



Electrolyte Assisted Hydrogen Storage Reactions

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Annual Merit Review

Project ID: ST137



Overview



Timeline:

- Project Start Date: 01/20/17
- Phase 2 End Date: 7/14/2019

Budget:

- 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, Stavila),
- Caltech (Solid-State NMR)
- Project lead: Liox Power, Inc. with subcontract to HRL Laboratories, LLC

Objectives:

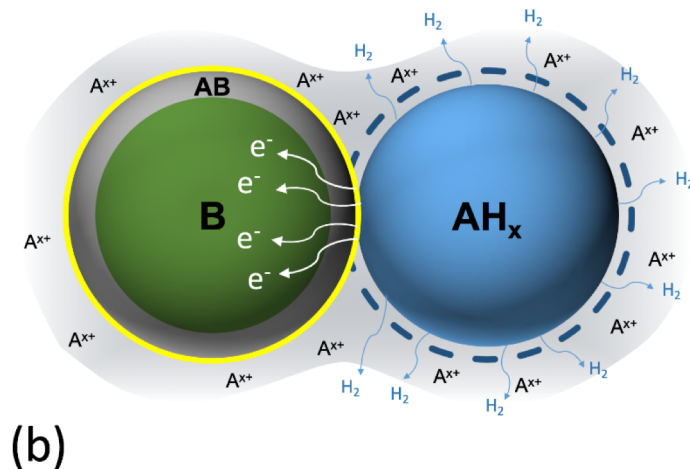
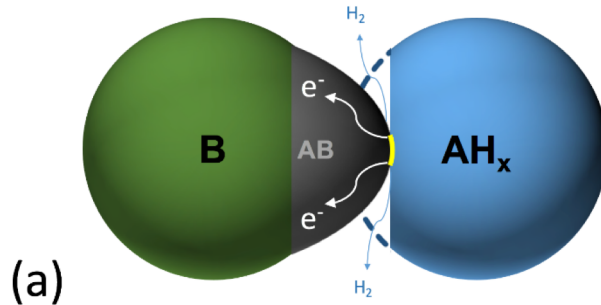
- Overcome kinetic barriers of hydrogen storage candidates with high capacities (and appropriate thermodynamics) for PEM fuel cell use that otherwise contain multiple solid phases that must nucleate, grow, and be consumed during cycling.
- Specific use of salt and borohydride electrolytes to promote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

Fulfillment of Phase 1 Accomplishments in 2018:

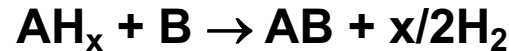
- Demonstrated electrolyte assisted hydrogen storage material with
 - 1) cycling of ≥ 1 wt% H₂;
 - 2) $\geq 10\times$ rate of hydrogen evolution as compared to systems without an electrolyte and
 - 3) favorable assessment of results indicating a pathway to meet storage targets.
 - 4) Reported on accomplishments, “Electrolyte-Assisted Hydrogen Storage Reactions,” Vajo, et al, *J. Phys. Chem. C*, 2018, 122 (47), pp 26845–26850 DOI: 10.1021/acs.jpcc.8b08335

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.

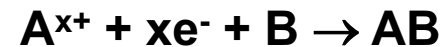
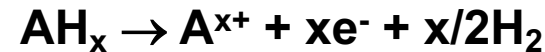


- **Solid-state reactions**



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

- **Electrolyte assisted reactions**



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)*

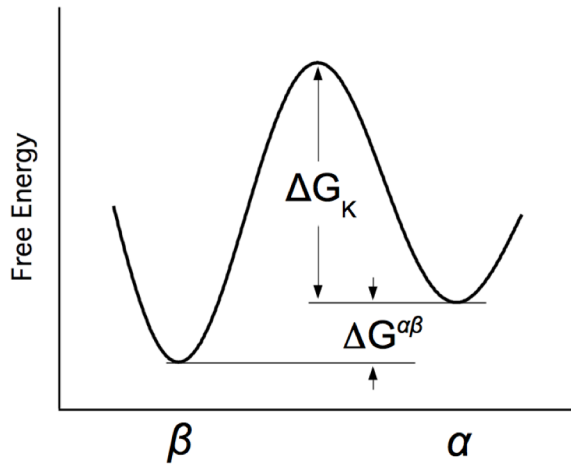


Approach: Electrolyte Assisted Hydrogen Storage Reactions (cont'd)



Budget Period 2 and 3 Tasks:

- 1) Lower the electrolyte content in consort with other processing approaches in order to achieve a full material gravimetric density of $\geq 8\text{wt}\%$ while maintaining Phase 1 kinetic improvements, and reduce hydrogenation and dehydrogenation pressure/temperature levels in Mg-B-H system levels to normal laboratory attainable conditions, minimizing reliance on the high-pressure system at Sandia.
- 2) Survey and test promising systems with $\geq 4\text{wt}\%$ full material density that better fulfill the goal of technological viability, but that have not been used due to limitations in cycling, contamination, or kinetics and where these limitations might be overcome through the use of electrolytes.
- 3) Test and evaluate electrochemical systems to supplement or supersede the solely thermochemical (i.e., temperature- and pressure-based) free energy driving forces currently used to direct hydrogen exchange reactions.

