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# HyMARC Seedling: Electrolyte-Assisted Hydrogen Storage Reactions

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HRL Laboratories, LLC, Malibu, CA

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Project End Date: June 19, 2018 (Phase 1)

## 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) 2018 Objectives

- Survey electrolytes to determine thermal and electrochemical stability, ionic conductivity, solubility (salt and hydrogen), and vapor pressure.
- Demonstrate electrolyte-assisted hydrogen evolution based on  $\text{Li}^+$  and/or  $\text{Mg}^{2+}$  cations (or other) storage materials.

- Demonstrate electrolyte-assisted reversible hydrogen uptake based on  $\text{Li}^+$  and/or  $\text{Mg}^{2+}$  cations with endothermic hydrogen evolution.

## 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 Plan,<sup>1</sup> 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 better understand their mechanisms and kinetics.
  - 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 Multi-Year Research, Development, and Demonstration Plan in Table 1, this project is conducting fundamental studies on the role of enhanced kinetics through the use of electrolyte-assisted 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

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

of nearing thermodynamic temperatures for relevant materials systems.

### FY 2018 Accomplishments

- Demonstrated 10× dehydrogenation kinetic improvement using electrolyte over non-electrolyte-containing samples: MgH<sub>2</sub>/Sn with Li/K-BH<sub>4</sub> eutectic, Mg(BH<sub>4</sub>)<sub>2</sub> with Li/K-BH<sub>4</sub> eutectic, MgH<sub>2</sub>/Si with Li/K/Cs-I ternary.
- Demonstrated rehydrogenation (at Sandia National Laboratories) of ≈2% in dehydrogenated MgH<sub>2</sub>/Sn in Li/K-BH<sub>4</sub> electrolyte-containing sample as compared to likely no (or very little) rehydrogenation of dehydrogenated MgH<sub>2</sub>/Sn containing no electrolyte under the same rehydrogenation conditions (1,000 bar).
- Demonstrated significant hydrogenation (6.3 wt%) of MgB<sub>2</sub> with electrolyte after Sandia hydrogenation and negligible hydrogenation (0.22 wt%) without eutectic (25× improvement).

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

Storage Parameter	Units	DOE 2020	Project Status
<b>System Gravimetric Capacity</b> Usable, specific energy from hydrogen (net useful energy/max system mass)	kWh/kg (kg H <sub>2</sub> /kg system)	1.8 0.055	TBD
<b>System Volumetric Capacity</b> Usable energy density from hydrogen (net useful energy/max system volume)	kWh/L (kg H <sub>2</sub> /L) system	1.3 (0.040)	TBD
<b>Charging/Discharging Rates</b> System fill time (5 kg)	min	3.3	TBD

TBD – to be determined

## INTRODUCTION

State-of-the-art hydrogen storage material studies supported by DOE-funded projects have included complex hydrides and destabilized systems, both of which typically involve multiple solid phases [1]. While these materials can exhibit high hydrogen densities and tunable thermodynamic properties, the rates of hydrogen exchange (i.e., the rates of dehydrogenation and rehydrogenation) are too kinetically limited for relevant applications. These limitations occur in part because multiple component materials are typically formulated as solid-state powder mixtures where reaction between the phases can only take place across solid-solid interfaces where particles are in direct atomic-scale contact. Nanoscale engineering, using mechanical milling or templates, and additives or catalysts have been employed to increase reaction rates by decreasing diffusion distances and increasing interfacial contact area and mobility. While significant kinetic improvements have been achieved and are still undergoing refinement, they have thus far been insufficient for practical applications.

## APPROACH

Given the interface-controlled processes of solid-state destabilization reactions that normally require thermal activation, we have defined a free energy difference that needs to be overcome before any relevant transformation or reaction can take place. Noting the difference between the effective empirically determined temperature required to promote a reaction in comparison to what might be expected on a purely thermodynamic basis, we note that the free energy barrier is typically >20 kJ. However, in so-called electrochemical conversion battery reactions that involve diffusing species in an electrolyte, the activation barrier has been observed to be as low as 4 kJ. Given the similarity of compounds used in both electrochemical and hydrogen storage reactions, the expectation is that the use of electrolytes will help lower the free energy barrier height by promoting solubilization of the diffusing species so that reactions are no longer controlled by limited interfacial areas.

