HyMARC: Metal Hydrides for Stationary Storage Applications

2020 DOE Hydrogen Annual Merit Review

May 30, 2020

HyMARC
Hydrogen Materials Advanced Research Consortium

Enabling **twice the energy density** for onboard H_2 storage

PI: Tae Wook Heo

Team: *B. Wood, S. Kang, N. Keilbart, A. Jana, P. Xiao*

Lawrence Livermore National Laboratory

Project ID# ST208

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LLNL-PRES-810838

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under contract DE-AC52-07NA27344. Lawrence Livermore National Security, LLC

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Overview

Timeline

Project start date: 03/02/2020

Project end date: 02/28/2021

Barriers addressed

- Difficulty in initial activation for hydrogenation
- Lack of understanding of surface mechanisms

Budget

Fuel Cell Technologies Office

Total Funds: $236,783

EERE Program Manager: Jesse Adams

Collaborators

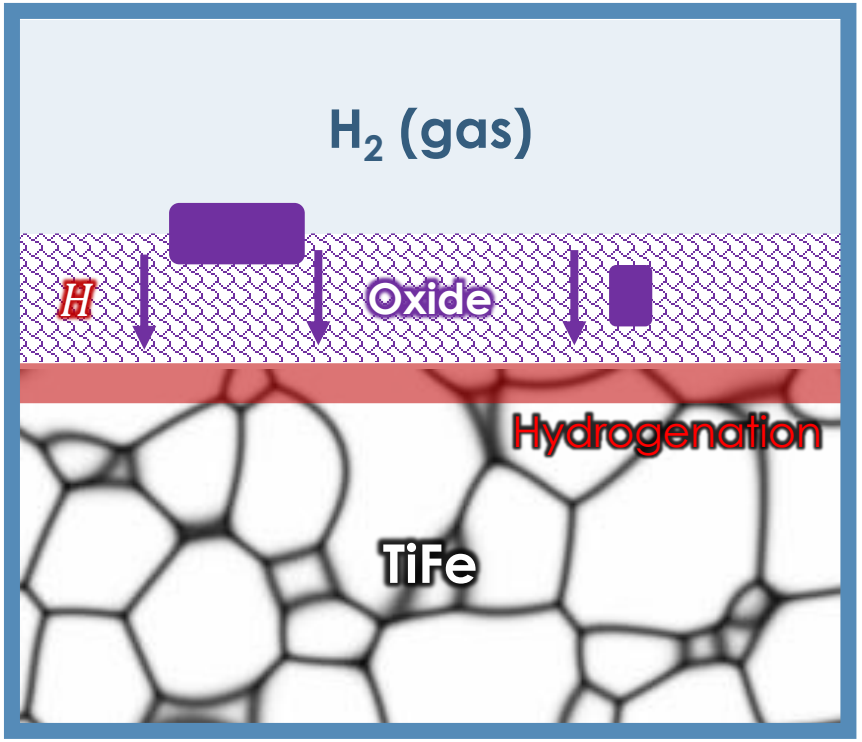
- KIST (Korea)
- HZG (Germany)

HyMARC Hydrogen Materials Advanced Research Consortium

Relevance

Source: https://www.energy.gov/

Source: https://apac-hydrogen.org



- **TiFe-based intermetallic hydrides**
  - Stationary hydrogen storage applications
  - Low cost, earth abundance, and reasonable capacity (~1.8 wt%)
- **Difficult initial activation for hydrogenation**
  - High temperatures and pressures
  - Long incubation times
  - Dopants (*e.g.*, Mn, Cr, Zr) for improving activation
  - Poorly understood mechanisms
- **Surface passivating oxide layer**
  - Potential roles in determining initial activation thermodynamics and kinetics
  - Processing-dependent oxide features
  - Second phase precipitates

Approach: Identification of key factors for activation

Oxide microstructures & chemistry

- Grain boundaries
- Grain morphology
- Oxide fractions/chemistry
- Precipitate microstructure

