HyMARC Seedling: Electrolyte Assisted Hydrogen Storage Reactions

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2017 DOE Hydrogen and Fuel Cells Annual Merit Review

Project ID: ST137

Overview

Timeline:

- Project Start Date for Phase 1: 01/20/17
- Phase 1 End Date: 06/19/18[a]
- Phase 2 End Date: 01/19/20

  [a] Project continuation to Phase 2 based on achieving Go/No-Go criterion.

Budget:

- Phase 1 Project Budget: $ 312,500
- Total Recipient Share: $ 62,500
- Total Federal Share: $ 250,000
- Total DOE Funds Spent[b]: $ ~18,760
  [b] as of 3/31/17
- Phase 2 Project Budget:[c] $937,500
- Total Recipient Share: $ 187,500
- Total Federal Share: $ 750,000

 [c] Project continuation to Phase 2 based on achieving Go/No-Go criterion.

Barriers

O. Lack of Understanding of Hydrogen Physisorption and Chemisorption.

- Decomposition pathways and products of materials to better understand their mechanisms and kinetics.
- H_2 storage capacity of potential storage materials and demonstrate reproducibility of their synthesis and capacity measurements.
- Develop reversible metal hydrides that improve kinetics while maintaining high gravimetric capacity at relevant release temperatures and pressures.
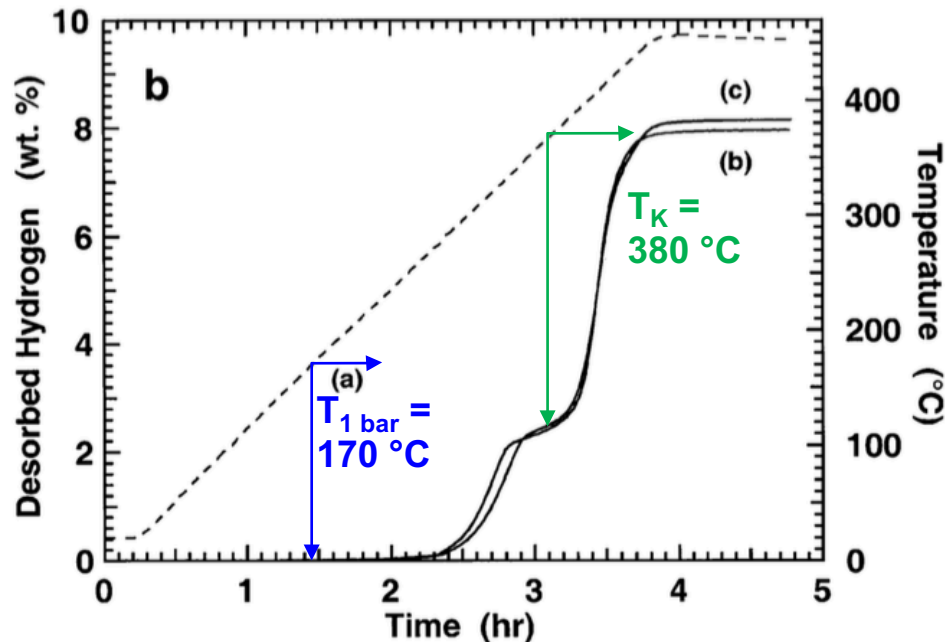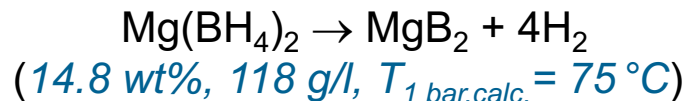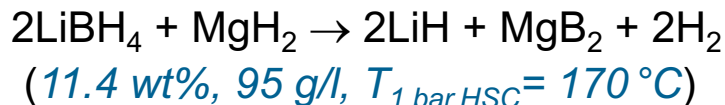
Partners/Collaborations

- HyMARC (Sandia, Stavila), HySCORE (PNNL, Autrey and Bowden)
- Project lead: Liox Power, Inc. with subcontract to HRL Laboratories, LLC

Relevance: Address kinetics of multi-phase hydrogen storage reactions… severely limited

- Most hydrogen storage candidates with high capacities and appropriate thermodynamics for PEM fuel cell use, contain multiple solid phases that must nucleate, grow, and be consumed during cycling.
- Presence of multiple phases hinders kinetics.
- For example: $2MgH_2 + Si \rightarrow Mg_2Si + 2H_2$ (*5.0 wt%, 83 g/l, $T_{1 bar,HSC} \sim 15\ °C$*)
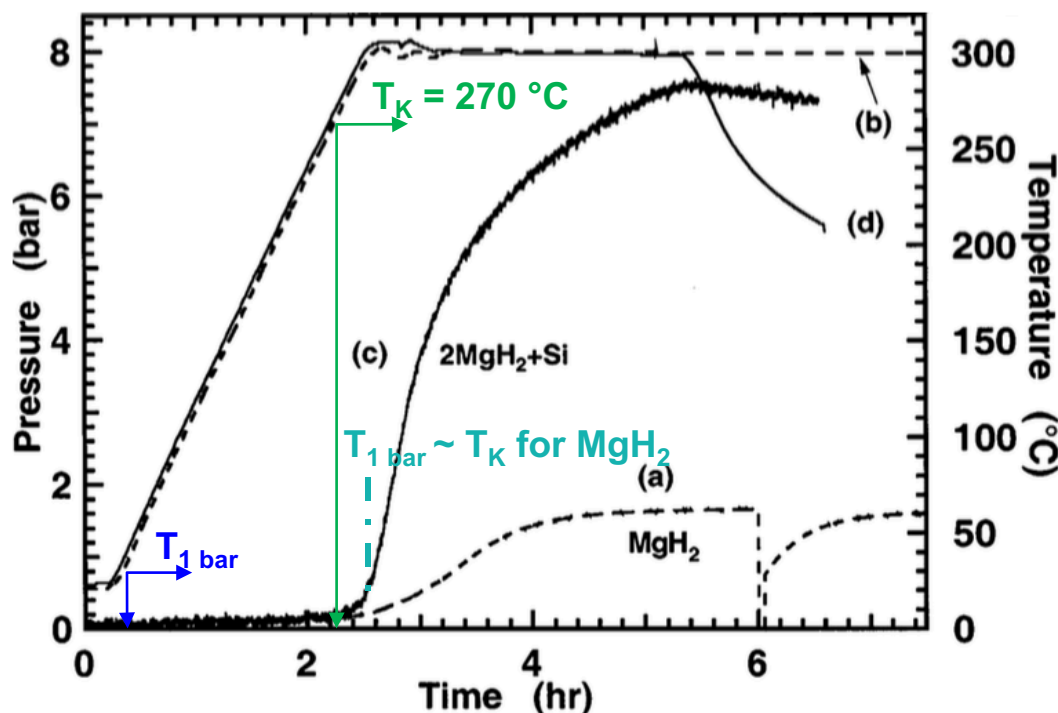
- $T_{1 bar} = 15\,°C << T_K = 270\,°C$ indicates kinetic limitation
- Working from T_K, we define a free-energy activation barrier for observable kinetics: ΔG_K

