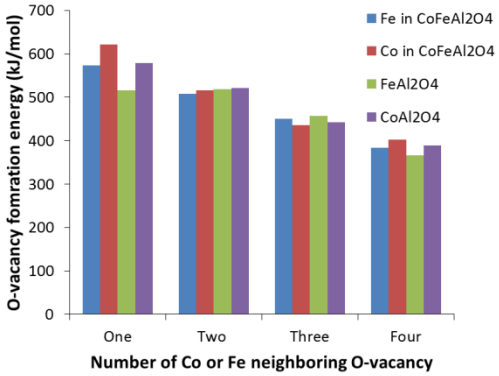
ΔH_{red} = 384 to 621 kJ/mol
ΔH_{ox} = -102 to -335 kJ/mol

Thermodynamically viable

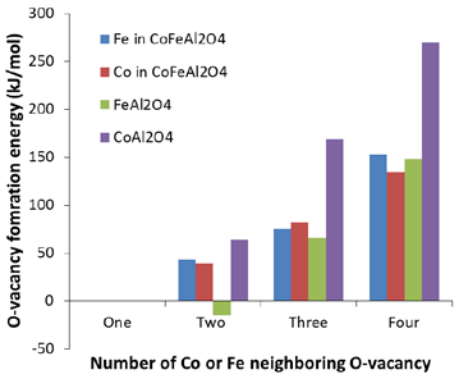
Predicted H_2 Generation of MAl_2O_4

Predicted O-vacancy relative H_2 production capacity:

O-vacancy formation energy



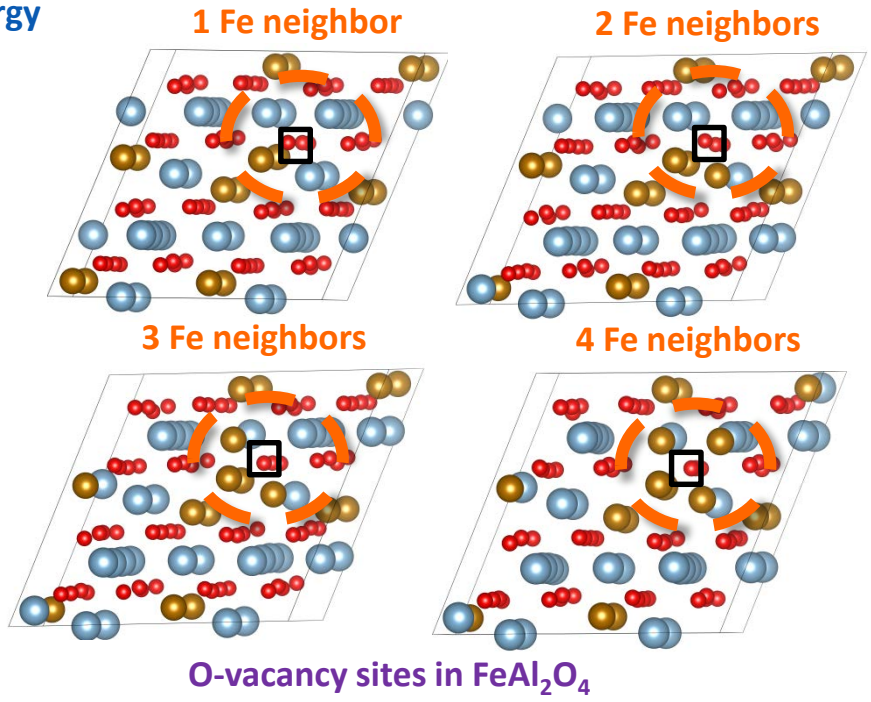
O-vacancy site formation energy



Assuming full reduction of all reducible sites at 1500 C and using the relative availability of the sites, we predict the relative H_2 generation capacity of the aluminates operating via O-vacancy mechanism to be:

$$FeAl_2O_4 \geq Co_{0.5}Fe_{0.5}Al_2O_4 > CoAl_2O_4$$

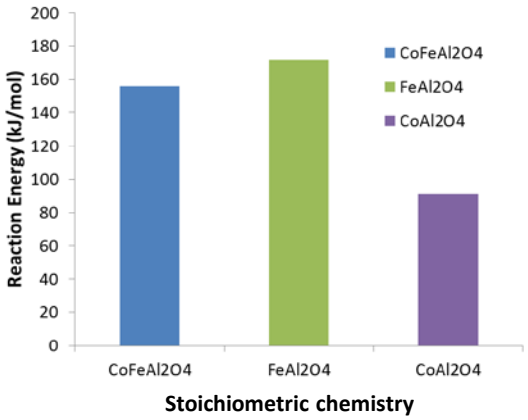
Relative H_2 production: 1: 0.7 : 2×10^{-4}



O-vacancy sites in $FeAl_2O_4$

Predicted Stoichiometric Reaction Relative H_2 Production Capacity:

Stoichiometric reaction energy



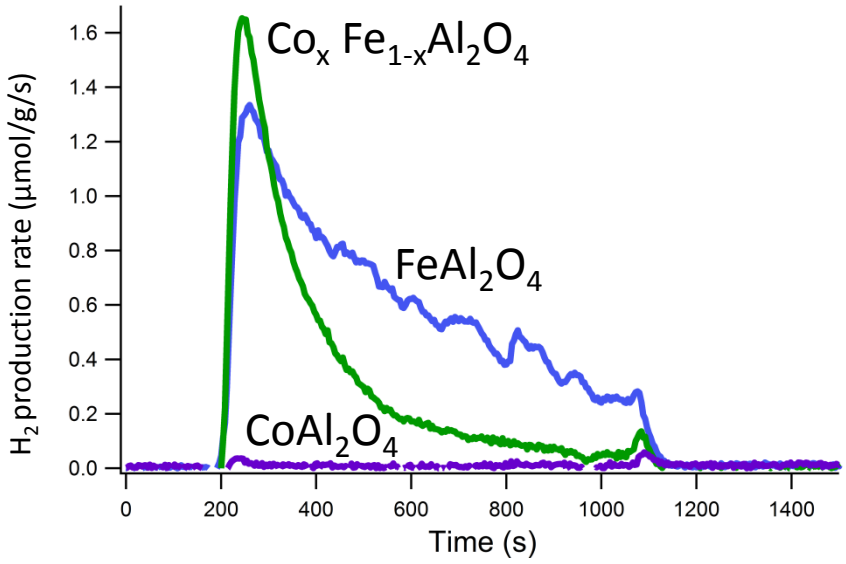
If we assume that the STWS criterion (ΔH > 286 kJ/mol) does not hold, and therefore any material can split water, we predict a relative H_2 generation capacity for the aluminates operating via a stoichiometric reaction mechanism to be:

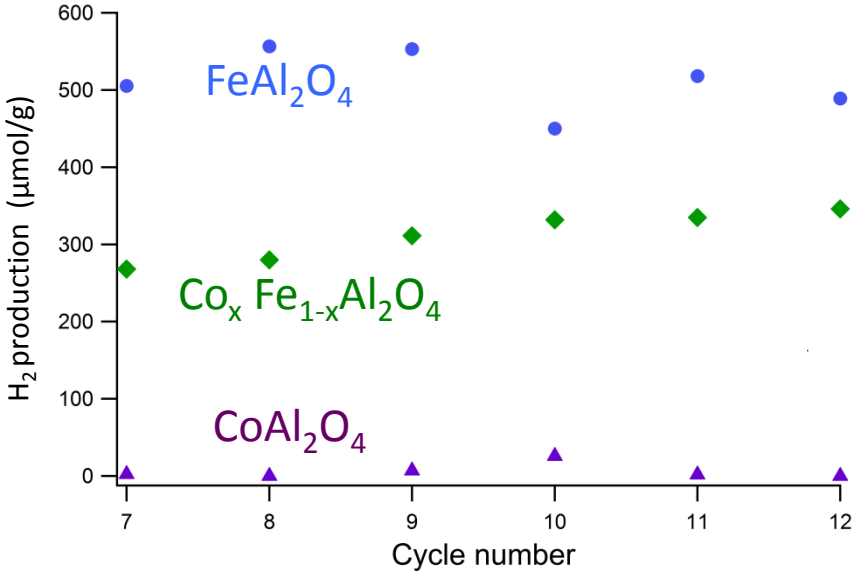
$$CoAl_2O_4 > Co_{0.5}Fe_{0.5}Al_2O_4 > FeAl_2O_4$$

Relative H_2 production: 1: 0.13: 0.004

Experimental Validation of Predicted STWS Behavior and Mechanism

1500/1350°C Near-isothermal Water Splitting





Relative H_2 production capacity:

