HyMARC: Addressing Key Challenges to Hydrogen Storage in Advanced Materials Through a Multi-Lab Collaboration

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Question and Answer

• Please type your questions to the chat box. **Send to: (HOST)**
Acknowledgements

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Enabling twice the energy density for onboard H₂ storage
Outline

- **FCTO Introduction**

- **HyMARC**
  - Objectives & goals
  - Phase 1 accomplishments
    - Moving the state-of-the-art
    - Seedlings

- **HyMARC Phase 2**
  - Tasks
  - Research projects

- **HyMARC Capabilities**
  - Modelling
  - Advanced characterization

- **HyMARC**
  - Examples of on-going research

- **Questions and Answers**
HyMARC performs foundational research, develops capabilities to accelerate materials discovery, and supports Seedling projects

Objectives:

• **Develop** and **Enhance** Hydrogen Storage Core Capabilities:
  - **Computational models and databases** for high-throughput materials screening
  - **New characterization tools and methods** (surface, bulk, soft X-ray, synchrotron)
  - **Tailorable synthetic platforms** for probing nanoscale phenomena

• **Validate** claims, concepts and theories of hydrogen storage materials

• **Accelerate** the path forward to development of hydrogen storage materials for transportation
Principal Investigators and Lead Researchers

- Mark Allendorf
  Co-Director
  SNL PI

- Vitalie Stavila

- Tom Gennett
  Co-Director
  NREL PI

- Phil Parilla

- Brandon Wood
  LLNL PI

- Tae Wook Heo

- David Prendergast
  LBNL PI

- Jeff Long
  LBNL PI

- Tom Autrey
  PNNL PI

- Mark Bowden

- Craig Brown

- Terry Udovic

- Jeff Urban
Accelerating materials discovery

- **Strategy assessments**: identified most promising material improvement strategies
- **Missing/inaccurate data**: e.g. thermodynamic data essential for material assessment
- **Modeling tools**: filling major gaps in understanding of key processes
- **Enabling Seedling Projects by providing**:  
  - Access to experimental resources essential to their success (e.g., hi-P reactors and PCT)  
  - Computational modeling in support of experiments (outside Seedling budget)  
  - Assisting with data interpretation (e.g., computational spectroscopy)

**Material development strategies we evaluated indicate progress toward several DOE targets**
HyMARC foundational research addresses all phenomena potentially influencing reaction thermodynamics and kinetics.

Effective thermal energy for $\text{H}_2$ release:

$$\Delta E(T) = \Delta H^\circ(T) + E_a$$

Thermodynamics          Kinetics
Phase 1: Some Examples of how HyMARC moved the bar for specific materials or strategies

- **Interface engineering**: Li$_3$N@(6nm-C) H$_2$ cycling T reduced by >180 °C (bulk is 430 °C)
- **Nanoconfinement (porous host)**: Mg(BH$_4$)$_2$@(6-nm C) H$_2$ desorption T reduced > 100 °C
- **Nanoencapsulation**: Mg(BH$_4$)$_2$@rGO >10 wt% (record for nanoscale hydride)
- **Sorbent Capacity**: Ni (m-dodbc) Highest volumetric/gravimetric room temperature capacity to date.
- **Hydrides**: Improved reversibility of Mg(BH$_4$)$_2$ to temperatures below 200 °C
- **Binding energies**: Established ability to alter hydrogen binding energies approaching 15 kJ/mole in sorbent materials
- **Desorption control**: Established that desorption temperatures can be controlled with dynamic sorbent materials (e.g. phonon vibrational modes, expansion, etc.)
- **Multiple molecular H$_2$ adsorption**: First sorbent material with validated existence of two hydrogen molecules adsorbed per metal center
Two major publications from HyMARC Phase 1 document perspectives on sorbent strategies and nanoscale metal hydrides

**HyMARC FY17/Q2 Go/No-go Milestone**

Rank improvement strategies for sorbents. Decision criterion: select 2 with greatest potential for increasing $\Delta H^\circ$. **Top strategies:**
- Open metal sites in MOFs
- Lewis acid/Lewis-base sites

**Energy & Environ. Sci. 2018, 11, 2784**

“An Assessment of Strategies for the Development of Solid-State Adsorbents for Vehicular Hydrogen Storage”

Topics include:
- Usable gravimetric and volumetric capacities
- The importance of binding strength
- Theoretical calculations of $H_2$ physisorption
- Considerations for adsorbent synthesis and characterization
- Revisiting the results of the 2010 HSCoE final report
- Perspectives on current material strategies

