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

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Project ID: PD120

NSF CBET-1433521

Overview:
Year 3 of 3-Year Project

Timeline

Project Start Date: 9/1/2014

Project End Date: 8/31/2017

Percent Complete: 80%

Technical Barriers Addressed

W. Materials and catalysts development

Budget

Total project funding: $525,371 (NSF)

Funding received: $275,321

Total funding remaining: $250,050

Partners/Collaborators

National Renewable Energy Laboratory (NREL), Golden, CO

- High-performance computing facilities

Weimer Group, CU Boulder

- Active materials synthesis and testing

Relevance:
Renewable Efficient Hydrogen Generation

***Project Objective:* Develop novel reactor materials capable of producing 50,000 kg H_2/day at a cost < \$2/kg H_2 in a particle solar thermal water splitting system.**

Specific 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.

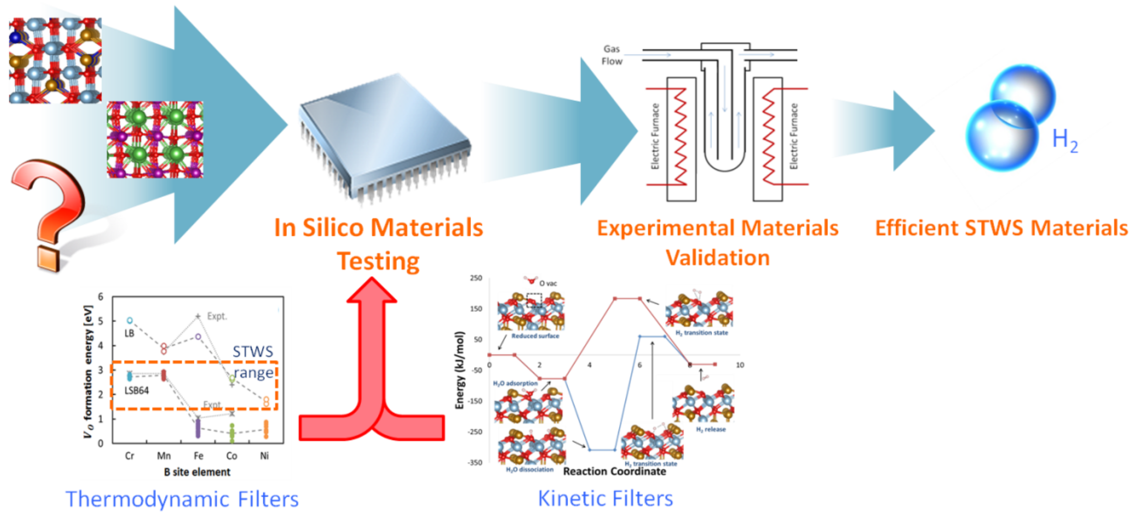
This Reporting Period:

- ✓ Studied the effect of inversion on spinel STWS behavior (**Barrier W**)
- ✓ Investigated the effect of dopants on hercynite H_2 production (**Barrier W**)
- ✓ Tested an effect of crystal structure and magnetic ordering on accuracy of computational screening in binary perovskites (**Barrier W**)
- ✓ Investigated origins of high surface oxidation reaction barriers (**Barrier W**)

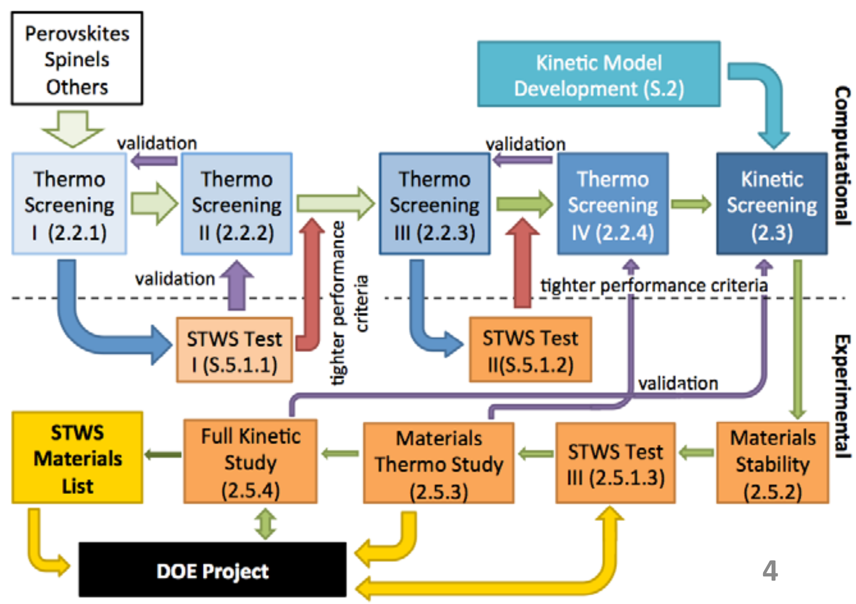
Approach:
Computational Prototyping of Oxide RedOx Materials

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



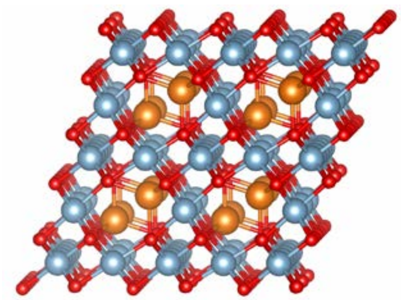
Apply fundamental materials science, chemistry and physics to develop materials design rules and discover promising materials using state-of-the-art electronic structure theory. For this objective, quantum simulations require careful, expert application due to limitations of the methods, effects of spin,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



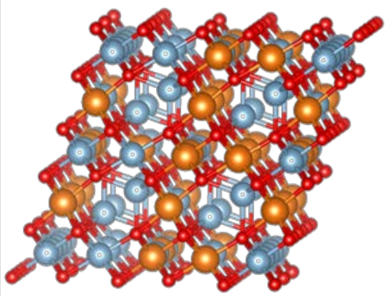
Accomplishments and Progress: Screening Spinel Materials – Inversion

- Normal spinel – Ordered structure where all oxygens are equivalent
- Inverse spinel – Disordered structure leads to different cation environments surrounding each oxygen