$FeAl_2O_4 \geq Co_{0.5}Fe_{0.5}Al_2O_4 > CoAl_2O_4$

Relative H_2 production: 1: 0.6 : 0

Predicted O-vacancy H_2 production capacity:

$FeAl_2O_4 \geq Co_{0.5}Fe_{0.5}Al_2O_4 > CoAl_2O_4$

Relative H_2 production: 1: 0.7 : $2X10^{-4}$

Predicted stoichiometric H_2 production capacity:

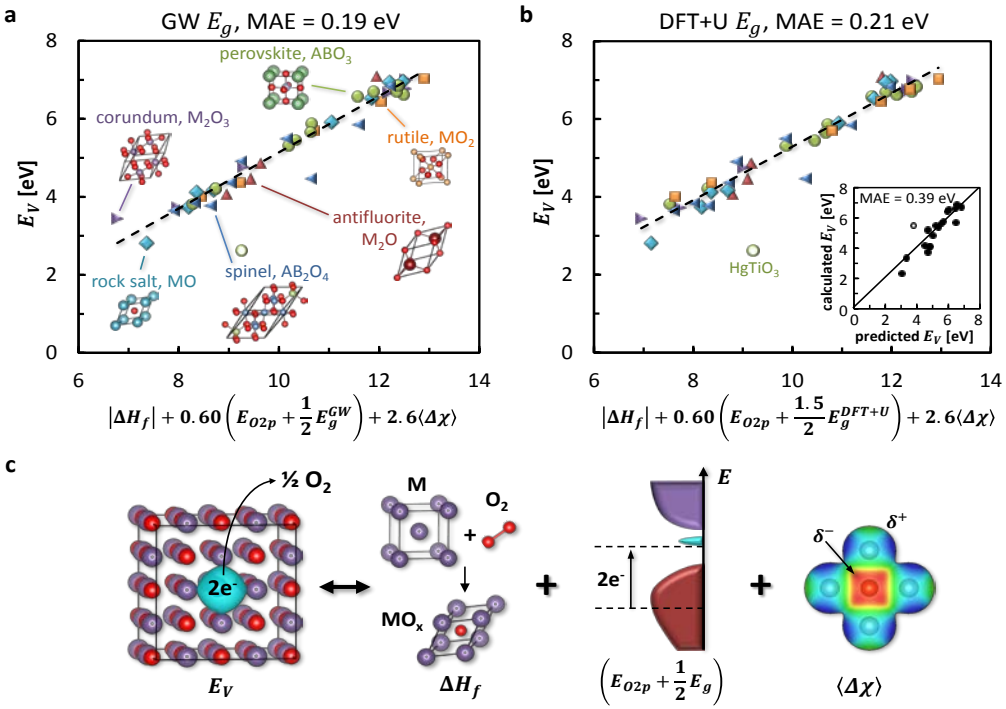
$CoAl_2O_4 > Co_{0.5}Fe_{0.5}Al_2O_4 > FeAl_2O_4$

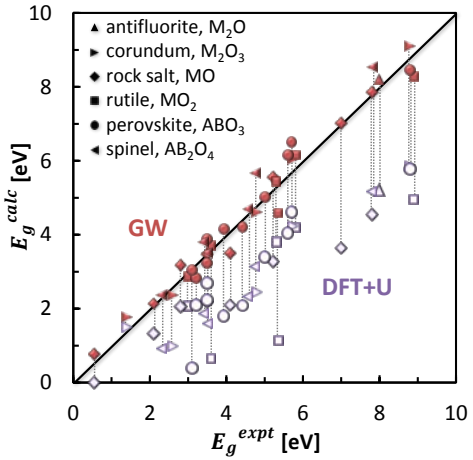
Relative H_2 production: 1: 0.13: 0.004

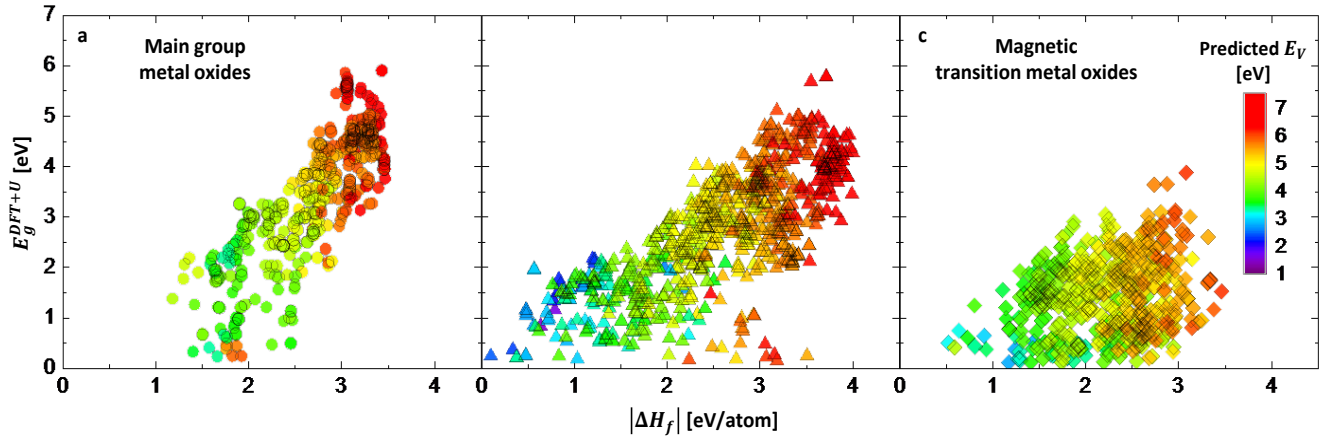
Experimental H_2 generation matches our predicted O-vacancy mechanism H_2 generation values. Therefore, the aluminates likely operate via an O-vacancy mechanism and the thermodynamic criteria developed for assessing STWS materials and mechanism is valid. Additionally, a new STWS material $FeAl_2O_4$ has been shown to be active.

Simple Descriptor Model Predicts ΔH_f(O 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.



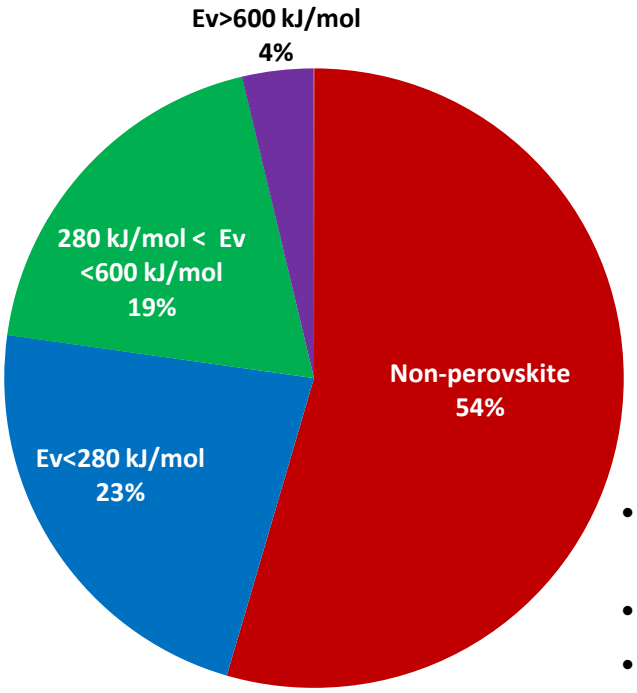




Deml, Holder, O'Hayre, Musgrave and Stevanovic, Submitted 2015.