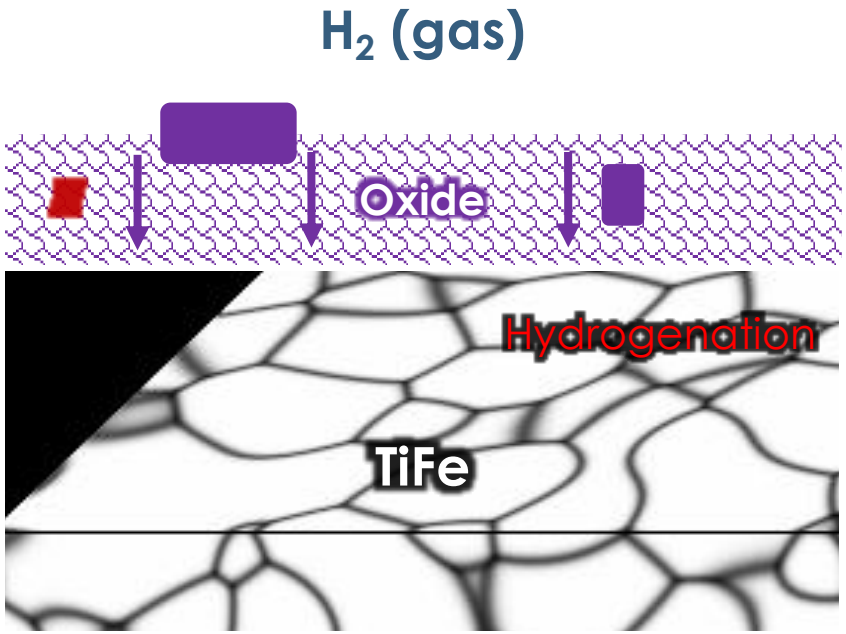
Oxide non-stoichiometry & crystallinity

- Ti/O ratio
- Fe/O ratio
- Crystalline/Amorphous

Oxide mechanics

- Strain in surface oxide due to underlying TiFe hydrogenation
- Strain-induced cracks

Surface oxide features play key roles in initial activation



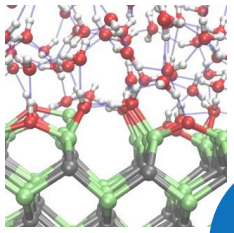
We focus on ***chemo-mechanical effects*** on ***hydrogen permeation*** through ***realistic surface oxide microstructures***

Approach: HyMARC modeling & Collaboration

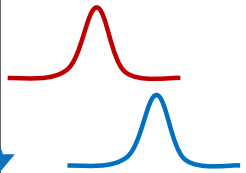
We leverage **1)** ***HyMARC modeling capabilities***, **2)** ***LLNL's leadership-class HPC facilities***, and **3)** ***international collaboration*** for theory-experiment integration

