
Electrolyte Assisted Hydrogen Storage Reactions

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Project ID: ST137

Timeline:

- Project Start Date: 01/20/17
- Phase 2 End Date: 05/01/2020
- Phase 3 End Date: TBD

Budget:

- Phase 3 Budget: \$ TBD
- Phase 2 Budget: \$ 486,750
- Total Recipient Share: \$ 93,750
- Total Federal Share: \$ 375,000
- Total DOE Funds Spent since project start: \$ 271,396 as of 12/31/2018
- Total Recipient Funds Spent since project start \$ 67,849 as of 12/31/2018

Barriers (from 2015 MYRDD)

- O. Lack of Understanding of Hydrogen Physisorption and Chemisorption.

Partners/Collaborations

- HyMARC (Sandia, high pressure hydrogenation),
- Caltech (Solid-State NMR)
- Liox Power, Inc. (project lead, moderate pressure hydrogenation)
- HRL Laboratories, LLC

Objectives:

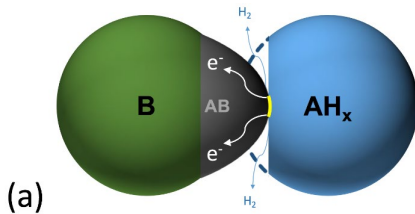
- Overcome kinetic barriers of hydrogen storage candidates with high capacities (and appropriate thermodynamics) for PEM fuel cell use that otherwise contain multiple solid phases that must nucleate, grow, and be consumed during cycling.
- Use 1) solvent with dissolved salt, 2) molten salt, or 3) molten salt eutectic electrolytes to promote solubilization and diffusion of species relevant to hydrogen storage release and uptake.

Technical Targets (for budget period 2):

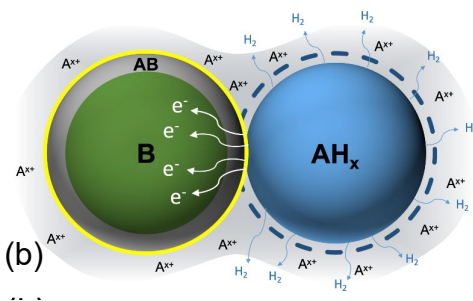
- 1) Demonstrate ≥ 8 wt% H_2 (hydride basis) at ≤ 350 bar H_2 and $\leq 300^\circ C$, 3 cycles
- 2) Demonstrate ≥ 4 wt% H_2 (hydride basis) at ≤ 100 bar H_2 and $\leq 150^\circ C$, 3 cycles

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.

Overcome interface-controlled process that normally requires thermal activation.



- **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:**
 $AH_x + B \rightarrow A^{x+} + xe^- + x/2H_2 + B \rightarrow AB + x/2H_2$
Electrolyte that can solvate A^{x+} facilitates transport and enables reaction to occur over full surface area of B exposed to electrolyte (*electron transport still solid-solid, but faster*)

Budget period 1 (Seedling phase) Demonstrated...

- 1) >10 wt% H_2 uptake (hydride only basis) for MgB_2 at $320^\circ C$ and 1000 bar (20x greater than for samples without electrolytes)
- 2) $\geq 10x$ rate of dehydrogenation (w.r.t systems without electrolytes) for $Mg(BH_4)_2$, MgH_2/Si and MgH_2/Sn with various electrolytes.

Electrolytes promote low activation barrier transport of heavy cations and anions effectively increasing interfacial area between reacting particles



Accomplishments and Progress Overview



Budget Period 2 (2019/20) Go/No-Go Criteria (either #1 or #2 must be met)

#1 Demonstrate ≥ 8 wt% H_2 (hydride basis) at ≤ 350 bar H_2 and ≤ 300 °C for 3 cycles

#2 Demonstrate ≥ 4 wt% H_2 (hydride basis) at ≤ 100 bar H_2 and ≤ 150 °C for 3 cycles

Summary of Budget Period 2 Accomplishments

- 1) Demonstrated hydrogenation of MgB_2 at $\sim 310^\circ C$ and ~ 350 bar in Li-K-CsCl eutectic with almost 70% conversion to BH_4 (previously 1000 bar)
- 2) Demonstrated 3 cycles of hydrogenation/dehydrogenation at >4 wt% H_2 using $NaAlH_4$ in the presence of diglyme electrolyte with dehydrogenation at $150^\circ C$ and hydrogenation at significantly reduced temperature and pressure hydrogenation ($75^\circ C$, 50 bar) **Meets Go/No-Go Criterion #2**
- 3) Obtained initial proof-of-concept for electrolyte-aided enhancement of performance from an alternative high-capacity material ($LiAlH_4$, ~ 7.8 wt% H_2)
- 4) Provided initial inputs for system-level model with K. Brooks (PNNL); preliminary results (US06 Drive Cycle) showed a 30% tank volume reduction using $NaAlH_4$ with an electrolyte

