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Sandia National Laboratories

Quarterly Progress Report

Project Title: Hydrogen Materials Advanced Research Consortium (HyMARC): Sandia Technical Effort

Total Project Period: October 1 – December 31, 2024

Date of Report: January 30, 2025

Recipient: Sandia National Laboratories

Working Partners: Lawrence Berkeley National Laboratory; Lawrence Livermore National Laboratory; National Renewable Energy Laboratory; Pacific Northwest Laboratory; Sandia National Laboratories, Livermore; SLAC National Accelerator Laboratory.

Cost-Sharing Partners: N/A

Contact: Mark D. Allendorf, SNL, (925)294-2895, mdallen@sandia.gov

DOE Managers: Dr. Zeric Hulvey

Key Project-Level and Technical Highlights

- Milestone completed: Shakedown tests of he Large Sieverts apparatus (aka Scale-up Reactor) were completed using using an AB_2 material with composition $Ti_{0.95}Zr_{0.05}Mn_{1.56}V_{0.31}Fe_{0.11}Al_{0.02}$ (Task 2B). This completes the Sandia FY25/Q1 milestone "Commission new large-scale Sieverts apparatus using a conventional hydride (e.g. HydralloyC5)."
- New project: A trilateral agreement has been finalized involving research institutions in Korea, Japan, and the U.S. The project partners are Sandia, LLNL, KIST, KAIST, and AIST. The project title is "Structure-Property Relationships in Metal Alloys for Hydrogen Storage and Processing." Funding for the U.S. portion of the effort is through NNSA; the PI is Vitalie Stavila. The overall objective of this project is to identify detailed structure-property relationships governing hydrogen separation, purification, storage, and compression in compositionally complex metal alloys.

Research Progress

Task 2: Materials Co-Design, Scale-up and Integration

Sandia Contacts: Vitalie Stavila, (925)294-3059, vnstavi@sandia.gov; Matthew Witman (925)294-3024, mwitman@sandia.gov.

Focus Area 2B: Scale-up of HyMARC-2 materials

Hydrogen capacity measurements were conducted using a custom-built Large Sieverts Apparatus (LSA) designed at Sandia to measure large sample sizes, from grams to several kilograms of H_2 storage material. The system is equipped with high-accuracy transducers for accurate pressure measurements. A schematic of the LSA with the calibrated volumes for absorption and desorption measurements (in mL) shown in **Figure SNL-1**. Source volumes for absorption (S1-S4) are 383.5, 931.7, 2098.1, and 5057.8 mL. These can be used individually, or combined for larger samples. Reservoir volumes for desorption (D1-D6) are 43945.1, 43925.3, 44263.0, 10993.0, 10890.0, and 3363.0 mL, and can similarly be used in any combination. The total calibrated volume available for desorption tests is 157379.4 mL or 157.3794 L, which is about 125 larger than the total volume available in the commercial PCTPro instrument. This setup can allow testing of kg-scale materials and hydrogen tanks. The testing was performed using a AB_2 material with a composition $Ti_{0.95}Zr_{0.05}Mn_{1.56}V_{0.31}Fe_{0.11}Al_{0.02}$ synthesized by arc-melting. An amount of 325.072 g of $Ti_{0.95}Zr_{0.05}Mn_{1.56}V_{0.31}Fe_{0.11}Al_{0.02}$ was loaded into a stainless-steel vessel, connected to the LSA, and the volume was calibrated using He gas. The sample was activated at 200 °C in vacuum, and hydrogenation

was performed under 75 bar hydrogen. Due to large temperature fluctuations during tests without active temperature control, the sample holder was immersed into a chilled bath with the temperature set to 22 °C to minimize the temperature fluctuations during the test. The sample holder was separated from the rest of the manifold, after which a hydrogen desorption experiment was conducted. A thermocouple, positioned in a well on the holder, was used to monitor the temperature of the sample holder, and the results are illustrated in **Figure SNL-2**. The temperature fluctuations during the test are due to the exothermal hydrogen release and endothermic hydrogen release. The LSA underwent comprehensive testing under different conditions, is leak-proof, and is ready for testing and validation experiments.