$FeAl_2O_4$ Normal Spinel



$FeAl_2O_4$ Inverse Spinel



Legend:
- A Atom (Fe)
- B Atom (Al)
- Oxygen

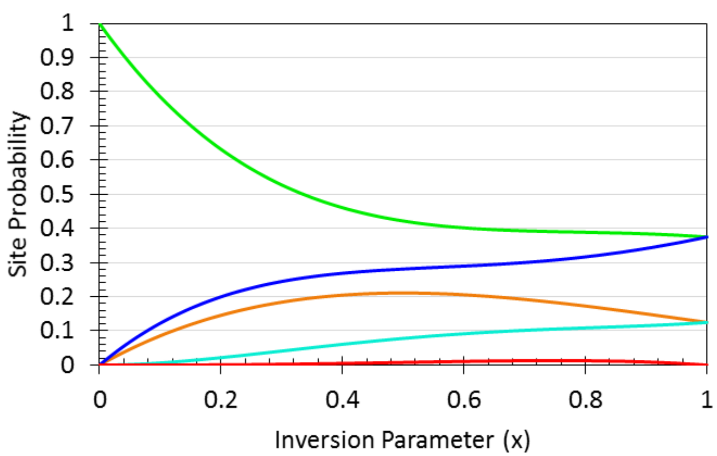
Inversion Parameter (x)

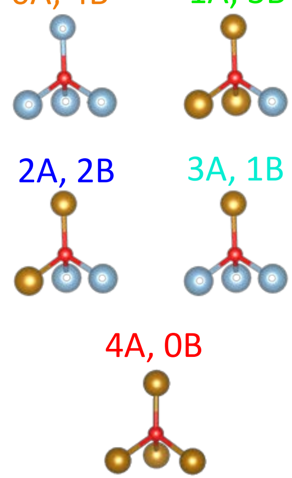
$$(A_{1-x}B_x)[A_xB_{2-x}]O_4$$

Tetrahedral Octahedral

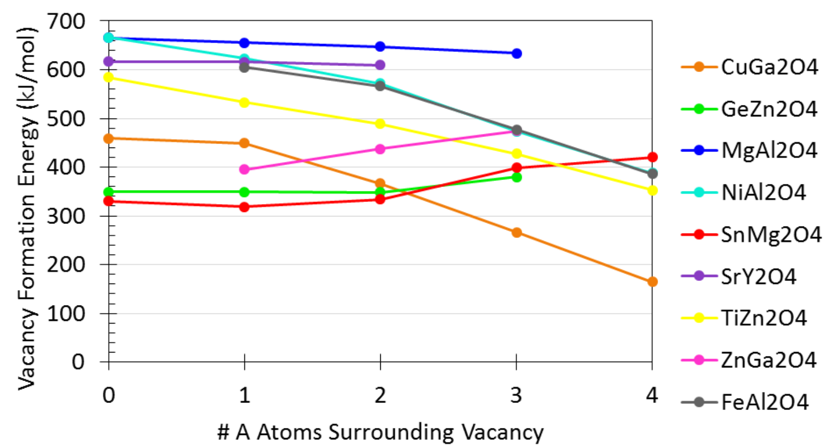
0 (normal) ≤ x ≤ 1 (inverse)

Inverse Spinel Site Probability





Inversion Effect on Vacancy Formation Energy



- Number of sites available for STWS depends on inversion parameter
- O vacancy formation energy can vary by 300 kJ/mol, depending on the cation environment

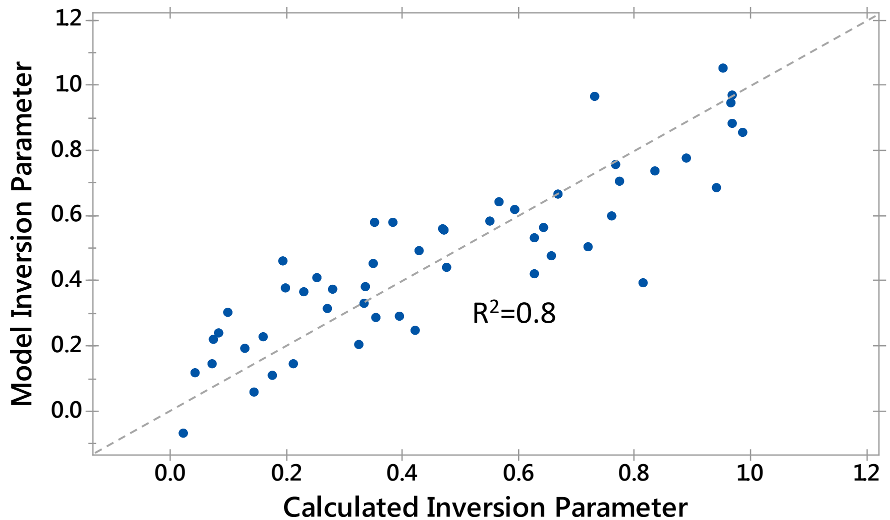
Accomplishments and Progress: Screening Spinel Materials – Inversion

- Inversion parameter depends on a variety of factors including:
  - Temperature
  - Cation size
  - Crystal field stabilization energy

$$x_{eq} = \frac{\sqrt{9+8(c-1)}-3}{2(c-1)}, \qquad c = e^{\Delta E/kT}$$

- Exact relationship between all these factors and x_{eq} not well defined

Predicted vs. Computed Inversion Parameter



Inversion Parameter (x)

$(A_{1-x}B_x)[A_xB_{2-x}]O_4$

Tetrahedral Octahedral

0 (normal) ≤ x ≤ 1 (inverse)

- Calculated the inversion parameter for 60 materials at STWS temperatures
- Preliminary model developed for predicting inversion parameter at STWS temperatures
- Model will significantly reduce number of required calculations for inverse spinels

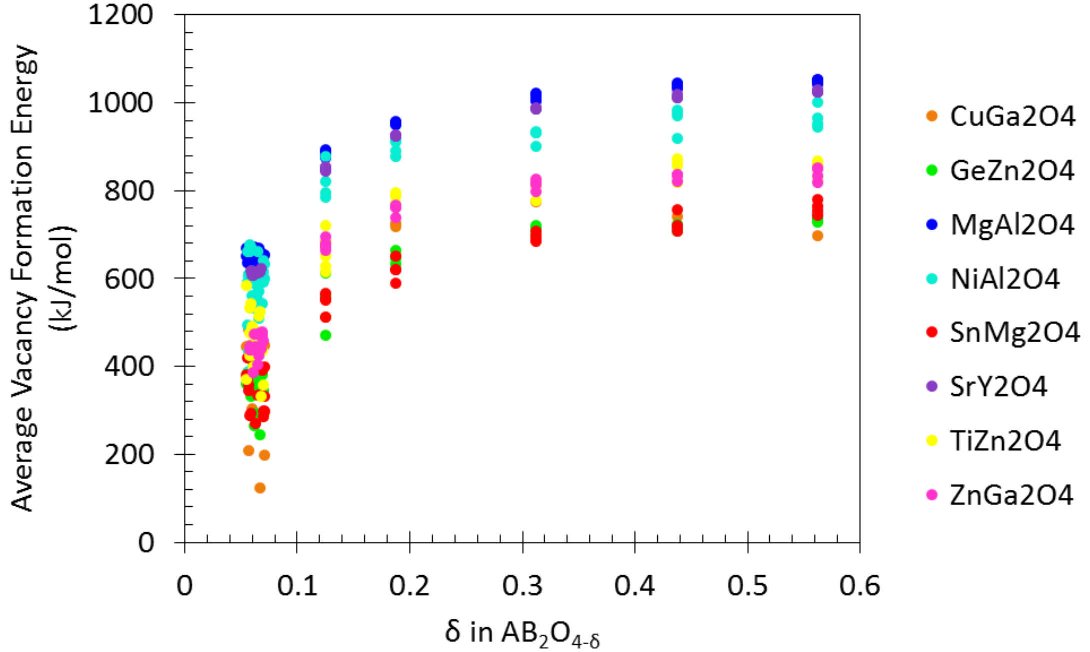
Accomplishments and Progress: Spinel Materials – Nonstoichiometry