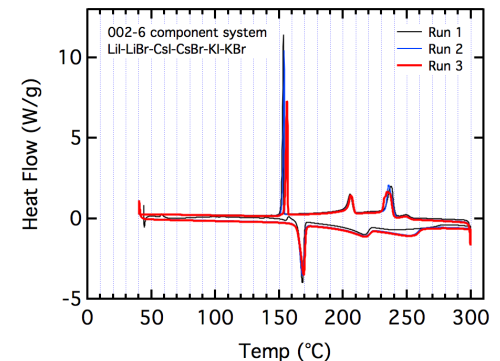
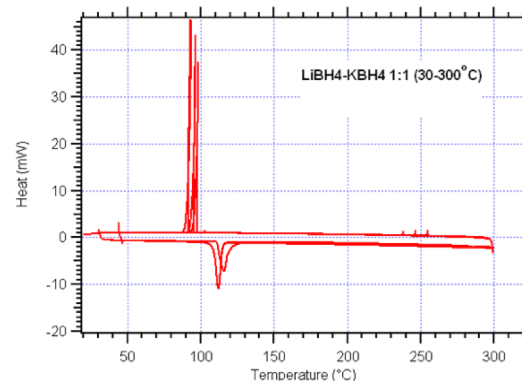
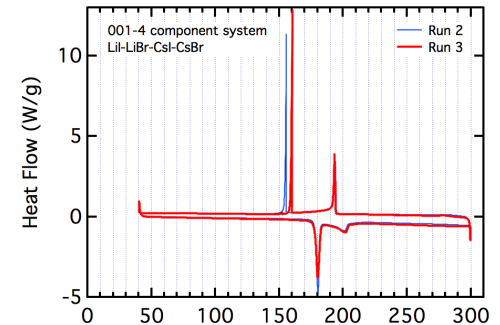
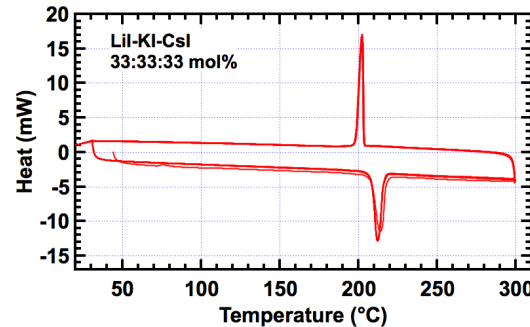


Left: Hypothesize that electrolytes significantly lower the free energy driving force for measurable rates as seen in conversion reactions, e.g.

$\Delta G_K, \text{solid-state} \sim 20 \text{ kJ}$; $\Delta G_K, \text{electrolyte} \sim 4 \text{ kJ}$

- Inorganic molten salts have high level of thermal stability over wide temperature range for (de)hydrogenation.
- 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.

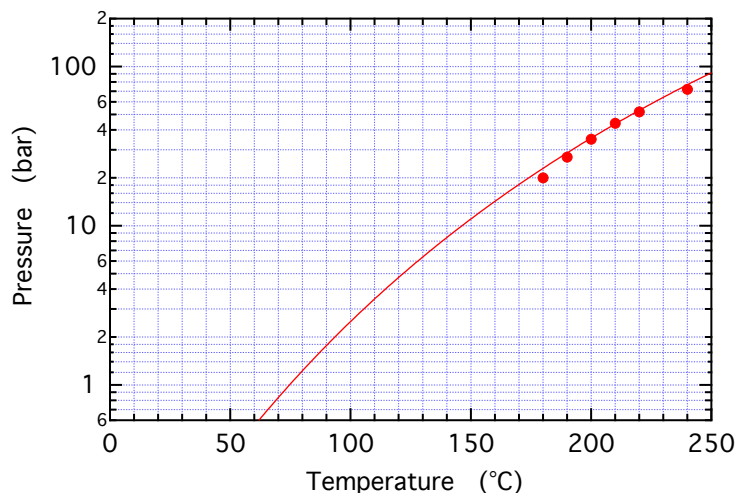


Assessment of candidate electrolyte-assisted hydrogen storage systems with 4 wt% full material basis hydrogen capacity and ≤ 150 °C/100 bar cycling

Criteria:

- 1) 4 wt% capacity on a full material basis, which including hydride + electrolyte + any catalysts or additives;
- 2) equilibrium dehydrogenation pressure appropriate for input to a fuel cell of at least 1 bar and preferably 2 bar to 5 bar at ≤ 150 °C;
- 3) hydrogen release rate at ≤ 150 °C enabling full release in a typical 300-mile drive time of ~5 hr to 6 hr, which for hydride materials with ~5 wt%-H₂ corresponds to rates of ~1 wt%/hr;
- 4) pressure for rehydrogenation of ≤ 100 bar at ≤ 150 °C.

Accomplishments: Assessment of Electrolyte-Assisted systems with 4 wt% capacity at <150 °C 100 bar cycling (cont'd)



Above: Equilibrium pressure for the $\text{Mg}(\text{NH}_2)_2 + 2\text{LiH}$ system. Experimental points from IJHE **37** 6646 (2012).

