HyMARC Seedling: Electrolyte Assisted Hydrogen Storage Reactions

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2018 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]: $ 165,342

  [b] as of 3/31/17
- Total Recipient Funds Spent $ 41,335

Barriers (from 2015 MYRDD)

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

Objectives:

- Overcome kinetic barriers of hydrogen storage candidates with high capacities (and appropriate thermodynamics) for PEM fuel cell use that otherwise contain multiple solid phases that must nucleate, grow, and be consumed during cycling.
- Specific use of salt and borohydride electrolytes to promote solubilization and diffusion of species relevant to hydrogen storage release and uptake.

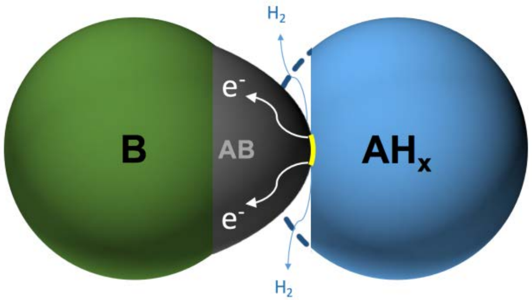
Impact since 2017:

- 10× dehydrogenation kinetic improvement using electrolyte over non-electrolyte containing samples: (MgH_2/Sn with Li/K-BH_4 eutectic, $Mg(BH_4)_2$ with Li/K-BH_4 eutectic, MgH_2/Si with Li/K/Cs-I ternary)
- Rehydrogenation (at Sandia) of ≈ 2% in dehydrogenated MgH_2/Sn in Li/K-BH_4 electrolyte containing sample. Likely no (or very little) rehydrogenation of dehydrogenated MgH_2/Sn containing no electrolyte under same rehydrogenation conditions (1000 bar).
- Significant hydrogenation (6.3 wt%) of MgB_2 with electrolyte after Sandia hydrogenation. Negligible hydrogenation (0.22 wt%) without eutectic. (25× mass improvement).

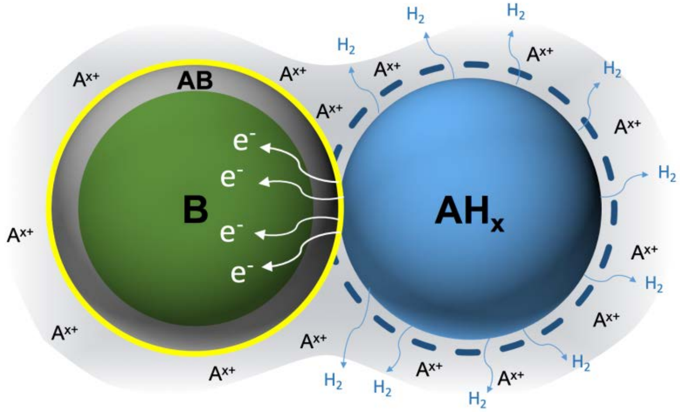
Approach: Electrolyte Assisted Hydrogen Storage Reactions

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

Addresses Technical Barrier “O” from 2015 MYRDD, specifically “Develop reversible metal hydrides with improved kinetics while maintaining high gravimetric capacity at relevant release temperatures and pressures,” from Table 3.3.8.



(a)



(b)

- **Solid-state reactions**

  $\mathbf{AH_x + B \rightarrow AB + x/2H_2}$

  Reaction rate and transport are limited by relatively small solid-solid interfacial surface area (yellow).

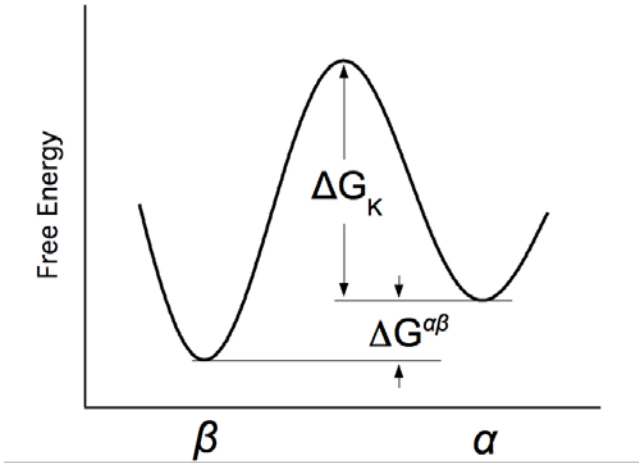
- **Electrolyte assisted reactions**

  $\mathbf{AH_x \rightarrow A^{x+} + xe^- + x/2H_2}$

  $\mathbf{A^{x+} + xe^- + B \rightarrow AB}$

  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*)

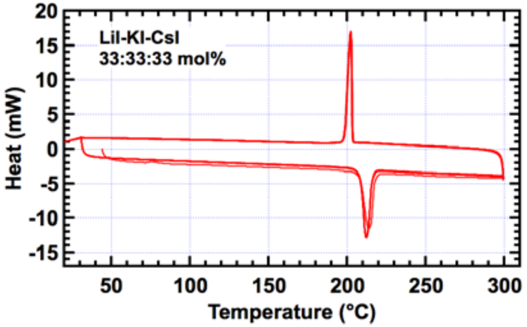
Approach: Salt and borohydride electrolytes most stable for this application.

