
HyMARC Seedling: Electrolyte-Assisted Hydrogen Storage Reactions

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Overall Objectives

- Address critical deficiencies of hydrogen storage systems design based on hydride materials, as determined by the Hydrogen Storage Engineering Center of Excellence (HSECoE).
- Obviate the need for high-temperature release of hydrogen in complex hydride and destabilization reactions through electrolyte use.
- Demonstrate a 10× improvement in dehydrogenation kinetics.

Fiscal Year (FY) 2019 Objectives

- Build from proof-of-concept results for electrolyte use in previous FYs on the Mg-B-H or similar system to achieve a full material gravimetric density of ≥ 8 wt % while maintaining the previously reported kinetic improvements with reduced electrolyte loading and cycling at ≤ 350 bar, $\leq 300^\circ\text{C}$ hydrogenation, and $\leq 350^\circ\text{C}$ dehydrogenation.

- Survey and assess promising systems with ≥ 4 wt % full material density capable of cycling at ≤ 100 bar and $\leq 150^\circ\text{C}$ 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.
- 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.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration (MYRDD) Plan¹, with sub-listings from Technical Task Description Table 3.3.8:

- (O) Lack of Understanding of Hydrogen Physisorption and Chemisorption
 - Determine the decomposition pathways and products of materials to understand their mechanisms and kinetics better.
 - Determine the hydrogen 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.

Technical Targets

While we note the system targets from the Hydrogen Storage section of the Fuel Cell Technologies Office MYRDD Plan in Table 1, this project is conducting fundamental studies on the role of enhanced kinetics through the use of electrolyte-assisted

¹ <https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22>

hydrogenation/dehydrogenation on complex hydride and destabilization hydride reactions. While the systems being studied, at least on a materials basis, show capacities in excess of system targets for volumetric and gravimetric densities, the kinetics required for hydrogenation/dehydrogenation are too slow under technologically relevant temperatures. Our effort explores the improvement in kinetics with the aim of nearing thermodynamic temperatures for relevant materials systems:

FY 2019 Accomplishments

- Demonstrated conversion of MgB_2 to $Mg(BH_4)_2$ at ~350 bar, 320°C in the presence

of electrolytes (compared to the FY 2018 result of 1000 bar at 320°C).

- Achieved three cycles of hydrogenation/dehydrogenation at >4 wt % hydrogen on a hydride-only basis and a favorable assessment for >4 wt % hydrogen on a total material basis using $NaAlH_4$ in the presence of diglyme electrolyte, with dehydrogenation at a maximum temperature of 150°C and hydrogenation at low temperature and pressure (75°C, 50 bar). These results satisfy a sufficient Go/No-Go Decision Point for proceeding to Phase 3.
- Demonstrated electrochemically-driven dehydrogenation reaction.

Table 1. Technical System Targets: Onboard Hydrogen Storage for Light-Duty Fuel Cell Vehicles

Storage Parameter	Units	DOE 2020	Project Status
System Gravimetric Capacity Usable, specific energy from hydrogen (net useful energy/max system mass)	kWh/kg (kg H_2 /kg) system	1.8 0.055	TBD
System Volumetric Capacity Usable energy density from hydrogen (net useful energy/max system volume)	kWh/l (kg H_2 /l) system	1.3 (0.040)	TBD
Charging/Discharging Rates System fill time (5 kg)	min	3.3	TBD

INTRODUCTION

The goal of this project is to address critical deficiencies of hydrogen storage systems design based on hydride materials, as originally identified by the DOE Hydrogen Storage Engineering Center of Excellence (HSECoE). Baseline hydrogen storage technology presently relies on compressed gas operating at ~700 bar pressure, which imposes huge demands on fuel delivery, fuel storage, and system cost. For onboard storage applications, Type IV composite overwrapped pressure vessels and associated balance-of-plant components are necessary to ensure safe and effective fuel delivery. However, such compressed gas technology falls well-short of volumetric targets even at 700 bar, given the density of gaseous molecular hydrogen is only 40 g· H_2 /l at ambient temperatures. One alternative is to utilize hydride materials that accommodate hydrogen in an atomic form. Certain hydrides can attain volumetric densities that exceed the density of liquid hydrogen (71 g· H_2 /l) while also offering advantageous thermodynamic properties. However, such material systems presently rely on solid-state diffusion for hydrogen release, which has a very high activation barrier for atom mobility and, thus, requires impractically high temperatures for operation.