- $\Delta G_K \equiv (T_K - T_{1 bar})\cdot\Delta S$
  $= 33$ kJ

- Best case (*catalyzed, nano-scale*)
  $T_K = 200\,°C$; $\Delta G_K = 24$ kJ

"Altering hydrogen storage properties by hydride destabilization through alloy formation: LiH and MgH_2 destabilized with Si," J.J.Vajo, F.Mertens, C.C. Ahn, R. C. Bowman, Jr., B. Fultz, J.Phys.Chem.B 108 (37) 13977 (2004).

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$2LiBH_4 + MgH_2 \rightarrow 2LiH + MgB_2 + 2H_2$

(*11.4 wt%, 95 g/l, $T_{1\,bar,HSC}$ = 170 °C*)

$Mg(BH_4)_2 \rightarrow MgB_2 + 4H_2$

(*14.8 wt%, 118 g/l, $T_{1\,bar,calc.}$ = 75 °C*)

$\Delta G_K = \Delta G\,(T_K = 380\,°C) \sim 22\,kJ$

$\Delta G_K = \Delta G(T_K = 250\,°C) = 20\,kJ$

"Reversible Storage of Hydrogen in Destabilized LiBH$_4$ J.J. Vajo and S.L. Skeith and F. Mertens, J. Phys. Chem. B Lett., 109, 3719 (2005).
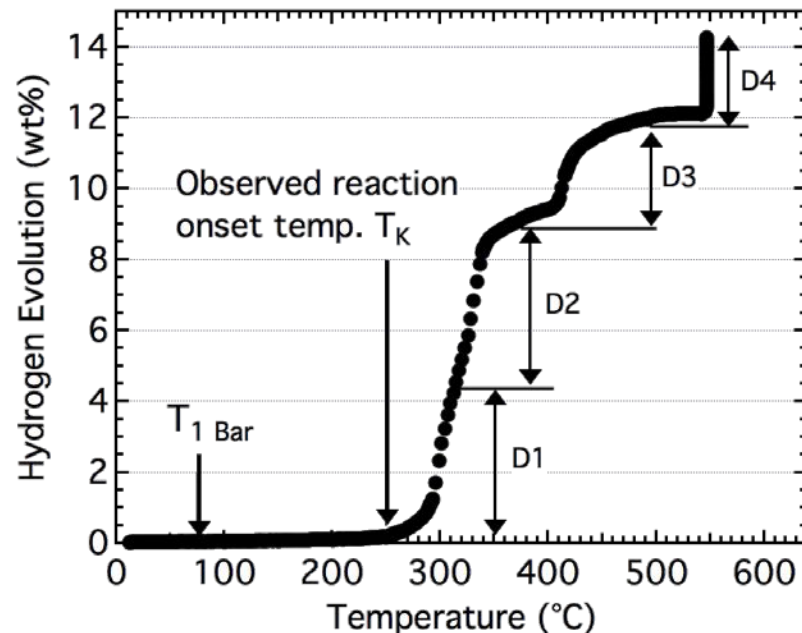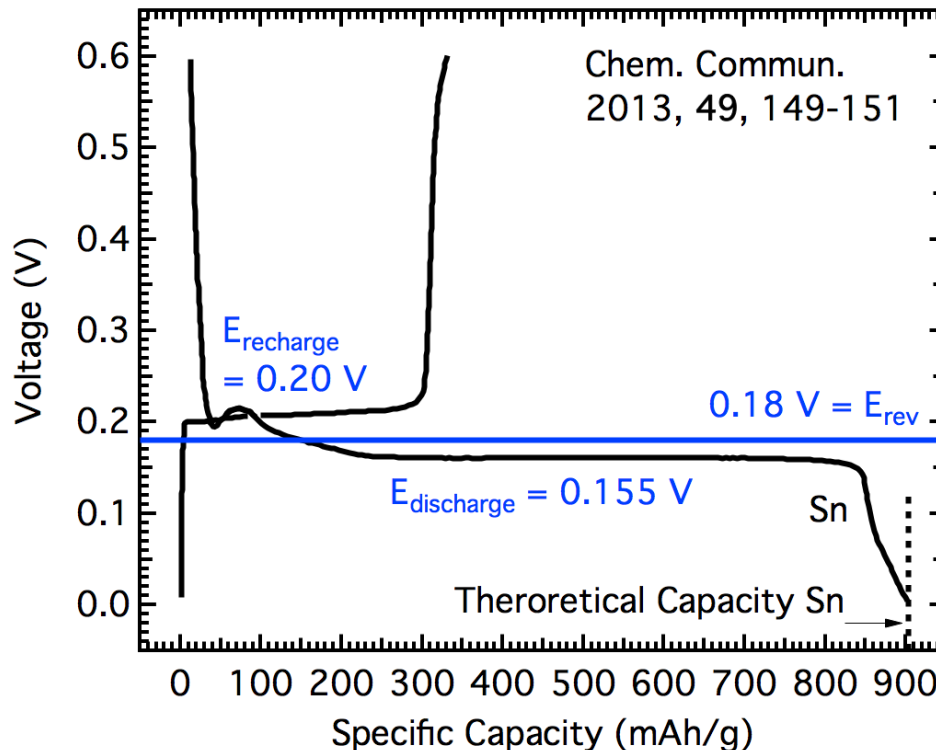
"Magnesium borohydride as a hydrogen storage material: Properties and dehydrogenation pathway of unsolvated Mg(BH$_4$)$_2$" G.L. Soloveichik, et al., Intl. J. Hydrogen Energy, 34, 916–928, (2009).

