Multiscale modeling of interface kinetics within HyMARC

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Enabling twice the energy density for onboard H₂ storage

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Timeline	Barriers addressed	
Project start date: 10/01/2018 Phase II end date: 09/30/2022	 Lack of understanding of hydrogen physisorption and chemisorption (Barrier O) System weight and volume (Barrier A) Charge/discharge rate (Barrier E) 	
Budget	Partners	
Phase I DOE funding: \$3040K Phase II FY19 DOE funding (expected): \$1250K Funding determined annually by DOE	Sandia (lead) NREL (lead) PNNL LBNL	NIST SLAC ORNL



Relevance: Multiscale features of storage mechanisms

HyMARC provides <u>i) community tools</u> and <u>ii) foundational understanding</u> of multiscale phenomena for hydrogen storage mechanisms



Approach: Validated multiscale modeling

Modeling approach prioritizes (i) bridging scales via multiscale integration; (ii) improving descriptions of "real" materials; and (iii) leveraging experiment-theory feedback



Roles of multiscale modeling within HyMARC



Accurate thermodynamic description of complex hydrides



- Compared to SNL PCT, our model predicts Δ S with 97% agreement and Δ H with 88% agreement.
- Phase equilibrium between Mg(BH₄)₂ and MgB₁₂H₁₂ is correctly predicted to within 10°C.
- Calibrated phase diagram can be used to:
 - Identify thermodynamic conditions for avoiding intermediates
 - ✓ Understand high-P hydrogenation
 - Extrapolate to hard-to-access P/T conditions
 - Inform kinetic models





Beyond-ideal thermodynamics: Internal interfaces

Theoretical framework for predicting equilibrium phase fractions as function of temperature, pressure, and particle size





Beyond-ideal thermodynamics: Internal interfaces

Demonstrated thermodynamic phase fraction prediction for Li-N-H



Large particles

 $\begin{array}{l} \mathsf{Li}_{3}\mathsf{N}\mathsf{+}\mathsf{H}_{2}\longleftrightarrow \mathsf{Li}_{2}\mathsf{N}\mathsf{H} + \mathsf{Li}\mathsf{H} \\ \mathsf{Li}_{2}\mathsf{N}\mathsf{H} + \mathsf{Li}\mathsf{H} & \mathsf{+}\mathsf{H}_{2}\longleftrightarrow \mathsf{Li}\mathsf{N}\mathsf{H}_{2} + 2\mathsf{Li}\mathsf{H} \end{array}$

Small particles

 $Li_3N+2H_2 \leftrightarrow LiNH_2 + 2LiH$

Predicted size-dependent phase fractions for hydrogenation of Li₃N/[LiNH₂+2LiH] system in core-shell microstructure



Successfully predicted experimentally characterized reaction pathway in nanoconfined Li-N-H and confirmed relevance of interfaces in determining phase stability



Mass transport kinetics: concurrent chemical & materials processes



Multiscale approach for computing effective diffusion property

Developed efficient modeling approach for extracting effective transport properties of realistic hydride microstructures

More realistic grain/phase microstructures



by phase-field simulations

Computational procedure

- Reconstruct a digital hydride microstructure using a *phase-field (PF) simulation* or using *experimental information*
- Assign individual diffusivities derived from atomistic simulations to corresponding grains/phases of the PF simulated microstructure
- Compute steady state profiles under macroscopic concentration gradients using the *Fourier-spectral iterative perturbation method*



Extract effective diffusivity tensor

$$D_{ij}^{eff} = - \langle j_i(r) \rangle / \overline{q}$$



Multiscale approach for computing effective diffusion property



Multiscale approach for computing effective diffusion property

Demonstrated flexibility of microstructural morphology in computation



transport properties.