#1 Demonstrated 10 wt% H_2 (hydride basis) at 350 bar and 310 °C (1 cycle)

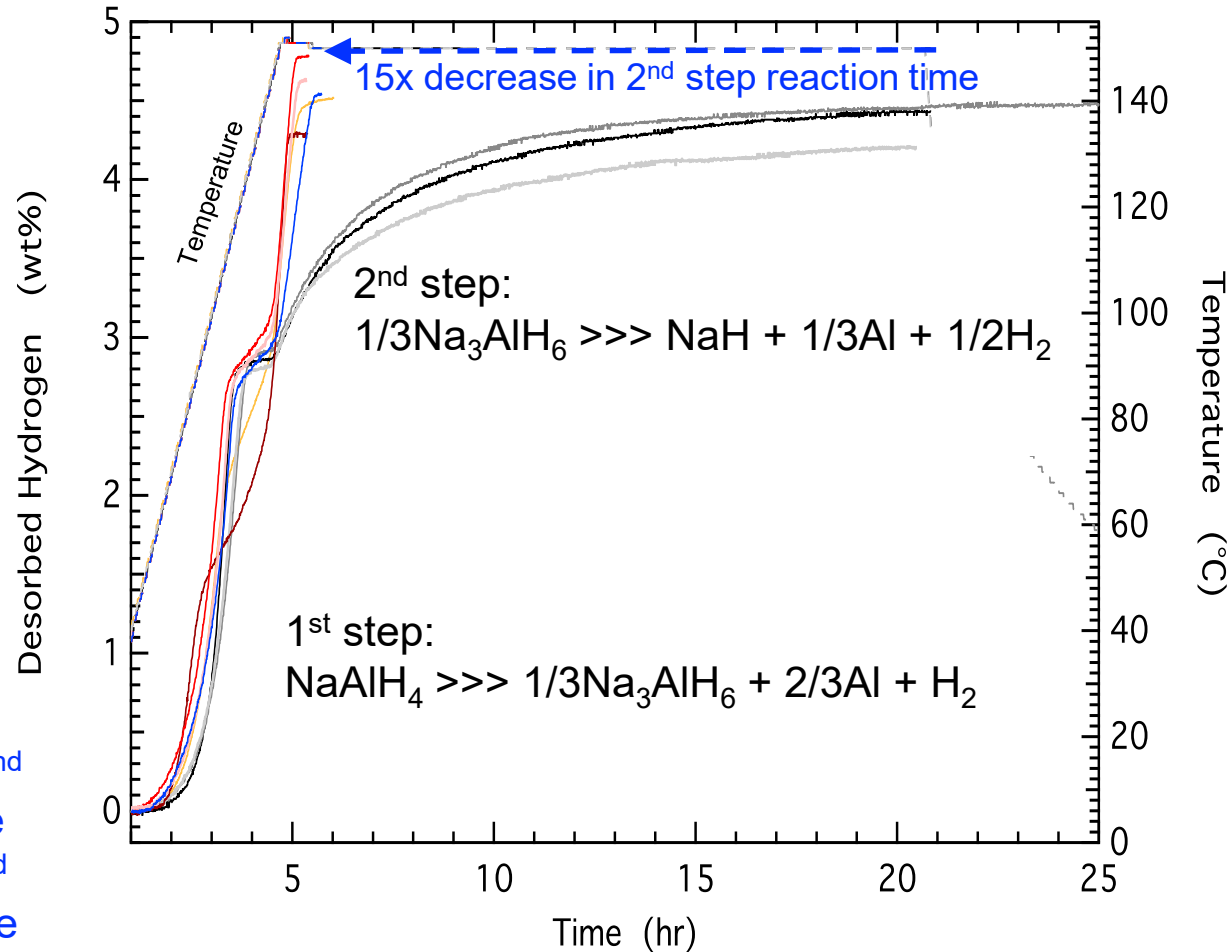
#2 Demonstrated 4.5 wt% H_2 (hydride basis) at 50 bar and 75 °C (3 cycles)

Electrolyte-Assisted Hydrogen Storage Reactions in Alanates:

- 1) Reversible cycling of NaAlH_4 in electrolyte at low temperature and low pressure
- 2) Enhanced Desorption from LiAlH_4 in electrolyte at low temperature

