

IV.C.7 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 an improvement in dehydrogenation kinetics by 10X.

Fiscal Year (FY) 2017 Objectives

- Survey of electrolytes to determine thermal and electrochemical stability, ionic conductivity, solubility (salt and H₂), and vapor pressure.
- Demonstrate electrolyte assisted hydrogen evolution based on Li⁺ and/or Mg²⁺ cations (or other) storage materials.
- Demonstrate electrolyte assisted reversible hydrogen uptake based on Li⁺ and/or Mg²⁺ cations with endothermic H₂ evolution.

Technical Barriers

This project addresses the following technical barriers from the 2015 Hydrogen Storage section (3.3) of the Fuel Cell Technologies Office Multi-Year Research, Development, and

Demonstration Plan with sub listings from the Technical Task Description Table 3.3.8.

- (O) Lack of Understanding of Hydrogen Physisorption and Chemisorption.
 - Decomposition pathways and products of materials to better understand their mechanisms and kinetics.
 - H₂ 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

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 H ₂ (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 H ₂ (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

TBD – to be determined

While we note the system targets listed above from the DOE 2015 Multi-Year Research, Development, and Demonstration Plan hydrogen storage section, 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 of nearing thermodynamic temperatures for relevant materials systems.

FY 2017 Accomplishments

- Analysis of di-, tri- and tetraglyme solvent stability for use with Mg(BH₄)₂ using gas chromatography-mass

spectrometry at ambient and 80°C temperatures. This technique for solvent decomposition analysis is more sensitive than nuclear magnetic resonance.

- Residual gas analysis (RGA) from ambient to 200°C at modestly high Ar pressures (to suppress solvent boiling) of the same systems in order to evaluate specific decomposition products showing dimethyl ether product.
- 10X enhanced kinetics of the $\text{MgH}_2 + \text{Si}$ destabilization reaction using a eutectic molten iodide salt of Li-K-CsI that has a 210°C melting temperature for equimolar composition.



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 materials reaction kinetics.

RESULTS

Solvent Stability Results with $\text{Mg}(\text{BH}_4)_2$

Initial results from HRL on the use of diglyme with $\text{Mg}(\text{BH}_4)_2$ showed evidence of gas release but with some uncertainty over the relative level of hydrogen with possible solvent decomposition products. With the official start of this effort and Liox's several unique analytical capabilities for gas analysis that were developed as part of its electrolyte studies since 2009, both gas chromatography-mass spectrometry and RGA analyses were used to re-examine glyme- $\text{Mg}(\text{BH}_4)_2$ reactions.

To obviate the possibility of water reactions, di-, tri and tetraglyme solvents were initially analyzed using a Karl Fischer titration, to assess and reduce the quantity of water to below the 10 ppm level. These solvents were then used to determine the extent of reactivity or decomposition.

Cell pressure and RGA data for tetraglyme with $\text{Mg}(\text{BH}_4)_2$ are presented in Figures 1 and 2 and were evaluated due to the higher boiling point of this solvent, with the anticipation that it might show a higher level of stability against decomposition. Using the unique RGA

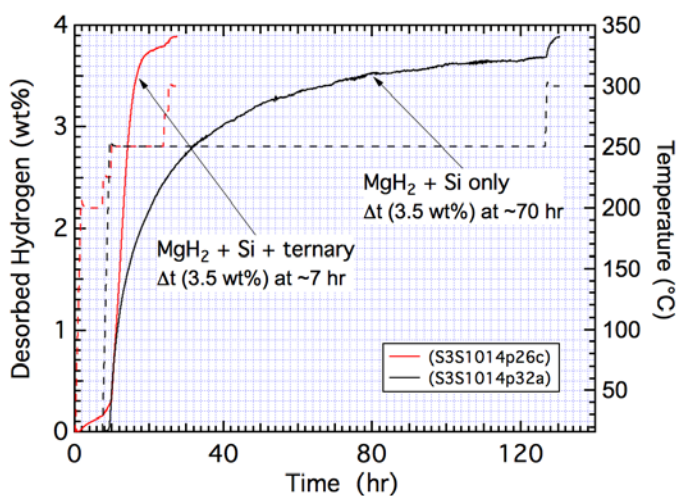


FIGURE 1. Cell pressure vs time for a cell containing $\text{Mg}(\text{BH}_4)_2$ with tetraglyme. Gas was extracted at dips and points indicated by the arrows and gas analysis data from these points is presented in Figure 2.