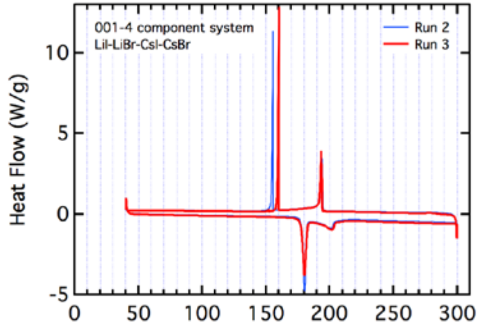


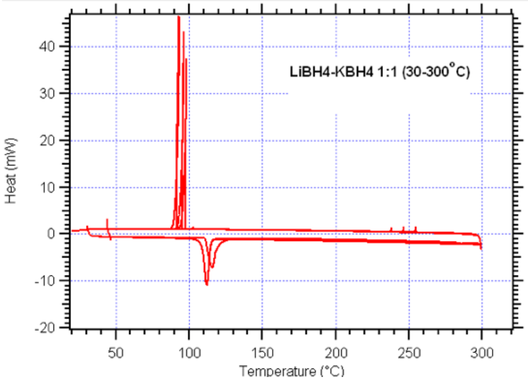
Left: Hypothesize that electrolytes significantly lower the free energy driving force for measurable rates as seen in conversion reactions, e.g. $\Delta G_{K,\ \text{solid-state}}$ ~ 20 kJ; $\Delta G_{K,\ \text{electrolyte}}$ ~ 4 kJ

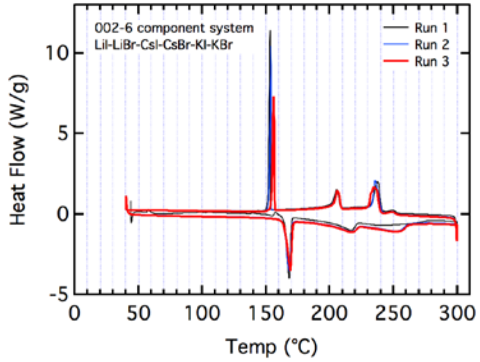
Inorganic molten salts have a high level of thermal stability over wide temperature range for (de)hydrogenation and can be formulated with components that are chemically inert to hydrogen storage compounds.

Right: DSC traces of some of the molten salt and borohydride mixtures synthesized/used in this effort.