- Reactions across solid/solid interfaces kinetically limited
- Required ΔG_K for measurable reaction is ~>20 kJ

Approach: **Based on kinetics of multi-phase battery reactions that appear less limited**

Battery analog reaction similar to the MgH_2/Si hydrogen storage reaction:
$Mg + 0.5\,Sn \leftrightarrow 0.5\,Mg_2Sn$, $\qquad \Delta G_{std,HSC} = -34.5$ kJ ($E_{rev} = 0.18$ V)
However, **this reaction occurs in liquid electrolyte**

Chem. Commun. 2013, 49, 149-151

$E_{recharge} = 0.20$ V

0.18 V = E_{rev}

$E_{discharge} = 0.155$ V

Sn

Theroretical Capacity Sn

Voltage (V) / Specific Capacity (mAh/g)

- From $\Delta G = -n \cdot F \cdot E$ ($n=2$), we determine free energy driving force for battery reactions (via *measurable discharge and recharge*)
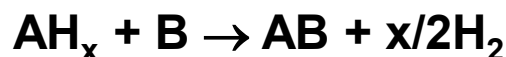
- $\Delta G_K = n \cdot F \cdot (E - E_{rev})$
- $\Delta G_{K,\,discharge} = 4.8$ kJ
- $\Delta G_{K,\,recharge} = 3.9$ kJ

- Hypothesize that electrolytes significantly lower the free energy driving force for measurable rates ($\Delta G_{K,\,solid\text{-}state} \sim 20$ kJ; $\Delta G_{K,\,electrolyte} \sim 4$ kJ)
- Hydrogen storage reactions formulated with electrolytes may act similarly

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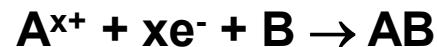Necessary to overcome interface-controlled process that normally requires thermal activation.
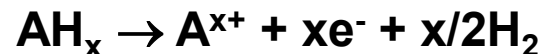

(a)

(b)
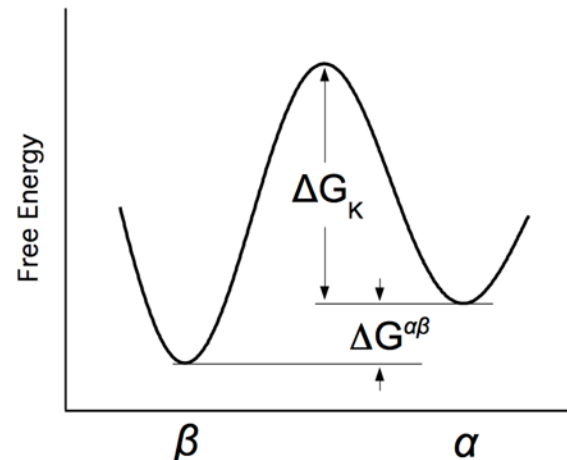
- **Solid-state reactions**
 $$AH_x + B \rightarrow AB + x/2H_2$$
  Reaction rate and transport are limited by relatively small solid-solid interfacial surface area (yellow).
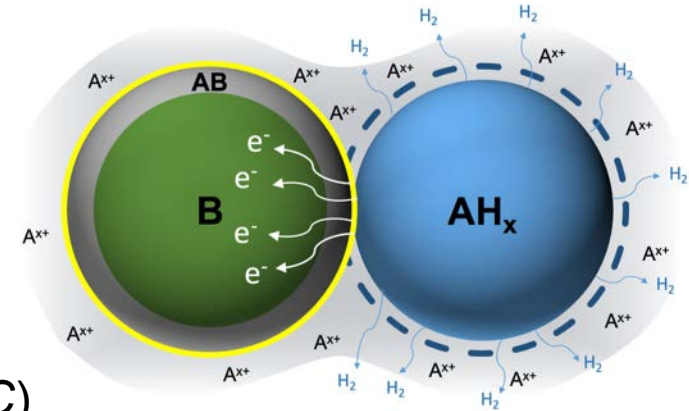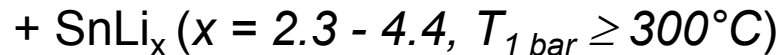
- **Electrolyte assisted reactions**
  $$AH_x \rightarrow A^{x+} + xe^- + x/2H_2$$
  $$A^{x+} + xe^- + B \rightarrow AB$$
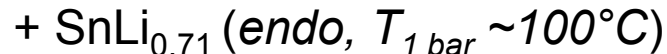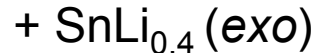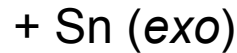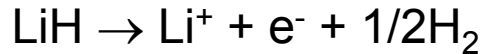 Electrolyte that can solvate A^{x+} facilitates transport and enables reaction to occur over full surface area of B exposed to the electrolyte. (*electron transport still solid-solid but much faster; conductive additives can also be included*)
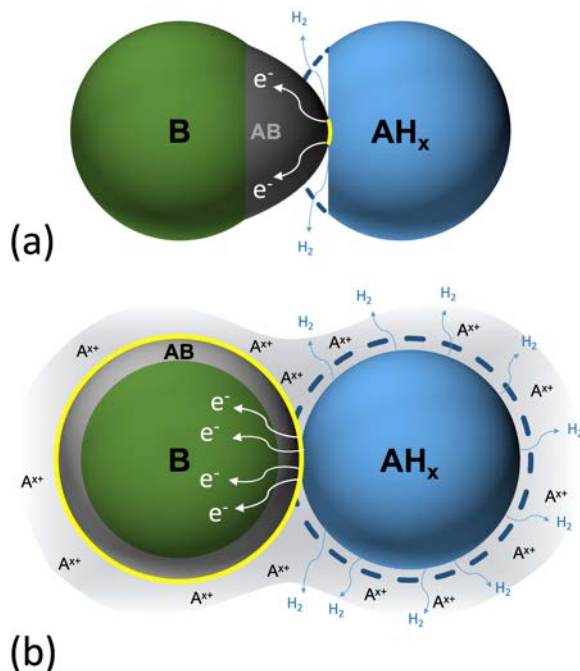
Similarity to battery conversion reactions

- **LiH/SnO$_2$ (***electrolyte for Li***)**

  $LiH \rightarrow Li^+ + e^- + 1/2H_2$

  $Li^+ + e^- + SnO_2 \rightarrow Li_2O + SnO$ (*exothermic*)

                   + Sn (*exo*)

                   + $SnLi_{0.4}$ (*exo*)

                   + $SnLi_{0.71}$ (*endo, $T_{1\ bar}$ ~100°C*)