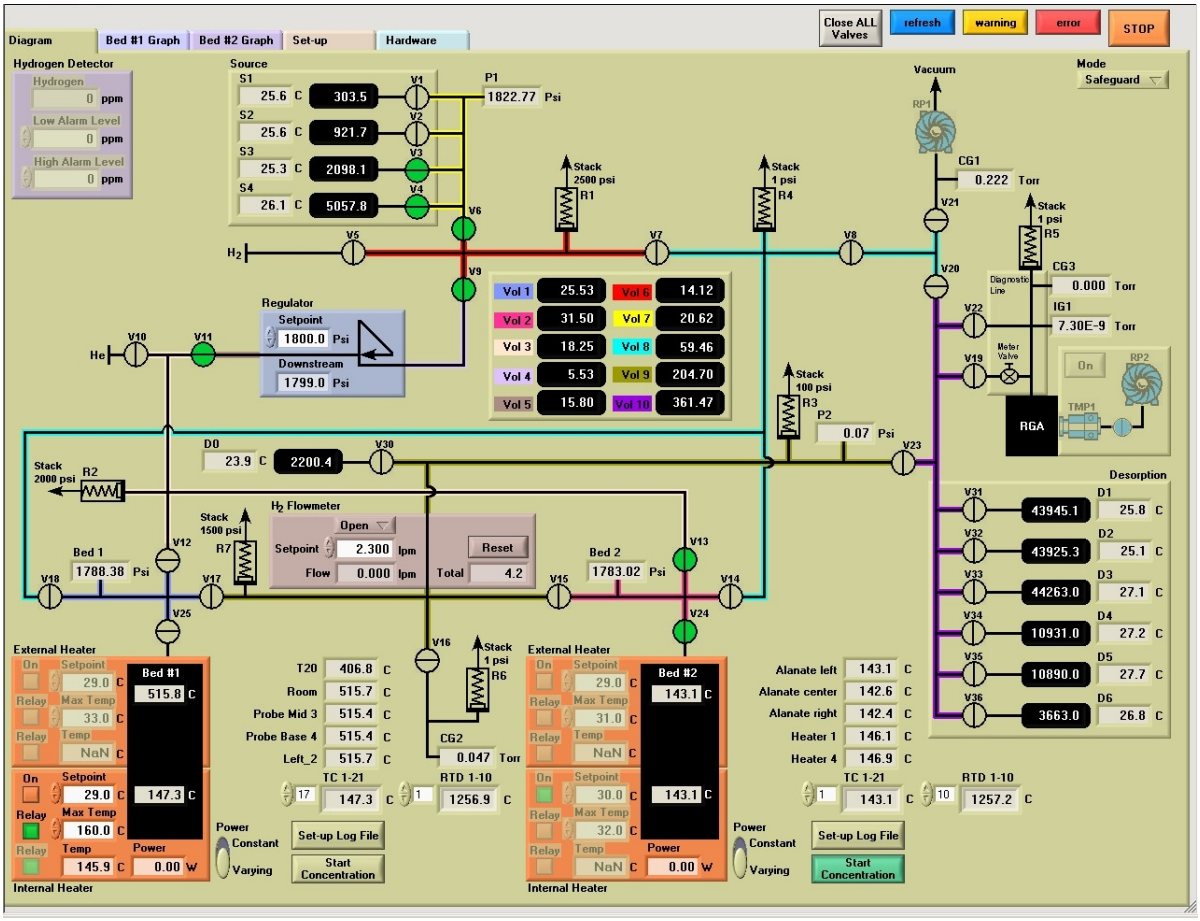

Figure SNL-1. Schematic representation of the Large Sieverts Apparatus and available calibrated volumes.

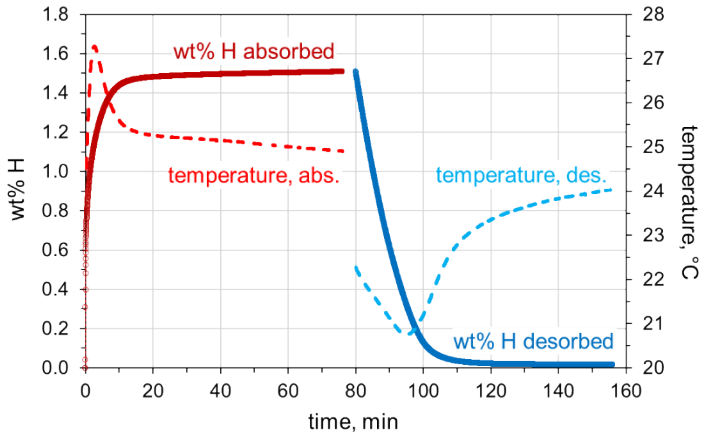

Figure SNL-2. Hydrogen uptake and release (and the corresponding temperature changes of the sample holder) for $Ti_{0.95}Zr_{0.05}Mn_{1.56}V_{0.31}Fe_{0.11}Al_{0.02}$ measured on the LSA.