Computational and **Experimental XPS** analysis

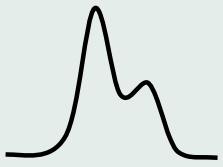
Develop model



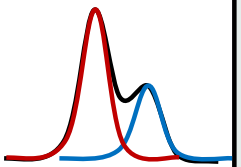
Compute representative spectra



Measure spectrum



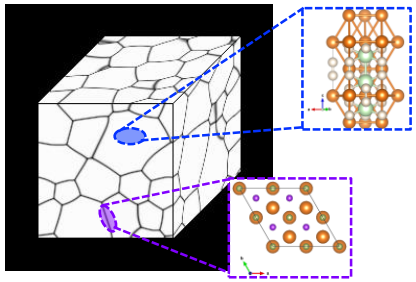
Interpret spectrum

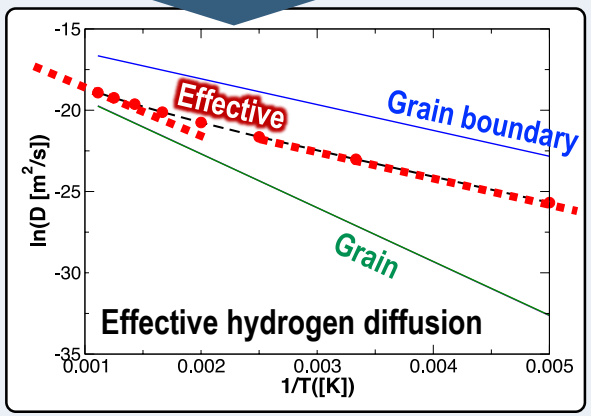


Surface oxide chemistry

Multiscale modeling of hydrogen transport

Polycrystalline oxide microstructure model





HyMARC Hydrogen Materials Advanced Research Consortium

Korea Institute of Science and Technology

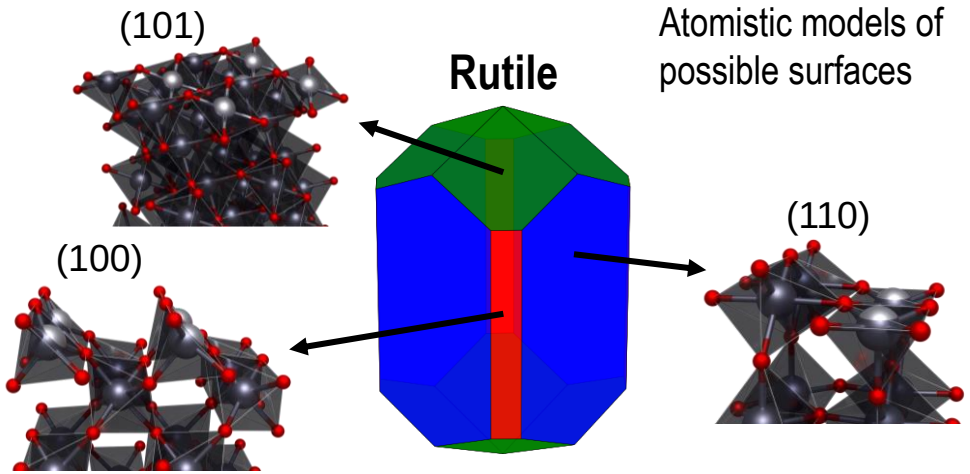
Helmholtz-Zentrum Geesthacht
Centre for Materials and Coastal Research

Accomplishments: Surface oxide structure & chemistry

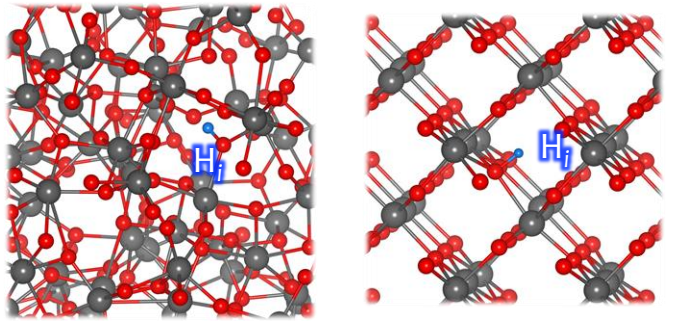
Atomistic approach

We constructed atomistic models of Ti oxides and Fe oxides for investigating hydrogen-surface oxide interactions, including solubility and transport of hydrogen