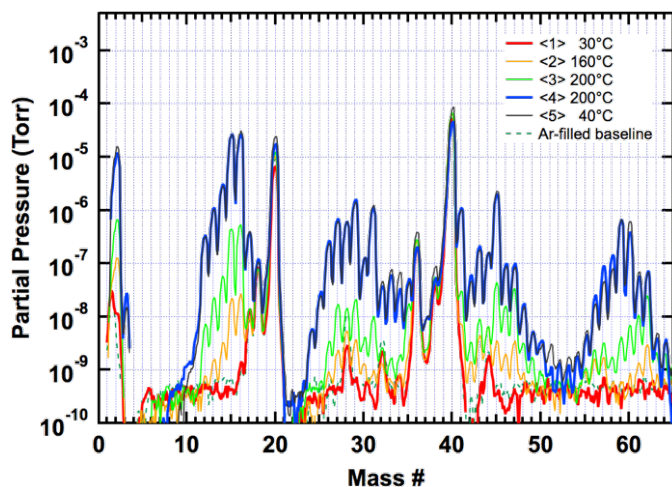


FIGURE 2. RGA data for points indicated from the gas extraction points shown in Figure 1. Decomposition to dimethyl ether (RGA peaks at mass numbers 13–15, 29–31, 45–46) is indicated, in addition to hydrogen evolution when tetraglyme is added to $\text{Mg}(\text{BH}_4)_2$. These peaks do not appear in the RGA in the absence of $\text{Mg}(\text{BH}_4)_2$.

instrumentation at Liox for determining gas compositions we determined that solvent decomposition does occur in the presence of $\text{Mg}(\text{BH}_4)_2$. Dips in the pressure data of Figure 1 indicated points where gas was extracted for the RGA analysis. Figure 2 shows the RGA plot for gas extraction times and temperatures from Figure 1. We note that the dimethyl ether reaction product peaks do not appear in the RGA in the absence of $\text{Mg}(\text{BH}_4)_2$. Similar results for di- and triglyme and hexamethylphosphoramide were presented in the ST137 Annual Merit Review 2017 presentation for this project.

Eutectic Molten Salt Analyses

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

We have used iodide salts of Li, K and Cs in an attempt to find a low temperature eutectic (melting) point composition to probe for the effectiveness of these salts in improving the kinetics of dehydrogenation. Binary phase diagram data for these iodides are available for the most part from computed values so an initial identification of an equimolar ternary melting point was determined by calorimetry and is shown in Figure 3.

To test for the effectiveness of this mixture in promoting kinetics, an equimolar salt ternary was combined with the MgH_2+Si destabilization reaction system and a comparison of this reaction with and without the ternary is shown in Figure 4.