Criterion 1, 4 wt% capacity: Capacity of $\text{Mg}(\text{NH}_2)_2 + 2\text{LiH}$ system is 5.5 wt%- H_2 . Thus, up to ~25%-by-weight of electrolyte/additives can be accommodated while maintaining a full material basis capacity of 4 wt%- H_2 .

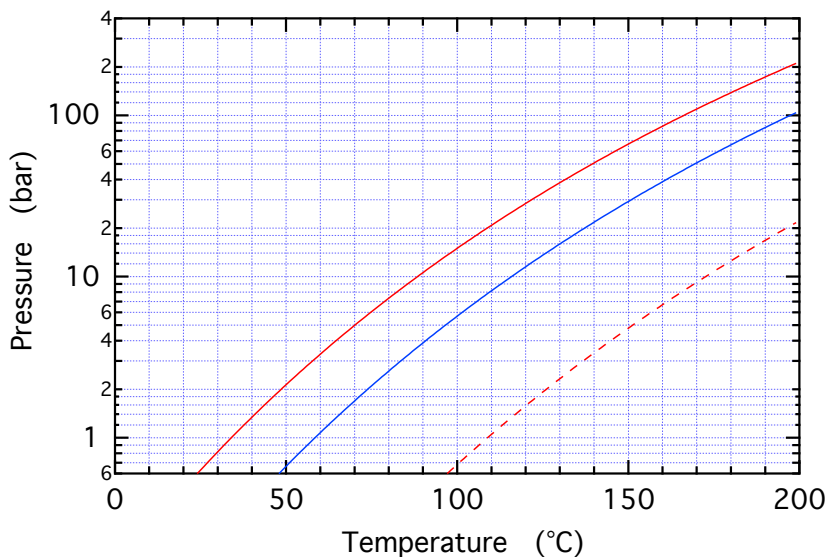
Criterion 2, ≥ 1 bar at ≤ 150 °C: Equilibrium pressure for this system characterized using isotherms measured at 180 °C to 240 °C [IJHE **37** 6646 (2012)]. Equilibrium pressure ($P(\text{NH}_2/\text{NH})$) is given by:

$$P(\text{NH}_2/\text{NH}) = \exp(-4683.7/T(\text{K}) + 13.47)$$

and shown fig at left. Extrapolation gives 11 bar pressure at 150 °C and 2.5 bar at 100 °C. Equilibrium pressure is nearly ideal for both dehydrogenation and rehydrogenation.

Criterion 3, ~1 wt%/hr at ≤ 150 °C: Kinetics not characterized extensively. Original isotherms were reported down to 190 °C, while newer formulations containing 4 mol% KH enabled measurements at 180 °C. Using catalyzed material, isothermal dehydrogenation at 200 °C showed 4 wt%- H_2 in 2 hr. The rate was decreasing significantly with the extent of reaction, nevertheless, the average rate was ~2 wt%- H_2 /hr. Rate increase by ~10× needed using an electrolyte, cycling at 150 °C possible.

Criterion 4, ≤ 100 bar at ≤ 150 °C: As discussed above the equilibrium pressure nearly ideal at temperatures between 100 °C and 150 °C.



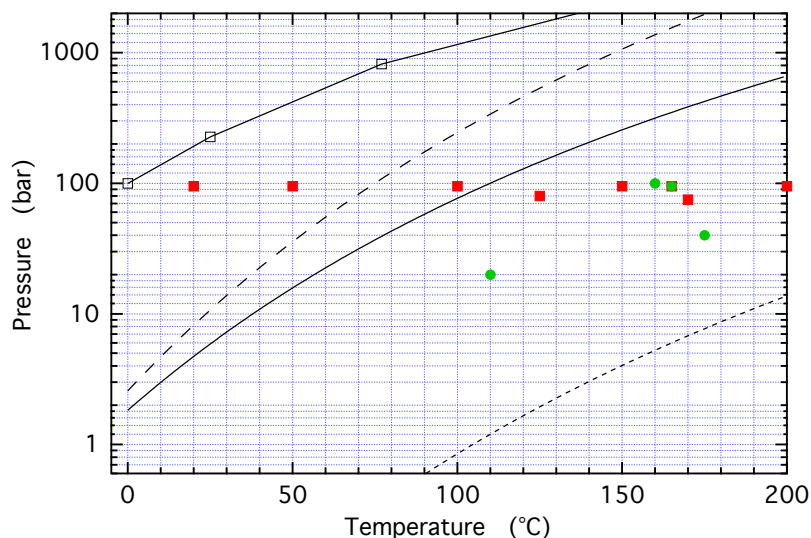
Equilibrium pressures for the sodium alanate system. (solid red) NaAlH₄/Na₃AlH₆; (dashed red) Na₃AlH₆/NaH; and (solid blue) NaAlH₄/NaH, which represents dehydrogenation and rehydrogenation in a single step.

Criterion 1, 4 wt% capacity: Capacity considering first two dehydrogenation steps from NaAlH₄ to Na₃AlH₆ and further to NaH is 5.6 wt%. Thus 4 wt% full material basis capacity can still be expected with up to 30%-by-weight added electrolyte. Our budget period 1 effort suggests that desired improvements in kinetics can be realized with this level of additives.