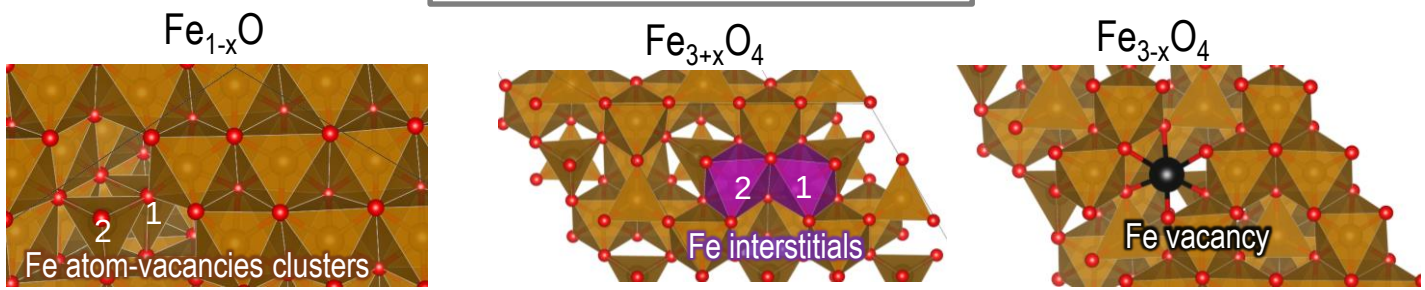
Models of possible Ti oxide surfaces



Models of ordered/disordered Ti oxides



Models of defective Fe oxides

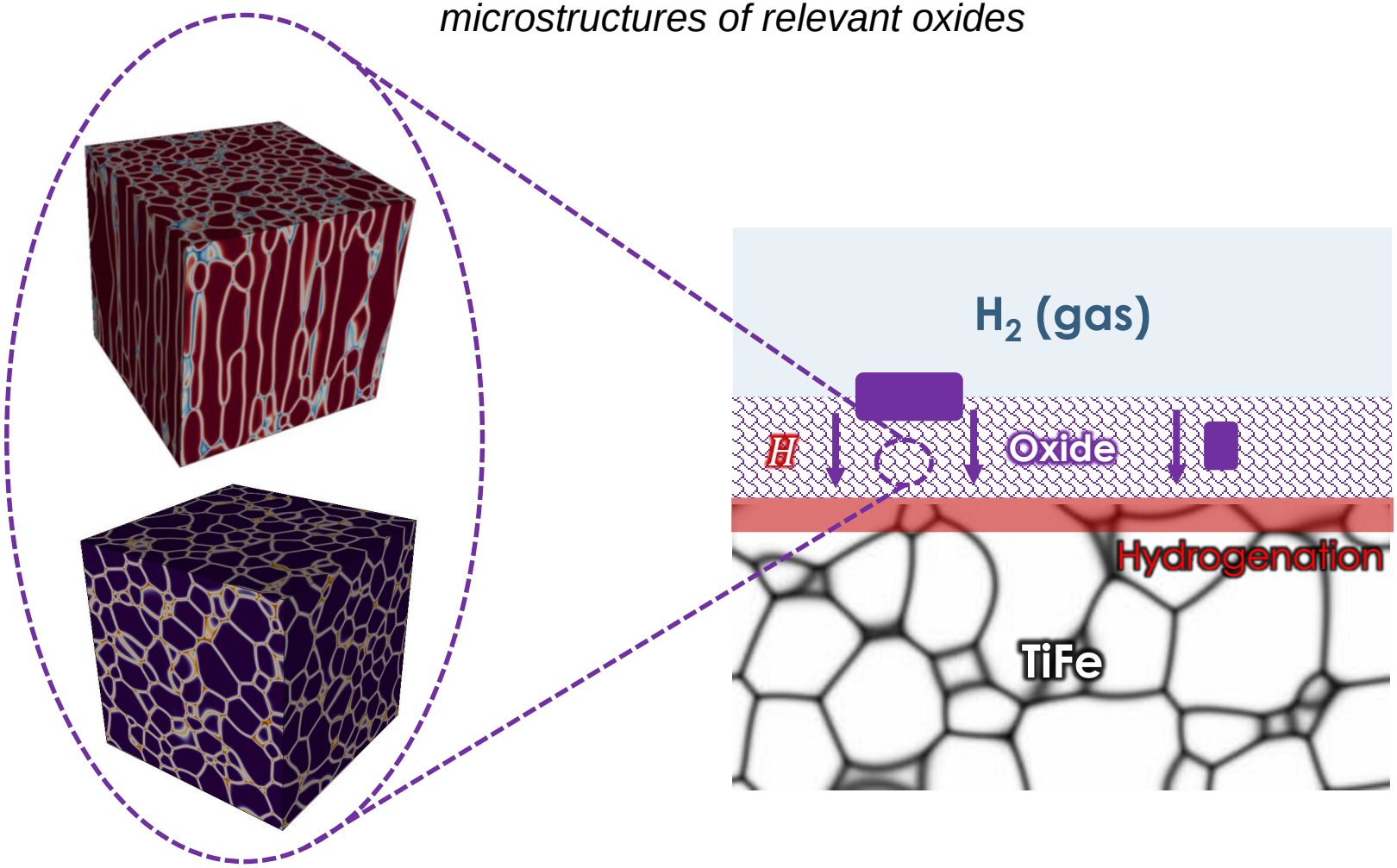


Surface oxide model and chemistry will be refined by combined computational and experimental XPS analysis through collaboration with KIST.

Accomplishments: Surface oxide structure & chemistry

Mesoscale approach