Electrolytes under consideration for this effort will ultimately require redox stability, low vapor pressure, high hydrogen permeability, and relatively low mass and volume with respect to the reacting species. Our effort is aimed at evaluating and testing electrolyte suitability to enhance hydrogen storage material reaction kinetics.

## RESULTS

### 10× Desorption Kinetic Improvement in the Mg/Si System

In fulfillment of the Phase 1 go/no-go requirements of this effort, we have demonstrated a 10× improvement in desorption kinetics in the Mg/Si destabilization system through the use of a ternary iodide salt, using an identical temperature ramp (setpoint). Data for this system is shown in Figure 1. The arrows in the plot indicate the point at which an identical 3.5 wt% desorption is achieved. In the case of the “neat” reaction in the absence of our electrolyte salt, the time required is 70 h, whereas when the electrolyte is added, the same desorption yield is achieved in 7 h.

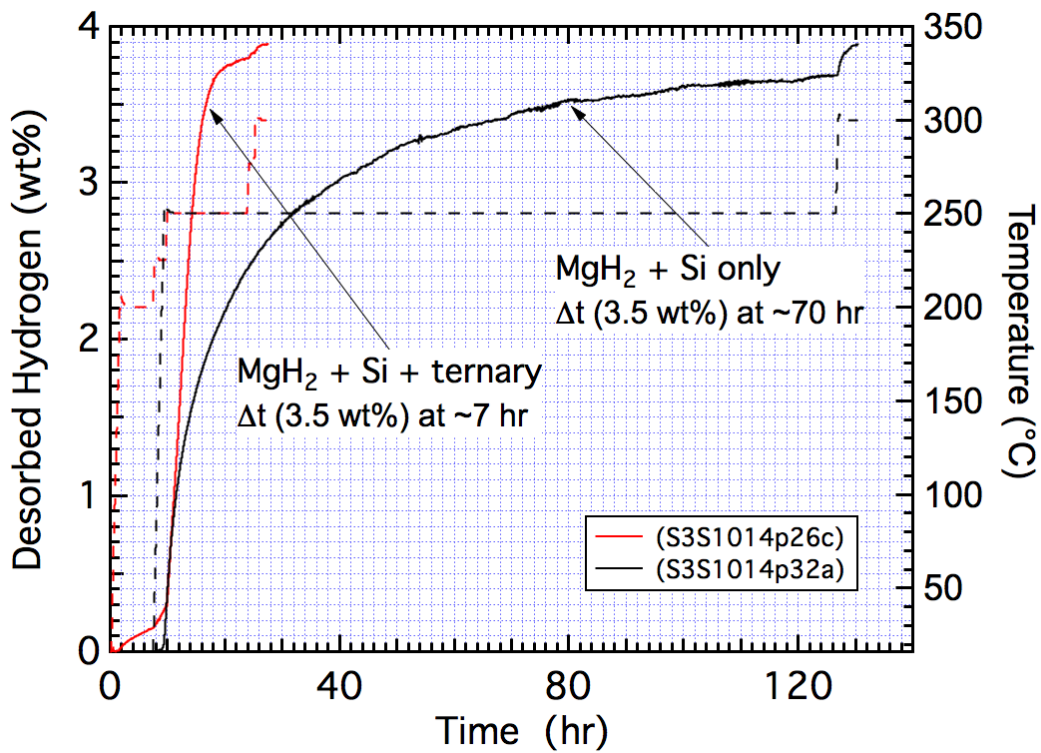


Figure 1. Hydrogen desorption as a function of time for the temperature ramps as indicated by the dotted traces. The use of an iodide ternary salt improves desorption kinetics by 10x.