Criterion 2, ≥ 1 bar at $\leq 150\text{ }^\circ\text{C}$: The equilibrium hydrogen pressures for the two dehydrogenation steps have been well established. As shown in at left, both of these pressures are $>\sim 5$ bar at $150\text{ }^\circ\text{C}$.

Criterion 3, ~ 1 wt%/hr at $\leq 150\text{ }^\circ\text{C}$: Reported rates for NaAlH₄ catalyzed with 4% TiCl₃ meet Criterion 2 and are likely close to the best rates achieved for this system [J Alloy Com **339** 299 (2002)].

Criterion 4, ≤ 100 bar at $\leq 150\text{ }^\circ\text{C}$: Achieving rehydrogenation at $120\text{ }^\circ\text{C}$ by including an electrolyte would lower the pressure to ~ 28 bar.



Above: Compilation of reported equilibrium pressures for dehydrogenation of Li_3AlH_6 to LiH . Open squares: computational estimates at discrete temperatures¹. Long dash: computational estimate using experimental input². Solid line: estimate from HSC. Short dash: experimental estimate³. Filled green circles: various reports claiming hydrogenation. Filled red squares: various reports claiming no hydrogenation.

¹PRB **76** 024112 (2007),

²J Alloy Com **420** 286 (2006),

³J Phys Chem B **105** 11214 (2001)

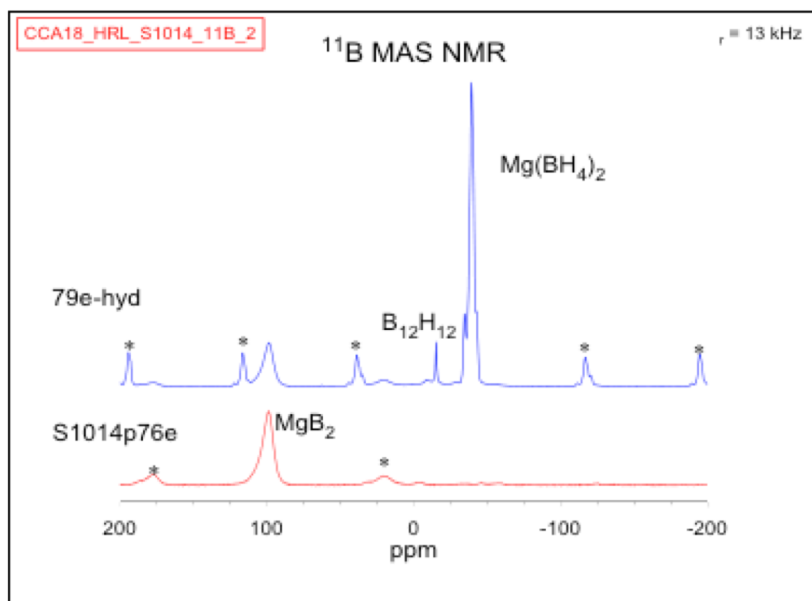
Criterion 1, 4 wt% capacity: The capacity for dehydrogenation Li_3AlH_6 to LiH is 5.5 wt%- H_2 . Up to ~25%-by-weight of electrolyte/additives can be accommodated maintaining full capacity of 4 wt%- H_2 .

Criterion 2, ≥ 1 bar at ≤ 150 °C: Large uncertainty in dehydrogenation thermodynamics for Li_3AlH_6 to LiH with reported equilibrium pressures at 100 °C (lines in fig at left), from 1 to 1000 bar. Despite uncertainty, equilibrium pressures likely sufficient for dehydrogenation.

Criterion 3, ~1 wt%/hr at ≤ 150 °C: Rates for dehydrogenation of Li_3AlH_6 not quantified thoroughly. Reported dehydrogenation of LiAlH_4 to LiH occurs by ~200 °C in TGA (Li_3AlH_6 step starting at about 120 °C to 150 °C), which corresponds to ~2 wt%/hr.

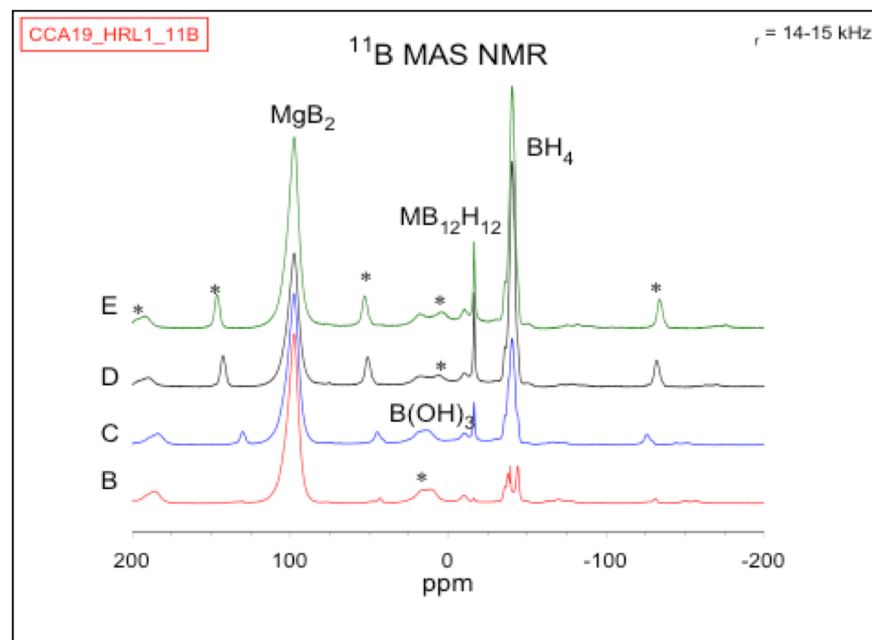
Criterion 4, ≤ 100 bar at ≤ 150 °C: Issue of Li_3AlH_6 as a hydrogen storage material is hydrogenation pressure. Marginally acceptable uptake could be achieved at 75 °C by increasing rate by 20 \times . In budget period 1, such an improvement was seen for hydrogenation of MgB_2 using a Li/K/CsI eutectic electrolyte.