- Vacancy formation energies depend on oxygen nonstoichiometry δ ($AB_2O_{4-\delta}$)
- Extent of reduction (and corresponding H_2 production) will depend on this dependence

$$AB_2O_4 \rightarrow \frac{\delta}{2} O_2 + AB_2O_{4-\delta}$$

$$AB_2O_{4-\delta} + \delta H_2O \rightarrow AB_2O_4 + \delta H_2$$

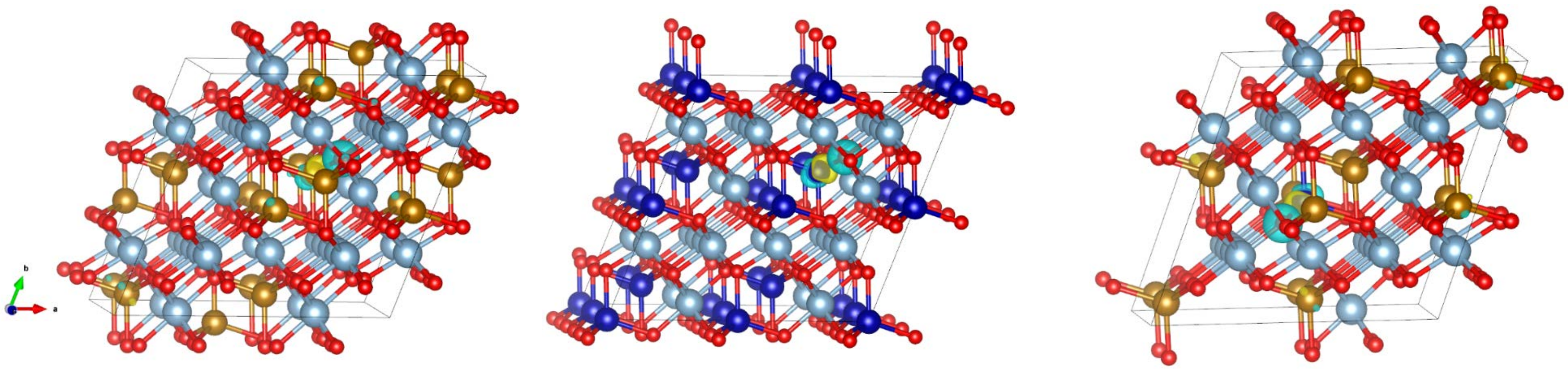
Effect of Nonstoichiometry on Vacancy Formation Energy

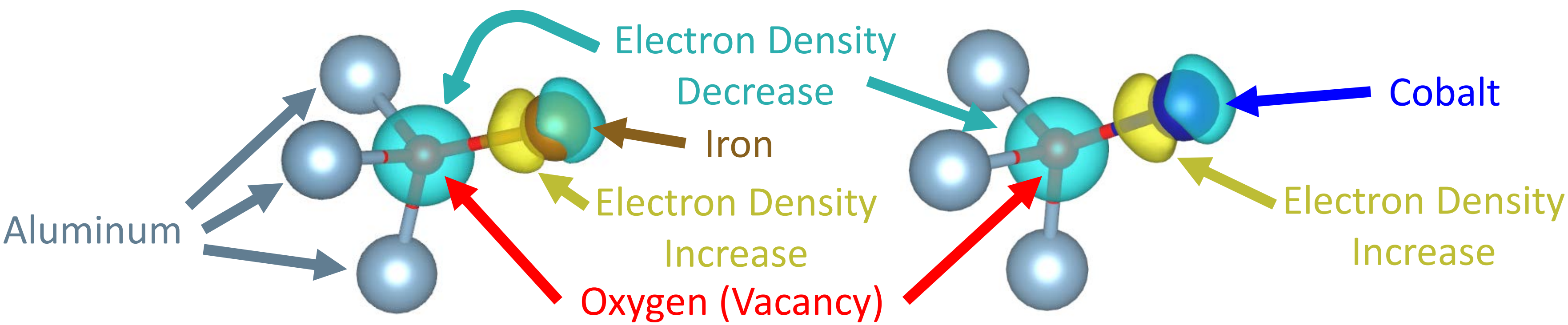


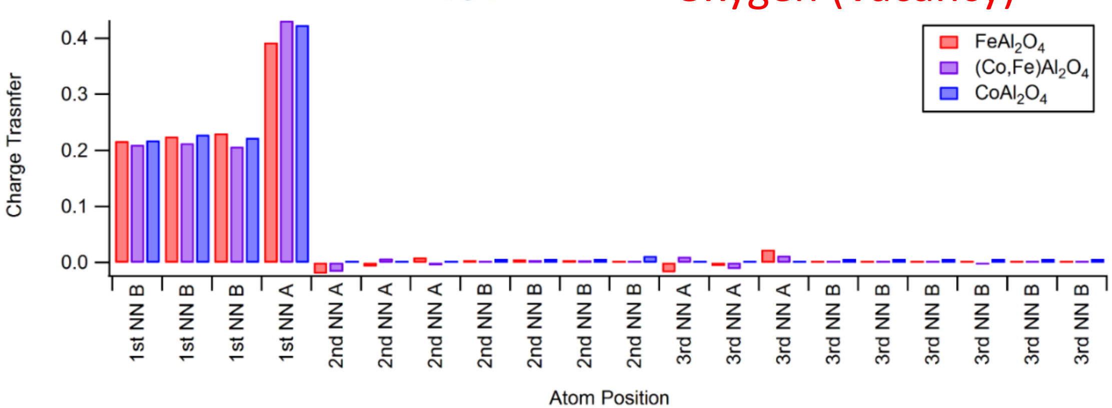
Average vacancy formation energy changes similarly with respect to oxygen nonstoichiometry for different spinel compounds

Accomplishments and Progress: Screening Spinel Materials – Doping

- Dopant effects on electron charge transfer studied for $FeAl_2O_4$, $CoAl_2O_4$ and $(Co,Fe)Al_2O_4$