### 10× Desorption Kinetic Improvement in the Mg/Sn System

Similar desorption kinetic improvement is seen in the Mg/Sn system at 150°C, in this case using a borohydride eutectic electrolyte. The plots demonstrating this improvement are shown in Figure 2. While higher temperatures with a somewhat lower improvement are required for more complete dehydrogenation of this destabilization system, clear kinetic improvements can be discerned. In addition, complete rehydrogenation of this system in the presence of an electrolyte was achieved, we believe for the first time, in the MgH<sub>2</sub>/(Si or Sn) destabilization system as reported at the 2018 Storage Tech Team Meeting (Southfield, Michigan, Sept. 12, 2018).

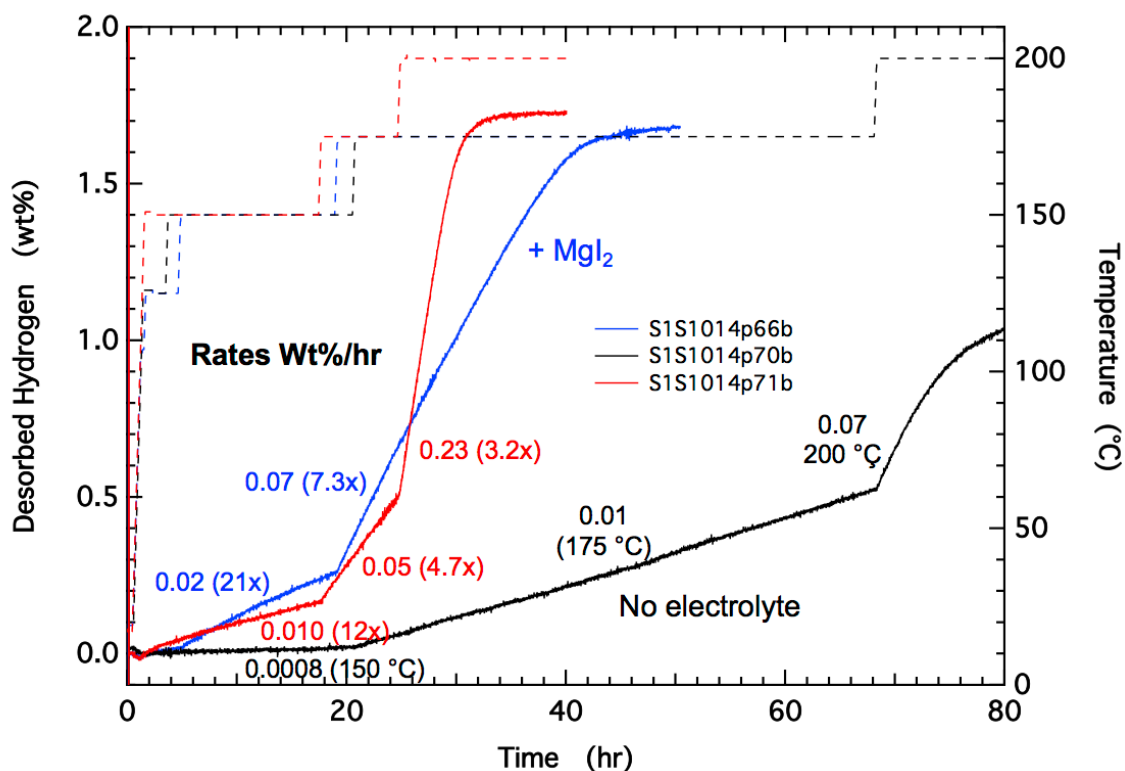


Figure 2. Hydrogen desorption in the Mg/Sn system in the presence of a borohydride electrolyte showing improved kinetics over the range of desorption temperatures. For this effort the addition of  $MgI_2$  appeared to further improve desorption kinetics.

### 10× Desorption Kinetic Improvement in the $Mg(BH_4)_2$ System

The use of a borohydride electrolyte also improved the kinetics of desorption in the  $Mg(BH_4)_2$  system as shown in Figure 3. The temperature maximum used in this case is  $225^\circ\text{C}$  (we note that  $>350^\circ\text{C}$  is required to fully dehydrogenate this compound). This particular system will be studied further as the borohydride electrolyte might also be a source of desorbed hydrogen. Nonetheless, clear differences between the “neat” compound and the use of borohydride additives greatly improve the yield in this system. We note also that from prior differential scanning calorimetry work performed in 2017, no obvious dehydrogenation of the eutectic could be seen, and the eutectic was stable to three cycles.