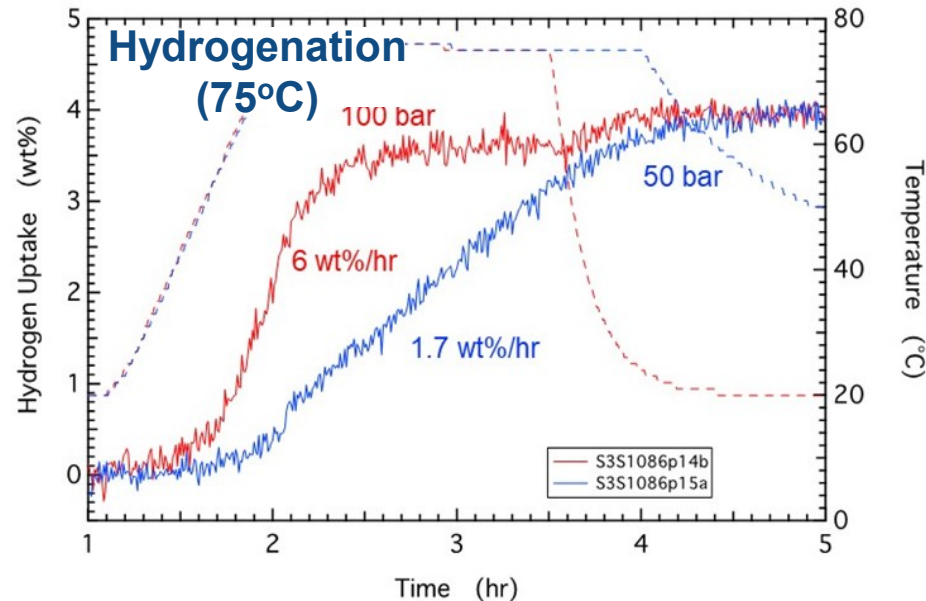
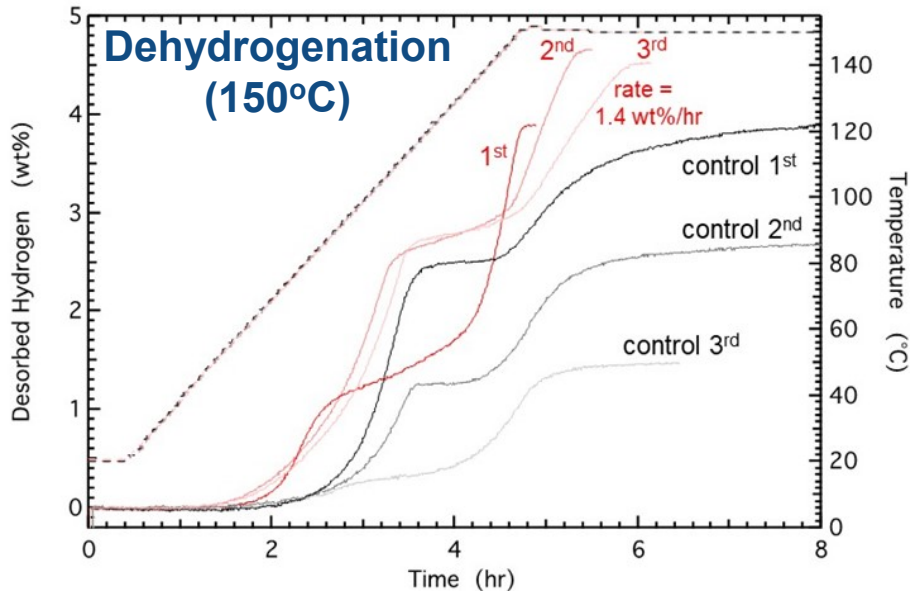
Low temperature ($\leq 150^\circ\text{C}$) hydrogen cycling in NaAlH_4 (theo. 50 g- H_2 /L, 5.6 wt%)

- **SOA control:** NaAlH_4 milled with 3 at% TiCl_3
- **Added electrolyte:** 47 wt% $\text{TiCl}_3/\text{NaAlH}_4$ mixed with 53 wt% diglyme electrolyte
- Hydrogenation treatments: ~ 110 bar, 130°C , 15 hr)
- Both control and electrolyte samples cycle well
- The initial rates and kinetics for the 1st step are similar
- However, the initial rate for the 2nd step is ~ 2 x higher with electrolyte and time required to complete 2nd step is 15x shorter with electrolyte



Electrolyte increases rate for second step with kinetics that are maintained (as opposed to decreasing) throughout the full extent of reaction