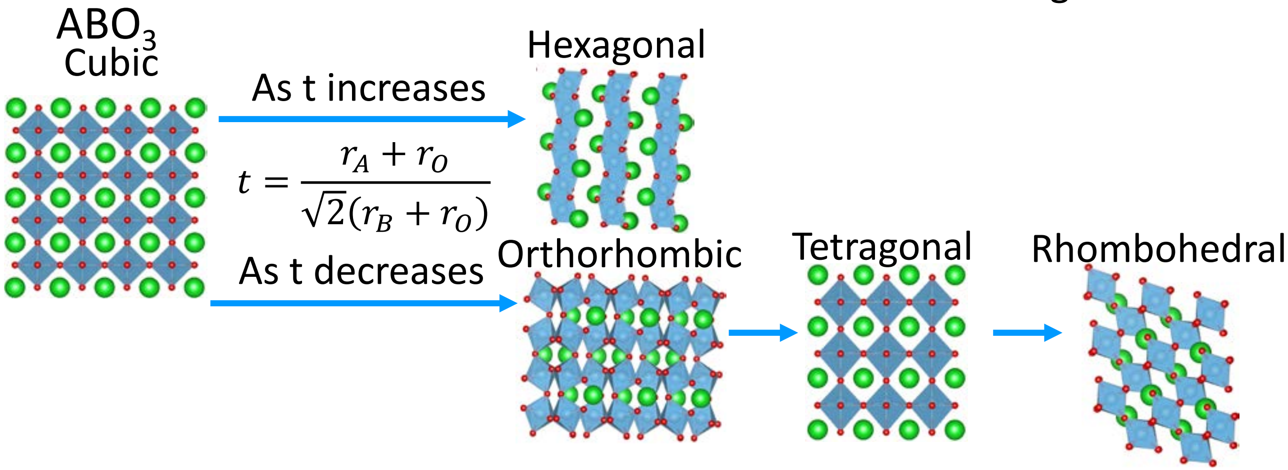




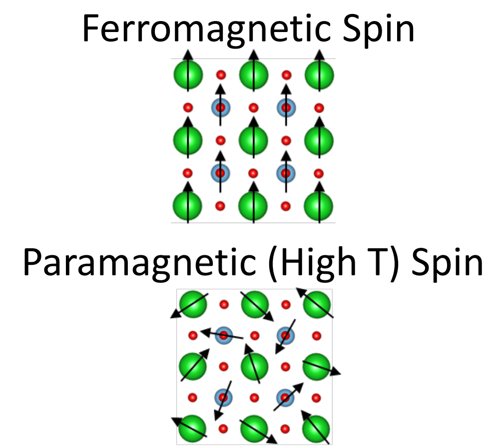
Charge transferred to 1st nearest neighbors only.
Simplifies required calculations for doped materials

Accomplishments and Progress: Perovskite Screening

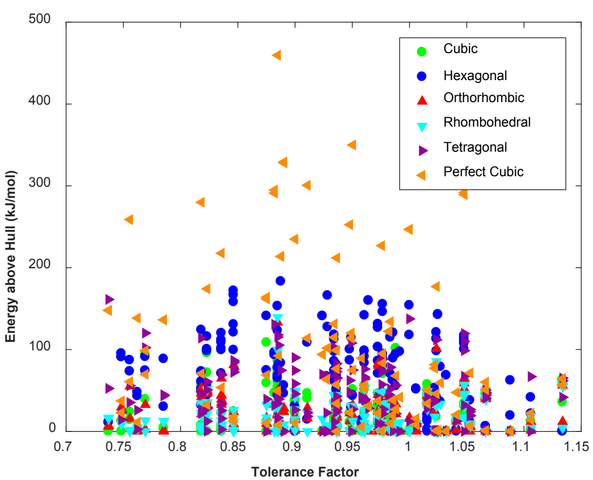
- Evaluated 1343 materials for the effect of structure and magnetic ordering on STWS behavior



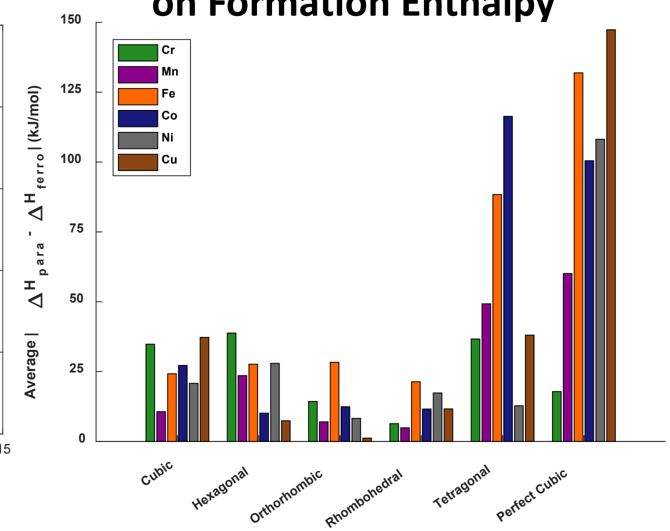
$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)}$$