We performed preliminary mesoscale simulations for generating complex microstructures of relevant oxides

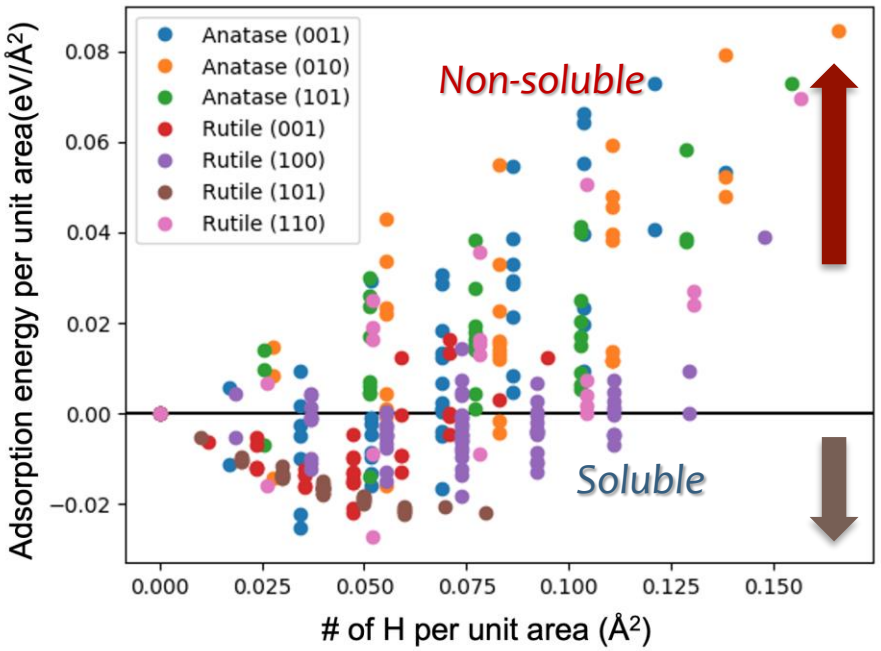


Experimental microstructure characterizations (SEM, TEM) will be combined to refine microstructure models through collaboration with HZG.

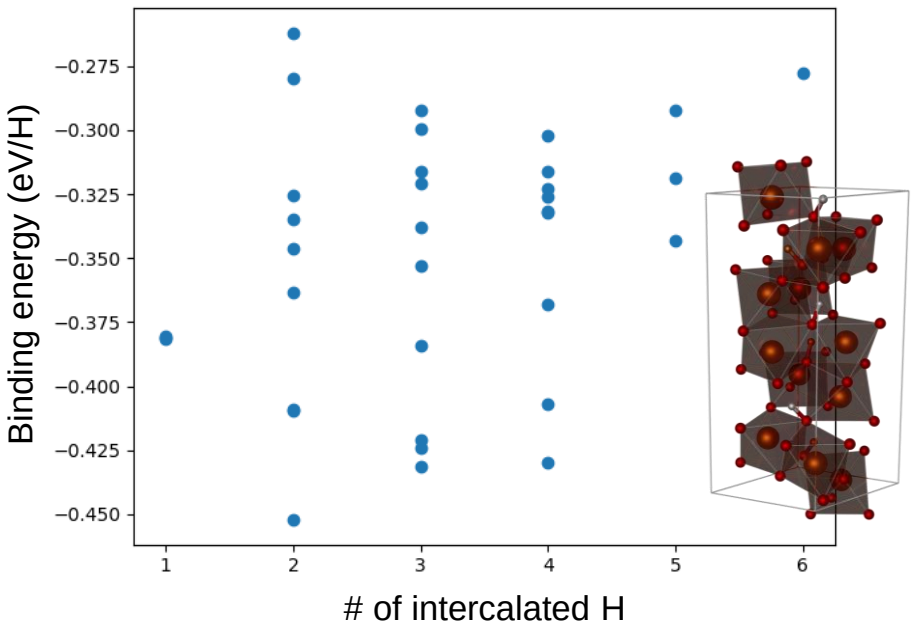
Accomplishments: Energetics for hydrogen solubility and transport
Atomistic approach