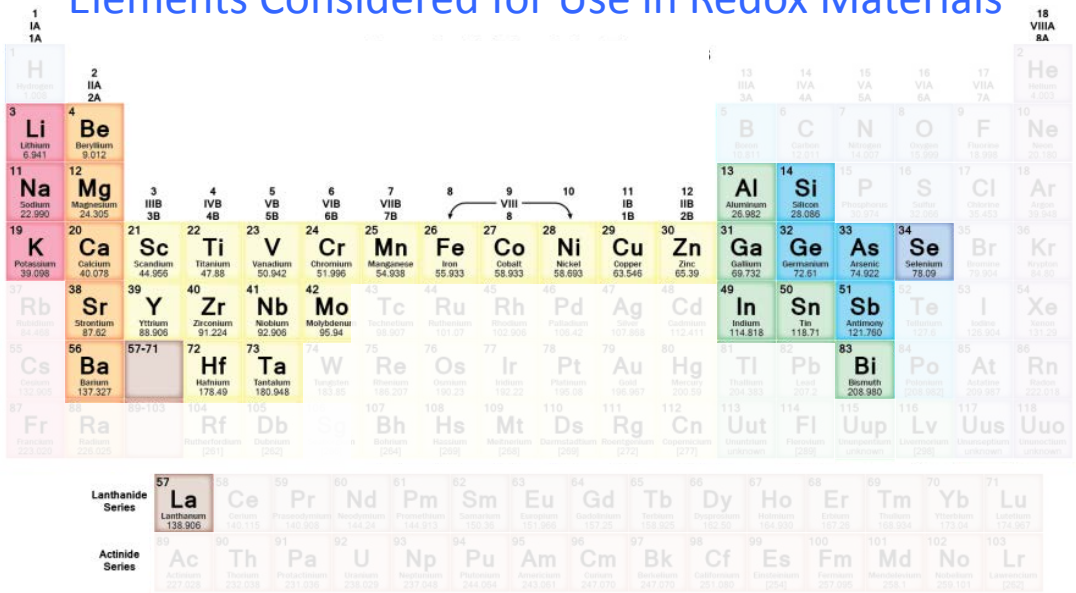
Binary Novel Perovskite Screening

Binary Perovskite Screening Results



1045 materials screened
As of 4/10/2015

Elements Considered for Use in Redox Materials



- 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)

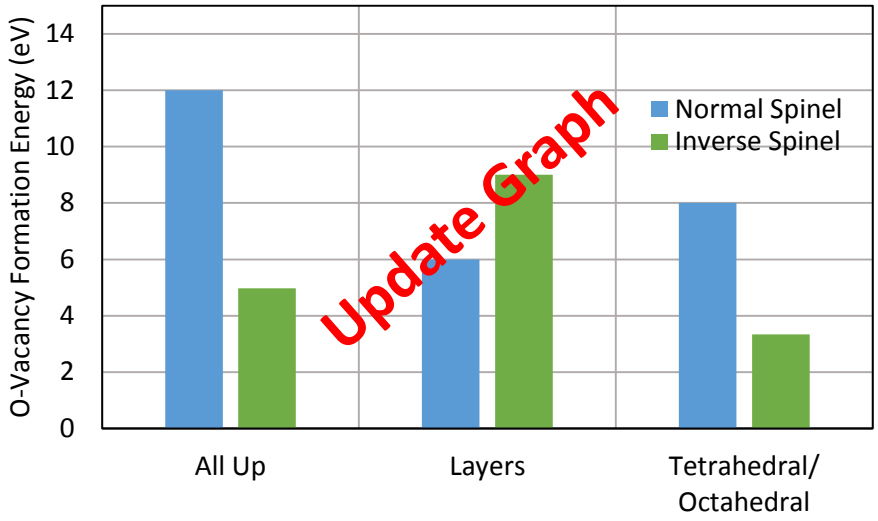
* *Materials were not analyzed for thermal stability or fabrication practicality*

Spin Considerations

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

Configuration		Co_3O_4	$CoAl_2O_4$	$CoFe_2O_4$	Fe_3O_4	$FeAl_2O_4$
Inverse[a]	All up[c]	135	**0.0**	71	52	**0.0**
	Alternating layers[d]	57	0.7	19	**0.0**	0.3
	Tetrahedral and octahedral[e]	83	N/A	**0.0**	8	N/A
	Other	**0.0**[f]	N/A	N/A	N/A	N/A
Normal[b]	All up[c]	N/A	19	34	N/A	**0**
	Alternating layers[d]		**0**	**0**		54
Inversion energy[g]			85	-14		33
Inversion parameter (x) at 1200 °C			0.02	0.85		0.23

[A,b]Energy differences in kJ/mol
[c]All electrons for Co and Fe atoms initially set to spin up
[d]Electrons in every other layer of Co and/or Fe atoms initially set to alternate spin up & spin down.
[e]Electrons of all tetrahedral atoms initially set to spin up. Electrons of all octahedral atoms initially set to spin down.
[f]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).
[g]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:

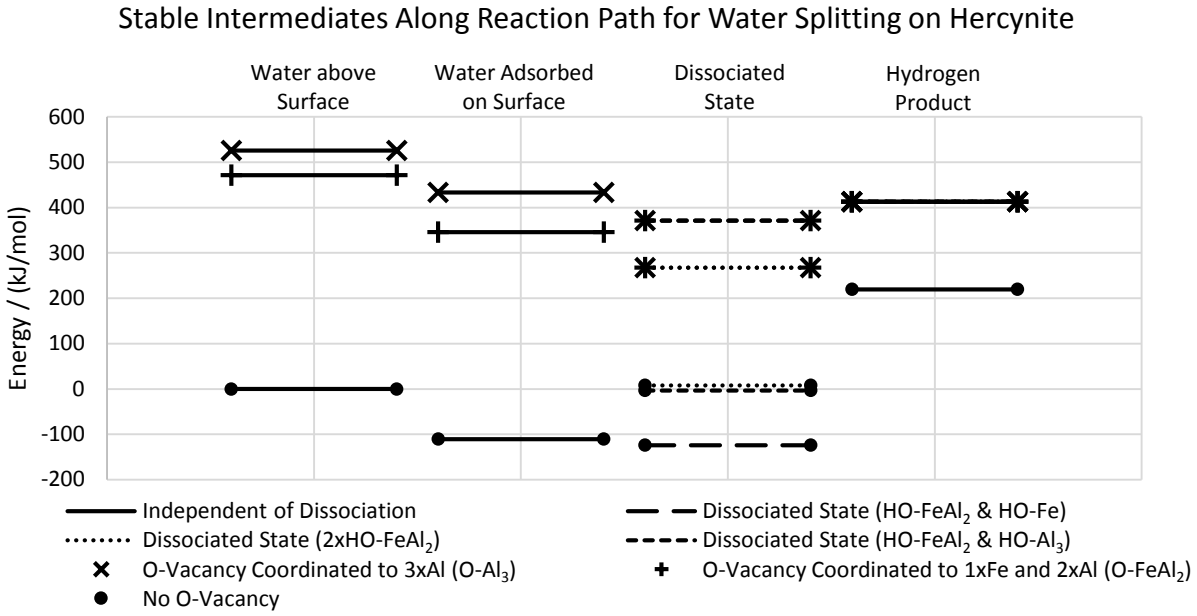
- Lowest energy spin state may vary between normal and inverse structure
- Lowest energy spin states may vary between host structure and O-vacancy defect structure
- Finding spin states currently requires manually testing of multiple configurations followed by multiple runs near minimum for verification

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

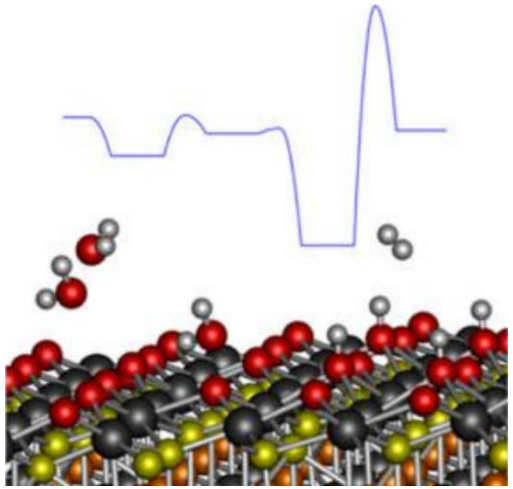
Approach to Kinetic Determination



Started analysis with stable adsorbed intermediates for water splitting on hercynite with and without oxygen vacancies.

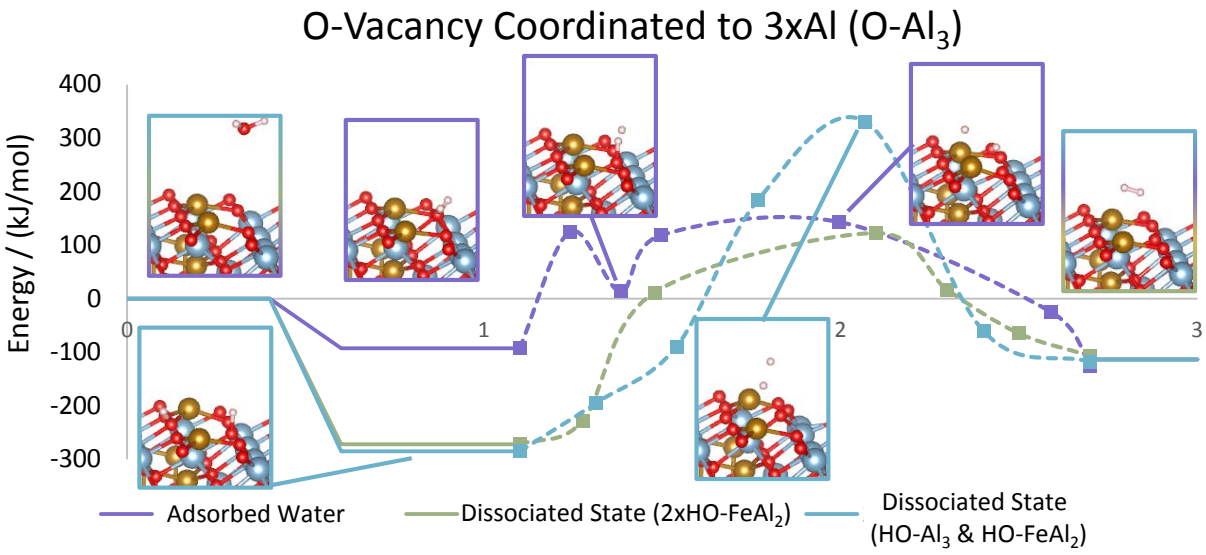
Hydrogen formation appears unfavorable without the oxygen vacancies. The activation barriers along this pathway will not be calculated.