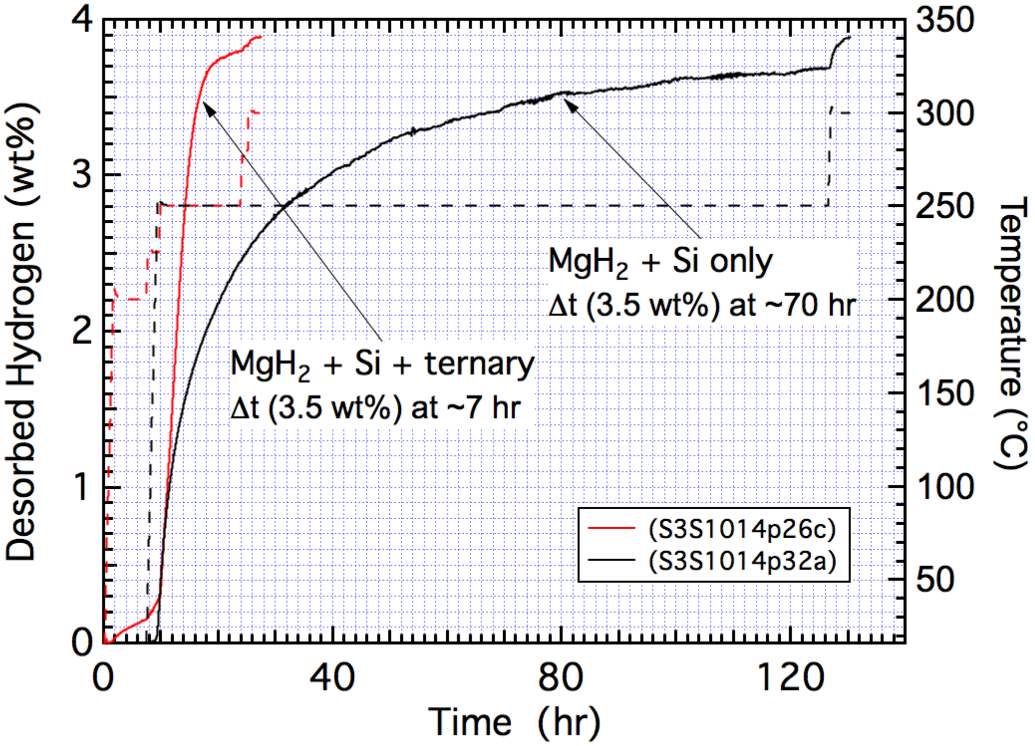




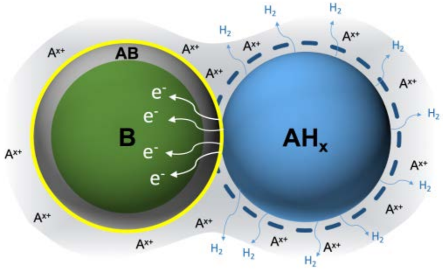




Accomplishments: 10× desorption rate in the Mg/Si system

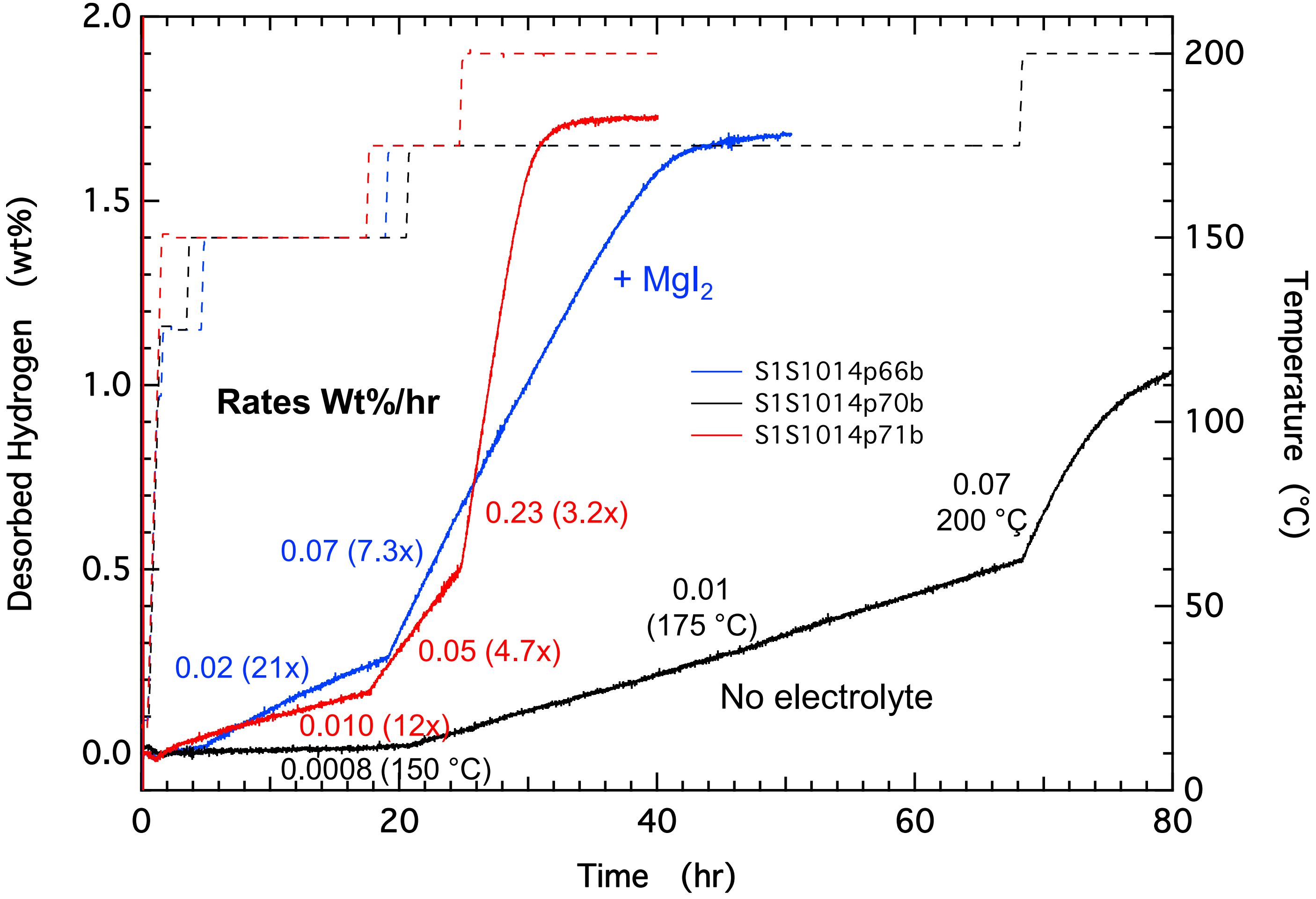


$AH_x + B \rightarrow AB + x/2H_2$



Hydrogen desorption as a function of time for the temperature ramps as indicated by the dotted traces. The use of an iodide ternary salt improves desorption kinetics by 10 ×. The fall-off in the “neat” reaction shown in the black trace is typical for destabilization reactions. The nearly straight line dehydrogenation shown in the presence of the ternary salt has not been observed before and gives evidence for enhanced solubility of the reactants.