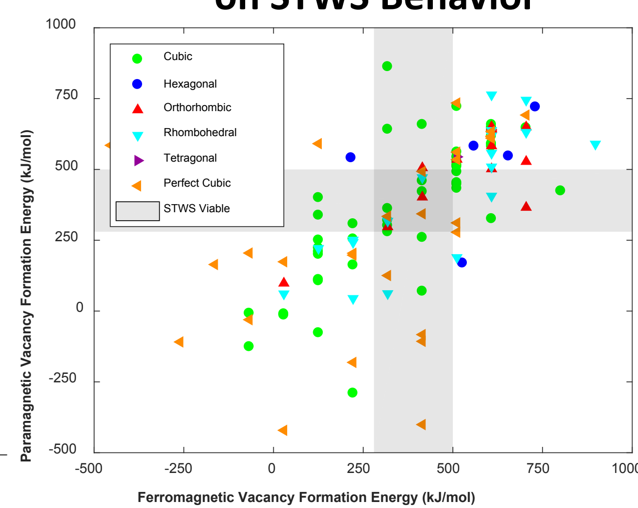
Effect of Structure



Effect of Magnetic Ordering on Formation Enthalpy

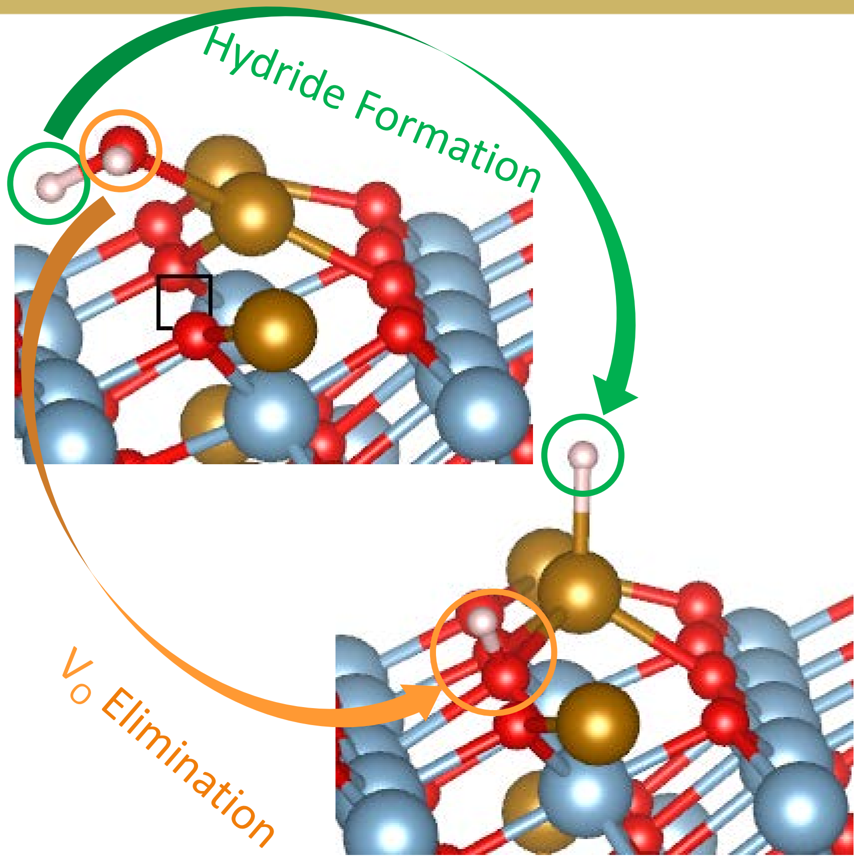


Effect of Magnetic Ordering on STWS Behavior

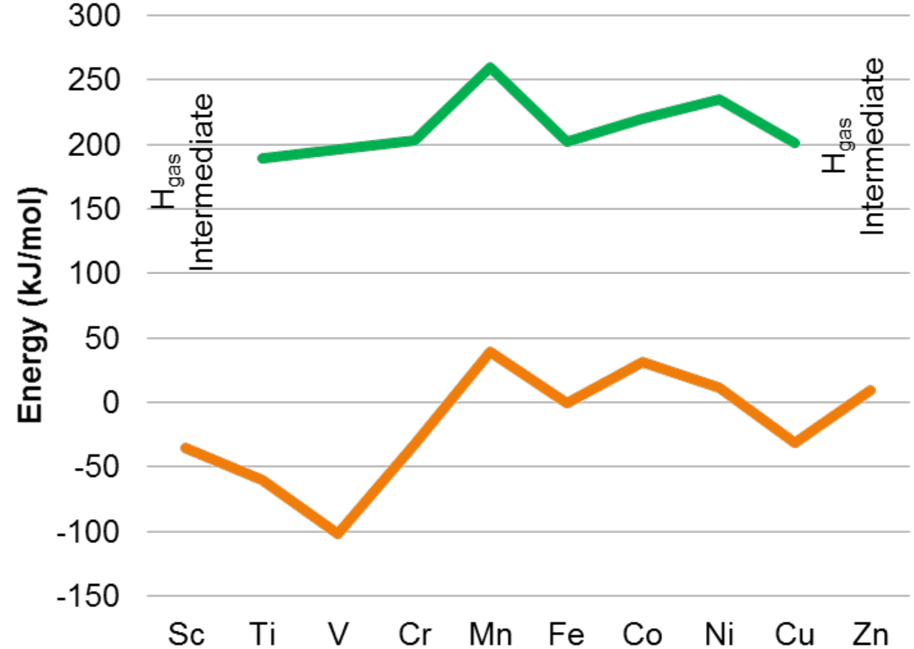


Both structure and magnetic order significantly affect the predicted STWS abilities of perovskites

Accomplishments and Progress: Decomposing Surface Reaction



Hydride Formation Reaction Barrier

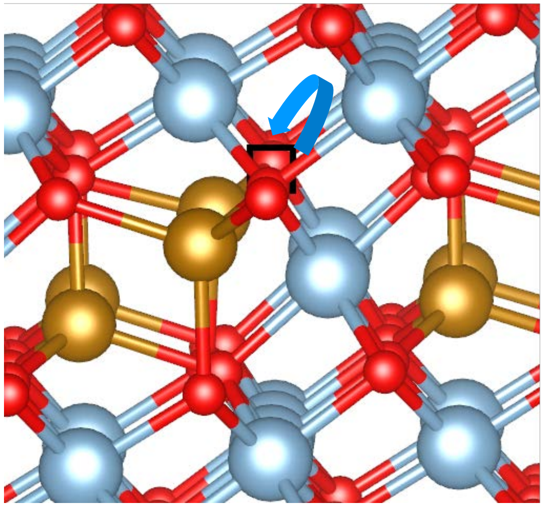


V$_O$ Elimination Reaction Energy (relative to Fe)

- H^- formation limits surface reaction, but is not severely impacted by dopants.
- Reaction barrier for separate V$_o$ elimination (not shown) is barrierless or near barrierless.
- The dissociation barrier for Sc-V and Mn-Zn are, separately, well correlated to the V$_O$ elimination energy.

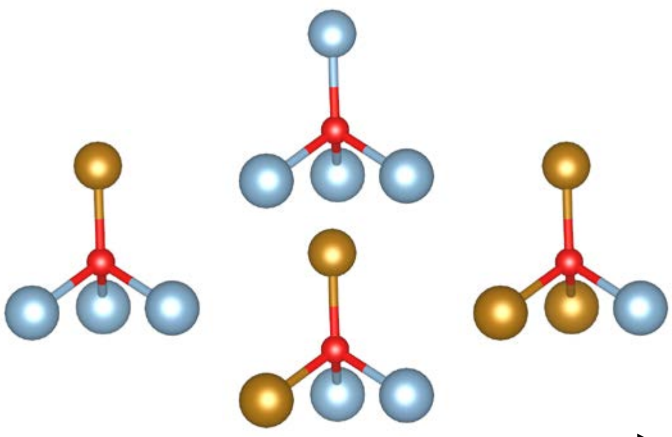
Accomplishments and Progress:
Kinetic Modeling of Disordered Hercynite Systems