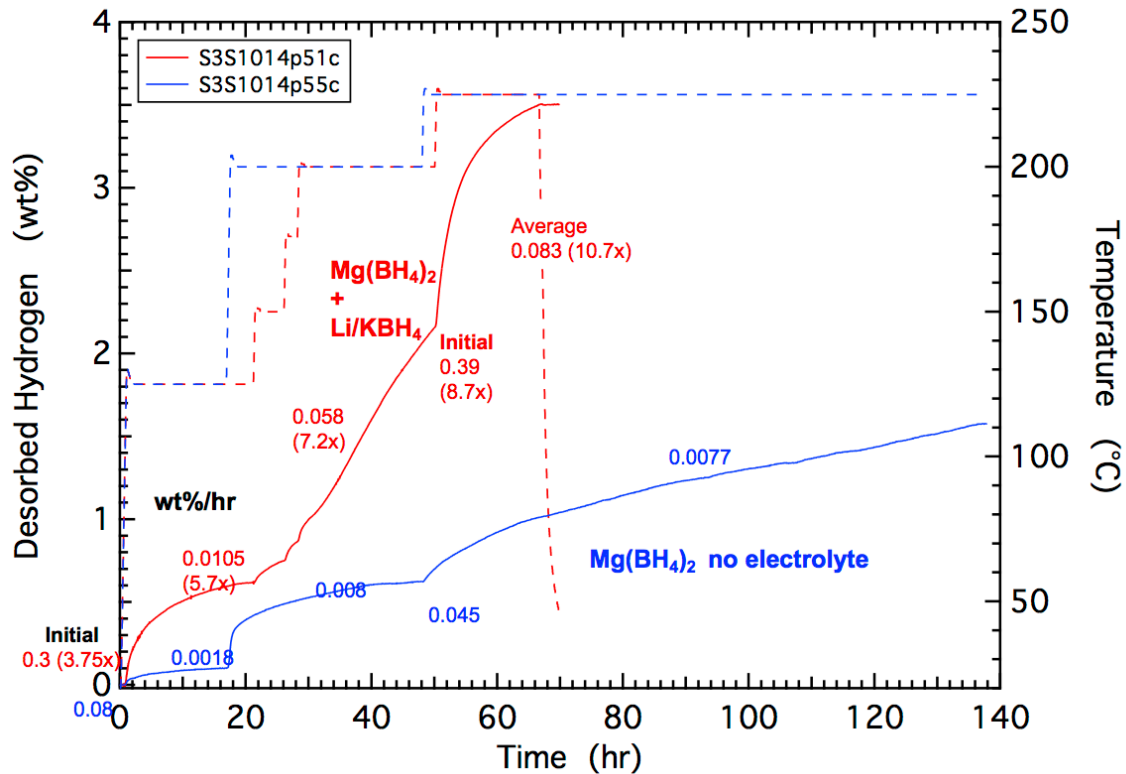


Figure 3. Desorbed hydrogen from the  $\text{Mg}(\text{BH}_4)_2$  compound with (red) and without (blue) a borohydride electrolyte. The final temperature for these traces of  $225^\circ\text{C}$  is below the  $>350^\circ\text{C}$  temperature necessary for complete dehydrogenation.

#### Confirmation of the Conversion of $\text{MgB}_2 \rightarrow \text{Mg}(\text{BH}_4)_2$ System Using an Iodide Electrolyte

With the help of Vitalie Stavila at Sandia National Laboratories, hydrogenation of  $\text{MgB}_2$  both with and without an iodide electrolyte was performed using 1,000 bar pressure at  $320^\circ\text{C}$  over 50 h. Subsequent dehydrogenation of these samples showed significant hydrogenation (6.3 wt%) using the electrolyte, whereas negligible (0.22 wt%) hydrogenation occurred in the absence of an electrolyte. Nuclear magnetic resonance spectroscopy was used to confirm the Sieverts results, and traces of the eutectic-containing sample before and after hydrogenation treatment are shown in Figure 4.