                   + $SnLi_x$ (*x = 2.3 - 4.4, $T_{1\ bar} \geq 300°C$*)

  Preliminary experiments:
  - Hand ground LiH/SnO$_2$ evolves H$_2$ at ~200 °C
  - LiH/SnO$_2$ evolves H$_2$ during high energy milling
  - Hand ground LiH/SnO$_2$ in LiClO$_4$/EC-DMC did not seem to evolve H$_2$ at 20 °C
  - Hand ground LiH/SnO$_2$ in 2M BEt$_3$/DEE evolves H$_2$ at 20 °C

    (*Note: BEt$_3$ solvates both Li$^+$ and H$^-$ forming LiBEt$_3$H*)

- **MgH$_2$/SnO$_2$ (***electrolyte for Mg***)**

           $\rightarrow$ MgO + SnO (*exo*) + Sn (*exo*) + Mg$_2$Sn (*endo, $T_{1\ bar}$ ~ 40 °C*)
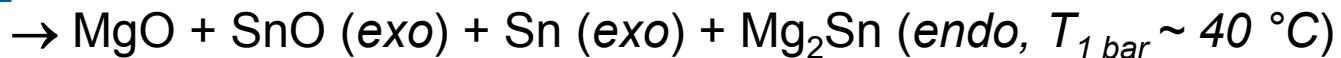
- **MgH$_2$/Si (***electrolyte for Mg***)**

           $\rightarrow$ Mg$_2$Si (*$T_{1\ bar}$ ~ 15 °C, 5 wt% H$_2$*)

Reactions not strictly following schematic concept

$$AH_x + B \rightarrow AB + x/2 H_2$$

- **Mg(BH$_4$)$_2$** (*electrolyte or just solvent?*)
  Can be solubilized completely
  Single (de-)hydrogenated phases (*simply/ideally*)

Preliminary experiments:
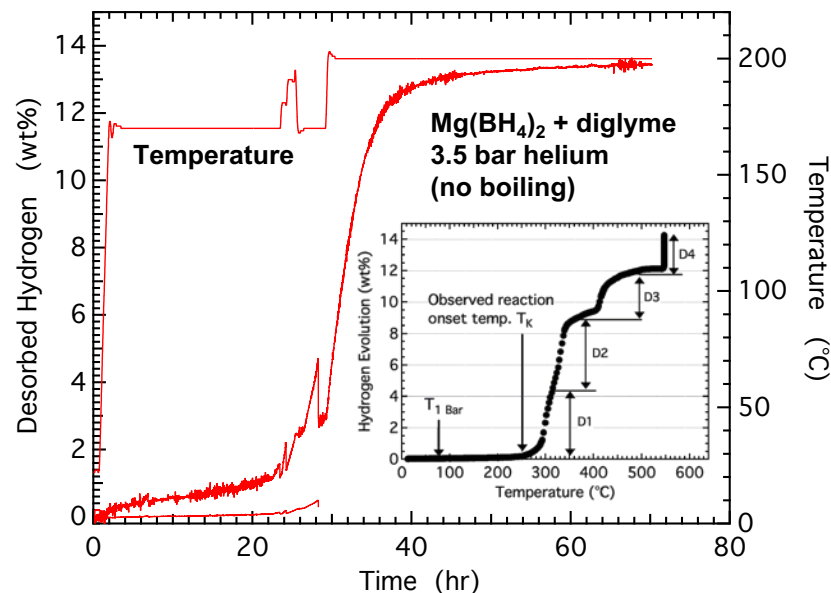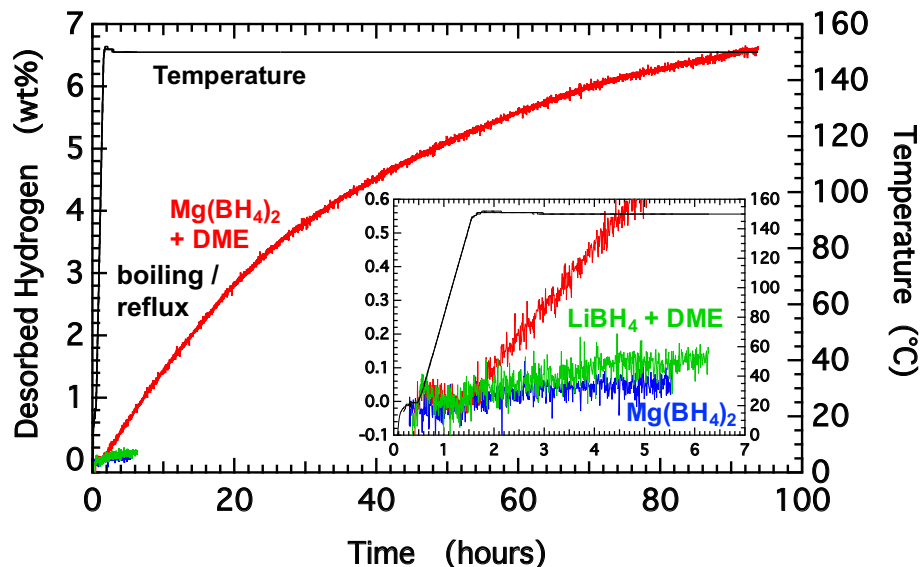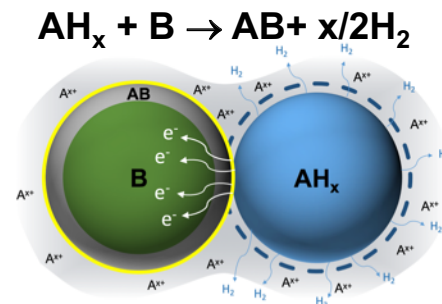
Results could be artifacts from solvent decomposition or complexation
(*analysis underway*)

- **LiBH$_4$/MgH$_2$** (*implementation being explored*)
- **NaAlH$_4$ and LiAlH$_4$** (*previous work in literature*)

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Approach: Electrolyte Criteria / Practicality Issues

- **Redox stability**
    - already developed for batteries with metallic Li and Mg
    - however, stability with H^- has not yet determined
    - also typically near room temperature, likely 50 °C or higher will be needed

- **Vapor pressure**
    - sufficiently low for recovery of pure H_2
    - organic carbonates and ethers may
      not work – possibly ok for proof of concept
    - many ionic liquids are being developed
      higher temperature batteries