Phase 1 effort below showed 71% conversion of MgB_2 to $\text{Mg}(\text{BH}_4)_2$ under 1000 bar, 320 °C for 50 hrs.



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.



Initial Phase 2 effort above for MgB_2 to $\text{Mg}(\text{BH}_4)_2$ under 700 bar, 300 °C for 50 hrs (Stavila). 50 wt% ternary iodide eutectic.

- E) 37% conversion (MgI_2 added).
- D) 42% conversion (milled with $\text{TiF}_3/\text{MgB}_2$ with iodide).
- C) 27% conversion (TiF_3 catalyst added, milled with MgB_2).
- B) 13% conversion compared to 71%

From last year
 70 wt% eutectic, 1000 bar, 320 °C
 BH₄/(BH₄ + B₁₂H₁₂) ratio
 ----- 95%

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

Integration ratio				
	MgB2	intermediates	BH4	
B	1	0.05	0.16	
C	1	0.14	0.43	
D	1	0.22	0.87	
E	1	0.17	0.68	

From this year (50 wt% eutectic, 700 bar, 300 °C)
 BH₄/(BH₄ + B₁₂H₁₂) ratio
 --- 76%
 --- 75%
 --- 80%
 --- 80%

- Lower ratios (i.e. more B₁₂H₁₂) could be from kinetic limitations lower pressure (700 vs 1000 bar) and/or from lower temperature (300 vs 320 °C) or thermodynamic limitations from lower pressure
 - next round 350 bar and 320 °C may help clarify

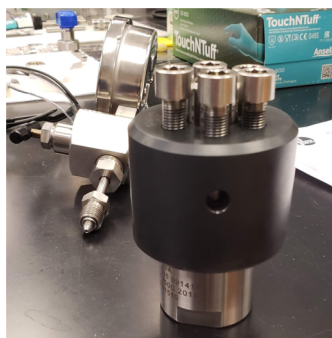
Accomplishments and Progress: In-house Parr reactor system completed and pressure tested

Valves:

V1: $\frac{1}{8}$ taper open/close valve

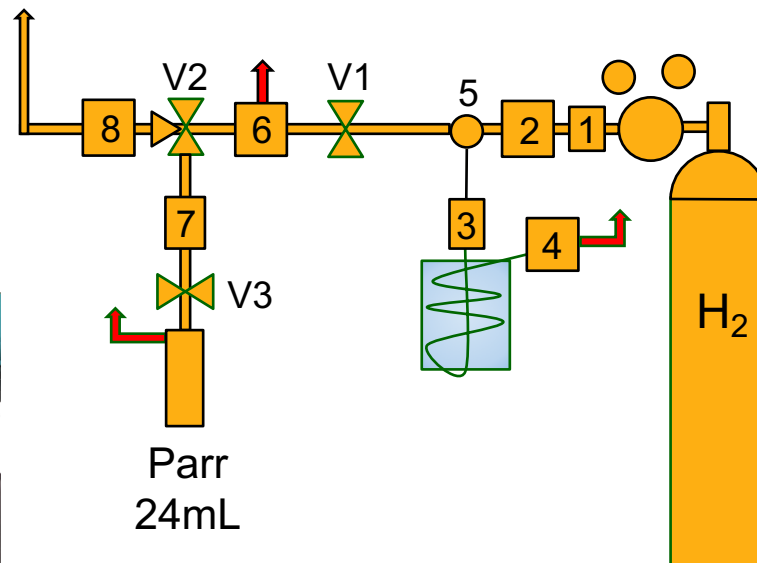
V2: $\frac{1}{8}$ 3-way valve regulated, purge is normally closed, other directions always open

V3: valve on Parr reactor



Procedure:

- 1) Open V1,V3
- 2) Cool dead vol to 77K
- 3) Apply 50 bar H₂
- 4) Close Reg (Parr, dead vol connected)
- 5) Remove dewar (pressure goes to 175 bar)
- 6) Close V1,V3 (Parr isolated)
- 7) Heat Parr to 600 K (pressure goes to 350 bar)
- 8) Cool to 300K
- 9) Open V3, V2 (Parr, purge connected)
- 10) Open V1 (Parr, purge, dead vol connected)