**Chem. Rev. 2018, 22, 10775**

“Nanostructured Metal Hydrides for Hydrogen Storage”

Topics include:
- Classes of nanostructured metal hydrides
- Synthesis routes
- Structure
- Morphology
- Mechanistic effects

**HyMARC FY18/Q4 Go/No-go Milestone**

Rank improvement strategies for hydrides. Decision criterion: select 2 with greatest potential for reducing effective $\Delta H$ (article addresses a major strategy considered in the Go/No-go)
HyMARC is currently collaborating with Phase 2 Seedling Projects and facilitating their research

The HyMARC team assists individual projects with:

• A designated HyMARC point-of-contact
• Technical expertise concerning specific scientific problems
• Access to HyMARC capabilities
  – Note that HyMARC collaborates and is not an analytical service

• Development of Magnesium Boride Etherates as Hydrogen Storage Materials (U. Hawaii)
  – Instability in MgB$_2$ B sheets explained (LLNL modeling investigation)
  – High-P hydrogenation, XRD, and FTIR performed for 43 MgB$_2$(etherate) samples

• Electrolyte Assisted Hydrogen Storage Reactions (Liox Power)
  – High-P experiments and sample characterization

• ALD Synthesis of Novel Nanostructured Metal Borohydrides (NREL)
  – Mg(BH$_4$)$_2$ nanoparticle samples sent to NREL for ALD coating

• Optimized Hydrogen Adsorbents via Machine Learning & Crystal Engineering (U. MI)
  – Discussions on crystal engineering of OMS in MOFs
HyMARC Phase 2 Task Structure

Task 1: Sorbents
- PI: Tom Gennett (NREL, Golden, CO)

Task 2: Metal Hydrides
- PI: Mark Allendorf (Sandia, Livermore, CA)

Task 3: Hydrogen Carriers
- PI: Tom Autrey (PNNL, Richland, WA)

Task 4: Advanced Characterization Capabilities
- PI: Phil Parilla (NREL, Golden, CO) and David Prendergast (Molecular Foundry, LBNL)

Task 5: Research Support for Seedling Projects
- PI’s: Mark Allendorf and Tom Gennett

Task 6: HyMARC Data Hub
- PI: Kristin Munch (NREL, Golden, CO)
HyMARC Phase 2 Focus Areas: designated high-priority research topics

**Sorbents:**
1.A Enthalpy / Entropy
1.B Optimizing Sorbent Binding Energies
1.C Optimizing Sorbent Packing
1.D. Dynamic Sorbent Materials
1.E Multiple Hydrogens Per Metal
1.F Nanoscale Defects in Sorbents

**Metal hydrides:**
2.A Thermodynamics
2.B Solid Interfaces and Surfaces
2.C Activation of bonds in hydride materials to improve kinetics (e.g. B-B, B-H, etc.)
2.D Nanoscaling to Improve Thermodynamics and Kinetics
2.E Microstructural Impacts of Complex Metal Hydride Reactions
2.F Machine Learning and Data Science

**Advanced Characterization:**
4.A High-Temperature Validated PCT System
4.B PCT Calorimetry,
4.C NMR Spectroscopy
4.D *In-situ* and *ex-situ* Synchrotron, Neutron and DRIFTS Techniques
HyMARC Modeling capabilities: tools that now cover all relevant length scales and many important phenomena

- **Atomic/molecular (0 – 1 nm)**
  - Computational Spectroscopy
  - Surface chemistry
  - Interatomic potentials
  - Example: NaAlH₄ surface chemistry: role of oxide

- **Molecular/micro (0.5 – 2 nm)**
  - Simulation
  - Microstructure
  - Example: Time-dependent simulations of MgH₂ formation

- **Mesoscale (2 - 100 nm)**
  - Nucleation kinetics
  - Phase microstructures
  - Example: Nano-alloying of Ni-doped Mg

- **Grains (≤ 10 μm)**
  - Grain boundaries
  - Particle size effects
  - Stress/strain
  - Example: H diffusion in PdHₓ
  - Diffusion in NaBH₄

- **Macroscale/Bulk**
  - Thermodynamics
  - Example: Mg(BH₄)₂ phase diagram

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**Diagram:**

- MgB₂ phase diagram
- Mg(BH₄)₂
- MgB₂ + 4 H₂
- 1/6 MgB₁₂H₁₂ + 5/6 Mg + 3 H₂

**Graph:**

- Energy level diagram
- Reaction pathways

**Scale:**

- Length (m) range from 10⁻¹⁰ to 10⁻²
Characterization tools: expanded and extended to in-situ, in-operando probing and mesoscale resolution