  Possible electrolytes:
  - **Organic carbonates**
  - **Ethers (***glyme, di-, tri-, tetra-***)**
  - **Ionic liquids**
  - **Eutectic molten salts**
  - **Grignards**

- **Hydrogen gas exchange and transport**
    - solvent must not limit H_2 availability
    - gas exchange electrodes are well-developed for fuel cells and air batteries
    - solubility is generally low but permeation is high

- **Weight and volume**
    - amount of electrolyte must not overly comprise hydrogen density
    - commercial batteries are ~12 wt% electrolyte, 40 wt% active material
    - electrolyte typically occupies space within powder; therefore
      negligible volumetric change

Approach: Electrochemical Potential Assisted Hydrogen Storage Reactions

Thermo-chemical reactions

- For an endothermic dehydrogenation reaction, i.e. $\Delta S > 0$, at fixed pressure, an increased free energy driving force (*more negative ΔG*) originates from the term $T \cdot \Delta S$.
  For $\Delta S = 125$ J/K-mol, an increase of 25 kJ requires ~200 K increase in temperature.
- For an exothermic hydrogenation reaction, i.e. $\Delta S < 0$, an increased free energy driving force originates from increased pressure via the term $R \cdot T \cdot \ln P$.
  At 100 °C, 25 kJ requires ~3200 bar.
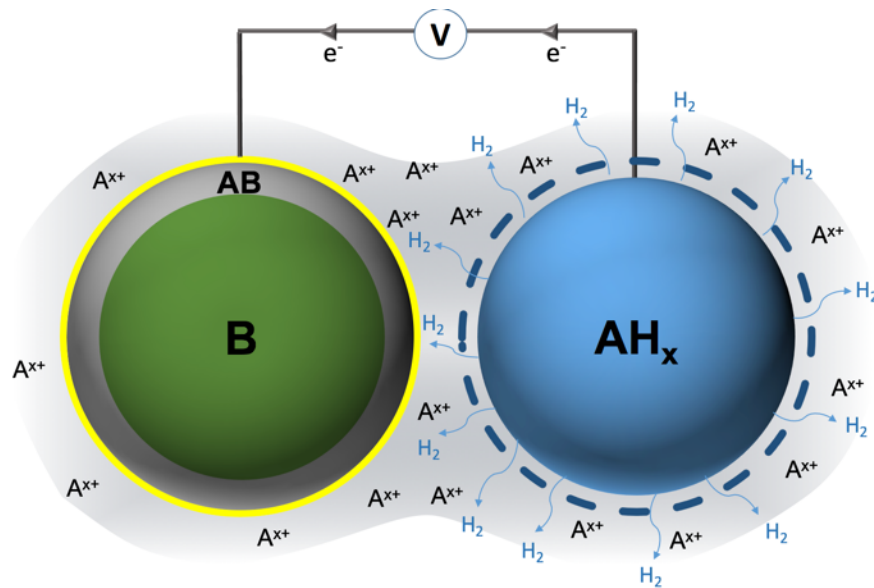
Electro-chemical reactions

- Increased free energy driving force originates directly from applied potential through the term $n \cdot F \cdot E$. For 25 kJ and $n = 1$ electron transfer, required potential E = 0.26 V.

Limited effort at this time

- *Written assessment and viability experiments for now*
- *Subject to results, more thorough investigation and demonstration from binary (or other) hydride with comparison of over-potentials for electrochemical and onset temperature.*

Accomplishments and Progress:
Organic Electrolyte Analyses

**GCMS Screening Data of Di-Tri- and Tetraglyme and HMPA and DMA**

Solvent only screening: Water level for glymes: <10 ppm, HMPA: 19 ppm, DMA: 14 ppm

Solvent + 0.1M Mg(BH4)$_2$ — 5 days at room temperature under Ar

Solvent + 0.1M Mg(BH4)$_2$ — 5 days at 80°C under Ar

Exemplary Solvents Tested:

- Diglyme (G2):   MW 134.17, bp 162 °C, auto-ignition temp: 188 °C
- Triglyme (G3):   MW 178.23, bp 216 °C, auto-ignition temp: 191 °C
- Tetraglyme (G4): MW 222.28, bp 275 °C, auto-ignition temp: 266 °C
- HMPA: MW 179.20, bp 233 °C, auto-ignition temp: 230 °C
- DMA: MW 87.12,   bp 165 °C, auto-ignition temp: 490 °C
- THF: MW 72.11,   bp   66 °C, auto-ignition temp:
   Flash point: -14 °C
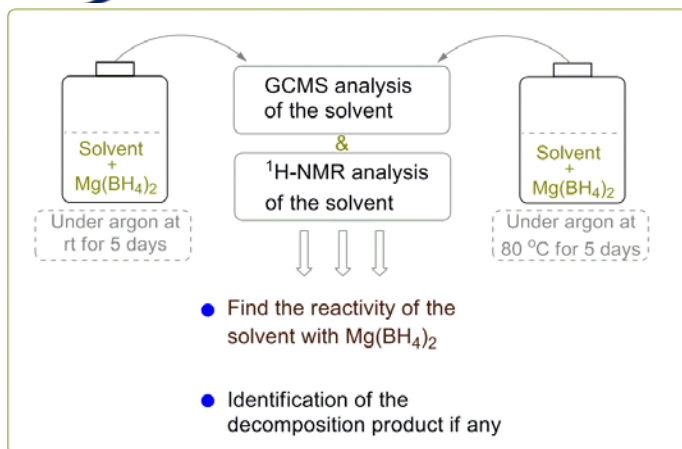
Above: Schematic for solvent analysis using GCMS to probe for solvent stabilities. For similar peak intensities — no solvent decomposition.
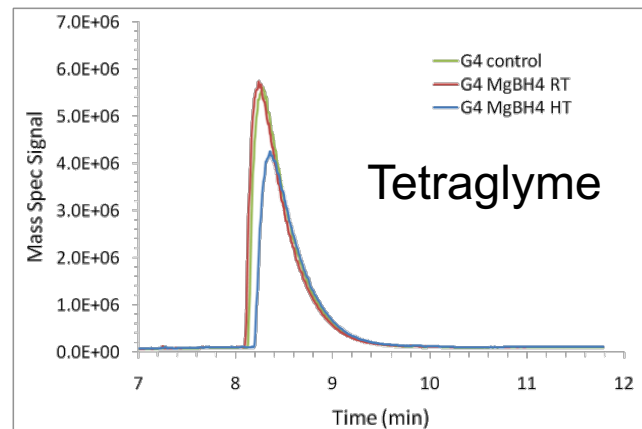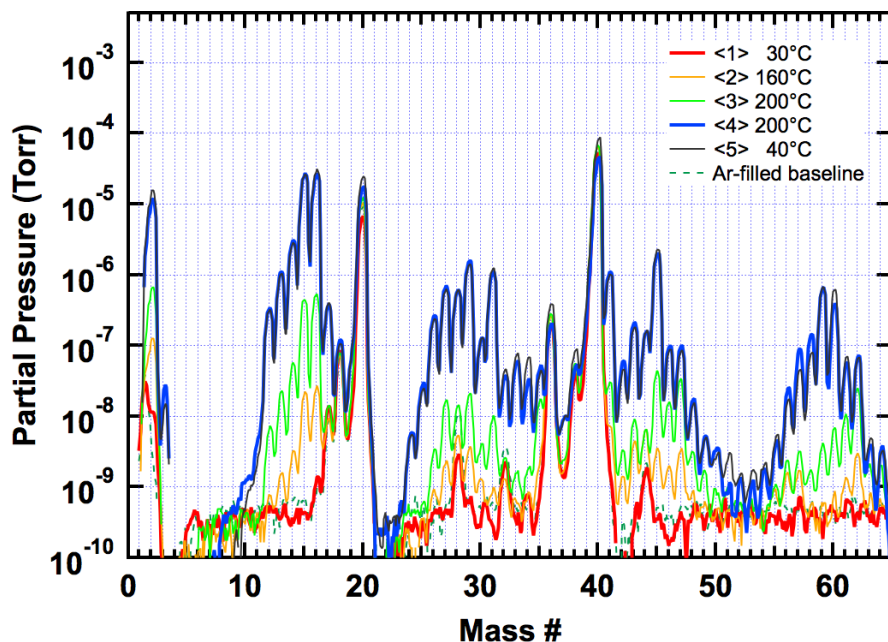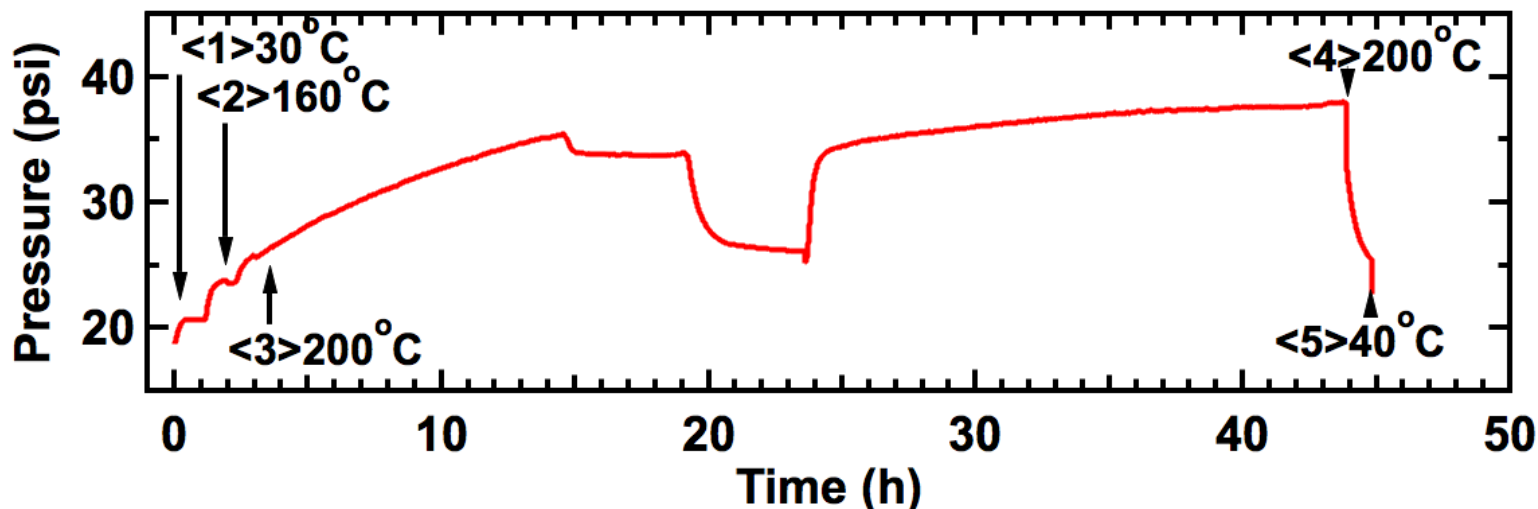

Tetraglyme

Above: No significant peak intensity change at RT for tri- and tetraglyme for 5 days. At 80 °C, peak intensity change, signs of degradation, but no extra peak indicating decomposition.

Diglyme:
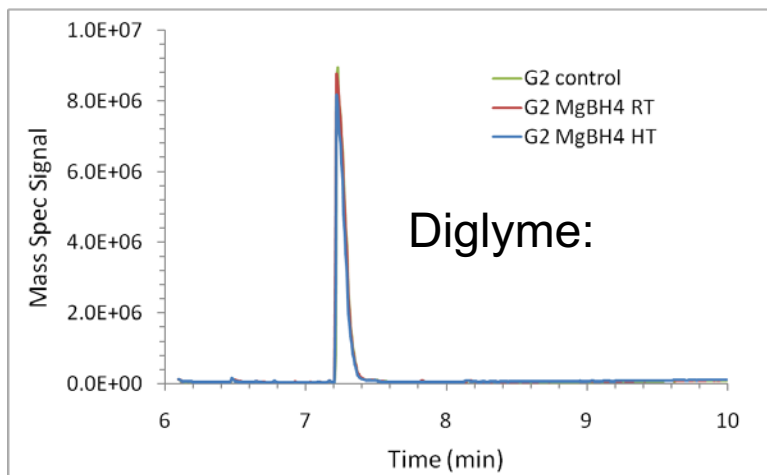
Above: With 0.1M Mg(BH$_4$)$_2$, no significant peak intensity change or no extra peaks — at RT or 80 °C after 5 days.