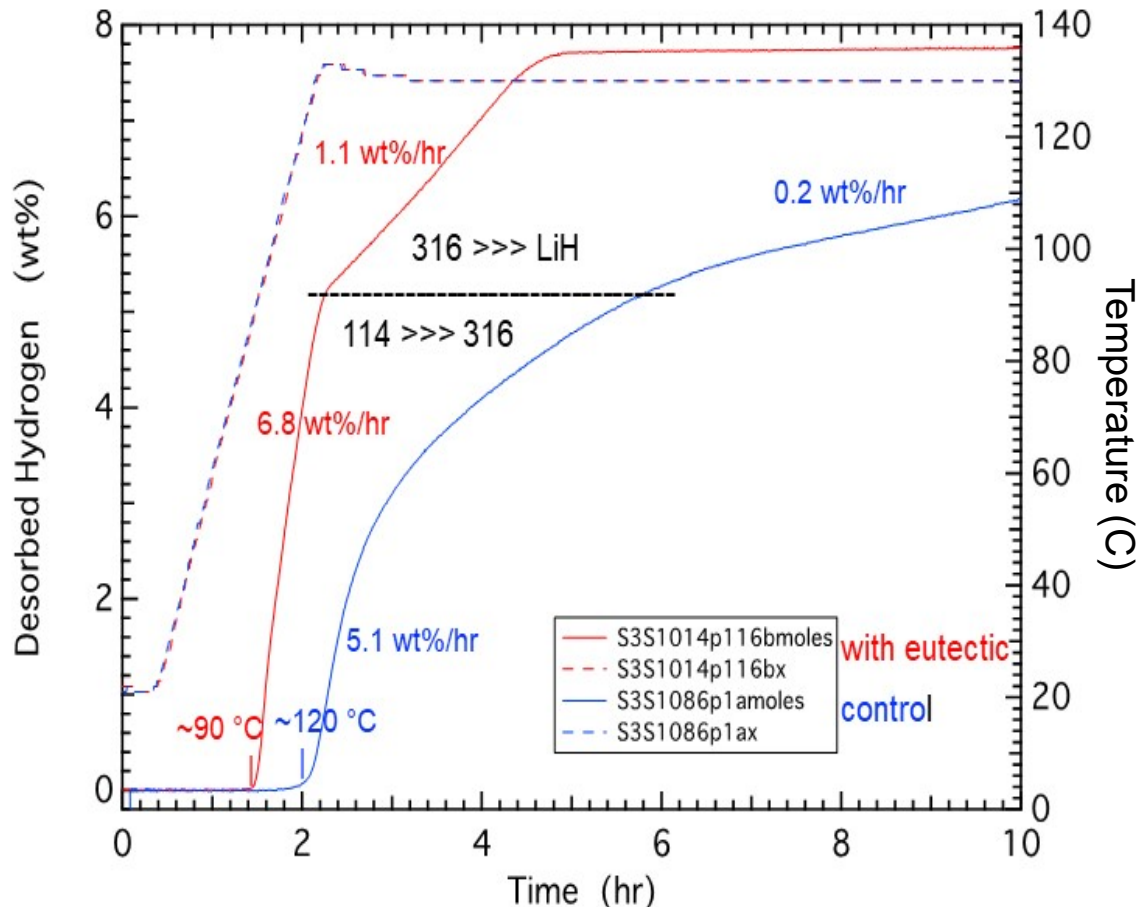
Low temperature and low pressure cycling of NaAlH_4 in the presence of electrolyte (50 wt% diglyme)



- **1st dehyd**: 3.9 wt% H (faster w/electrolyte)
- **2nd dehyd** (after 100 bar hyd): 4.6 wt% H w/electrolyte and 2.7 wt% H for control
- **3rd dehyd** (after 50 bar hyd): 4.5 wt% H w/electrolyte and 1.5 wt% H for control

- **100 bar**: 4 wt% H uptake at 6 wt%/hr
- **50 bar**: 4 wt% H uptake at 1.7 wt%/hr
- No reduction in total H uptake down to 50 bar hydrogenation pressure

Electrolyte improves dehydrogenation & rehydrogenation (rate & uptake)