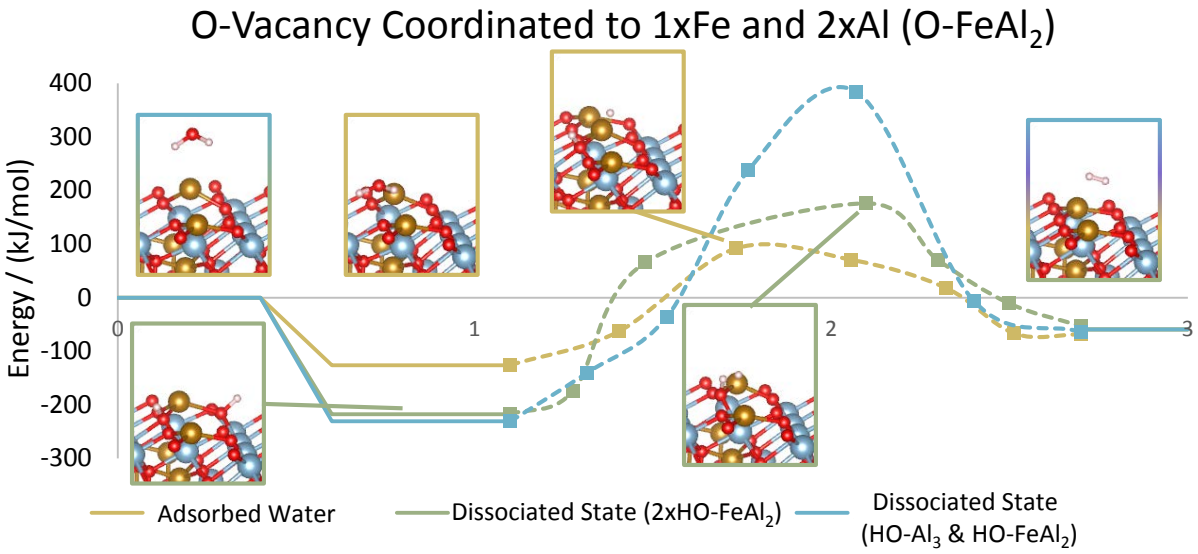
On ceria, the formation of hydrogen is the rate limiting process in the water splitting reaction.* We expect that it will be the most important activation barrier for other materials as well.



*Hansen, H. A., & Wolverton, C. (2014). Kinetics and Thermodynamics of H2O Dissociation on Reduced CeO2(111). *The Journal of Physical Chemistry C, 118*(47), 27402-27414. doi: 10.1021/jp508666c

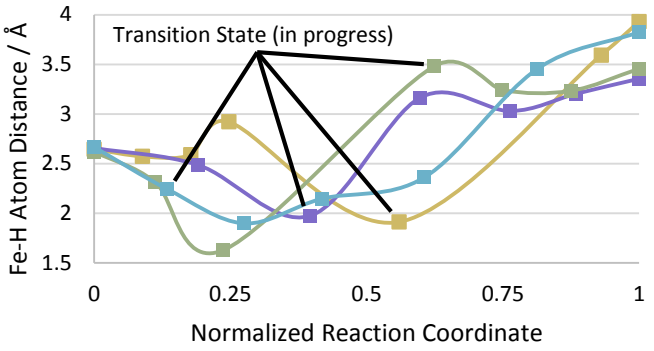
Preliminary Kinetics Results





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 H_2 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 H_2 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 H_2 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 H_2 formation kinetics (which are rate-limiting) based on fundamental materials descriptors.

Acknowledgements

Amanda Hoskins (Univ. of Colorado Boulder)

Brian Ehrhart (Univ. of Colorado Boulder)

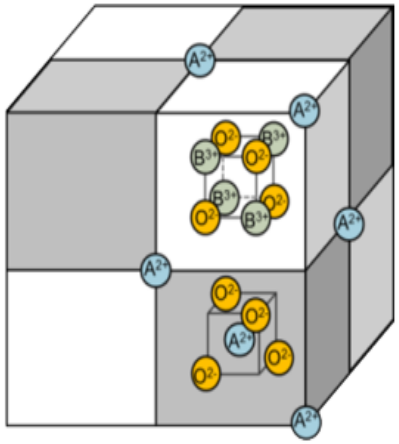
Aaron Holder (NREL)