HMPA:
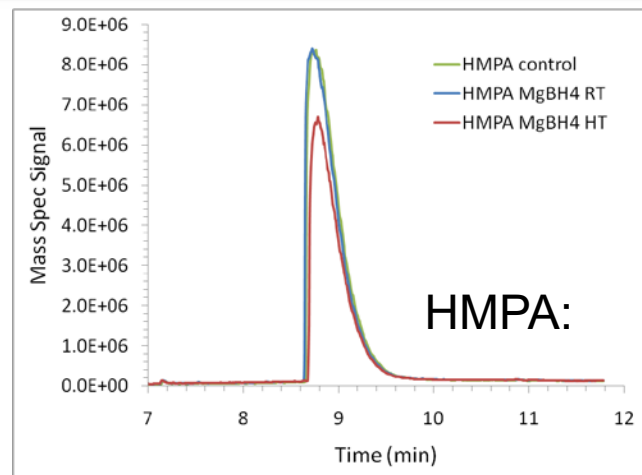
Above: With 0.1M Mg(BH$_4$)$_2$, at room temperature, no peak intensity change but at 80 °C for 5 days GCMS peak intensity change, signs of degradation.

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Accomplishments and Progress:
$Mg(BH_4)_2$ + Tetraglyme

To validate assumption of H_2 evolution only as in Slide 8, residual gas analysis performed vs temperature as shown above. Dips in pressure data indicate RGA sampling points. Tetraglyme analyzed here given its higher boiling point than diglyme with assumption of higher solvent stability.

RGA data at left indicate that tetraglyme decomposes to Dimethyl ether RGA peaks at mass # 13-15, 29-31, 45-46.
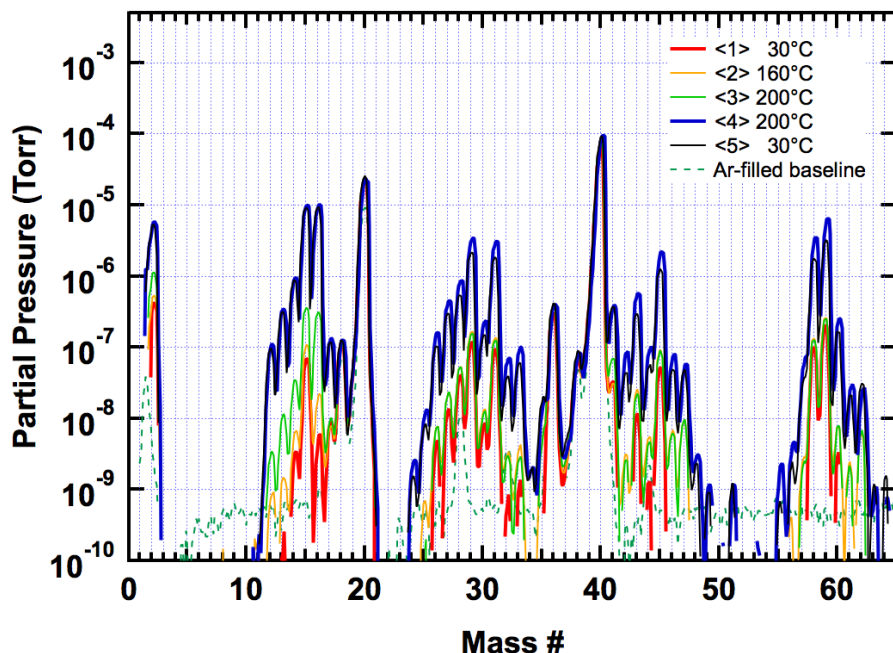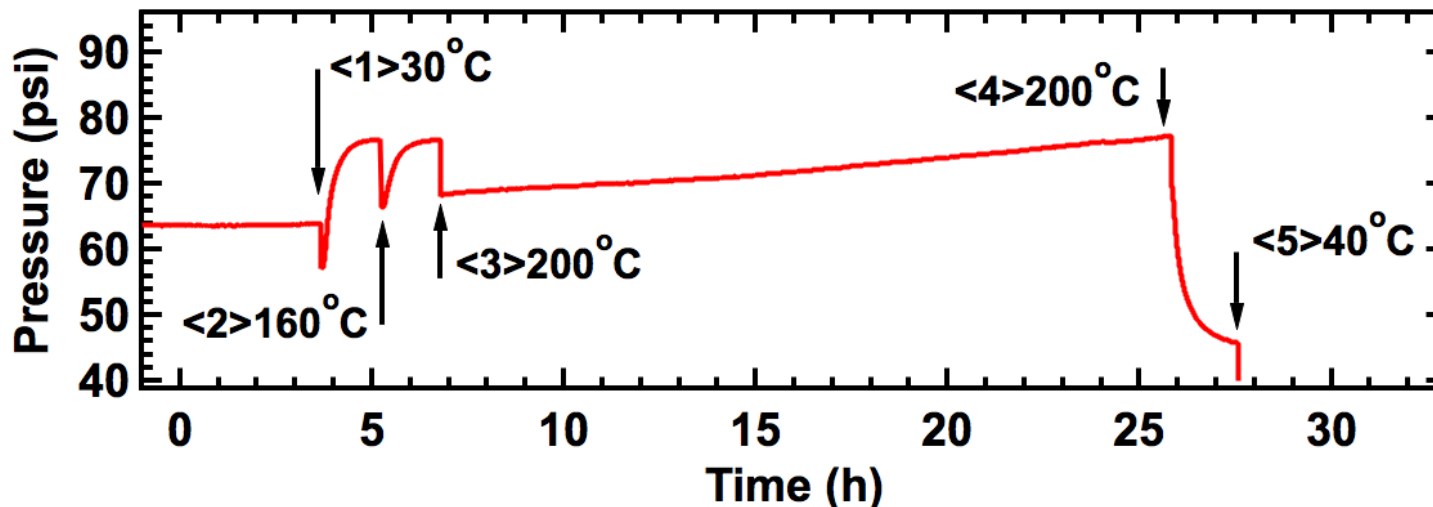
RGA performed vs temperature as shown above for diglyme under pressure to suppress boiling. Dips in pressure data indicate RGA sampling points.

At left, dimethyl ether decomposition product present under all conditions but not seen for di- or tetraglyme - RGA analysis in absence of Mg(BH$_4$)$_2$.