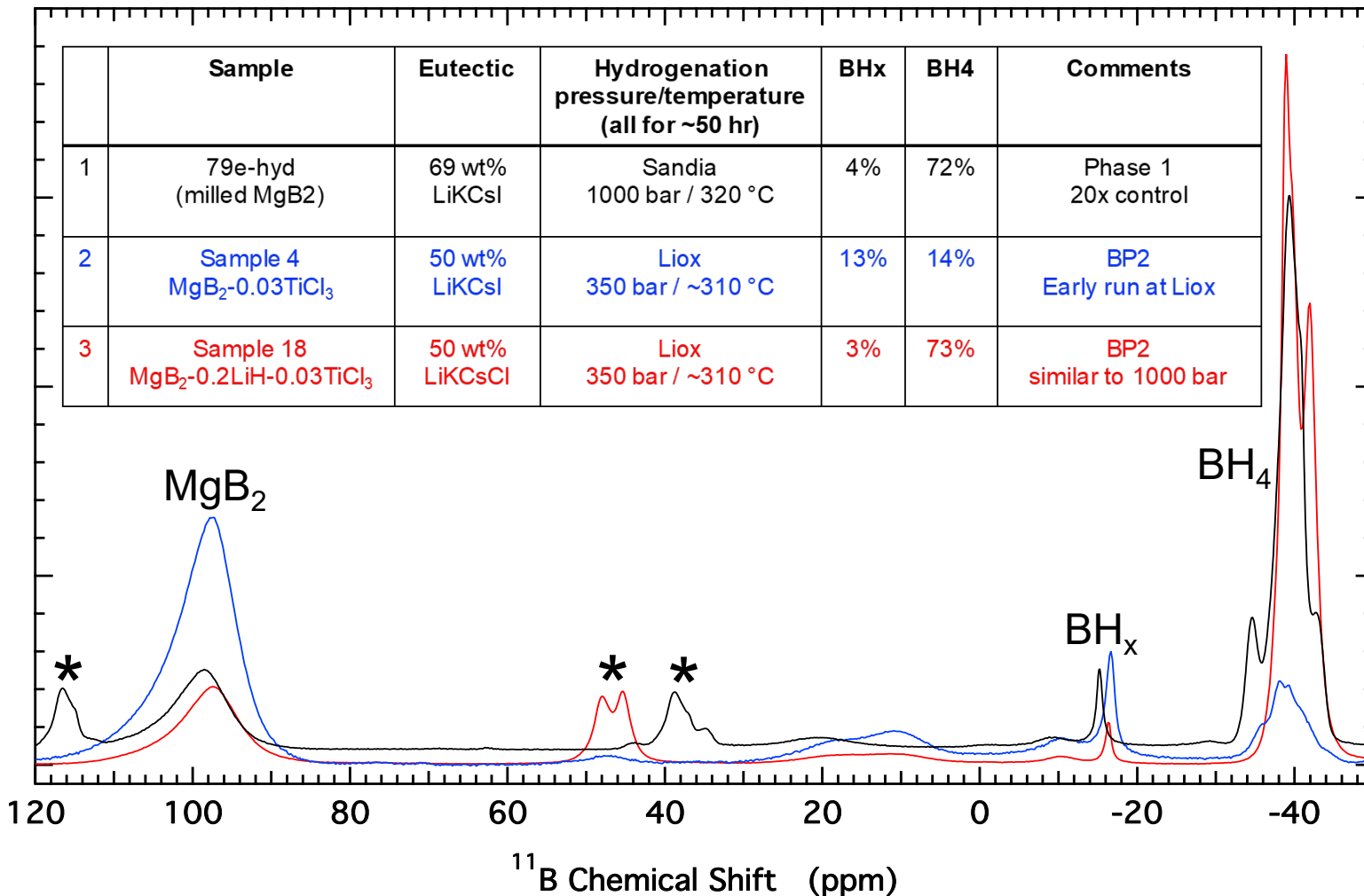


- Hydrogen desorption from LiAlH_4 in Li-KBH_4 electrolyte compared to control sample; both with 3 mol% TiF_3
- Onset temperature for hydrogen release is reduced by about 30°C in sample with electrolyte
- LiAlH_4 + electrolyte: 7.8 wt% H_2 desorption over 5 hrs
- LiAlH_4 control: 7.8 wt% H_2 desorption over 25 hrs
- More pronounced rate difference in 2nd decomp step (similar to NaAlH_4)