Diffusion in Hercynite

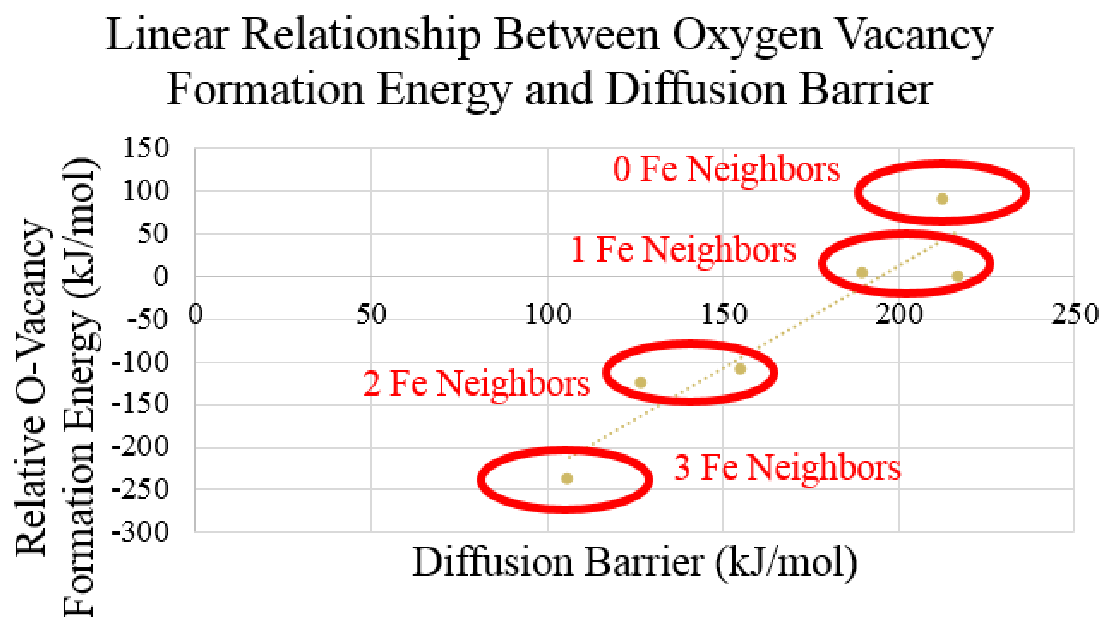


- Cation distribution in hercynite has a significant impact on the diffusion barrier
- Barrier shows strong correlation to both the O vacancy formation energy, and the number of Fe cations that neighbor the diffusion site
- This shows promise for modeling of disordered systems without explicit calculations for every state.

Impact of Inversion on Local Environment



Increasing Inversion

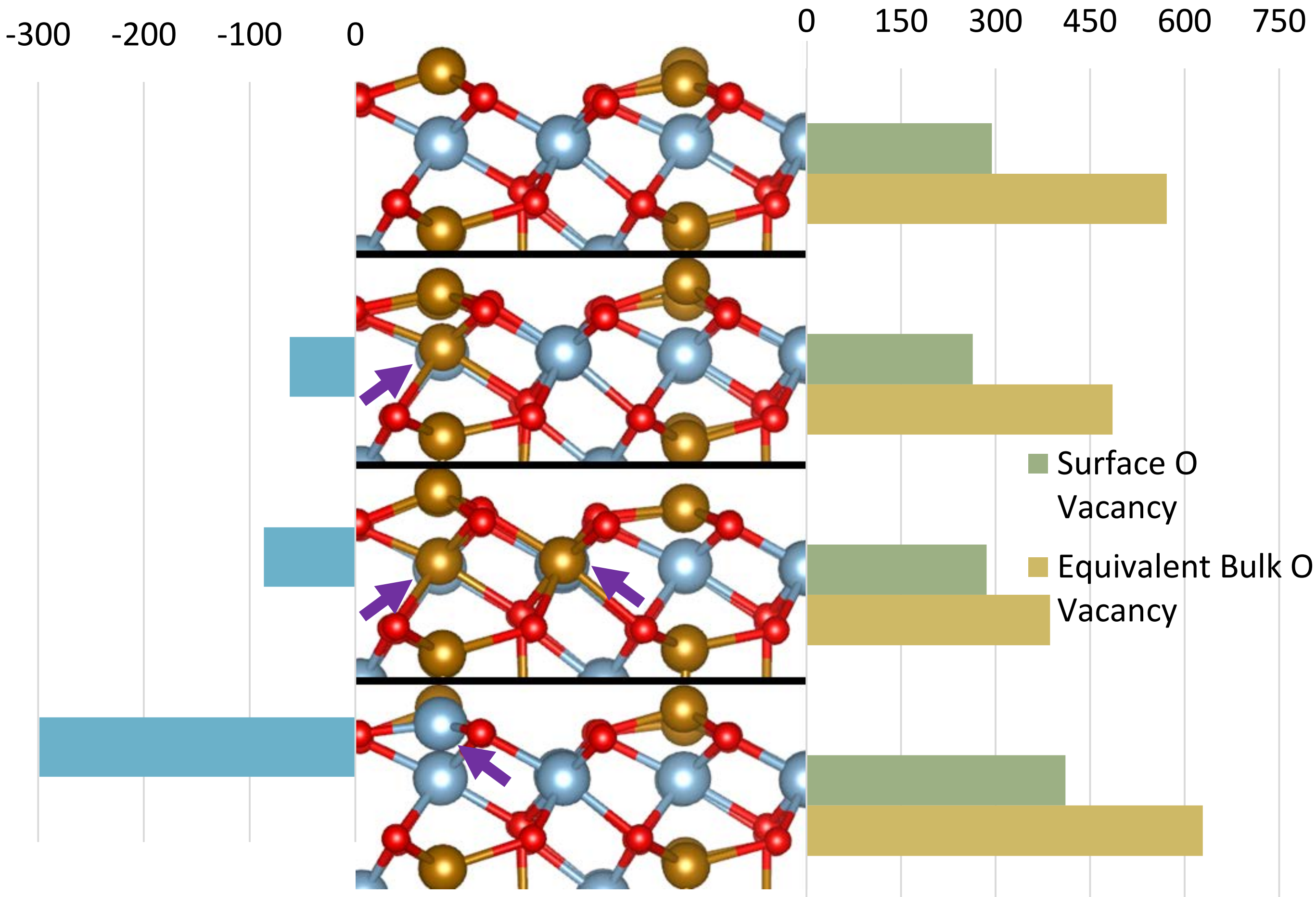


Accomplishments and Progress: Introducing Inversion to Surface Structures

Inversion Energies of Surface Relative to Bulk (kJ/mol)

Inverse Structures

O Vacancy Formation Energies (kJ/mol)

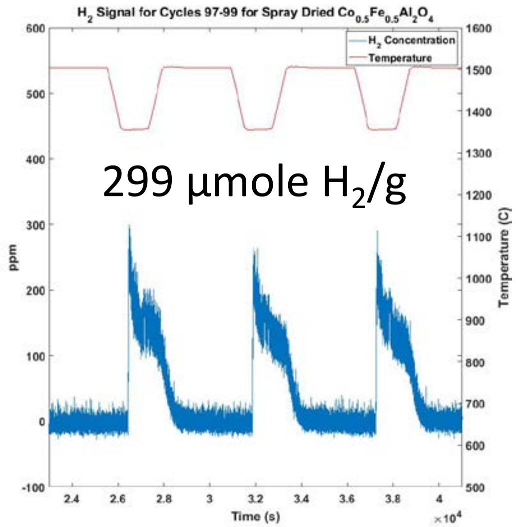


- Inversion is more likely to occur at the surface
- Strong preference for vacancies to occur at surface
- Beneficial for material oxidation, detrimental to material reduction