We conducted preliminary quantum-mechanical calculations of hydrogen adsorption and binding energy for relevant oxides based on constructed atomistic structures

H adsorption energies at various surfaces of TiO_2



H binding energy in crystalline Fe_2O_3

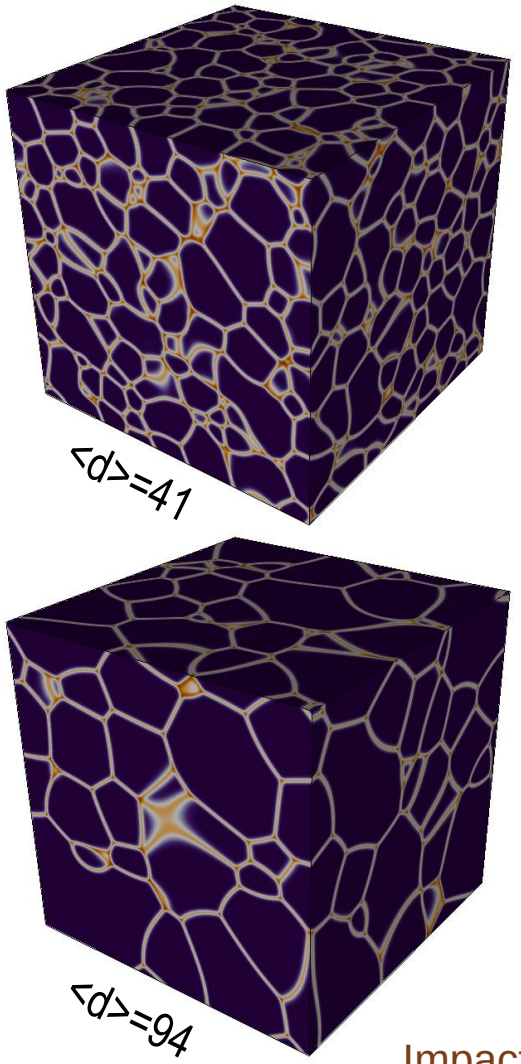


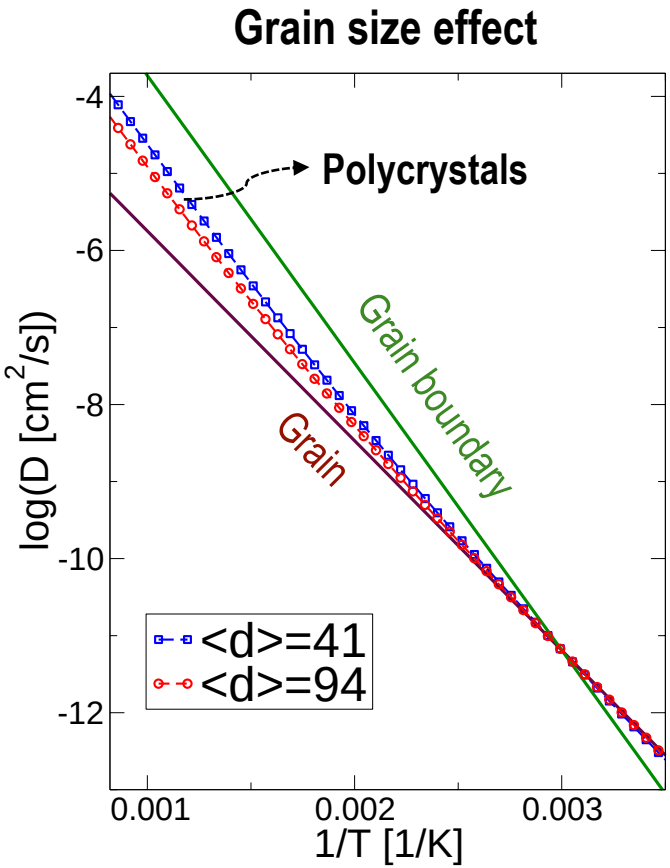
We are formulating a comprehensive statistical analysis method for investigating interactions (*e.g.*, solubility, diffusivity) between hydrogen and realistic oxide surface/grain boundaries