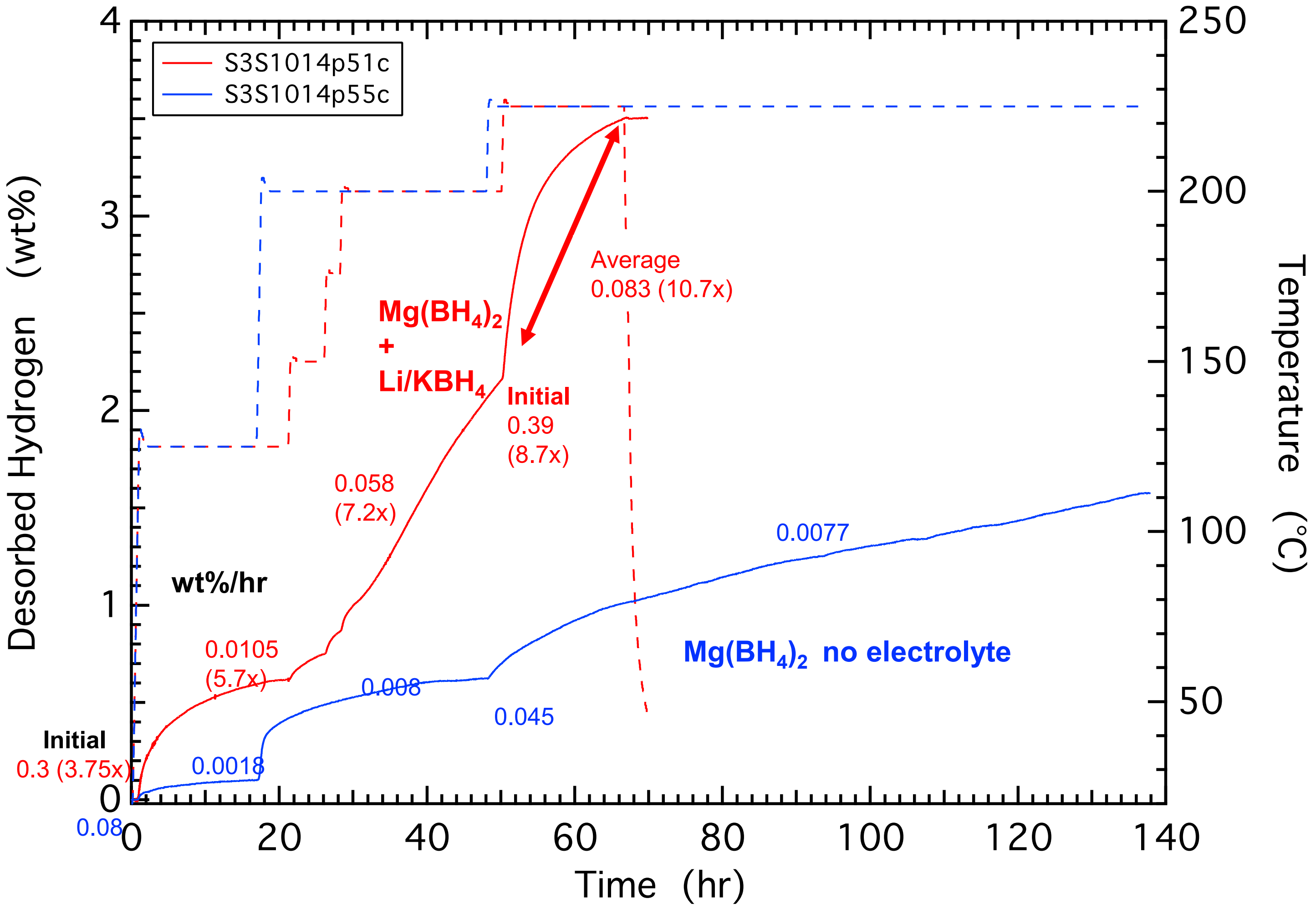
Accomplishments: 10× desorption rate in the Mg/Sn system



- >10× rate increase at 150 °C, ~5x at 175 °C, and 3x at 200 °C with Li/KBH_4 eutectic
- Addition of MgI_2 seems to further improve rates

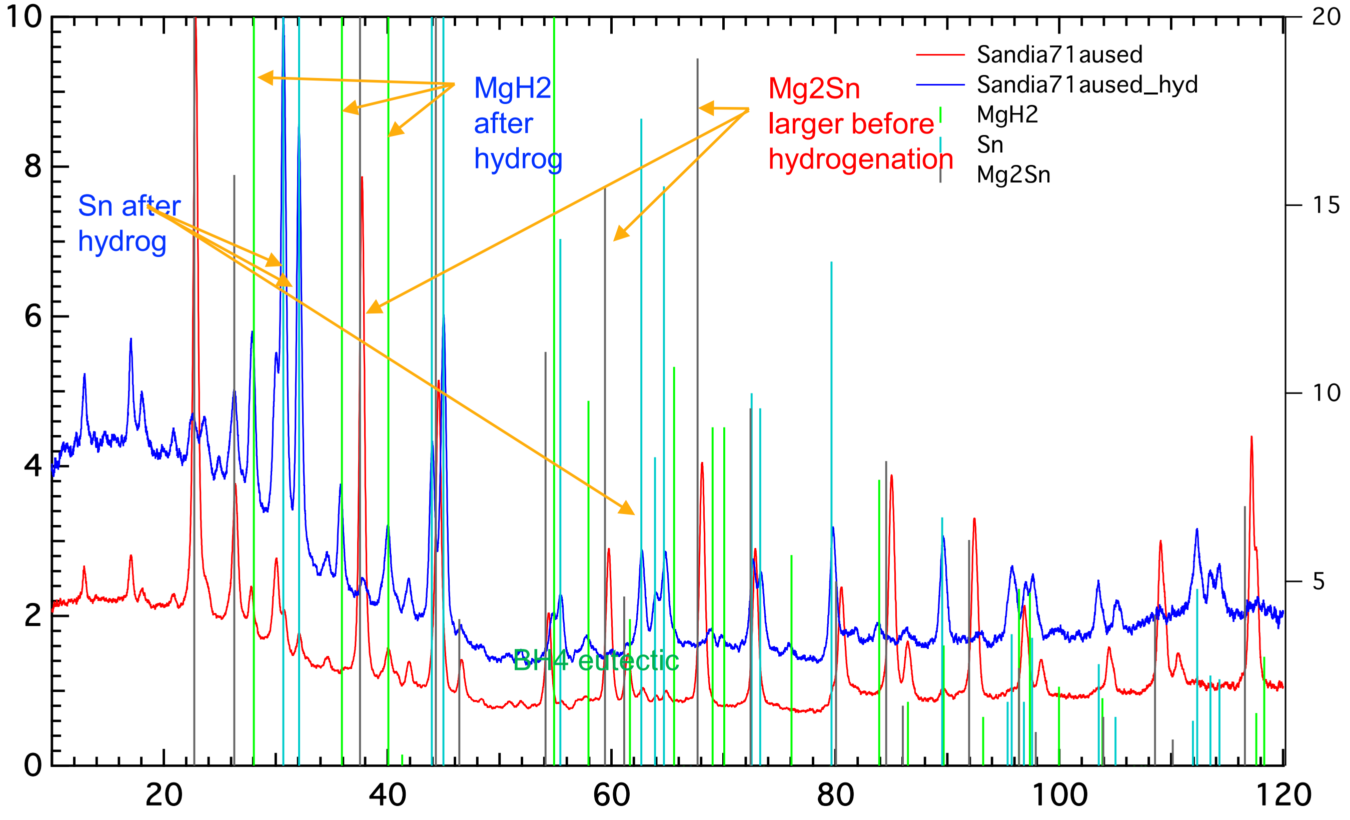
Accomplishments and Progress:

10× dehydrogenation kinetic improvement in $Mg(BH_4)_2$ using a borohydride electrolyte



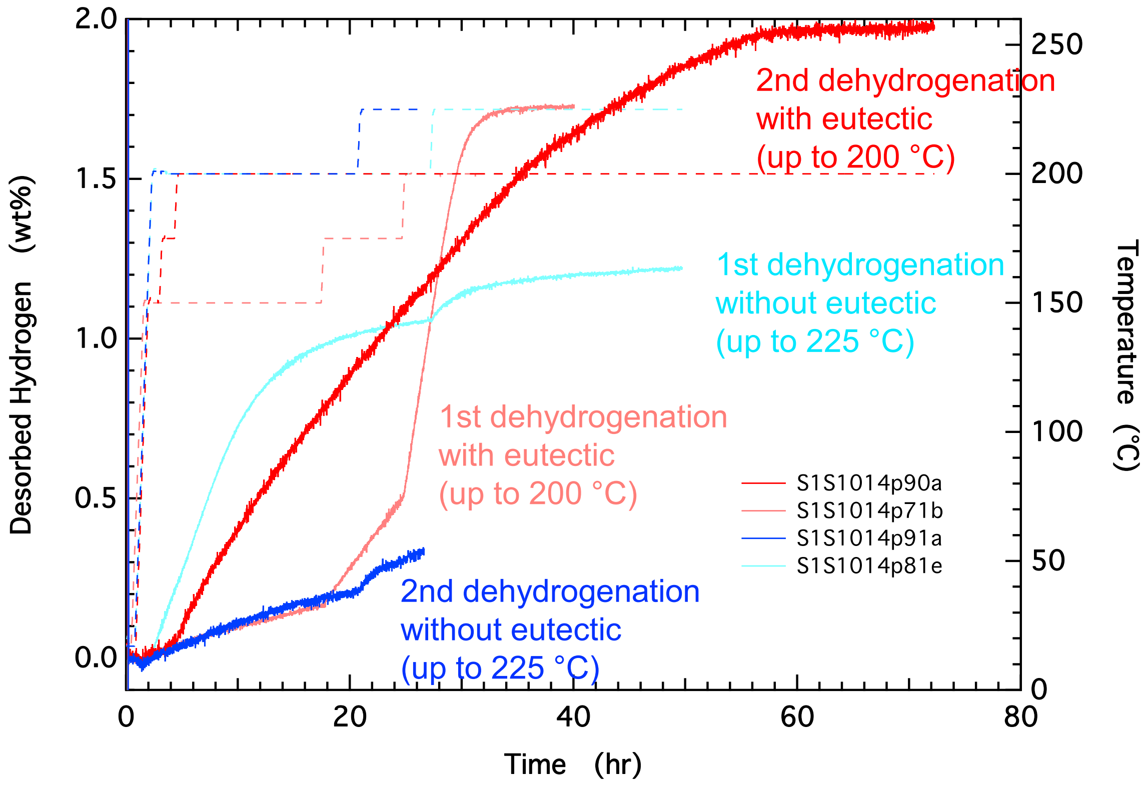
$Mg(BH_4)_2$ with (red) and without (blue) pre-melted Li/KBH_4 eutectic electrolyte

Accomplishments and Progress:
Rehydrogenation in the $MgH_2/Sn + Li/KBH_4$ eutectic system (Sandia)



XRD comparison of initially dehydrogenated MgH_2/Sn → hydrogenation cycle using eutectic, little or no hydrogenation occurred without eutectic

Accomplishments and Progress:
Dehydrogenation after hydrogen treatment at Sandia of dehydrogenated MgH_2/Sn