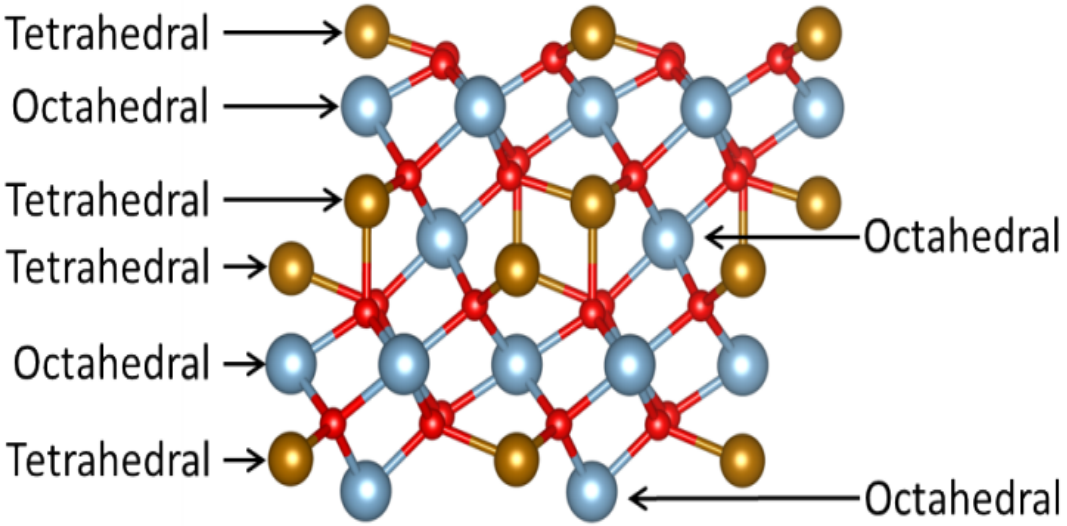
National Science Foundation - CBET

Back-up slides

Spinel structure

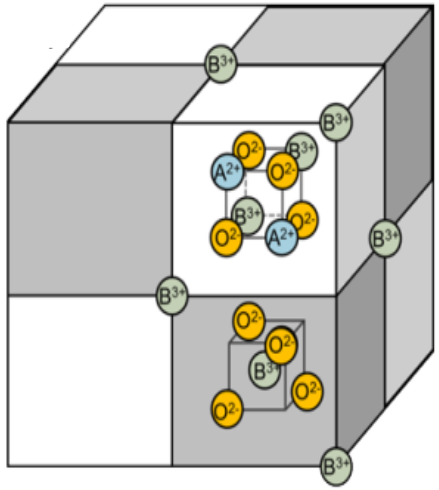
Normal

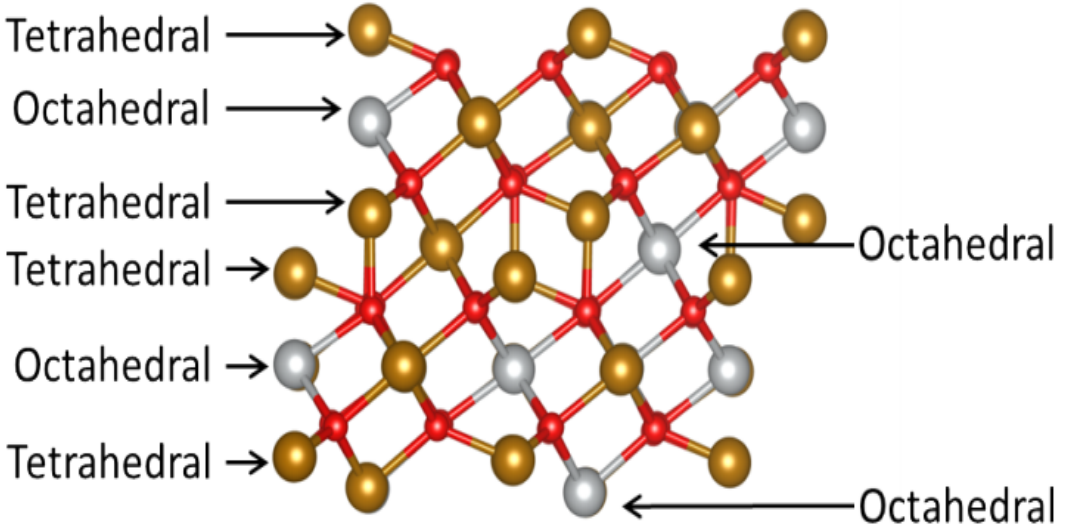




$FeAl_2O_4$

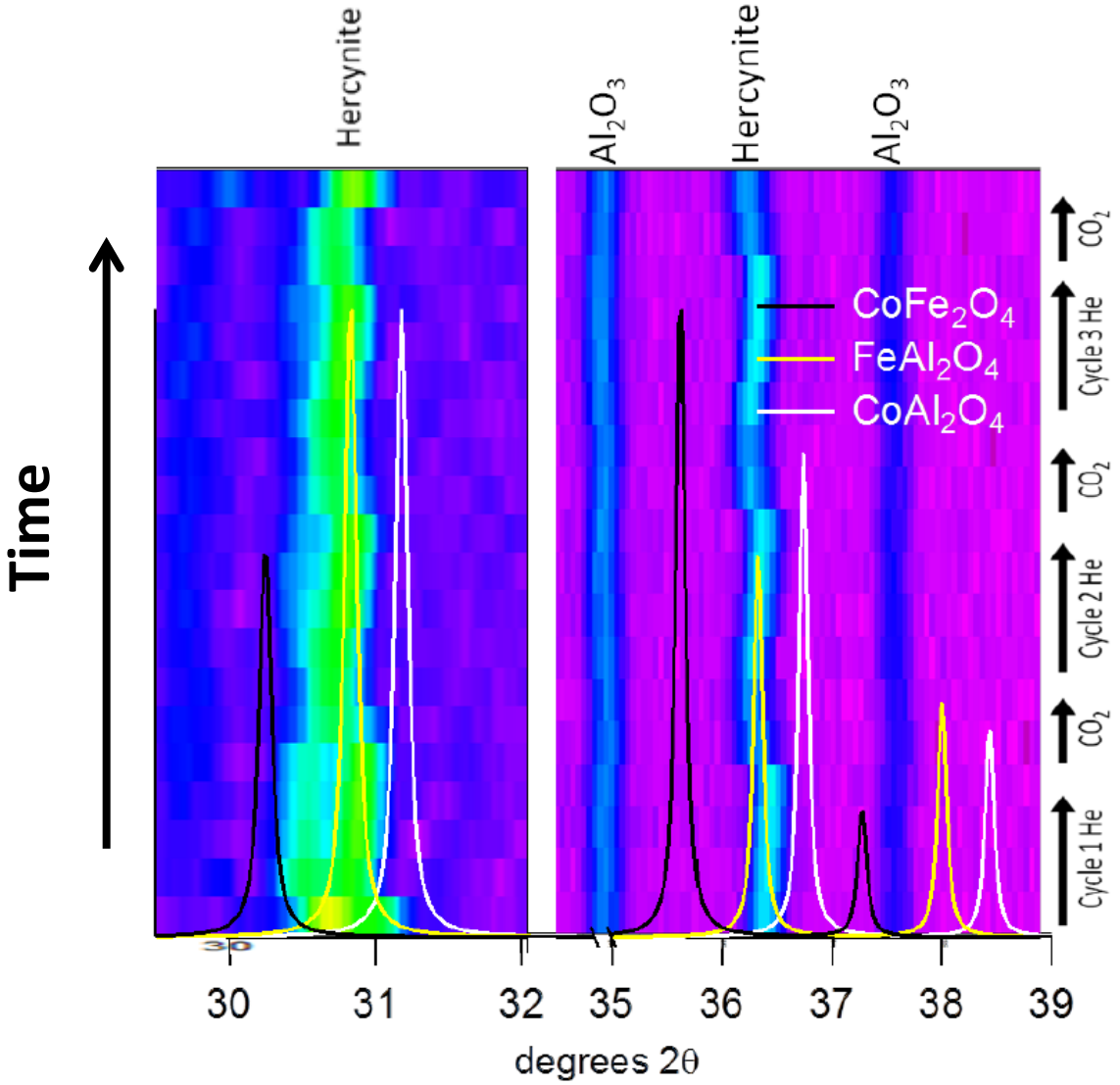
Inverse





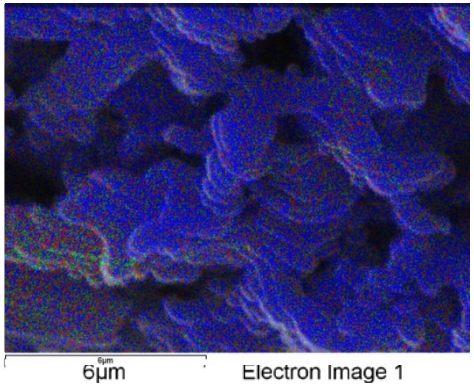
$CoFe_2O_4$

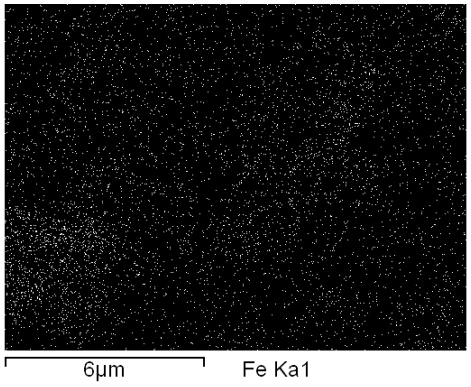
High temperature XRD also suggests an O-vacancy mechanism for the hercynite cycle

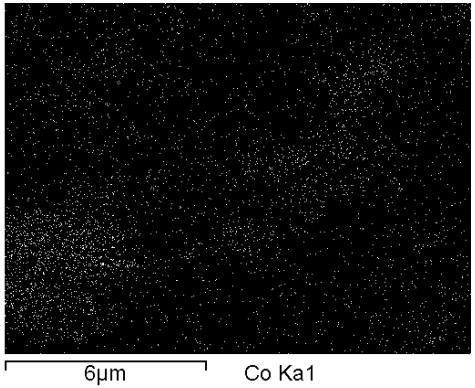


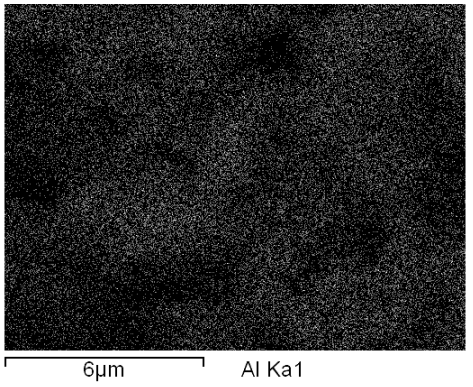
EDS analysis of phase segregation in the hercynite material