APPROACH

The initial focus of our research effort is to employ and demonstrate an electrolyte system to mediate the diffusion of species at lower temperatures relevant to transportation applications, with the goal of establishing the critical factors necessary to obviate the need for high-temperature release of hydrogen. A parallel goal of this exploratory effort is to determine the effectiveness of modest electrochemical potentials in overcoming any endothermic requirements for hydrogen release in a similar electrolyte-promoted scenario.

The FY18 report described initial results using MgB_2 , where cycling (hydrogen uptake, one cycle) of up to 8.1 wt % on a hydride mass basis (~4.1 wt % on a full-material mass basis) was achieved using a Li/K/CsI eutectic electrolyte. In addition, using a Li/ KBH_4 eutectic, uptake of ~6 wt % hydrogen on a hydride mass basis (~2.7 wt % on a full-material mass basis) was shown. Utilizations are approximately 20x greater than for samples

without electrolytes under the same conditions. We also showed for the first time nearly complete reversibility, including dehydrogenation, high-pressure rehydrogenation, and 2nd cycle dehydrogenation, of ~2 wt % (hydride mass basis) for MgH_2/Sn with a Li/KBH_4 eutectic electrolyte. In all cases, rates of >10x hydrogen evolution as compared to systems without an electrolyte were observed. Hence, the utility of our electrolyte approach was demonstrated in FY18, and our FY19 results described below build from this.

RESULTS

Hydrogenation of MgB_2 under lower-pressure conditions in the presence of an electrolyte

A laboratory setup was established at Liox, whereby hydrogen pressures of up to ~400 bar could be achieved, and this was used to hydrogenate MgB_2 at 350 bar and 320°C in the presence of $\text{Li}/\text{K}/\text{CsI}$ eutectic electrolyte and TiCl_3 catalyst. ^{11}B solid-state NMR spectroscopy (Figure 1) indicated that up to 14 % $\text{Mg}(\text{BH}_4)_2$ equivalent was formed under these conditions, which compares very well with the results obtained with electrolyte under much higher pressure conditions in the FY18 work.

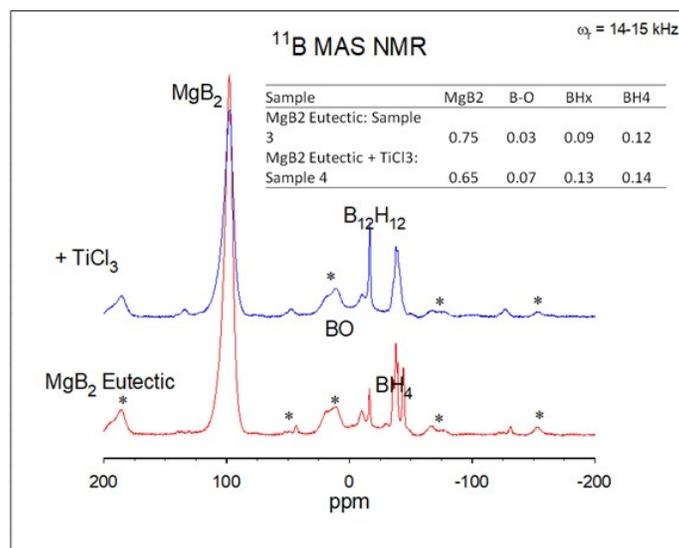


Figure 1: ^{11}B solid-state NMR data for hydrogenation of MgB_2 at 350 bar hydrogen in the presence of $\text{Li}/\text{K}/\text{CsI}$ eutectic electrolyte.

Low temperature and low-pressure cycling of NaAlH_4 in the presence of electrolyte

We prepared sodium alanate active material by milling NaAlH_4 with 3 mol % TiCl_3 (this is known to produce 3 mol % TiAl_x , which is catalytically-active to aid dehydrogenation). This was mixed with diglyme at 50/50 wt % and tested compared to a control NaAlH_4 material that did not comprise electrolyte, using a maximum temperature for hydrogen desorption of 150°C (Figure 2, left). This clearly shows the improved performance of the NaAlH_4 /diglyme material system across three cycles. The electrolyte-treated sample starts to desorb H_2 at a lower temperature than the control, and although the kinetics are complicated (a 2-step process with an induction period evident for desorption from the intermediate Na_3AlH_6 phase), the electrolyte-treated sample evidently demonstrates >4 wt % capacity with desorption rates >1 wt %/hr up to 150°C, in stark contrast to the control. Figure 2 (right) indicates the hydrogenation profiles used to treat the sample before the second and third desorption cycles (data for the electrolyte-treated sample shown). We used a maximum temperature of 75°C and pressures from 100 bar (1st hydrogenation) to 50 bar (second hydrogenation). This shows that the electrolyte-treated sample of NaAlH_4 can be re-hydrogenated at 75°C at pressures as low as 50 bar; both 100 bar- and 50 bar-treatments resulted in similar hydrogen uptake (~4 wt %) although the latter was slower, as might be expected. The control sample did not hydrogenate fully under these conditions, and hence the hydrogen-desorption capacity exhibited in cycles two and three is reduced accordingly (Figure 2, left). Thus, we conclude that the presence of electrolyte improves both hydrogenation and dehydrogenation performance.