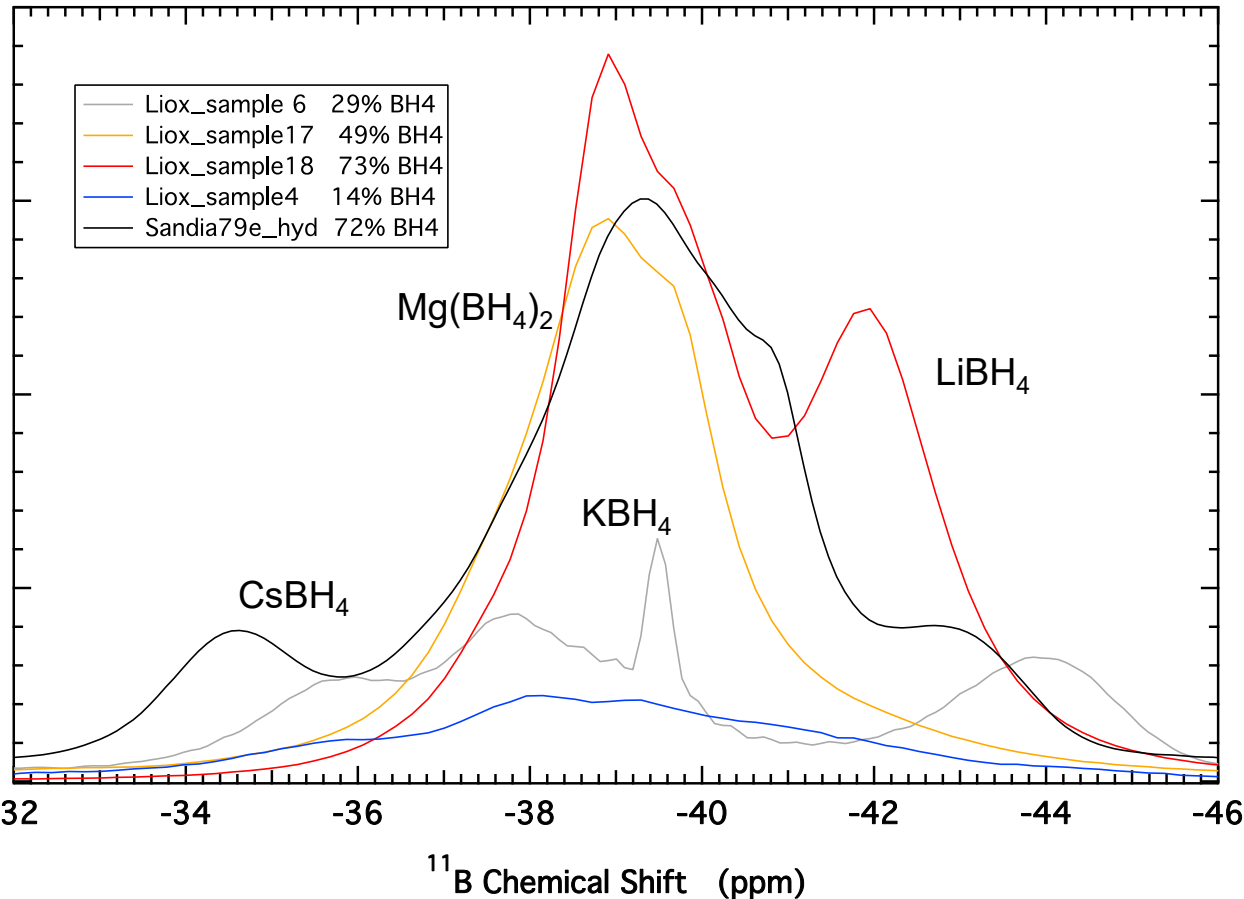
Complete dehydrogenation (7.8 wt% H) of LiAlH_4 occurs 5x faster in sample with electrolyte

Electrolyte-Assisted Hydrogen Storage Reactions in $\text{Mg}(\text{BH}_4)_2$:

Demonstrated hydrogenation of MgB_2 at $\sim 310^\circ\text{C}$, ~ 300 bar in 50 wt% Li-K-CsCl eutectic with $\sim 70\%$ conversion (previously 69 wt% electrolyte at 1000 bar)



Achieved conversion similar to 1000 bar/69 wt% eutectic at 350 bar/50 wt% eutectic



- ^{11}B NMR from a variety of different samples with two different eutectics (see list and DSCs in backup) shows multiple BH_4 species present at room temperature (solid state)
- System may be more homogeneous in molten state
- Variability in amount of BH_4 formation and different types of BH_4 species suggests eutectic (composition and concentration) is key to optimization

Depending on formulation, the hydrogenated sample after solidification contains a mixture of BH_4 phases

Reviewer's Comments

- More work on higher-capacity materials is warranted. [This work is ongoing](#)
- The team has yet to prove its conceptual model is correct. [This is a good point and needs to be addressed. This will be investigated further in Phase 3 in conjunction with modeling at LNL \(see below\)](#)
- A study of electrochemically driven hydrogen cycling compared to other electrochemical devices, such as batteries, should be done to identify the advantages (or disadvantages) of such a system. A practical study should be deferred until a better understanding has been gained and a more appropriate system demonstration has been performed; needs more justification; its advantages over other electrochemical systems are unclear; strategy is unclear; needs better definition. [Based on an internal assessment we have discontinued electrochemically-driven research efforts to focus on the thermochemical approach.](#)
- The work would benefit from the characterization and computational tools available at other HyMARC partners. The team's collaboration with other HyMARC members could be improved. [We have initiated a new collaboration with PNNL \(Kriston Brooks\) to perform system modeling of the sodium alanate/electrolyte system to assess system-level performance](#)
- It is suggested that the team provide a clear picture of how this will work in the vehicle system framework. More details of how this approach to the onboard generation of hydrogen will have an impact on the overall onboard, closed system energy balance. [Work with PNNL \(Kriston Brooks\) on system modeling should help us better understand how this will work in the vehicle system](#)
- The project lacks theory to guide the selection of additives (slide 11). Likewise, other factors should be considered. For example, the capillary forces between the particles that drive ionic motion (slide 2) could be important. [We have had discussions with Brandon Wood \(LNL\) regarding modeling to understand the mechanisms involved \(at a variety of scales\) and guide additive selection](#)
- Team should study the system in operando and verify the presence of the correct ions at the right concentration to be consistent with $\text{Mg}(\text{BH}_4)_2$ creation or desorption according to the project model. [In operando studies will be considered after full cycling over ~3 cycles has been established using an optimized electrolyte system. This work is planned for early phase 3.](#)