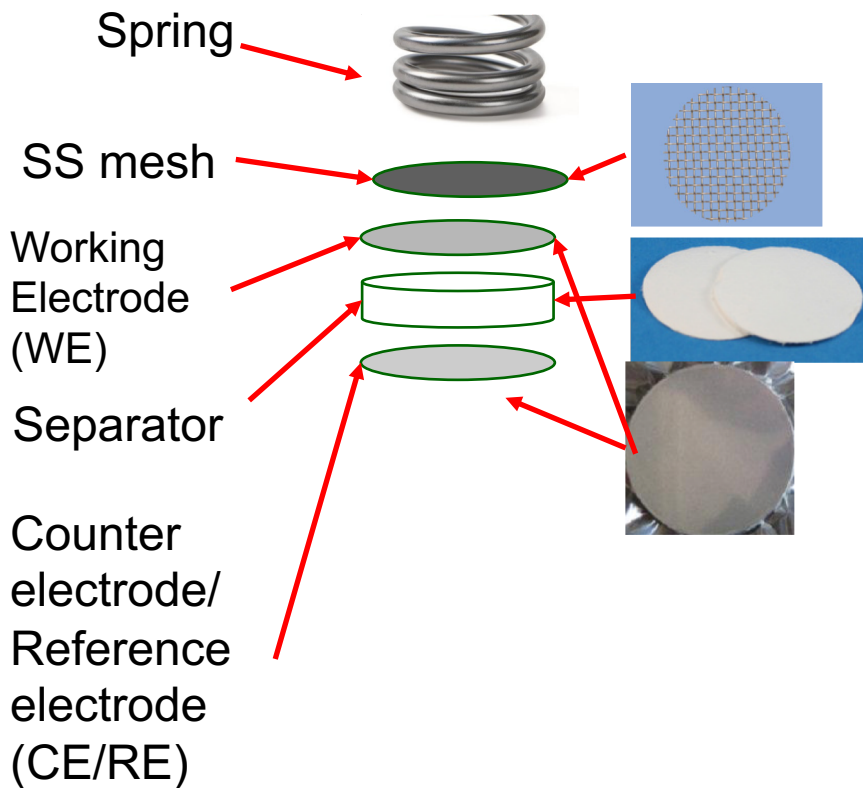


- 1) $\frac{1}{4}$ FNPT to $\frac{1}{8}$ taper seal
- 2) Check valve
- 3) $\frac{1}{8}$ taper seal to $\frac{1}{4}$ taper seal
- 4) Safety rupture disk (6000 psi burst)
- 5) $\frac{1}{8}$ taper seal tee
- 6) Safety rupture disk (6000 psi burst)
- 7) 2 micron inline filter
- 8) Check valve

Arrows indicate to fume hood
red=emergency

All tubing is $\frac{1}{8}$ inch unless noted

Experimental Cells:
 Setup allows for gas evolution and
 pressure/RGA monitoring *in situ*