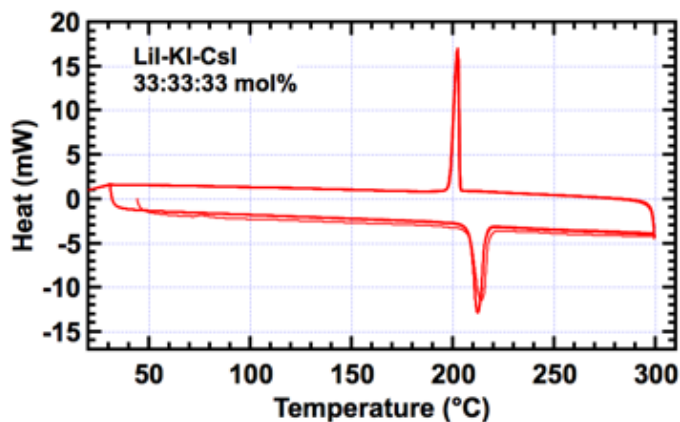


FIGURE 3. Differential scanning calorimetry trace of the ternary mixture of LiI, KI and CsI salts indicating a melting point of $\sim 210^\circ\text{C}$. A different composition based on tie-line analysis of the binary phase diagrams was performed but yielded the same melting temperature.

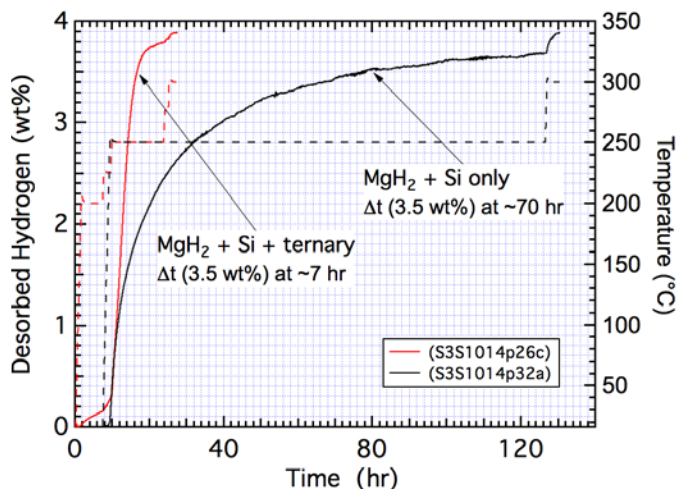


FIGURE 4. 10X improvement in dehydrogenation kinetics of MgH_2+Si in the presence of a ternary LiI:NaI:KI eutectic compared to no eutectic is shown for the neat reaction shown in the black trace in comparison to the reaction in the presence of the ternary shown in the red trace.

The fall-off in the “neat” reaction shown in the black trace of Figure 4 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. The ~ 10 -fold increase in kinetics demonstrated here in the presence of the ternary under these conditions points to the effectiveness of the iodide ternary in promoting the dehydrogenation of this system.

We have also examined the possibility of a $\text{LiBH}_4-\text{KBH}_4$ binary eutectic that has a melting point of $\sim 105^\circ\text{C}$ and anticipate other low temperature eutectic systems suitable

for fulfilling all of the electrolyte requirements that include (a) redox stability, (b) low vapor pressure, (c) suitable hydrogen gas exchange and transport, and (d) minimal weight and volume.

CONCLUSIONS AND UPCOMING ACTIVITIES FOR PHASE 1

Given our success in achieving a 10X kinetic improvement with the MgH_2+Si destabilization reaction through the use of an iodide salt ternary electrolyte, it appears that the electrolyte has provided the means necessary to solubilize the reactant phases.

- While the melting temperatures for the iodide ternary are still too high for applications, the observation of kinetic improvement suggests that our approach of electrolyte use provides a pathway for practical implementation.
- With existing funding, we plan to evaluate other systems using electrolytes that have lower melting temperatures that fall within the range of values where reactions are expected on the basis of equilibrium thermodynamic values.
- While the ternary iodide salt had a melting point of $\sim 210^\circ\text{C}$, we have already determined other systems with melting temperatures $< 110^\circ\text{C}$ and are poised to use these in systems where the kinetics under thermodynamic equilibrium conditions will benefit from electrolyte use.

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

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

FY 2017 PUBLICATIONS/PRESENTATIONS

1. Channing Ahn, “HyMARC Seedling: Electrolyte Assisted Hydrogen Storage Reactions,” ST137, presented at the 2017 DOE Hydrogen and Fuel Cells Annual Merit Review, Washington DC, June 7, 2017.

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.