**Atomic/molecular (0 – 1 nm)**

**Molecular/micro (0.5 – 2 nm)**

**Mesoscale (2 - 100 nm)**

**Grains (≤ 10 μm)**

**Macroscale/Bulk**

- **Microporosimetry/BET**
- **AP-XPS ALS/BL 11.0.2**
- **XAS In-situ flow cell (1 bar, max. 250°C)**
- **He bubbles seen by AC-TEM STEM res. 63 pm**
- **STXM (30 nm res.) LBNL/ALS**
- **LiNH₂**
- **Li₃N**
- **Ultrahigh Pressure Reactor (1000 bar)**
- **H-D exchange**

Length (m) range: **10⁻¹⁰** to **10⁻²**
HyMARC surface characterization capabilities include unique instrumentation to directly probe hydrogen on surfaces

Motivation:
Surfaces are believed to play an important role in hydrogen storage reactions; exact role and mechanisms remain unclear.

Technical Approach: *In-situ* techniques enable us to probe the surface chemistry for H₂ storage materials.

- **Low energy ion scattering (LEIS):**
  - Determine surface composition, H surface conc.
  - (First monolayer only, <1 nm)

- **Ambient pressure XPS:**
  - Characterize O, Na, Al, and Ti binding.
  - (Surface and near sub-surface, <10 nm)

- **Scanning trans. x-ray microscopy (STXM):**
  - Distribution of Ti within particles.
  - (Bulk)

What we can learn:
⇒ What is the exact surface composition of H₂ storage materials?
⇒ How do surfaces respond to temperature and H₂ environments?
⇒ What is the spatial distribution of species of interest?
⇒ Can surfaces be modified to improve H₂ storage properties?
Extended Characterization Capabilities

**DRIFTS**

Diffuse reflectance system coupled to cryostat and gas adsorption analyzer
Can collect data at 15-373 K and 0-100 bar (controlled dosing up to 1.2 bar)

**Thermal Conductivity**

H₂, He (other gases possible) from vacuum to 100 bar
Temperature Range: 40 K to 375 K
Sample types include solids & compressed pucks & powder

**Variable Temperature PCT**

Modified PCT Pro system with capabilities of hydrogen pressures up to 200 bar, and a controlled temperature range from 40 – 350 K. (other gases possible including CH₄)
High-pressure hydrogen station provides access to pressures in current fueling stations

- Up to 1000 bar $H_2$ and 400 °C
- Holds up to 4 different samples at once
- Employed for:
  - Synthesis of metal hydrides that cannot be synthesized in another way
  - Destabilization of $[B_{12}H_{12}]^{2-}$ and $[B_{10}H_{10}]^{2-}$ compounds
  - Hydrogenation of metal borides, e.g. $\text{MgB}_2$, $\text{MgB}_2$-etherates
  - Stability of hydrides and sorbents under high-pressure $H_2$
Synthetic capabilities: New sample formats for encapsulate complex hydrides, MgB$_2$ nanoparticles, graphene nanostructures

- **Atomic/Molecular** (0 – 1 nm)
  - Mg(BH$_4$)$_2$ film on Au for LEIS measurements

- **Molecular and microscales** (0.5 – 2 nm)
  - Model systems: GNR+(H$_2$ dissoc. catalyst)

- **Mesoscale** (2 - 100 nm)
  - MgB$_2$ nanoparticles
  - Encapsulation
  - Strain effects

- **Grains** (up to ~ 10 μm)
  - Nanoscaling

- **Macroscale/Bulk**
  - High-purity MOFs for model validation
  - New thermodynamics: Liquid-phase Mg(BH$_4$)$_2$
HyMARC has access to several user facilities

*Joint experiments may be planned on a limited basis*
Examples of experimental progress
NaAlH$_4$ surface chemistry understood using tools that probe the surface, near surface, and bulk material

*Novel approach mixes AIMD with XPS simulations via LLNL/LBNL collaboration to interpret SNL AP-XPS and obtain a reliable picture of how surface chemistry evolves*

**Simulated XPS shows that past work has incorrectly assigned chemical species, which does not always follow oxidation state!**

**Near-surface region chemistry involves oxide film on Na$_3$AlH$_6$, which evolves as hydrogen enriches and then depletes during dehydrogenation**
Understanding MgB$_2$ decomposition

HPC-enabled capability to directly observe chemical reactions upon hydrogenation of MgB$_2$ edges under high pressure illustrates competing pathways for $B_xH_y$ formation.