Reduced

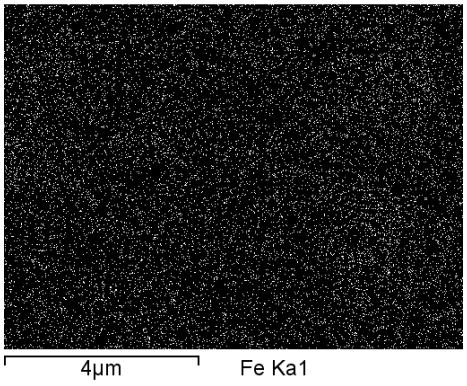


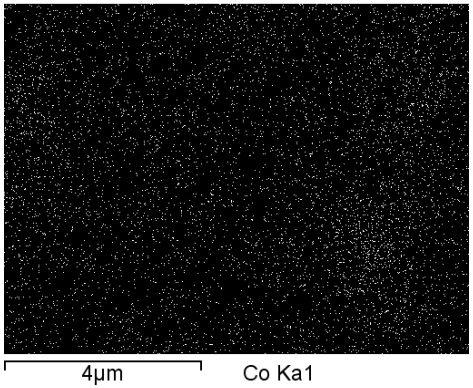


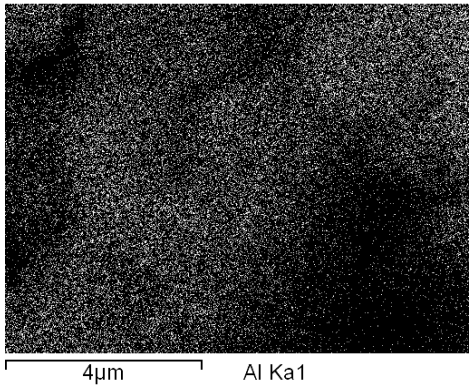




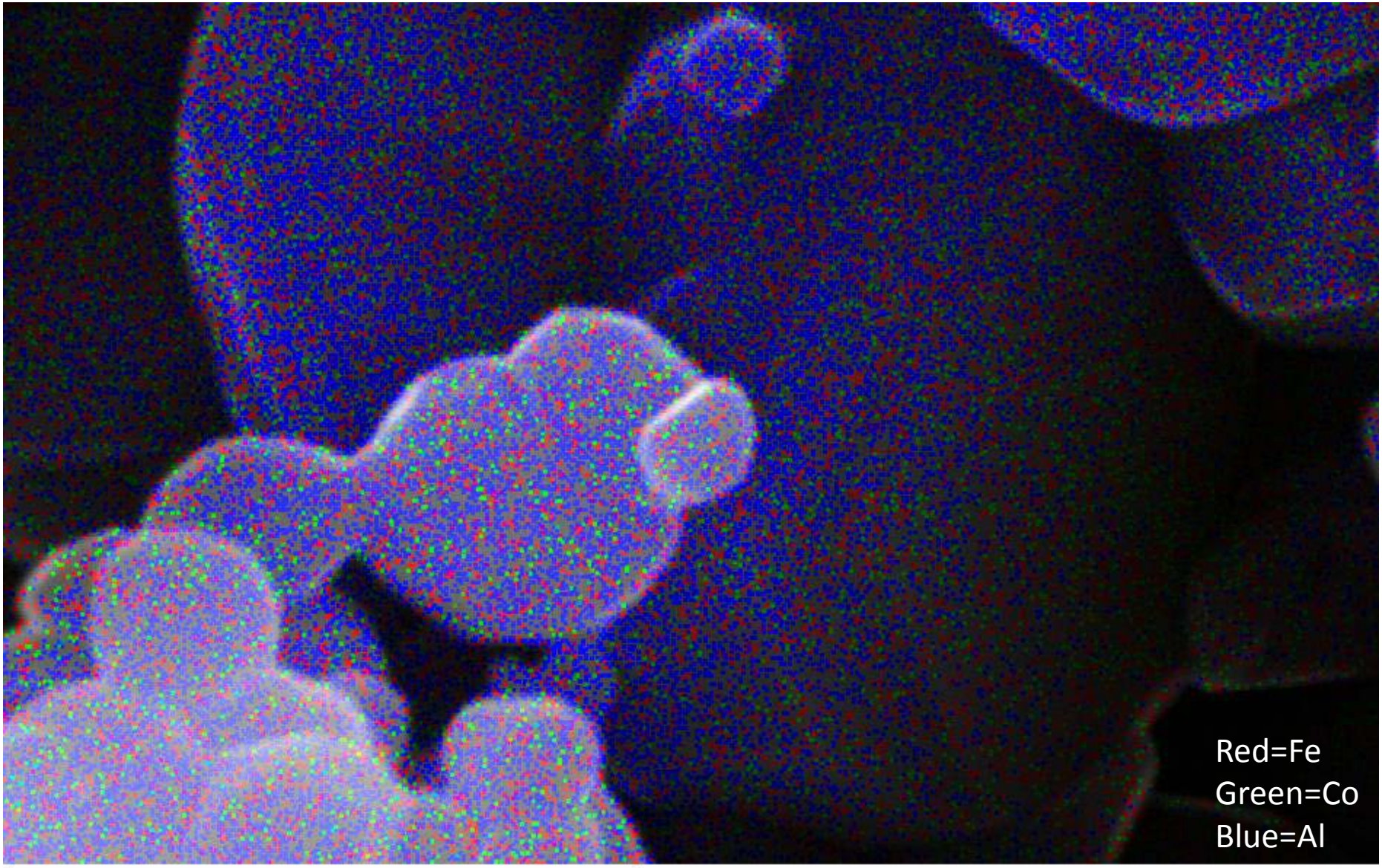
Oxidized in CO_2



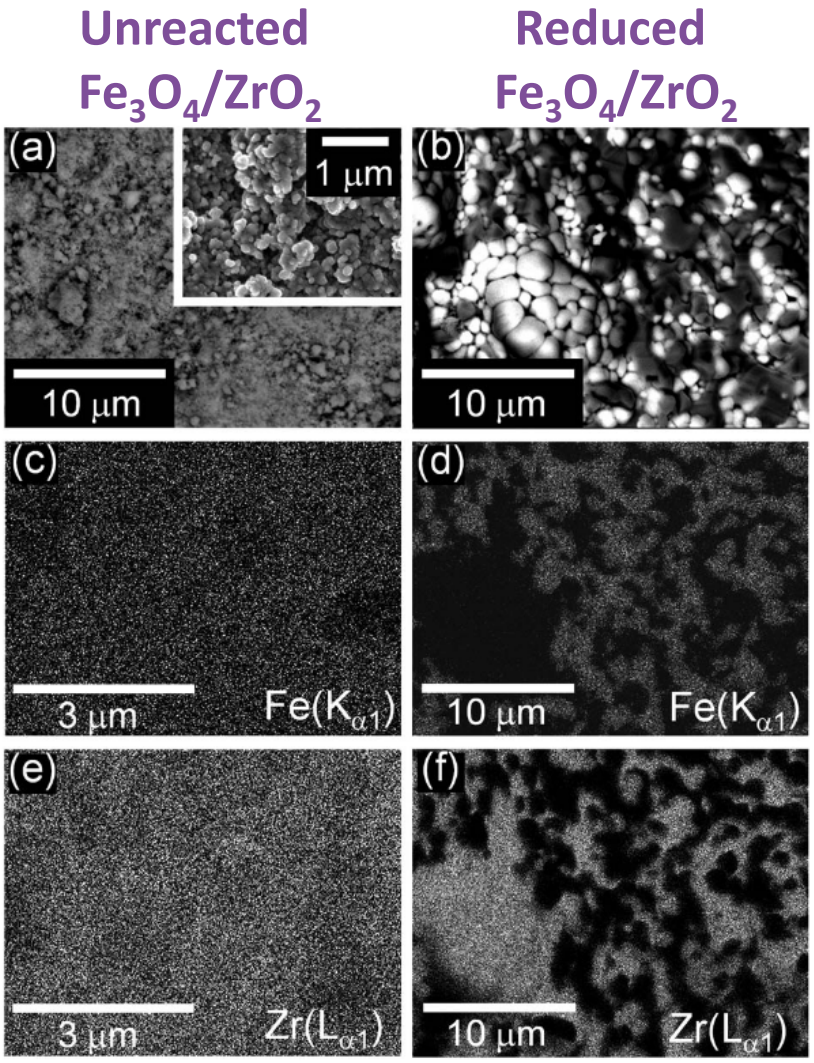


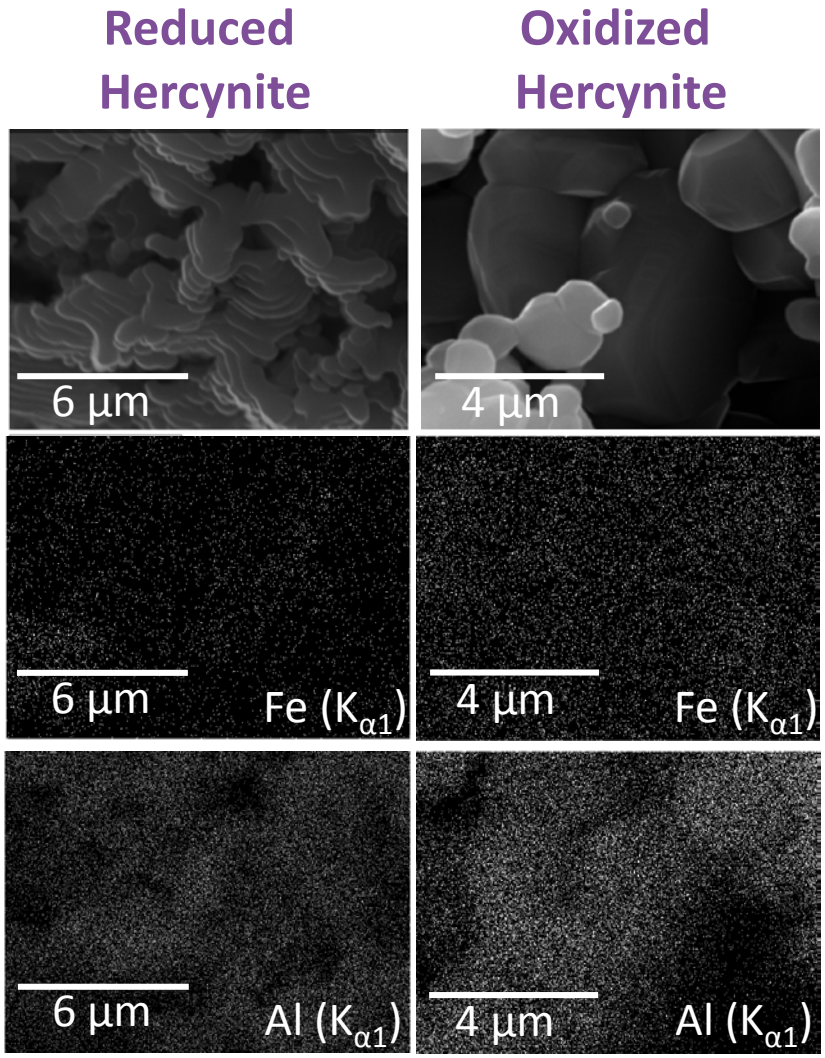