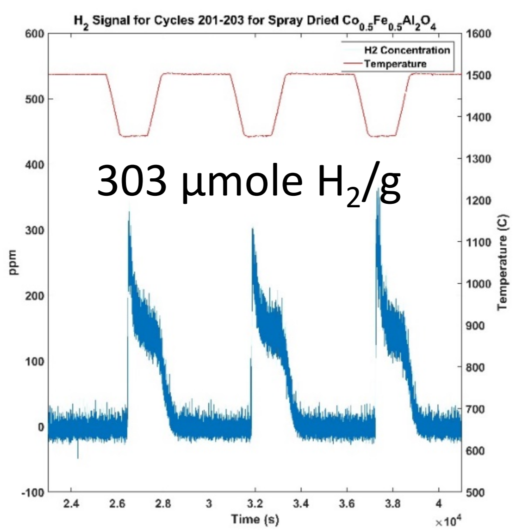
Accomplishments and Progress: Active Material Testing

Spray Dried $Co_{0.5}Fe_{0.5}Al_2O_4$

H_2 Production Cycles 97-99

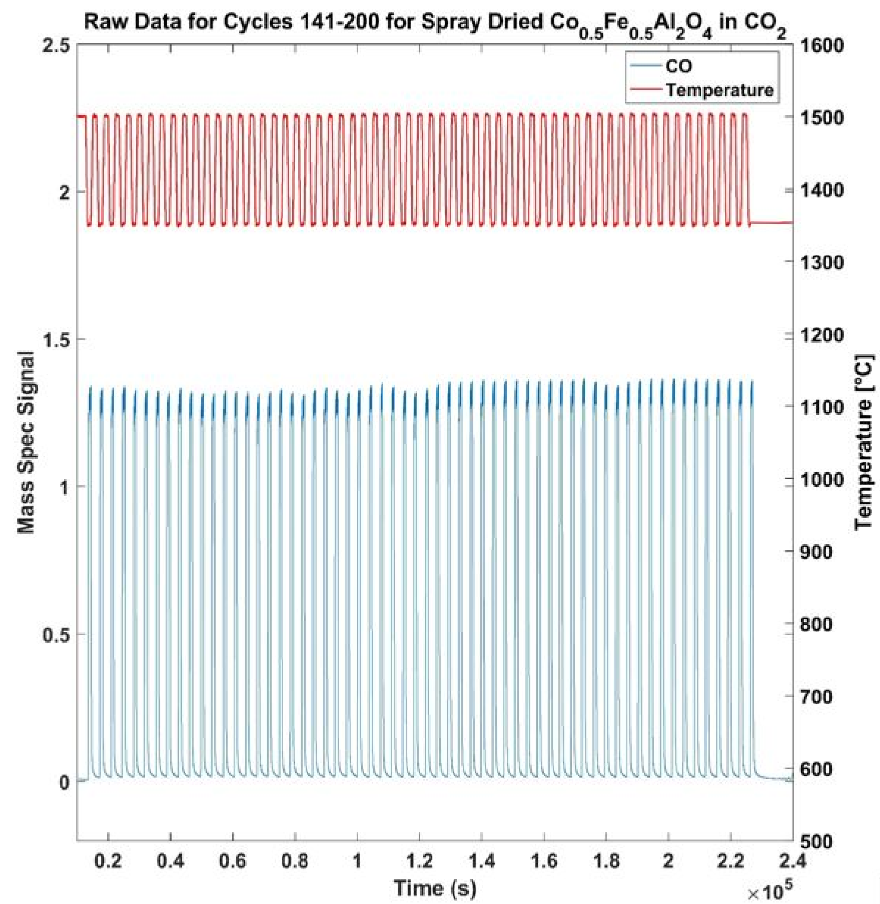


H_2 Production Cycles 201-203



Target: > 150 µmole/g & < 10% activity loss between 100th and 200th cycle
Actual: 300 µmole/g and no activity loss

CO Production Cycles 141-200



Collaborations

Collaborator		Project Roles
	National Renewable Energy Laboratory (NREL)	High-performance computing facilities (Peregrine). High-throughput computing consultaion
	Weimer Group, CU Boulder	Active material synthesis and testing through "sister" DOE project PD114

Accomplishments and Progress: Responses to Previous Year Reviewer' Comments

This project is funded by NSF. No reviewer comments were provided for this project.

Remaining Challenges and Barriers

- Thermodynamic Screening
  - Spinel inversion can be critical to predicted behavior and needs to be included into high-throughput modeling
  - Perovskite structure and magnetic ordering must be modeled at high-temperature conditions for accurate STWS predictions
  - Doped materials have additional computational complexities that must be considered
- Kinetic Screening
  - Faster reduction and oxidation kinetics required for feasible STWS processes
  - Developing a descriptor model for kinetics requires a large set of explicit kinetic calculations
  - Materials with random structure/occupancy have large space of possible structures
- Material Testing
  - New materials must be stable over many water splitting cycles and must be compatible with reactor containment materials

Project Objective: ***Develop novel reactor materials capable of producing 50,000 kg H_2/day at a cost < \$2/kg H_2 in a particle solar thermal water splitting system.***

Proposed Future Work

- Thermodynamic Screening
  - Incorporate cation inversion into screening methods for spinel materials
  - Complete screening of binary spinels and begin screening doped spinels
  - Utilize lessons learned from perovskite study to accurately screen perovskites
- Kinetic Screening
  - Expand study to new materials. Test that inversion or random doping can be modeled similarly to hercynite
  - Investigate reactions on perovskite surfaces
  - Begin investigating the reduction reaction
- Material Testing
  - Test perovskites in SFR and/or TGA to provide feedback to validation study
  - Synthesize and test H_2 production of various spinels in SFR