Note, the control sample can be completely re-hydrogenated at 130°C, 100 bar; its increasingly-poorer capacity in Figure 2 (left) reflects the re-hydrogenation conditions used.

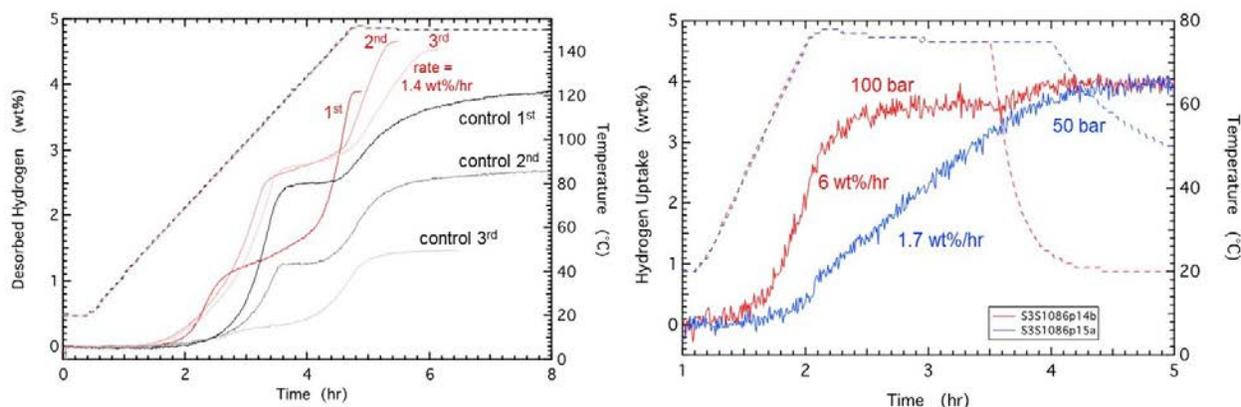


Figure 2: (left) Hydrogen desorption from 50/50 wt % NaAlH₄/diglyme (red, solid line) and NaAlH₄ control samples (black, solid line) across three cycles. Re-hydrogenation steps are discussed above; note that both NaAlH₄ materials were pre-filled with 3 mol % TiCl₃. Corresponding temperature profiles are indicated by the dashed lines. (right) Hydrogen uptake for the 50/50 wt % NaAlH₄/diglyme sample at the 1st hydrogenation step under 100 bar pressure for 90 minutes (red, solid line) and the second hydrogenation at 50 bar for 120 minutes (blue, solid line); both cycles were performed at 75°C (dashed lines).

Hence, we believe that we have established that our electrolyte-incorporation approach can enable reversible cycling of >4 wt % hydride material basis (excluding electrolyte) storage capacity at temperatures ≤150°C (desorption)/75°C (adsorption) under pressures as low as 50 bar hydrogen, successfully meeting the Go/No-Go criterion.

Electrochemically-assisted dehydrogenation

We have demonstrated a proof-of-concept dehydrogenation of LiBH₄ in an electrochemical cell in the presence of liquid electrolytes at room temperature (Figure 3). This remains a work-in-progress, and further results will be outlined in future reports.