- Subcontract: HRL Laboratories
- University: Caltech (Hwang, Solid State/NMR)
- HyMARC
 - Sandia NL: High pressure reversibility in presence of electrolyte (V. Stavila)
 - PNNL: Provided initial inputs for system-level model (K. Brooks) using US06 Drive Cycle

- Lower electrolyte content – currently 50 wt% with an ultimate target of 20-25 wt%
 - For MgB₂/Mg(BH₄)₂, assuming 74% conversion (11 wt % H on hydride basis) as demonstrated with best sample, 25 wt% electrolyte would provide >8 wt% (full material basis) hydrogen storage
 - For NaAlH₄, achieve >4 wt% full material basis with practical dehydrogenation rate (>~1 wt%/hr at <150 °C) and hydrogenation at < 100 bar
- Demonstrate complete cycling with borohydride system (is eutectic effective for multiple cycles?)
- Reduce time required for boride hydrogenation

- Improved (lower) electrolyte-to-active material ratio (e.g. alternative eutectics: lower molecular weight increases moles-per-mass; optimized hydride particle size: larger particles require less electrolyte to cover surface but have longer internal diffusion distances)
- Improve uptake (conversion) of MgB_2 at 350 bar and 300 °C (e.g., catalysts, mechanical milling). Current hydrogenation times fixed at ~50 hr, is hydrogenation still continuing or over much earlier?
- Experimentally test other electrolytes for NaAlH_4 system
- Experimentally test Mg amide/LiH and other low temperature systems with electrolytes

- Aim of the research and development effort described here is to take electrolyte 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.

- **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:** Achieved 11 wt% hydrogen uptake (MgB_2) with 50 wt% eutectic at 350 bar and 310°C. Demonstrated reversible hydrogen cycling in electrolyte-treated NaAlH_4 with a desorption rate 15x faster for 2nd step compared to control. Demonstrated hydrogenation (formation of NaAlH_4) at low pressure and temperature (50 bar, 75°C).
- **Collaborations:** Caltech (Solid-State NMR), PNNL (system modeling) and Sandia NL (high pressure hydrogenation)

Technical Backup Slides



Comparison of hydrogenation from Sandia and Liox



Sample	Eutectic	Hydrogenation pressure/temperature (all ~50 hr)	BHx	BH4	Comments
79e-hyd (milled MgB ₂)	69 wt% LiKCsI	Sandia 1000 bar / 320 °C	4%	72%	BP1 Original result: shows much higher conversion than control
79d-hyd (milled NgB ₂)	0 wt% control	Sandia 1000 bar / 320 °C	0%	3%	BP1 Control
p108d (MgB ₂ + 3 at% TiF ₃) milled with eutectic	50 wt% LiKCsI	Sandia 700 bar / 300 °C	11%	42%	BP2 Lower pressure: reduces conversion significantly
p108c (MgB ₂ + 3 at% TiF ₃)	50 wt% LiKCsI	Sandia 350 bar / 320 °C	11%	17%	BP2 Further lower pressure: even lower conversion, high BHx
Sample 4: MgB ₂ -0.03TiCl ₃	50 wt% LiKCsI	Liox 350 bar / ~310 °C	13%	14%	BP2 Early run at Liox: similar to Sandia
Sample 18: MgB ₂ -0.2LiH-0.03TiCl ₃	50 wt% LiKCsI	Liox 350 bar / ~310 °C	3%	73%	BP2 Current best: similar to original 1000 bar result



Tabulation of Liox hydrogenation experiments 1/2



Sample	Eutectic		MgB ₂	B-O	BH _x	BH ₄
Sample 1: MgB ₂	50 wt%		0.87	0.04	0.05	0.05
Sample 2: MgB ₂ -0.03TiCl ₃	50 wt%		0.78	0.08	0.13	0.01
Sample 3 MgB ₂	50 wt% LiKCsI		0.75	0.03	0.09	0.12
Sample 4: MgB ₂ -0.03TiCl ₃	LiKCsI 50 wt%		0.65	0.07	0.13	0.14
Sample 5: MgB ₂	75 wt% LiKCsI		0.66	0.07	0.10	0.17
Sample 6: MgB ₂ -0.03TiCl ₃	75 wt% LiKCsI	More eutectic compare 4	0.47	0.05	0.19	0.29
Sample 7: MgB ₂ -0.03TiCl ₃	50 wt% LiKCsI milled 2 hr	milled eutectic compare 4 little better	0.62	0.07	0.13	0.18
Sample 8: MgB ₂ -0.03TiCl ₃	50 wt% LiBH ₄ milled 2 hr	milled LiBH ₄ electrolyte little better	0.17	0.02	0.07	0.74
Sample 9: MgB ₂ -0.03TiCl ₃ No hydrogen treatment	50 wt% LiKCsI milled 2 hr	control	0.90	0.06	0.02	0.01
Sample 10: MgB ₂ -0.03TiCl ₃ No hydrogen treatment	50 wt% LiBH ₄ milled 2 hr	control	0.25	0.03	0.01	0.71

Early full run at Liox. Similar to Sandia p108c (previous slide).