EDS analysis of phase segregation in the hercynite material



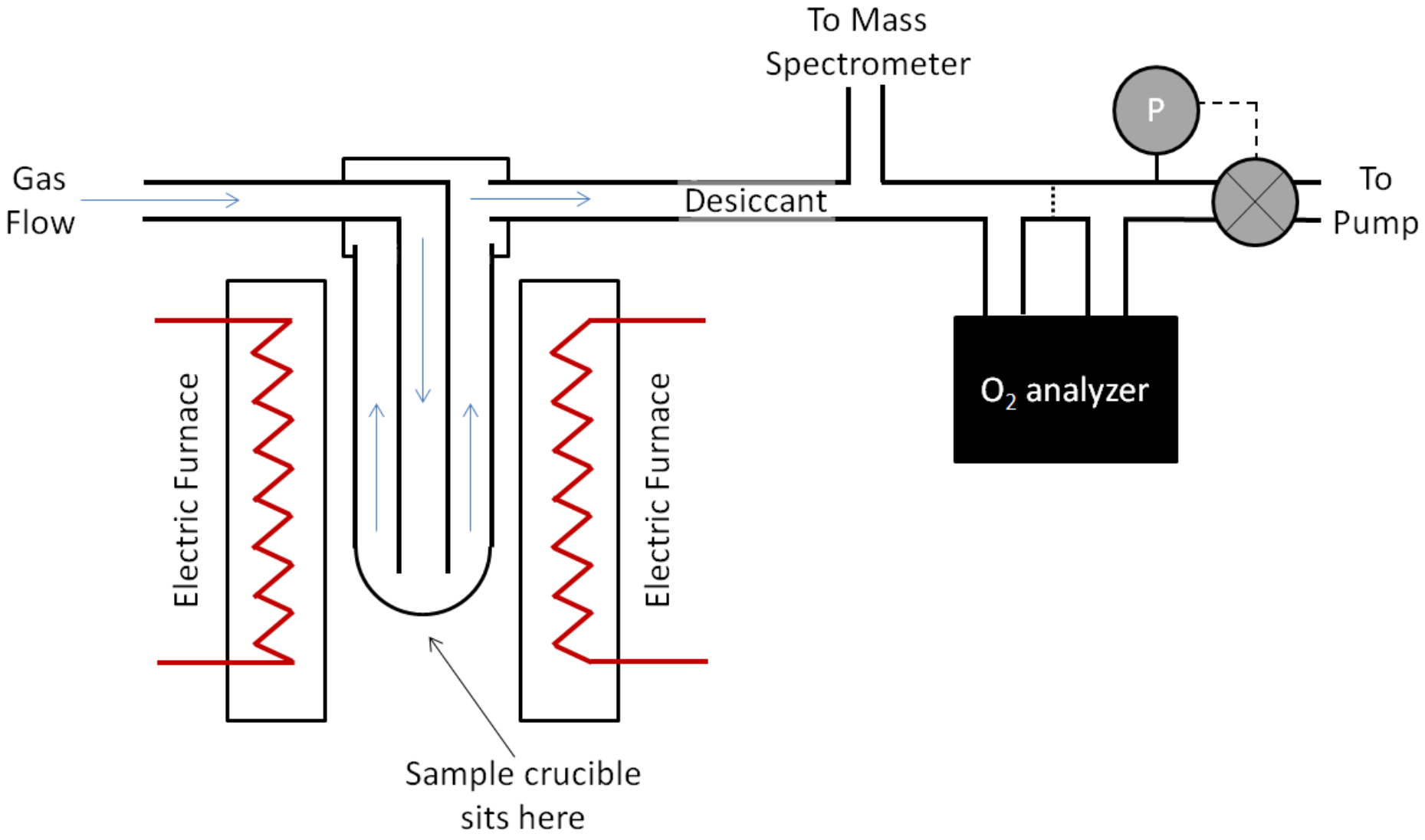
STWS phase separation or no separation



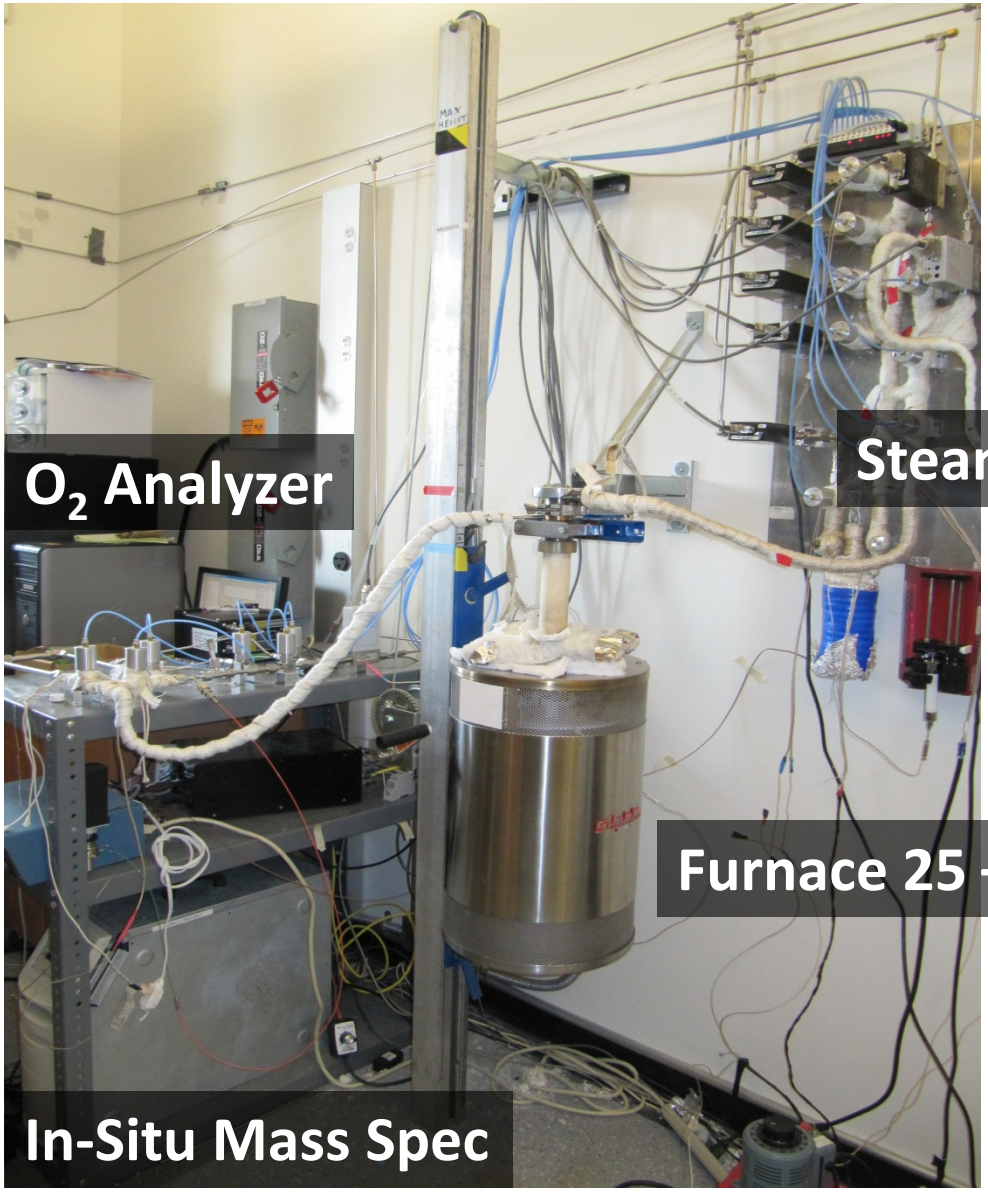


Scheffe et al. E&ES, 2013, **6**, 963

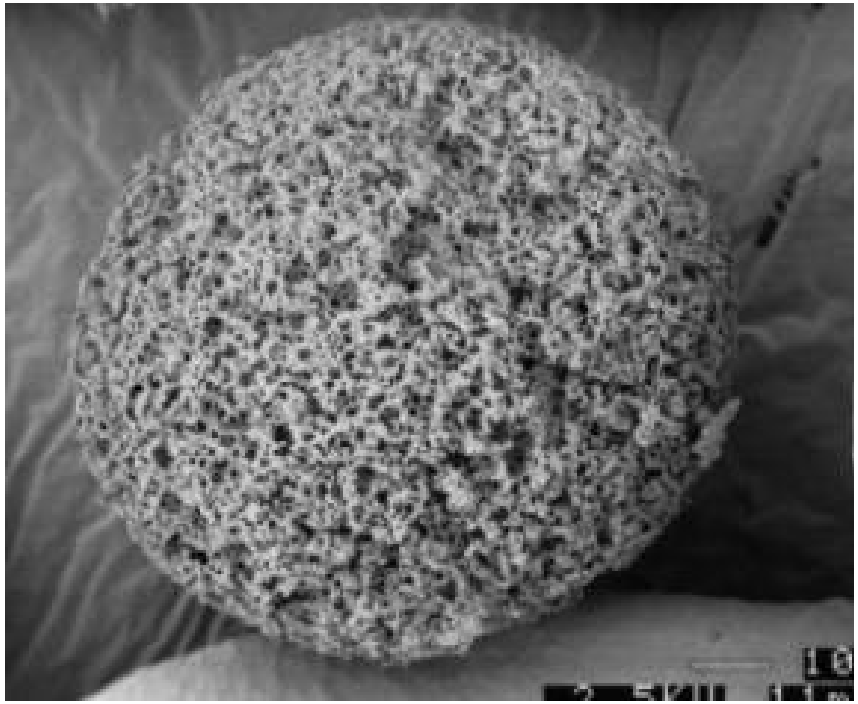