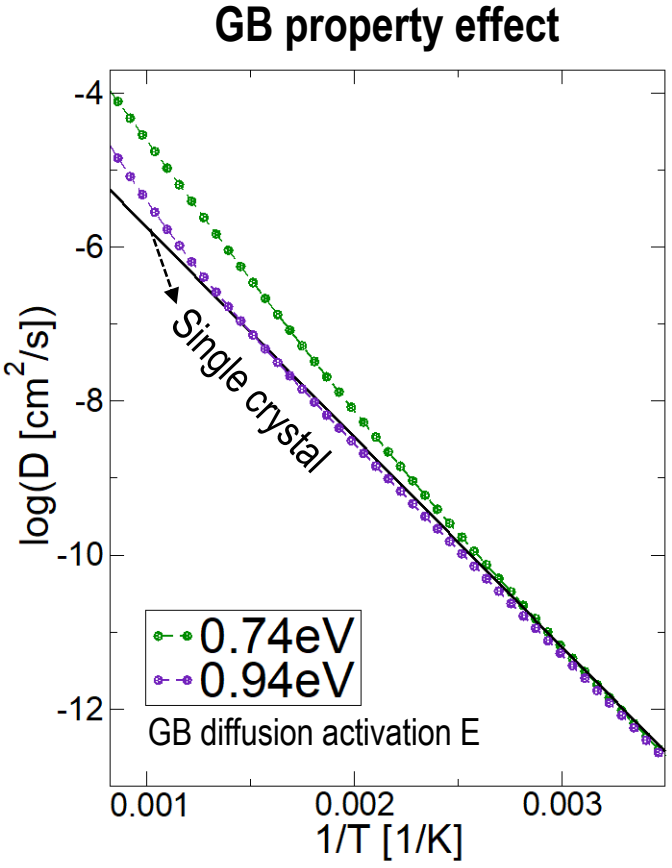
Accomplishments: Hydrogen permeation through oxide microstructures

Mesoscale approach

We investigated variability of effective hydrogen permeation through TiO_2 microstructures







Impacts of grain size and grain boundary diffusion properties on hydrogen diffusion were quantitatively analyzed.

Collaboration & Coordination

- **Collaboration with HZG (POC: Dr. Martin Dornheim, Germany):**
  - Coordinated regular-based teleconference schedules.
  - Established plans for remotely mentoring graduate students.
    - *1 student for atomistic modeling & 1 student for mesoscale modeling*
    - *Mitigation of issues associated with delayed visit schedules of HZG students and LLNL's researchers due to COVID-19.*

- **Collaboration with KIST (POC: Dr. Young-Su Lee, Korea):**
  - Initiated discussions for coordinating collaboration for surface oxide characterizations.
  - Coordinated plans for initial activities for refining/validating computational models.

Remaining Challenges and Barriers

- **COVID-19 related issues**
  - **Challenge**: Visit schedules of HZG students and LLNL researchers have been delayed.
  - **Mitigation**: We have established 1) plans for remotely mentoring graduate students; and 2) protocols for effective communication.