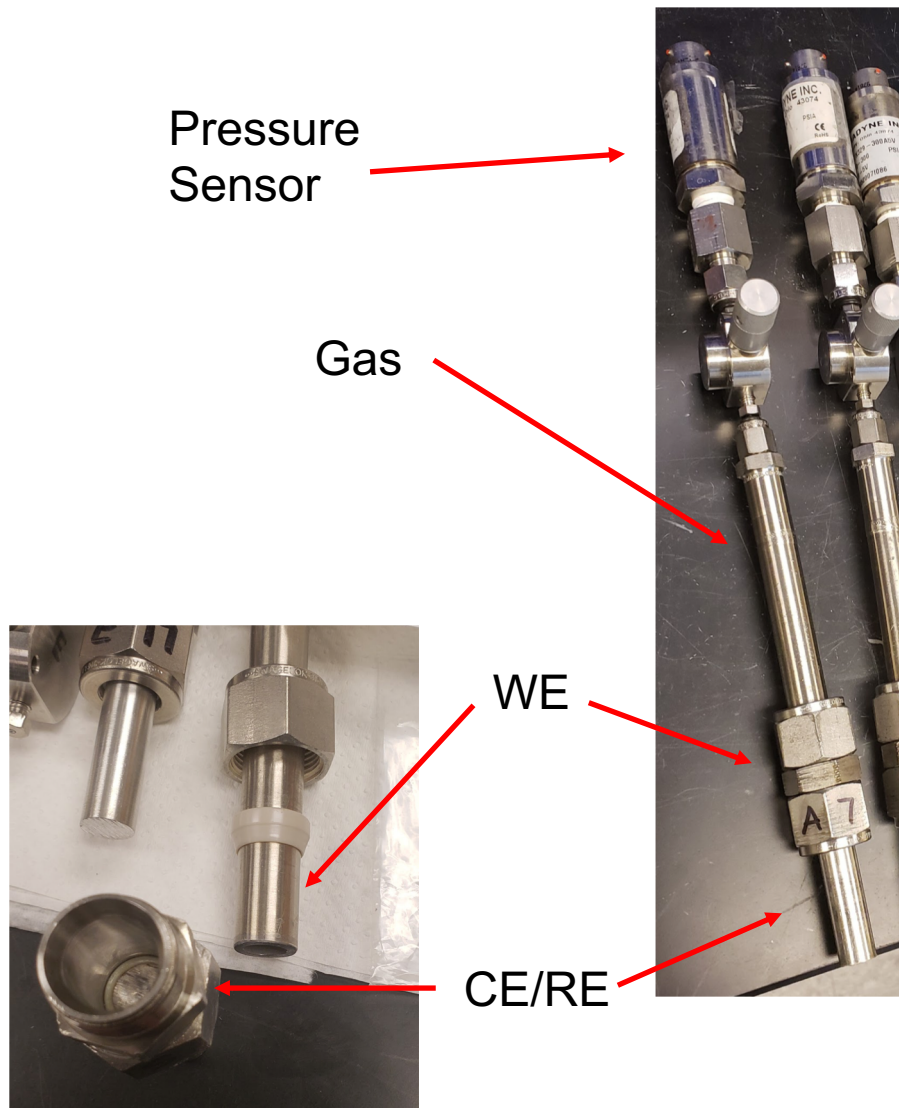


Pressure Sensor

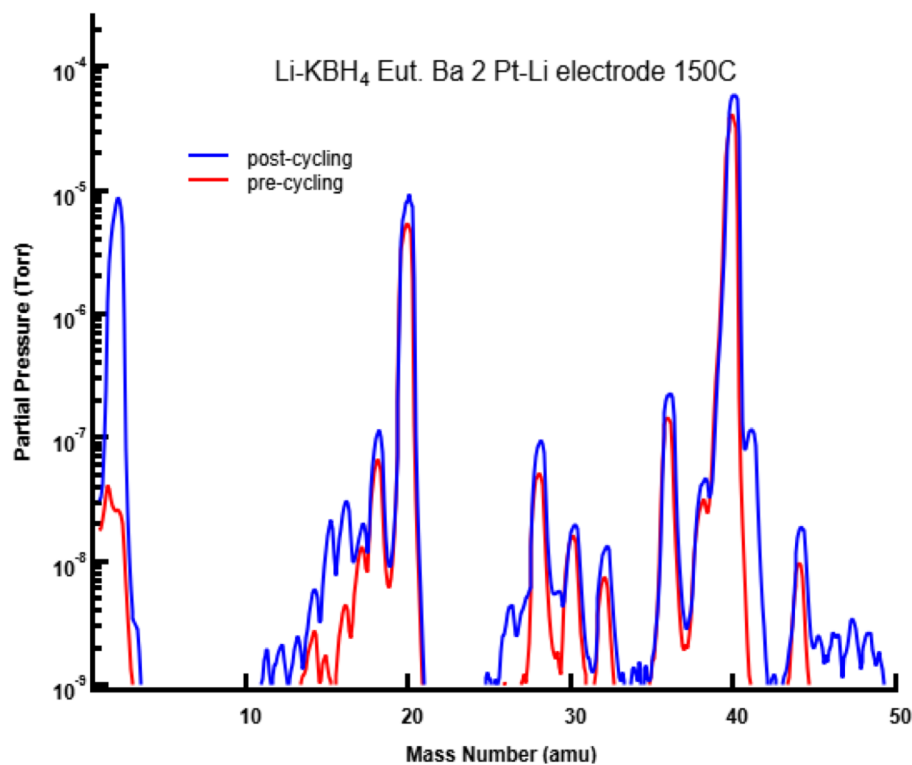
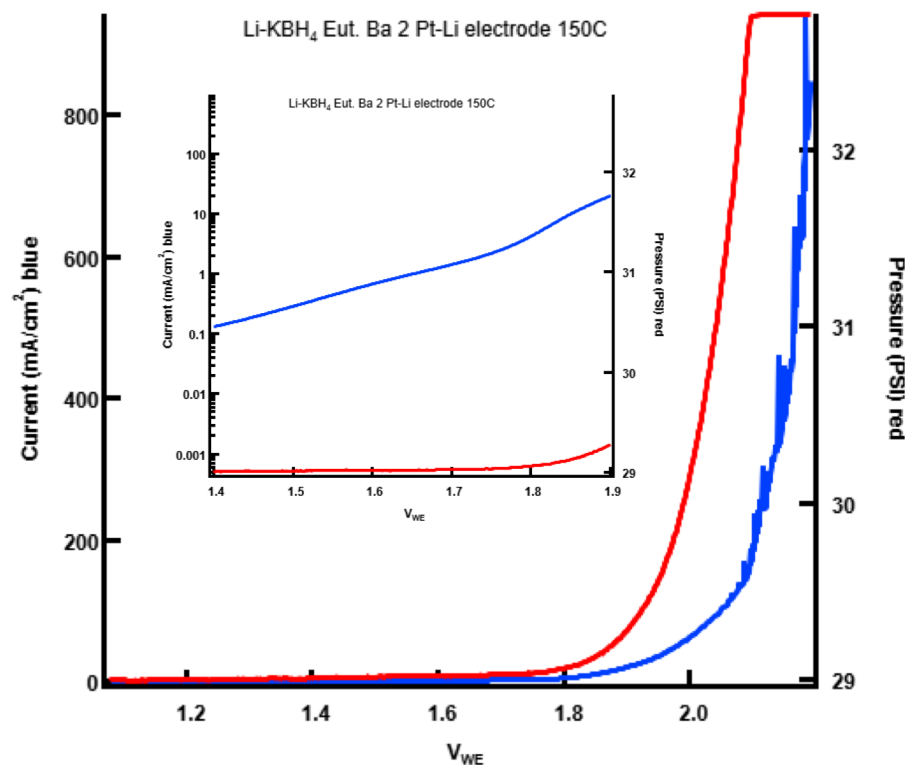
Gas