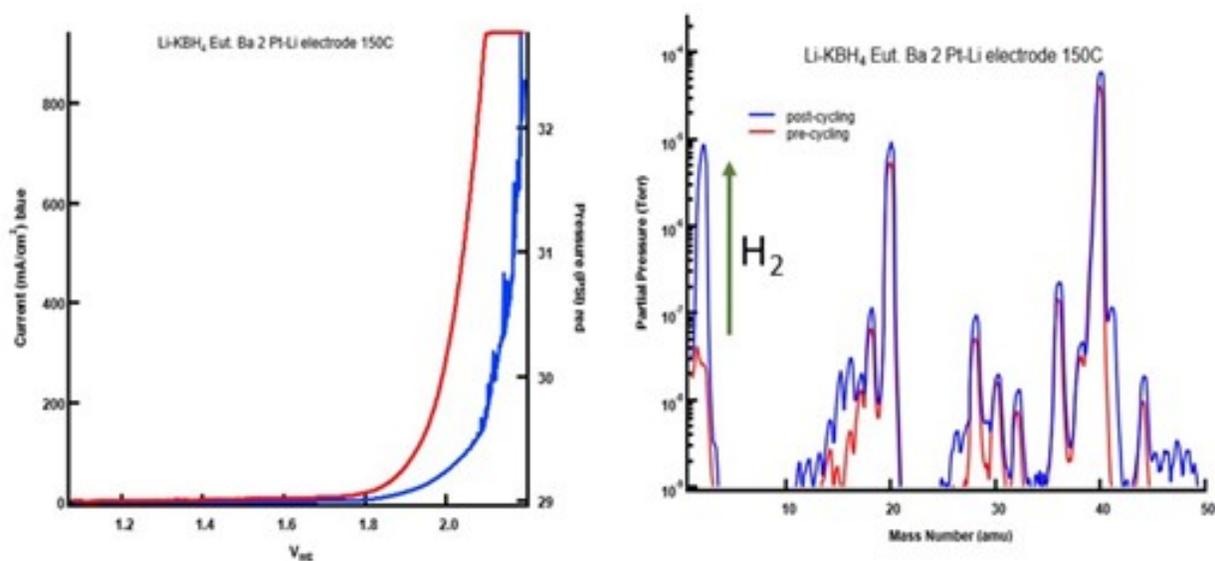


Figure 3: (left) Linear sweep voltammetry of Li electrode in LiBH₄/KBH₄ eutectic electrolyte at 150°C shows an increase in current concomitant with an increase in pressure measured by mass spectrometry (right) that indicates the electrochemically-assisted generation of hydrogen. Diborane was also detected in the mass spectrum.

CONCLUSIONS AND UPCOMING ACTIVITIES

Our electrolyte-assisted concept continues to demonstrate benefits in terms of lowering the temperature/pressure conditions required to enable hydrogenation and dehydrogenation reactions. In the case of NaAlH₄ with diglyme electrolyte, this has enabled reversible cycling of >4 wt % on a hydride-only basis at temperatures ≤150°C (desorption)/75°C (adsorption) at pressures as low as 50 bar hydrogen. Immediate tasks for the remainder of Budget Period 2 of the Phase 2 effort will include:

- Further lowering the pressure and temperature required for conversion of MgB₂/MgBH₄
- Characterizing the behavior of other materials capable of meeting the 4 wt % target at <150°C such as amide/imide systems with diglyme electrolyte
- Continued assessment of electrochemically-assisted hydrogenation/dehydrogenation reactions
- Integrating metrics from our demonstrated NaAlH₄ system into a system-level model, in collaboration with HyMARC partners at PNNL.

SPECIAL RECOGNITIONS AND AWARDS/PATENTS ISSUED

1. “Electrolyte-Assisted Hydrogen Storage Reactions” paper described below highlighted as the inside cover image for the issue of *J. Phys. Chem. C* in which it was published.

FY 2019 PUBLICATIONS/PRESENTATIONS

1. J. J. Vajo, H. Tan, C. C. Ahn, D. Addison, S. Hwang, J. L. White, T. C. Wang, V. Stavila, J. Graetz, “Electrolyte-Assisted Hydrogen Storage Reactions,” *J. Phys. Chem. C*, 122 (2018): 26845-26850.
2. J. Graetz, “HyMARC Seedling: Electrolyte Assisted Hydrogen Storage Reactions,” ST137, presented at the 2019 DOE Hydrogen and Fuel Cells Annual Merit Review, Washington DC, May 1, 2019.
3. J. J. Vajo, “HyMARC Seedling: Electrolyte Assisted Hydrogen Storage Reactions,” presented to the Storage Tech Team, Southfield, MI, September 19, 2019.

REFERENCES

1. Lennie E. Klebanoff and Jay O. Keller, “5 Years of Hydrogen Storage Research in the U.S. DOE Metal Hydride Center of Excellence (MHCoe),” *International Journal of Hydrogen Energy* 38 (2013): 4533–76.