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Quarterly Progress Report

Project Title: Fundamental Safety Testing and Analysis of Hydrogen Storage Materials and Systems

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Project Objective:

In order to design commercially viable solid state hydrogen storage systems, it is important to understand and quantify the environmental reactivity of the active species in possible environmental exposure scenarios. This report gives a summary of standardized UN tests along with calorimetric experiments performed in order to quantify both the rate and the amount of the energy released; as well as characterize the reaction products resulting from water exposure of a lithium borohydride and magnesium hydride combination ($2\text{LiBH}_4 + \text{MgH}_2$).

Status:

Calorimetry

The heat of reaction during hydrolysis for the single components MgH_2 , LiBH_4 and the mixture $2\text{LiBH}_4 + \text{MgH}_2$ were measured in a mixing cell using both neutral DI water and a 1M HCl acid solution. Figure 1. displays the maximum heat flow normalized per weight of hydride material (mW/mg) under acidic and neutral hydrolysis conditions. The remarkable increase in the reaction under acidic conditions points to the role of a hydroxide and/or oxide layer which may form on the surface of hydride particles in solution. This surface layer impedes the hydrolysis in neutral conditions, however strong acidic solutions seem to remove this layer allowing for quick reaction times. The effect of environmentally accessible conditions such as acid rain (pH 4) displayed similar results to neutral water.

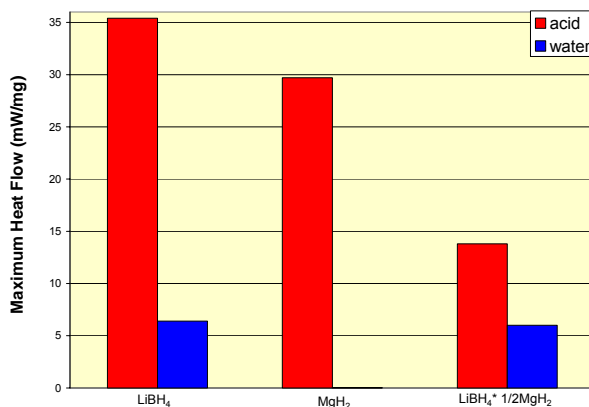


Figure 1. Maximum heat flow (mW/mg) during hydrolysis at 40°C with neutral DI water and 1M HCl acid.

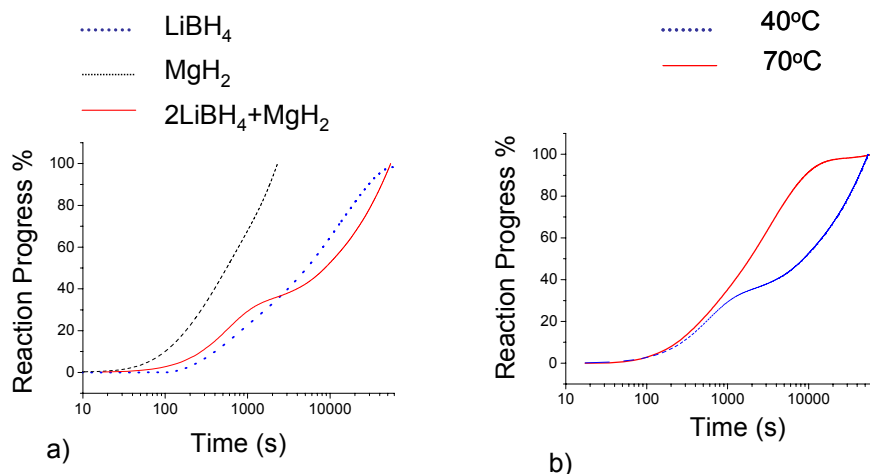


Figure 2. Reaction Progress as a function of time hydrolysis of materials with DI water at 40°C.

The time dependence of the heat flow signal was integrated resulting in the total enthalpy of the measured reaction. The integrated area under the heat flow signal as a function of time divided by the total reaction enthalpy was used to estimate the reaction progress in (%) as displayed in Figure 2. These experiments were independently confirmed using the volume hydrogen gas produced during hydrolysis as an additional measure of reaction progress. The hydrolysis of the single components as well as the mixture at 40°C under neutral DI water conditions is displayed in Figure 2 (a). It is noted that although the MgH_2 seems fast; this is derived from the extremely low measured heat flow. This was confirmed when MgH_2 was hydrolyzed with DI water where the volume of gas produced was barely measurable. Figure 2(b) shows the temperature dependence of neutral DI water hydrolysis in the mixed $2\text{LiBH}_4 + \text{MgH}_2$ system. A temperature increase of 30°C (from 40 to 70°C) resulted in an increase of reaction progress from 40 to 70% after 1 hour.

Standardized Testing

Estimations have been conducted to determine the amount of material that will be required to conduct the full array of testing procedures for the three materials that have been identified, based on the volume or size suggested by the United Nations Panel. The results of the calculations are shown in Table 1. It can be seen that the water contact tests require relatively small amounts of the materials (~10g) for completion of a given test. However, the air contact tests require a significantly larger amount of material per test, in particular the self-reactive tests. These materials are typically ball-milled prior to testing to render a controlled material size distribution; additionally, these tests are to be conducted in the fully charged, partially discharged, and fully discharged states. Material production and pre-treatment procedures have been developed to accommodate the tests.