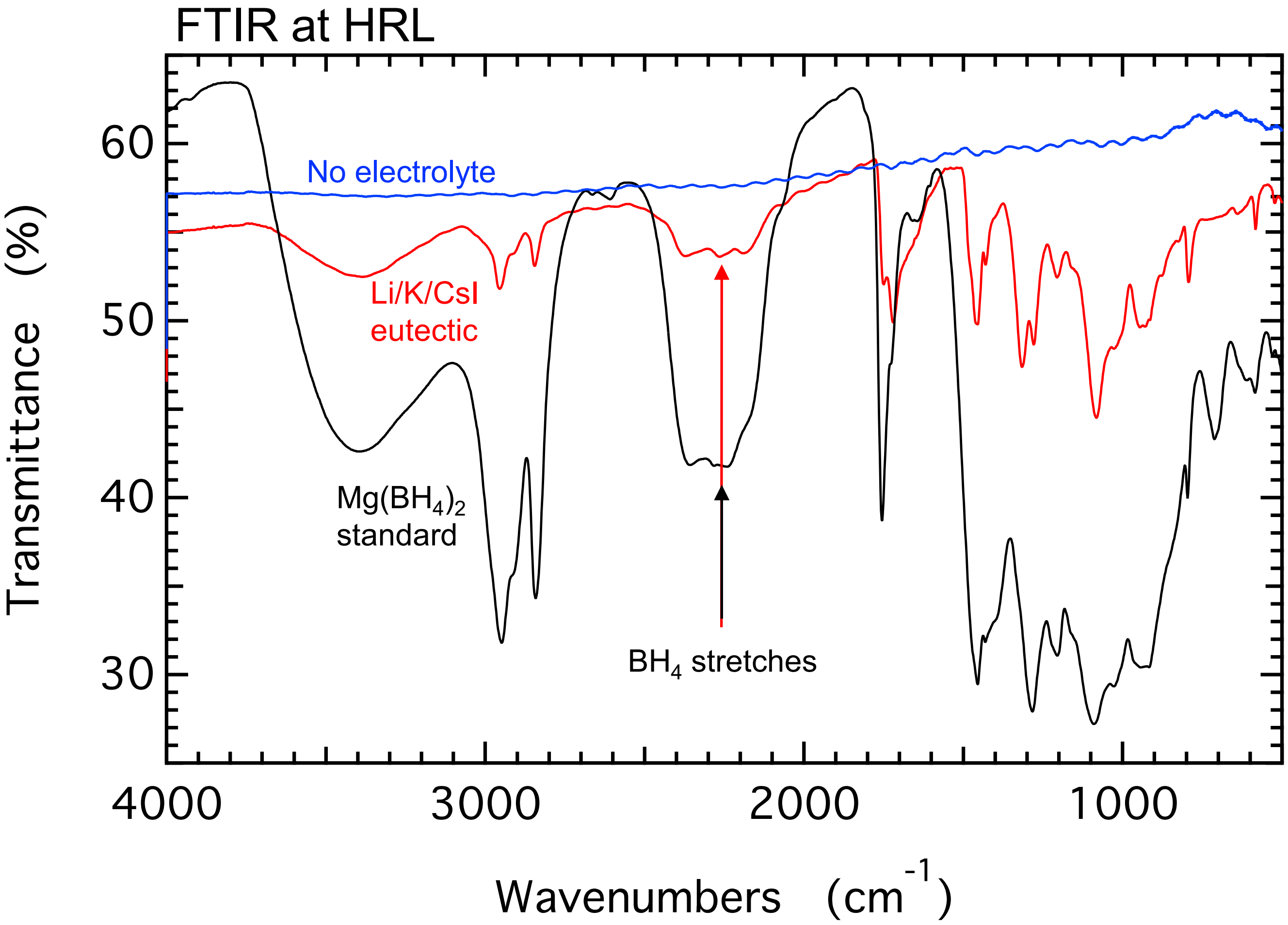
>3× smaller capacity for control sample (that had no electrolyte)

- **Likely complete rehydrogenation with Li/KBH_4 eutectic**

- first time really seen in MgH_2/X system (X = Si, Sn)
- Capacity 15% higher, due possibly to better attrition of sample after H_2 treatment and before measurement.
- Noise higher because of smaller sample mass