WE

CE/RE



Li || LiBH₄-KBH₄ Ba₂|| Pt cell, Ar, 150°C



- Linear Sweep Voltammetry shows large increase in current corresponding to a pressure increase
- Post sweep mass spec shows ~300x increase in H₂ partial pressure as well as some diborane
- Indicates possible electrochemical oxidation of BH₄⁻ (forming H₂ and B/BH₃/B₂H₆)



Collaborators



- ▶ Subcontract: HRL Laboratories
- ▶ University: Caltech (Hwang, Solid State/NMR)
- ▶ HyMARC (Stavila: High pressure reversibility in presence of electrolyte).

- Experimentally test Mg amide/LiH and other low temperature systems with electrolyte
- Improve uptake (conversion) of MgB_2 at 350 bar and 300 °C (e.g., catalysts, mechanical milling)
- Identify lower eutectic temperature systems consistent with electrochemical and thermal stability with engineering viability
- Improved electrolyte-to-active material ratio (e.g. alternative eutectics, hydride particle size)
- Demonstrate electrochemically-driven H_2 evolution and cycling from a solid hydride electrode
- 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



Milestone Accomplishments Budget Period 2



Milestone 4.1 (Q2): Hydrogenation pressure reduction. (80%)

Milestone 4.2 (Q3): Hydride/electrolyte formulation optimization. (20%).

Milestone 5.1 (Q1): Written Assessment of ≥ 4 wt% systems. (100%).

Milestone 5.2 (Q3): Empirical assessment for reversible storage of ≥ 4 wt% full material basis gravimetric H₂ capacity with hydrogen cycling under practical conditions. (0%).

Milestone 6.1 (Q2): Initial demonstration of electrochemically promoted hydrogen cycling. (80%).

Milestone 6.2 (Q3): Demonstrate electrochemically promoted hydrogen cycling (both dehydrogenation and rehydrogenation) of ≥ 1 wt% H₂ (materials basis) as determined by RGA of H₂ release during cycling. (0%).

Go/No-go Decision point Budget Period 2 (12 months):

- 1) Demonstrate pathway to ≥ 8 wt% H₂ at ≤ 350 bar pressure and $\leq 300^\circ\text{C}$. $\geq 10 \times$ rate of hydrogen evolution as compared to systems without an electrolyte (100%);
- 2) Demonstrate electrochemical pathway to ≥ 4 wt% H₂



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.

- **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 8 wt% hydrogen uptake (MgB_2) with 50 wt% eutectic at 1000 bar and 320 °C. Demonstrated hydrogen uptake at lower temperatures and pressures (700 bar, 300 °C). Demonstrated >3x increased uptake with catalysts and milling. Preliminary demonstration of electrochemically-driven dehydrogenation of BH_4^-
- **Collaborations:** Caltech (Solid-State NMR), and HyMARC (Sandia)



Reviewer-only slides



Data Management Plan



- **Data Types and Sources:** The data generated during the course of this work will consist of hydrogen evolution assessment based on gas analysis measurements of both thermochemically exothermic and endothermic-based hydride storage reactants in the presence of selected electrolytes. The data will consist specifically of gas evolution quantity as a function of time and possibly temperature. The data will identify the reactant vendors (as is typical for the scientific literature), their relevant quantities and the specific gas constituents (if gases other than hydrogen are evolved) relative to the quantity of reactants and the latter plotted against a time axis in order to validate improved kinetics.
- **Content and Format:** All experimental data will be documented in lab notebooks or collected automatically with automated gas analysis systems using data loggers. The data will be saved in tab delimited ASCII format that will be readable by any text editing software including Excel.
- **Sharing and Preservation:** In addition to reporting and submitting these data to HYMARC, we anticipate publishing the results in a peer-reviewed journal as a means of data dissemination and archival purposes. In addition to plots that appear in journal format, we anticipate that data in ASCII format as noted earlier will be added to any journal article supplement. We do not anticipate any permanent restrictions or limitations on data sharing unless our developments warrant the filing of a provisional patent, after which information will be released to HYMARC with the intent that validation experiments by HYMARC will be performed. We note also that non-proprietary data will be presented at the Annual Merit Review and to the Tech Team at USCAR when scheduled.
- **Protection:** We do not anticipate any confidentiality or personal privacy issues during the course of this work that have not already been addressed by Liox working on prior Dept. of Energy grants. In addition to the non-disclosure agreement with HYMARC, we anticipate that our effort, where additives to standard electrolytes are used, will be the subject of provisional patents that will be filed by Liox upon validation of results of relevance/significance to this effort.
- The DMP outlined above addresses the most critical aspect of data dissemination through the use of reporting of findings in peer reviewed publications and through oral presentations at the Program's Annual Merit Review and USCAR Tech Team. These presentation means offer the greatest conveyances for making available the findings to be discerned through this effort, that will be critical if the limitations of solid state hydrogen storage in hydride destabilization and/or complex hydride reactions that require activation barriers associated with solid state diffusion are to be overcome in identifying a practical hydrogen storage system.