Technology Transfer Activities

None to date

Summary

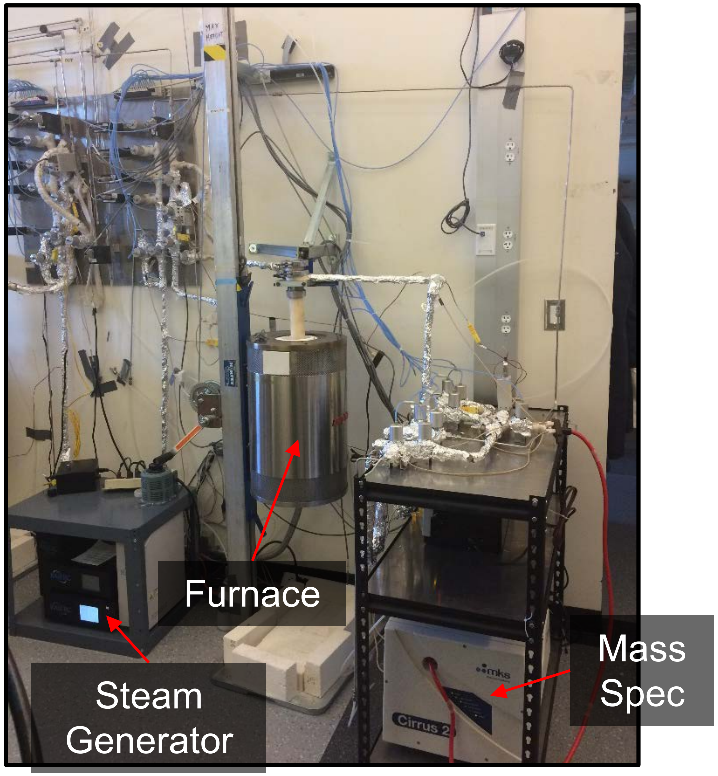
- Approach
  - Computational prototyping of metal oxide materials integrating theory and experimentation
- Thermodynamic Screening
  - Screened 60 new spinel materials to determine inversion parameter and available sites for water splitting. Developed preliminary model for inversion parameter
  - Electron density transferred to 1st nearest neighbors only in spinel aluminates
  - Structure and magnetic ordering play a critical role in predicting the STWS behavior of perovskite metal oxides
- Kinetic Screening
  - Identified important components of the oxygen evolution reaction
  - Determined the effect of inversion on hercynite reactions
  - Identified approach to minimize complexity required to fully model inversion
  - Identified potential model to minimize additional calculations necessary for future inverse or randomly doped materials (notably SLMA)
- Material Testing
  - Spray dried Co-doped hercynite particles stable over 200 redox cycles

Technical Backup Slides

Accomplishments and Progress – Material Testing

- Synthesis of materials using a citrate gel process
  - Homogeneous product with control of stoichiometry
- Materials tested using stagnation flow reactor (SFR)
  - Quantify H_2 production at different conditions
  - Can remove diffusion effects to fit kinetic models to data

New SFR for Long-Term Material Testing

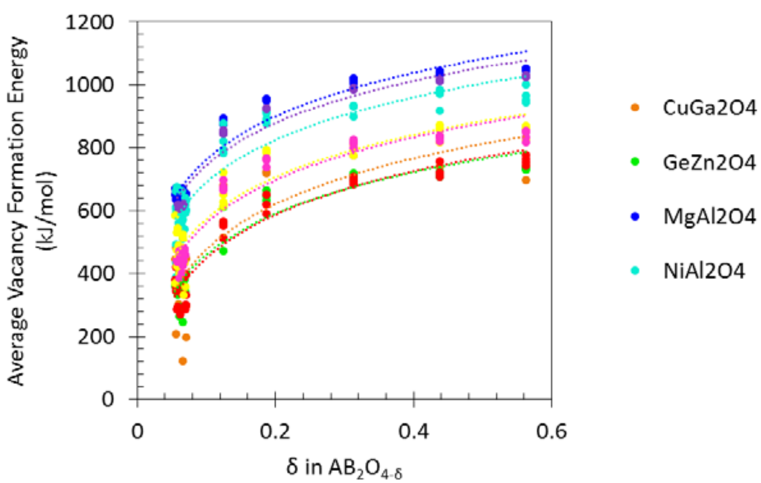


Accomplishments and Progress: Spinel Materials – Nonstoichiometry & Doping

- Vacancy formation energy depend on oxygen nonstoichiometry ($AB_2O_{4-\delta}$)
- Extent of reduction (and corresponding H_2 production) will depend on this change

$$AB_2O_{4-\delta} + \delta H_2O \rightarrow AB_2O_4 + \delta H_2$$

Effect of Nonstoichiometry on Vacancy Formation Energy



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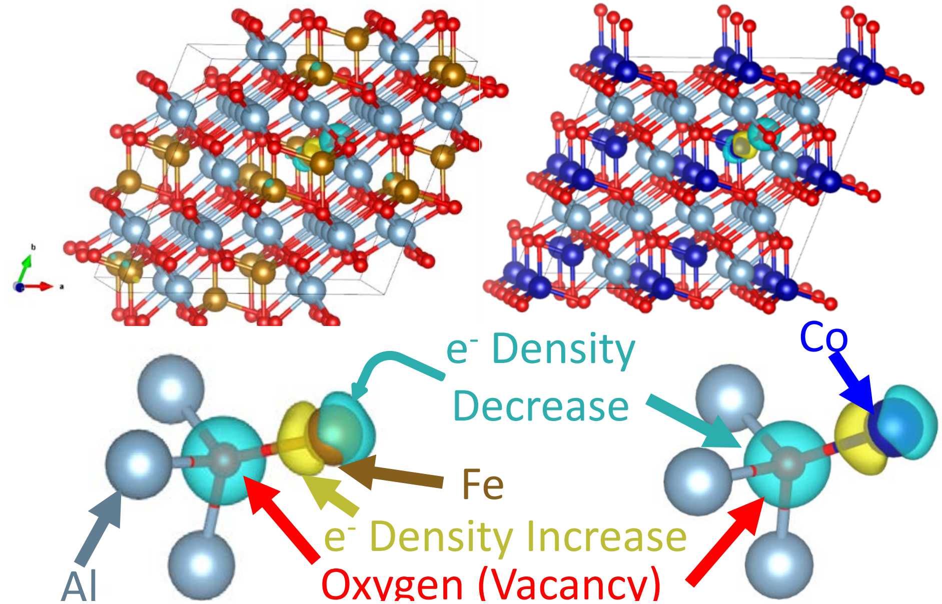

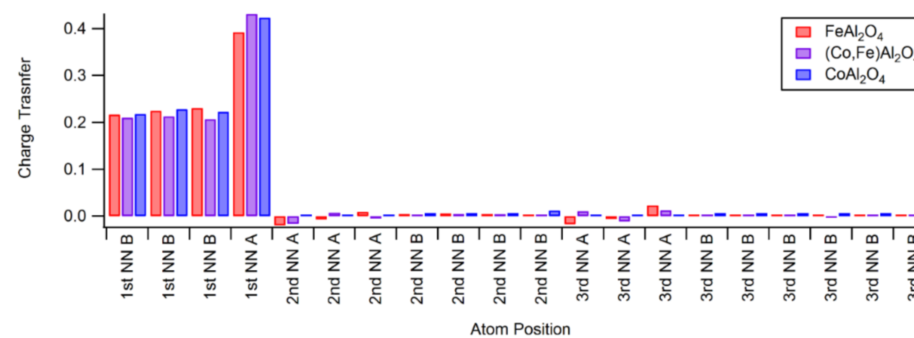

Charge transferred to 1st nearest neighbors only in all cases