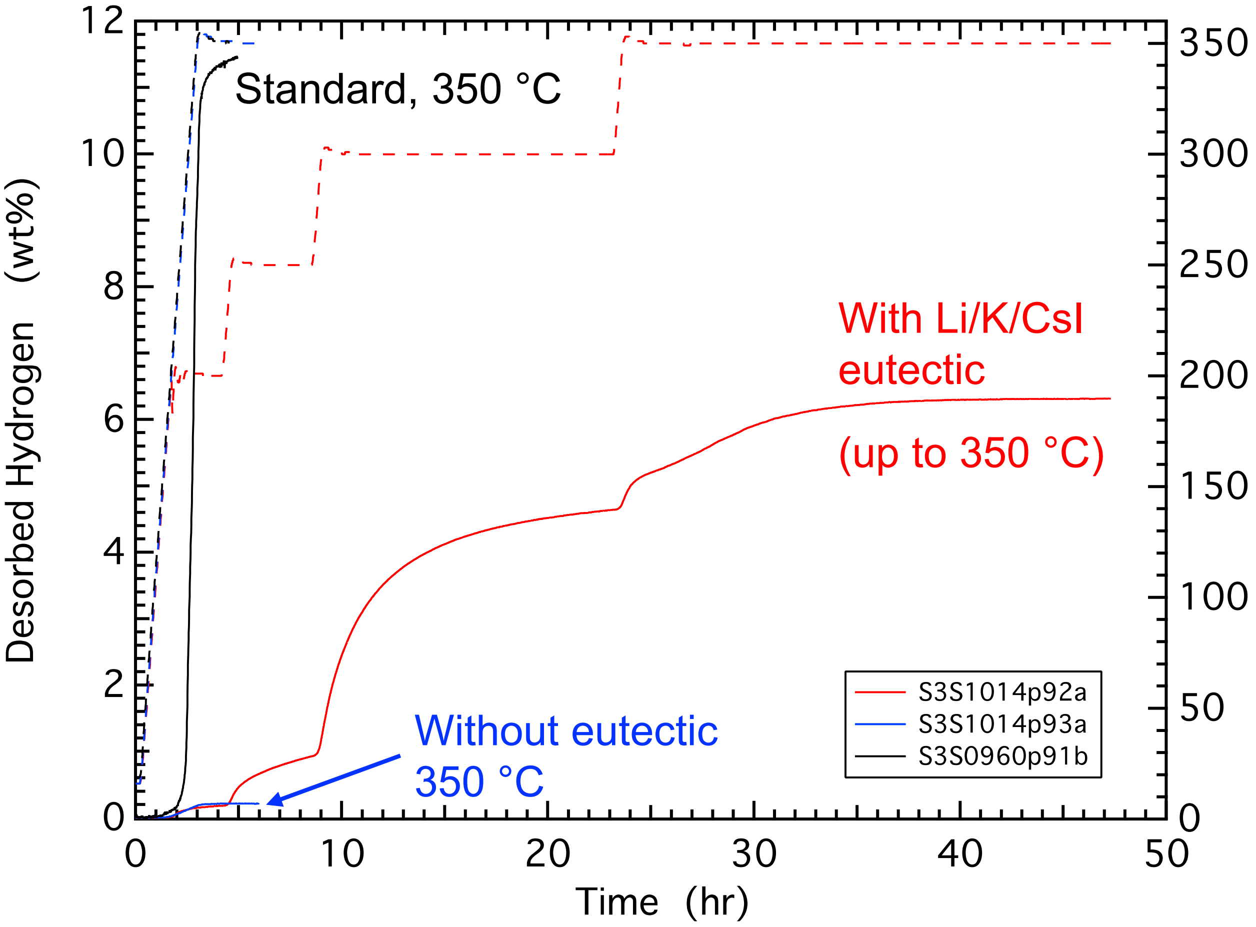
Accomplishments and Progress:

Initial qualitative FTIR measurements of Sandia hydrogenated MgB_2

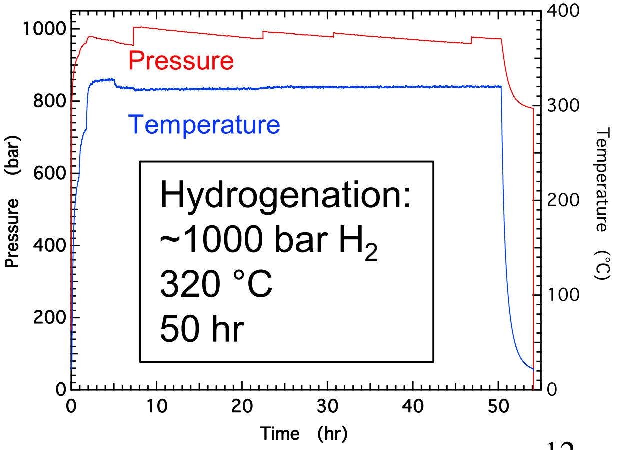


- Clear BH_4 stretches with Li/K/CsI eutectic containing sample
- No BH_4 stretches without eutectic

Accomplishments and Progress: Sieverts Analysis of MgB_2 after Sandia hydrogenation



- Significant (6.3 wt%) hydrogenation with eutectic
- Negligible (0.22 wt%) hydrogenation without eutectic
- > 25 × uptake with eutectic electrolyte
- Agrees with FTIR