Stagnation Flow Reactor

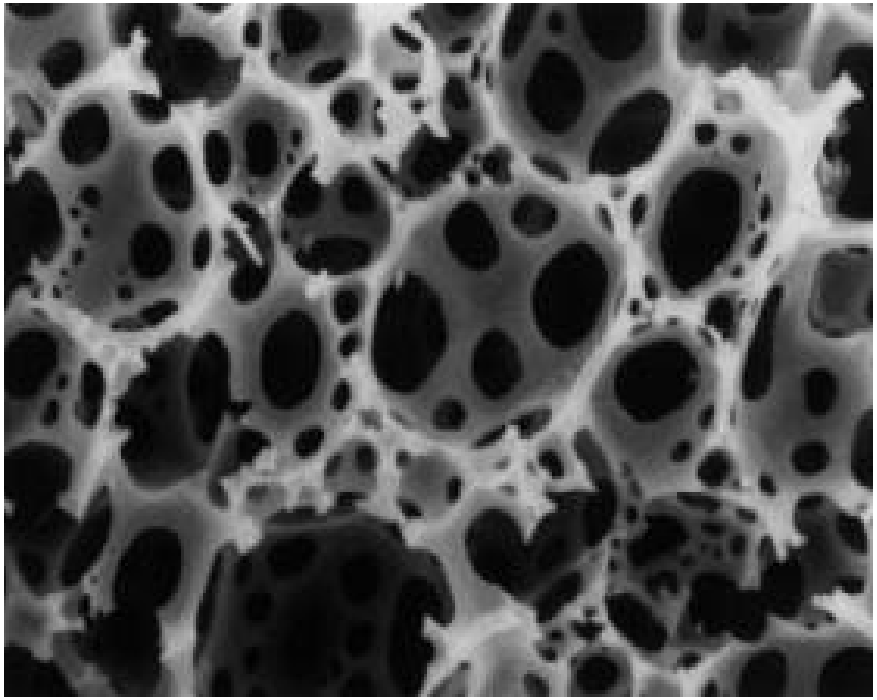


Water Splitting Reactor Set-up



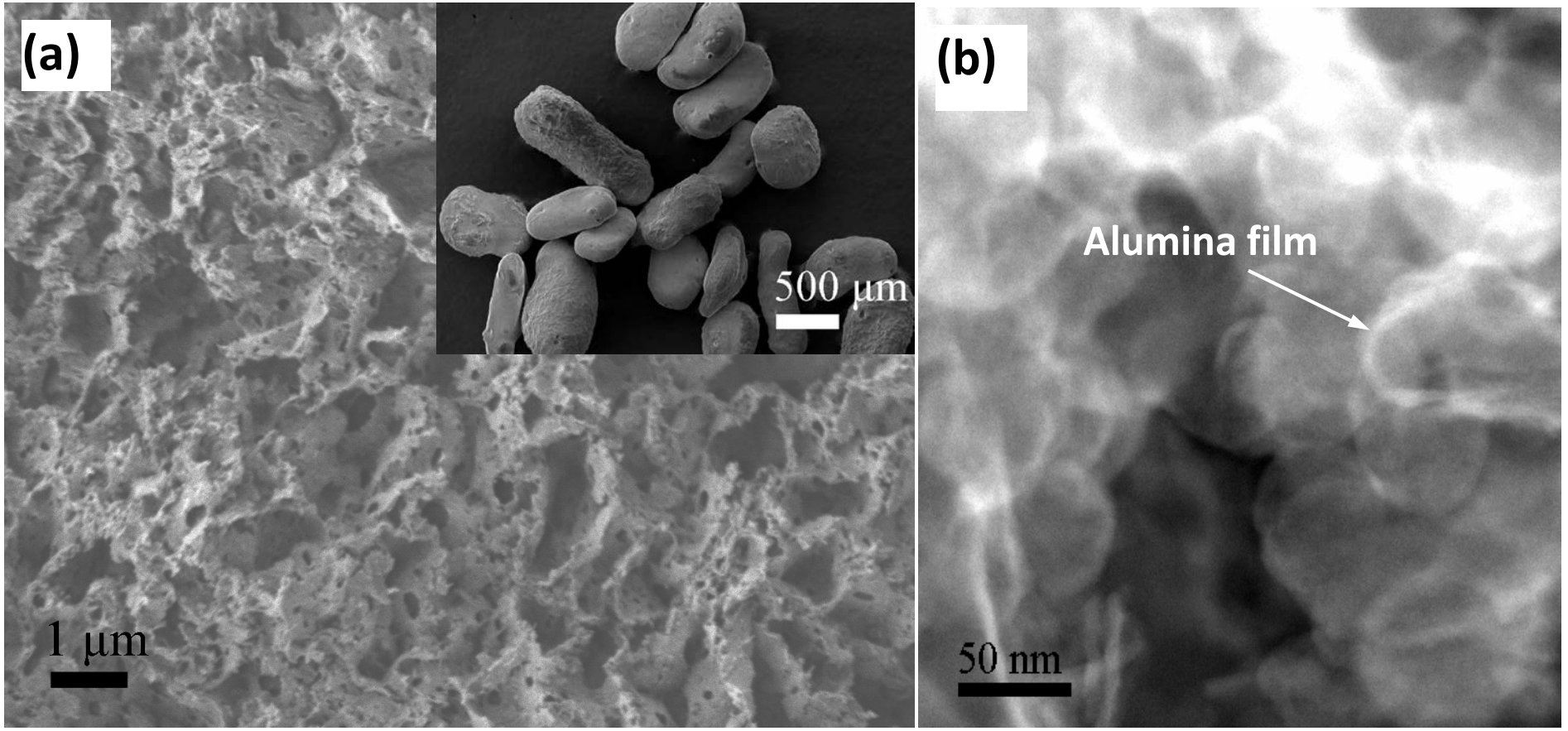
Highly Porous Scaffolding





- 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_2O_3 coatings on polymer Scaffolding