Proposed Future Work

Milestone	Description	End Date	Type
M1: Determine candidate surface oxide species from literature data and characterization through external partnerships	Generate atomistic and mesoscale models of surface oxides to be considered for doped and undoped TiFe	05/31/2020	Quarterly Progress Measure (Regular)
M2: Complete calculations of thermodynamics of bulk oxides and key spectroscopic signatures	Perform DFT calculations of oxide thermodynamics and simulate reference XPS spectra for bulk species to be compared with experiments	8/31/2020	Quarterly Progress Measure (Regular)
M3: Complete calculations of energetics of sub-stoichiometric surface oxides and key spectroscopic signatures	Perform ab initio molecular dynamics simulations of surface oxidation to generate configurations for additional XPS simulations to be compared with experiments	11/30/2020	Quarterly Progress Measure (Regular)
M4 (Go/No-Go): Demonstrate multiscale model for predicting hydrogen transport trends	Show ability to correctly predict trends in hydrogen transport and activation time compared to experimental results for 2-3 common dopants. Use multiscale model to suggest oxide properties that could reduce activation time to < 5 hours at 100 °C and 25 bar H_2.	02/28/2021	Annual Milestone (Regular)

Any proposed future work is subject to change based on funding levels.

Responses to Previous Year Reviewer Comments

Project was not reviewed last year.

Summary

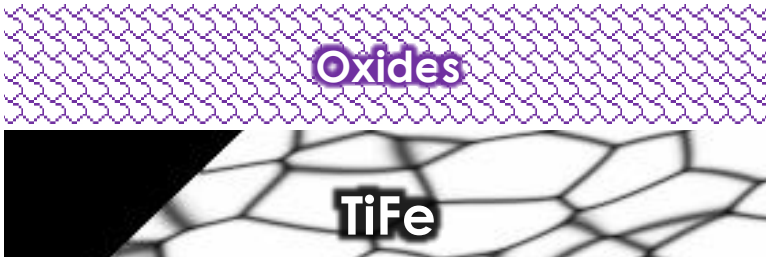
- **We have identified key chemo-mechanical factors that potentially determine initial activation of hydrogenation of TiFe.**
- **We focus on hydrogen permeation through realistic surface oxide microstructures, which is one of the key factors for initial activation.**
- **We have initiated activities for establishing collaboration with HZG (Germany) and KIST (Korea) for theory-experiment integration.**
- **We have carried out preliminary atomistic and mesoscale simulations.**
  - *We constructed atomistic models of Ti oxides and Fe oxides for investigating hydrogen-surface oxide interactions.*
  - *We performed preliminary mesoscale simulations for generating complex microstructures of relevant oxides.*
  - *We conducted preliminary quantum-mechanical calculations of hydrogen adsorption and binding energy for specific oxides (e.g., TiO_2 and Fe_2O_3), which determine initial hydrogen-surface oxide interactions.*
  - *We investigated variability of effective hydrogen permeation through TiO_2 microstructures due to grain size and grain boundary diffusion properties.*

Technical backup slides

Technical Backup

Reduction thermodynamics of relevant oxides upon exposure to hydrogen

H_2 (gas)



$3H_2 + TiO_2 \rightarrow TiH_2 + 2H_2O$ $\quad \Delta H_{calculated}$ = +44 kJ/mol

$2H_2 + TiO_2 \rightarrow Ti + 2H_2O$ $\quad \Delta H_{calculated}$ = +213 kJ/mol; $\Delta H_{experimental}$ = +372 kJ/mol

$4H_2 + Fe_2O_3 \rightarrow 2FeH + 3H_2O$ $\quad \Delta H_{calculated}$ = -321 kJ/mol

$3H_2 + Fe_2O_3 \rightarrow 2Fe + 3H_2O$ $\quad \Delta H_{calculated}$ = -298 kJ/mol; $\Delta H_{experimental}$ = -32 kJ/mol

Source: https://materialsproject.org

These thermodynamic data provide information about stabilities of relevant oxides under hydrogen environment.