- Utilized to improve strategies for performance/design of new materials

- AIMD simulations show that chemistry occurs preferentially at exposed edge planes, in agreement with our previous experiment-theory study
  Ray et al. *PCCP* 19, 22646, 2017

- Mg-rich edges lead to smaller molecules; B-rich edges lead to closo-borane formation
At low pressures spectra indicate only adsorption at Co$_2^+$ site (Site 1)

Secondary physisorption sites (Site 2) are populated after Site 1 is filled
Summary

HyMARC National Laboratory team activities

- Foundational research to accelerate materials discovery
- Development of advanced characterization tools
- Computational modeling across all relevant length scales
- Innovative material synthesis

HyMARC researchers collaborate and assist DOE-Fuel Cell Technologies Office Seedling projects

- Scientific expertise
- Joint experiments
- Access to cutting-edge capabilities when needed
- Validation measurements
Question and Answer

• Please type your questions to the chat box. **Send to: (HOST)**
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All relevant DOE offices and other federal agencies working on hydrogen and fuel cell technologies at Annual Merit Review (AMR)

2019 AMR – April 29 – May 1
Crystal City, VA
www.hydrogen.energy.gov

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www.energy.gov/eere/fuelcells/fuel-cell-technologies-office-newsletter
Thank you

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hydrogenandfuelcells.energy.gov
Additional slides if needed
Select onboard hydrogen storage targets

<table>
<thead>
<tr>
<th>Storage Parameter</th>
<th>Units</th>
<th>2020</th>
<th>2025</th>
<th>Ultimate</th>
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<tbody>
<tr>
<td><strong>System Gravimetric Capacity</strong>&lt;br&gt;Usable, specific-energy from H₂ (net useful energy/max system mass)</td>
<td>kWh/kg (kg H₂/kg system)</td>
<td>1.5 (0.045)</td>
<td>1.8 (0.055)</td>
<td>2.2 (0.065)</td>
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<tr>
<td><strong>System Volumetric Capacity</strong>&lt;br&gt;Usable, specific-energy from H₂ (net useful energy/max system volume)</td>
<td>kWh/L (kg H₂/L system)</td>
<td>1.0 (0.030)</td>
<td>1.3 (0.040)</td>
<td>1.7 (0.050)</td>
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<tr>
<td><strong>Storage System Cost</strong>&lt;br&gt;$/kWh&lt;sub&gt;net&lt;/sub&gt; ($/kg H₂)</td>
<td>$/kWh&lt;sub&gt;net&lt;/sub&gt; ($/kg H₂)</td>
<td>10 (333)</td>
<td>9 (300)</td>
<td>8 (266)</td>
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<tr>
<td><strong>Durability/Operability</strong></td>
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<td>Min/max delivery temperature °C</td>
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<td>-40/85</td>
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<tr>
<td>Min/max delivery pressure Bar (abs)</td>
<td>5/12</td>
<td>5/12</td>
<td>5/12</td>
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<tr>
<td><strong>Charging/Discharging Rates</strong></td>
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<tr>
<td>System fill time Minutes</td>
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<td>3-5</td>
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<td>Minimum full flow (g/s)/kW of FC</td>
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<td>0.004</td>
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<td><strong>Dormancy (at 95% of capacity)</strong></td>
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<tr>
<td>Min time to first release Days</td>
<td>7</td>
<td>10</td>
<td>14</td>
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<tr>
<td>Max boil-off loss after 30 days %</td>
<td>10</td>
<td>10</td>
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For the complete set of onboard hydrogen storage targets, see: [https://www.energy.gov/eere/fuelcells/doe-technical-targets-onboard-hydrogen-storage-light-duty-vehicles](https://www.energy.gov/eere/fuelcells/doe-technical-targets-onboard-hydrogen-storage-light-duty-vehicles)
Accurate Mg-B-H phase diagram prediction

- New method gives computed entropy and enthalpy within 3% and 12% of experiments, respectively, up from 11% and 50% for standard DFT
- Phase equilibrium between Mg(BH$_4$)$_2$ and MgB$_{12}$H$_{12}$ is correctly predicted to within 10 °C!