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Possible impacts of mechanical stress/strain



Reaction progress

- Destabilizing intermediates and product hydride
- Flattening the energy landscape
- Engineering thermodynamics (P · V term) for better reversibility & reaction kinetics



 $(J_i: \text{flux}, c_0: \text{total concentration}, M_{ij}: \text{mobility}, F_i: \text{Driving force}, \Delta\Omega: \text{atomic dilation}, P: \text{local pressure})$



* R. W. Balluffi, S. M. Allen and W. C. Carter, Kinetics of Materials, John-Wiley and Sons (2005)



Multiscale modeling approach for computing strain energy

Hydrogenation induces significant volume expansion/structural transformation, leading to mechanical stress within hydrides in a confining medium



Computational procedure Generate a metal hydride microstructure using a phase-field simulation Assign DFT-derived phase-dependent ideal elastic moduli & lattice parameters to corresponding grains/phases of the simulated microstructure Compute mesoscopic stress/strain fields for mechanical equilibrium under loads using the Microelasticity theory/computation method $\nabla_{j}\sigma_{ij} = \nabla_{j} \left[C_{ijkl}(\vec{r}) \cdot \left\{ \bar{\epsilon}_{kl} + \delta \epsilon_{kl}(\vec{r}) - \epsilon_{kl}^{0}(\vec{r}) \right\} \right] = 0$ Compute strain energy $E_{str}(\vec{r}) = \frac{1}{2} C_{ijkl}(\vec{r}) \cdot \left\{ \bar{\epsilon}_{ij} + \delta \epsilon_{ij}(\vec{r}) - \epsilon_{ij}^0(\vec{r}) \right\} \cdot \left\{ \bar{\epsilon}_{kl} + \delta \epsilon_{kl}(\vec{r}) - \epsilon_{kl}^0(\vec{r}) \right\}$

Impact of confinement strain energy on thermodynamics

HyMARC's multiscale modeling approach quantifies the destabilizing effect of confinement stress on reaction enthalpy due to volume expansion upon hydrogenation



Computed strain energy is relevant to the experimentally measured confinement effect on ΔT exhibited in TPD measurement of NaBH₄ (Interaction with ANL (D.J. Liu) seedling project).



Impact of confinement: Effect of loading









Loading can have a large effect on confinement stress

Impact of internal stress on diffusion property

Diffusion property differently responds to internal stress depending on grain/particle size



Modeling phase transformation mechanisms of metal hydrides



Phase nucleation kinetics modeling

Advanced nucleation model identifies three possible pathways of phase formation



Predicted phase morphologies are being compared with STXM to identify pathways



Phase nucleation kinetics modeling

Nucleation kinetics favor two-step condensation-crystallization mechanism with pressure-dependent rate limitations

Low H₂ pressure



High H₂ pressure





Modeling coupled processes of (re/de)hydrogenation

<u>D</u>iffuse <u>Reactive</u> <u>Interface</u> <u>N</u>onlinear <u>K</u>inetics (DRINK) model for (de)hydrogenation fronts controlled by materials & chemical kinetic processes



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DRINK model progress: PdH_x dehydrogenation kinetics

Diffuse Reactive Interface Nonlinear Kinetics model incorporates diffusion, phase transformation, stress, and chemistry to simulate (de)hydrogenation



T.W. Heo, X. Zhou, S. Kang, B.C. Wood, in preparation

Summary

- EMN multi-national labs consortium *HyMARC* currently include and is actively developing validated modeling capabilities for investigating multiscale chemical and materials processes for hydrogen storage.
- Multiscale modeling plays significant roles in combining and integrating *multiple chemical/materials processes* taking place at *various length and time scales* as well as *non-ideal* materials factors.
- Integrated multiscale approaches are applied to investigate simple and complex hydrides focusing on
 - Beyond-ideal thermodynamics
 - Mass transport kinetics
 - Solid-solid interfaces/phase transformations



Technical backup slides

Multi-scale modeling framework for simulating solid-solid phase transformation



Sources of mechanical stresses during hydride formation