More eutectic increases conversion but B₁₂H₁₂ (ie BH_x) is also high.

Milling the eutectic (as opposed to just mixing) improves conversion slightly

Using LiBH₄ as the electrolyte does improve the conversion slightly but the analysis is complicated because there is BH₄ to start with (see sample 10)



Tabulation of Liox hydrogenation experiments 2/2



Sample	Eutectic		MgB ₂	B-O	BHx	BH4
Sample 11: MgB ₂ -0.03TiCl ₃ + 50 wt% expanded graphite	LiKCsI 50 wt%	graphite to shear compare 4 somewhat better	0.58	0.06	0.16	0.20
Sample 12: MgB ₂ -0.2LiH-0.03TiCl ₃	none	added LiH more than LB/MH reduced BHx	0.61	0.04	0.03	0.32
Sample 13: MgB ₂ -0.2LiH-0.03TiCl ₃	LiKCsI 50 wt%	added LiH compare 4 significantly better	0.44	0.04	0.04	0.48
Sample 14: MgB ₂ -0.2LiH-0.03TiCl ₃	LiKCsI 75 wt%	added LiH compare 6 significantly better	0.26	0.04	0.04	0.67
Sample 15: 0.25MgB ₂ -0.73MgH ₂ - 0.02TiCl ₃	50 wt% LiKCsI	tried mostly MgH ₂ not better	0.72	0.02	0.01	0.25
Sample 16: 0.25MgB ₂ -0.73dMgH ₂ - 0.02TiCl ₃	50 wt% LiKCsI	same as 15 but dehydrogenated not better	0.71	0.02	0.02	0.25
Sample 17: MgB ₂ -0.03TiCl ₃	LiKCsCl 50 wt%	chloride eutectic compare 4 significantly better	0.35	0.05	0.11	0.49
Sample 18: MgB ₂ -0.2LiH-0.03TiCl ₃	LiKCsCl 50 wt%	LiH and Cl eutectic compare 13 significantly better	0.21	0.03	0.03	0.73

Tried milling with graphite to shear MgB₂, slightly better

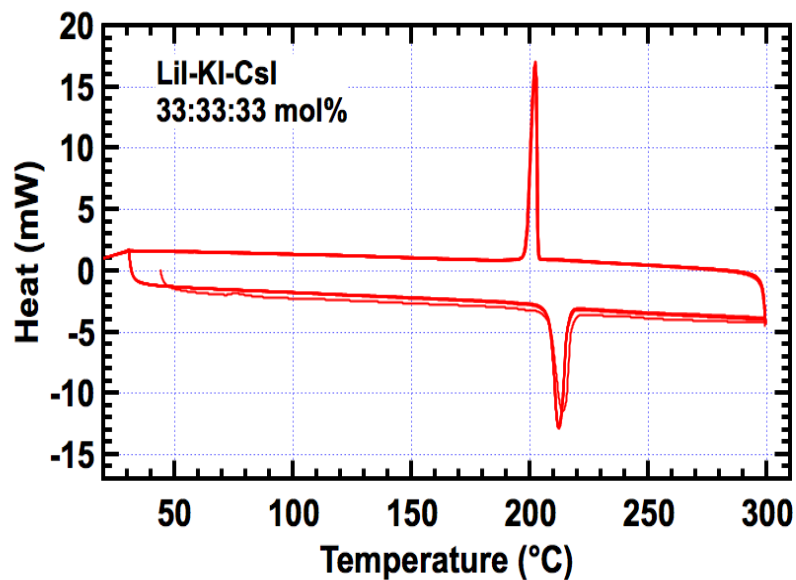
Added 0.2LiH increased conversion more than expected for just LiBH₄ formation while significantly decreasing B₁₂H₁₂. This needs to be studied further

Tried MgH₂ with a little MgB₂ to boost the capacity to >8 wt%. Did not really seem to help MgB₂ conversion

Lighter chloride increases conversion note: without LiH B₁₂H₁₂ goes up

With chloride and 0.2LiH achieved best conversion so far

Iodide eutectic
MW = 187 g/mol



(New) chloride-based eutectic
MW = 81 g/mol

- LiCl : KCl : CsCl (57.5 : 16.5 : 26 mol):
-Mixed them well and ball-milled for 2 min