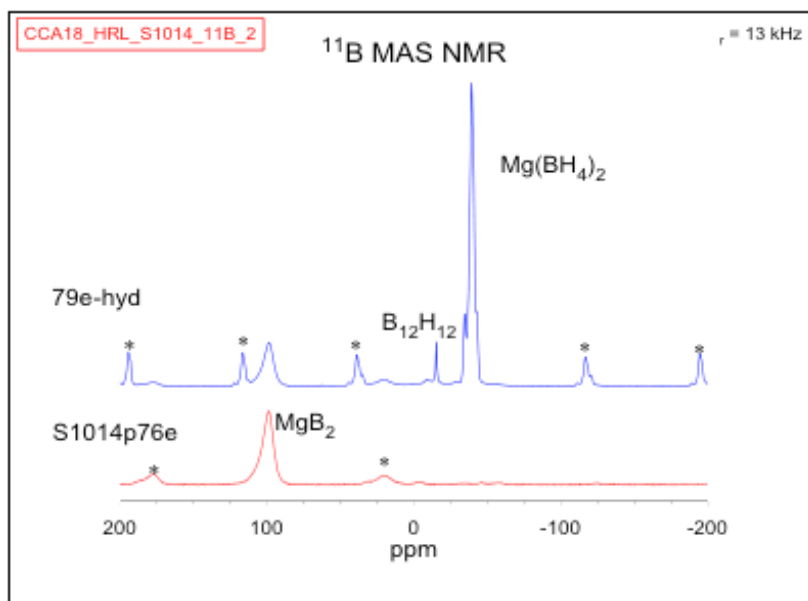


Figure 4.  $^{11}\text{B}$  NMR confirmation of  $\text{MgB}_2 \rightarrow \text{Mg}(\text{BH}_4)_2$  conversion comparing  $\text{MgB}_2$  before hydrogenation (red trace) and after hydrogenation (blue trace) in the presence of an iodide eutectic. We note that there was little uptake without the eutectic.

## PHASE 1 CONCLUSIONS AND UPCOMING ACTIVITIES FOR PHASE 2

Given our success in achieving a  $10\times$  kinetic improvement with the  $\text{MgH}_2/(\text{Si}$  and  $\text{Sn})$  destabilization reaction and kinetic improvement of the  $\text{Mg}(\text{BH}_4)_2$  compound through the use of electrolytes, solubilization of the reactant phases has enabled fulfillment of the go/no-go requirements for Phase 1 of this effort, which ended in June 2018.

Immediate tasks for Budget Period 2 of the Phase 2 effort will consist of:

- Lowering the temperature and pressure required for hydrogenation of  $\text{MgB}_2$  and the dehydrogenation of  $\text{Mg}(\text{BH}_4)_2$  or other systems (capable of  $\geq 8$  wt% hydrogen on a full material basis).
- Application of electrolyte assist to practical systems (capable of  $\geq 4$  wt% hydrogen on a full material basis).
- Demonstration of electrochemically promoted hydrogen cycling.

## SPECIAL RECOGNITIONS & AWARDS/PATENTS ISSUED

1. Patent Invention Disclosure: “Hydrogen storage material formulations containing electrolytes,” filed June 1, 2017.

## FY 2018 PUBLICATIONS/PRESENTATIONS

1. Channing Ahn, “HyMARC Seedling: Electrolyte Assisted Hydrogen Storage Reactions,” ST137, presented at the 2018 DOE Hydrogen and Fuel Cells Annual Merit Review, Washington DC, June 14, 2018.
2. Channing Ahn, “HyMARC Seedling: Electrolyte Assisted Hydrogen Storage Reactions,” presented to the Storage Tech Team, Southfield, MI, September 12, 2018.

## 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.