Water contact testing procedures have been conducted on the $2\text{LiBH}_4 \cdot \text{MgH}_2$ material, and were filmed using standard digital video recording techniques. In order to put the results of the Li/Mg mixture into perspective, these tests were also conducted on pure LiBH_4 and MgH_2 . The tests fell into three different scenarios, wherein there is 1. an excess of water and a small amount of hydride material (water immersion), 2. an excess of water and a small amount of hydride material; however the physical contact is retarded by the addition of filter paper on the surface of the water (surface contact), and 3. a small amount of water and an excess of hydride material (water drop). The results of these tests are given in Table 2. The results indicate the LiBH_4 is the most reactive of the substances tested, with the Li/Mg mixture and pure MgH_2 being much less reactive. Visual analysis of the video recordings (not included in this report, but can be made available if desired) indicates that the mixture seems to exhibit some properties of both of the constituent pure

materials. In all cases, the materials failed the United Nations testing procedures by virtue of the evolution of gas upon reaction or the emission of a flame event. The different scenarios of the water contact tests result in three different regimes for heat and mass transport. The rate at which the water and hydride mix, the exothermic heat generated during the contact of water and hydride, and heat transfer properties controlling the removal of heat dictate which type of failure mode the test exhibits. These test results are currently being considered for development of a numerical model to predict the failure mode for a given material and contact scenario.

	Mol Wt.	density [g/cc]		packing density [%]	Stoich H2
NH3BH3	30.8800	0.8500		0.5000	3.0000
AlH3	30.0100	1.4800		0.5000	1.5000
LiBH4	21.7900	0.6660		0.5000	
MgH2	26.3300	1.4500		0.5000	
2LiBH4.MgH2	69.9100	1.0403		0.5000	4.0000
density of H2 (0C,1atm) [g/L]	0.0899				

United Nations			Mass of Material per Test [g]			Total Mass Per Substance [g]			
Test Description	(d/l)_sample, if relevant [mm]	V_sample, if relevant [cm^3]	Number of Trials Per Material	NH3BH3	AlH3	2LiBH4.MgH2	NH3BH3	AlH3	2LiBH4.MgH2
1. Water Immersion	2.0000	0.0335	3.0000	0.0142	0.0248	0.0174	0.0427	0.0744	0.0523
2. Water Surface Exposure	2.0000	0.0335	3.0000	0.0142	0.0248	0.0174	0.0427	0.0744	0.0523
3. Water Drop	30x20 disk	4.7124	3.0000	2.0028	3.4872	2.4511	6.0083	10.4615	7.3533
5. Impact Sensitivity		0.0400	29.0000	0.0170	0.0296	0.0208	0.4930	0.8584	0.6034
6. Pyrophoricity		1.0000	3.0000	0.4250	0.7400	0.5201	1.2750	2.2200	1.5604
7. Self Heating		25.0000	2.0000	6.6406	11.5625	8.1272	13.2813	23.1250	16.2544
<i>measurements are</i>	25.0000	15.6250	2.0000	6.6406	11.5625	8.1272	13.2813	23.1250	16.2544
<i>for cubes</i>	25.0000	15.6250	2.0000	6.6406	11.5625	8.1272	13.2813	23.1250	16.2544
8. Burn Rate	b:20,h:10,l:250	25.0000	3.0000	10.6250	18.5000	13.0036	31.8750	55.5000	39.0107

All tests must be run in the charged, partially charged and uncharged state

Total Masses [g]	239.1537	416.4922	292.8870
[kg]	0.2392	0.4165	0.2929
30% overage [g]	310.8998	541.4399	380.7531
30% overage [kg]	0.3109	0.5414	0.3808

Table 2. Results of Water Contact Tests for 2LiBH4.MgH2, LiBH4, and MgH2.

UN Test	Material	Pass/Fail
Water Drop	MgH2	Fail – flame
	LiBH4	Fail – flame
	2 LiBH4.MgH2	Fail – flame
Surface Contact	MgH2	Fail – flame
	LiBH4	Fail – flame
	2 LiBH4.MgH2	Fail – flame
Water Immersion	MgH2	Fail – gas evolved
	LiBH4	Fail – gas evolved
	2 LiBH4.MgH2	Fail – gas evolved

Conclusions

Large differences in heat flow and reaction progress were observed when MgH_2 and LiBH_4 were hydrolyzed using neutral DI water compared to acid solutions of 1M HCl; this is attributed to a surface hydroxide/oxide layer. The mixed $\text{MgH}_2 + \text{LiBH}_4$ compound behaves similar to the LiBH_4 component and displayed a marked temperature dependence of hydrolysis with neutral water.

The amount of material to perform the United Nations testing procedures for air and water sensitive materials has been estimated and found to be significant but not insurmountable. Water contact tests have been conducted on $2\text{LiBH}_4 \cdot \text{MgH}_2$ and pure LiBH_4 and MgH_2 . All materials failed the United Nations testing procedures. The three different testing procedures used (water immersion, surface contact, and water drop) indicate that the volume of hydrogen generated, the exothermic heat generated during water contact, and the mode of heat transport determine whether or not a flame event is encountered.

Future Plans

Liquid Hydrolysis experiments will continue with partially dehydrated materials. Gas hydrolysis and oxidation studies will begin at various humidity levels and temperatures using a flow cell. Characterization of crystalline and amorphous solid products with X-ray and NMR, gas products with RGA connected to flow cell

The water contact tests will be repeated for the Li/Mg mixture to verify reproducibility. The air contact tests for pyrophoricity will be conducted next on the Li/Mg mixture, followed by the self-reactivity tests. Testing equipment to add thermocouple and gas composition measurements are being developed; additionally, the possibility of adding IR thermography to the procedures is being evaluated. Materials are being fully and partially dehydrated using a pressure manifold.