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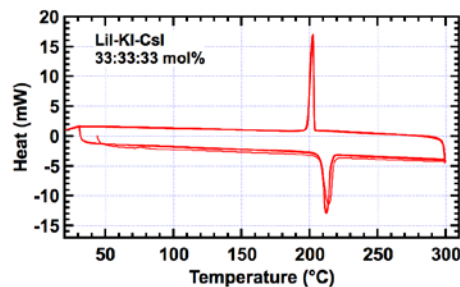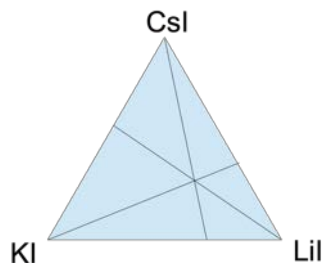
- Inorganic molten salts thermally stable over wide temperature range for dehydrogenation and may be formulated with components that are chemically inert to hydrogen storage compounds.

- $2MgH_2 + Si \rightarrow Mg_2Si + 2H_2$: System demonstrates <u>substantial</u> improvement in dehydrogenation kinetics in ternary LiI:NaI:KI eutectic compared to no eutectic.

- Combinatorial investigation of low melting point multicomponent (binary, ternary, quarternary) eutectics under investigation (example: $LiBH_4$:KBH_4 mp = ~110 °C).
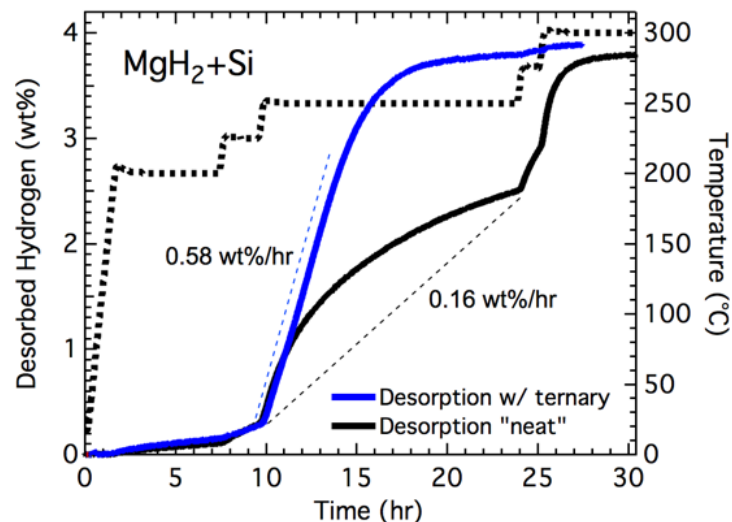
MgH_2/0.5Si (milled 5 hr) with Li, K, CsI ternary
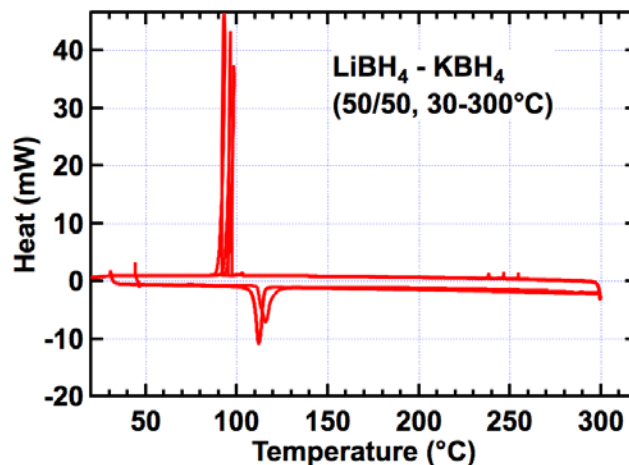
DSC of $LiBH_4$:KBH_4 eutectic

Collaborators

- ► Subcontract: HRL Laboratories

- ► University: Caltech (Hwang, Solid State/Solution NMR)

- ► HySCORE (PNNL: Autrey, Bowden, Solid State NMR)

- ► HyMARC (Stavila: High pressure reversibility in presence of electrolyte)

Remaining Challenges and Barriers

- Finding lower eutectic temperature systems consistent with electrochemical and thermal stability with engineering viability.

- Rehydrogenation in systems based on Li^+ and/or Mg^{2+} with endothermic H_2 evolution and exothermic H_2 uptake.

- Application to practical systems with high capacities and thermodynamics compatible with fuel cell systems with considerations that include base-material capacity, operating temperature, electrolyte requirements and estimates of ultimate capacity penalties.

Proposed Future Work: Milestones

Milestone 1.1 (Q1): Survey of electrolytes suitable for hydrogen storage reactions. (100%)

Milestone 1.2 (Q3): Demonstration of electrolyte assisted evolution of ≥ 1 wt% H_2 (materials basis) from an endothermic or exothermic reaction at a rate greater than for the equivalent dry powder as measured by residual gas analysis (RGA) of H_2 release during the reaction. (50%).

Milestone 1.3 (Q5): Demonstration of electrolyte assisted hydrogen cycling (both dehydrogenation and rehydrogenation) of ≥ 1wt% H_2 (materials basis) via RGA at a rate greater than for the equivalent the dry powder. (20%).

Milestone 2.1 (Q4): Written assessment of electrochemically promoted hydrogenation of a hydride material.

Milestone 2.2 (Q6): Initial demonstration of electrochemically promoted cycling (both dehydrogenation and rehydrogenation with electrochemical coupling) of ≥ 1 wt% H_2 (materials basis) as determined by RGA of H_2 release during cycling.

Go/No-go Decision point Phase 1 (18 months): Demonstrate electrolyte assisted hydrogen storage material with:

1) cycling of ≥ 1 wt% H_2 ;
2) ≥ 10 × rate of hydrogen evolution as compared to systems without an electrolyte and;
3) favorable assessment of results indicating a pathway to meet storage targets.

Technology Transfer Activities

- Aim of the research and development effort described here is to take electrolyte and electrochemical potential concepts from TRL 1 to TRL 3.

- If concepts prove viable, consideration of these approaches will require an engineering assessment for system and BOP although this may be premature until completion of TRL 5 .

- Liox posed to initiate product development, but broader range of markets in addition to transportation difficult to discern.

- IP to be developed as joint HRL/Liox invention.

Summary

- Objective: To address kinetics of multi-phase hydrogen storage reactions that are presently severely limited.

- Relevance: Lowering the free energy gap presently necessary to overcome interface-controlled process that normally requires thermal activation.

- Approach: Use of electrolytes and/or electrochemical approaches to "solubilize" or promote diffusion of reacting species.

- Accomplishments: Survey and initial studies of ether-type and eutectic salt reactivity/suitability with candidate material systems.

- Collaborations: Caltech, HySCORE (PNNL) and HyMARC (Sandia)