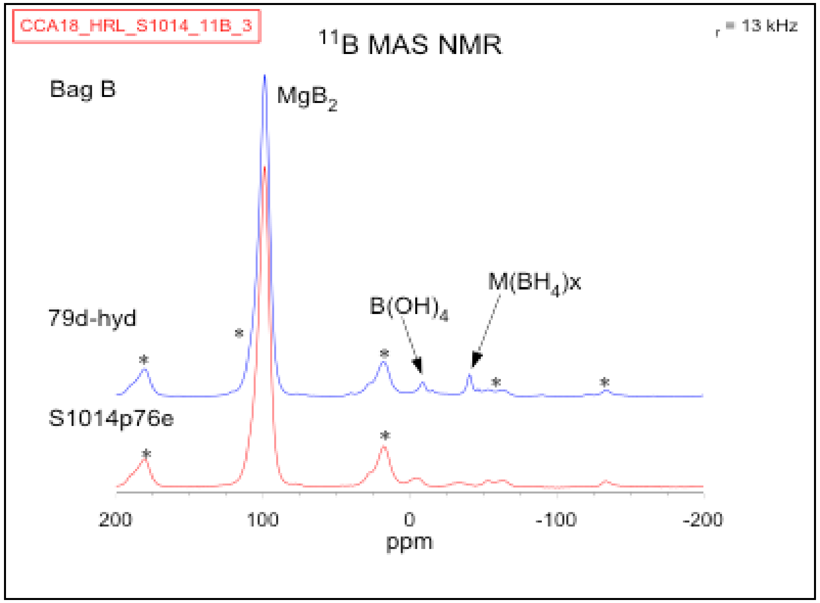


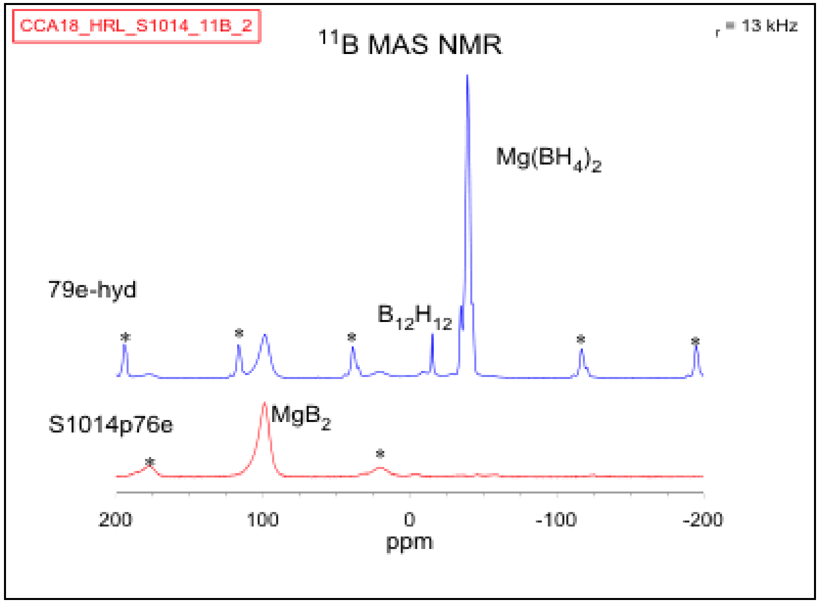
Hydrogenation:
~1000 bar H_2
320 °C
50 hr

Above: HRL Sieverts measurements after Sandia H_2 treatment.
Right: Sandia Pressure/Temperature treatment

Accomplishments and Progress:

NMR Confirmation of $MgB_2 \rightarrow Mg(BH_4)_2$ conversion



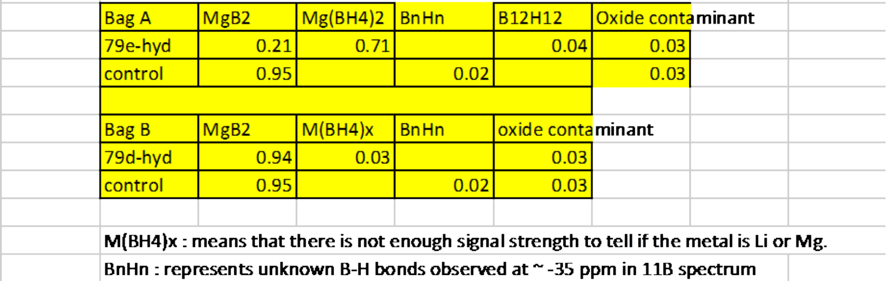


Control sample data: S1014p79d: MgB_2 (lower red trace) with no eutectic before Sandia hydrogen treatment, a control for 79d-hyd

79d-hyd: MgB_2 (upper blue trace) with no eutectic after Sandia hydrogen treatment, control sample for 79e-hyd

S1014p79e: MgB_2 with the Li/K/CsI eutectic (lower red trace) before hydrogen treatment, another control for 79e-hyd

79e-hyd: MgB_2 with the Li/K/CsI eutectic (upper blue trace) after hydrogen treatment at Sandia.



Relative ratio of 11B signal strength, not molar ratio of identified species

Bag A	MgB2	Mg(BH4)2	BnHn	B12H12	Oxide contaminant
79e-hyd	0.21	0.71		0.04	0.03
control	0.95		0.02		0.03

Bag B	MgB2	M(BH4)x	BnHn	oxide contaminant
79d-hyd	0.94	0.03		0.03
control	0.95		0.02	0.03

M(BH4)x : means that there is not enough signal strength to tell if the metal is Li or Mg.

BnHn : represents unknown B-H bonds observed at ~ -35 ppm in 11B spectrum

- Significant conversion to $Mg(BH_4)_2$ with eutectic
- Little uptake without eutectic
- Validates Sieverts data

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).

Proposed Future Work (contingent on advancement to Phase 2)

- Milestones have been completed for the Phase 1 effort.
- Finding lower eutectic temperature systems consistent with electrochemical and thermal stability with engineering viability.
- Rehydrogenation improvement in systems based on Li^+ and/or Mg^{2+} with endothermic H_2 evolution and exothermic H_2 uptake.
- Improved electrolyte to active material ratio through borohydride use.
- 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.

Any proposed future work is subject to change based
on funding level

Milestone Accomplishments

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. (95%).

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. (100%).

Milestone 2.1 (Q4): Written assessment of electrochemically promoted hydrogenation of a hydride material. (100%)

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

1) cycling of ≥ 1 wt% H_2 ; (100%)
2) ≥ 10 × rate of hydrogen evolution as compared to systems without an electrolyte (100%);
3) favorable assessment of results indicating a pathway to meet storage targets.
4) Any proposed future work is subject to change based on funding levels

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 has been 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: 10x improvement to dehydrogenation kinetics in three electrolyte containing material systems in comparison to control samples. Hydrogenation of electrolyte containing MgB_2 to $Mg(BH_4)_2$ under conditions where no hydrogenation occurs in non-electrolyte containing control sample.
- Collaborations: Caltech, HySCORE (PNNL) and HyMARC (Sandia)