Focus Area 2D: Hydrides

PCT prediction tools (SNL, Uppsala, AIST). We are currently wrapping up our paper on first-principles AB2 PCT predictions which will enable better compositional optimization of techno-economically relevant AB2 alloy metal hydrides [1], as we can now predict whether a desired plateau pressure will be achieved for a given composition, while simultaneously minimizing the cost of the raw materials. **Figure SNL-3** shows the validation predictions of the computational workflow (solid lines), vs. experiments (open circles). The tentative title of this preprint is "*Efficient pressure-composition-temperature diagram predictions to discover and optimize metal hydrides*" [2]. Simultaneously, we collaborated with Uppsala Univ. and AIST, who have helped make and test new predicted AB2 hydrides from this study. One such promising material (TiZrFeCrMnNi) has been extensively characterized in a parallel study led by Uppsala [3], which has been determined to be higher performing than HydralloyC5 (~10% higher H/M reversible capacity under identical temperature/pressure swing conditions), while being lower cost as it contains no vanadium. Therefore, we anticipate it to be a more competitive option than the TEA benchmark of HydralloyC5 discussed in [1].

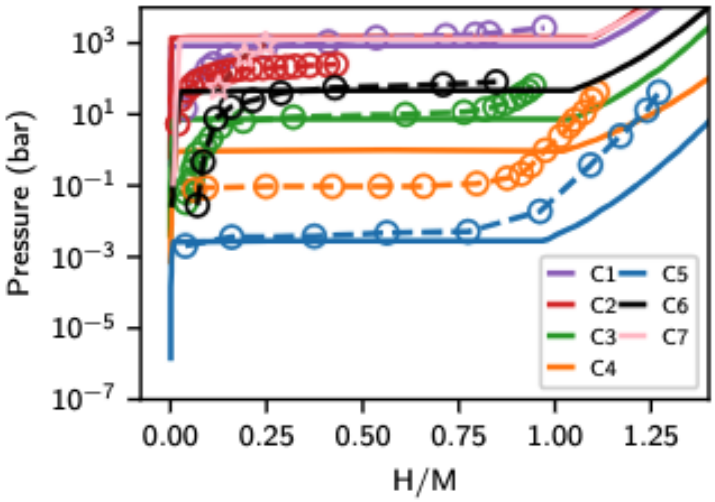

Figure SNL-3. Validation of predicted vs experimental PCT isotherms in [2]

Next steps: we plan to build an ML-accelerated tool to predict which high-entropy AB2 alloys are most likely synthesizable as a pure (no local composition enrichments), hypothesizing that this will allow us to not only optimize AB2 composition for overall plateau pressure and alloy cost, but also minimize "sloping-ness" of the plateau and increase working capacity for better TEA outlook.

Borohydride dopants improve desorption kinetics of Li-Mg amide. This quarter, we focused on finishing the manuscript for the research on borohydride doped 2:1 materials to finish up this project. Key data that were collected were the N 1s XPS data to analyze the surface (7 nm) of the material (**Figure SNL-4**). These data corroborate our N-K edge XAS data, which revealed that imide was forming in the bulk (TFY) of the desorbed material, but the surface was mostly amide (TEY) for all the doped and undoped materials. The main findings of this paper are the inverse core-shell mechanism of desorption occurring in the Li-Mg-N-H system and the borohydride catalysts that aid in the dehydrogenation by destabilizing N-H bonds near the surface of the amide/hydride dehydrogenating species. We also focused this quarter on scaling up the 2.9LiH + 1 $Mg(NH_2)_2$ + 0.1 KH material for large-scale Sieverts studies. We synthesized 50 grams of material and are currently undergoing activation processes.

Next steps: Activating the 2.9LiH + 1 $Mg(NH_2)_2$ + 0.1 KH material, contacting companies for large scale ball milling, and collecting thermal conductivity and packing density data for 2.9LiH + 1 $Mg(NH_2)_2$ + 0.1 KH to write a systems analysis paper on this material.

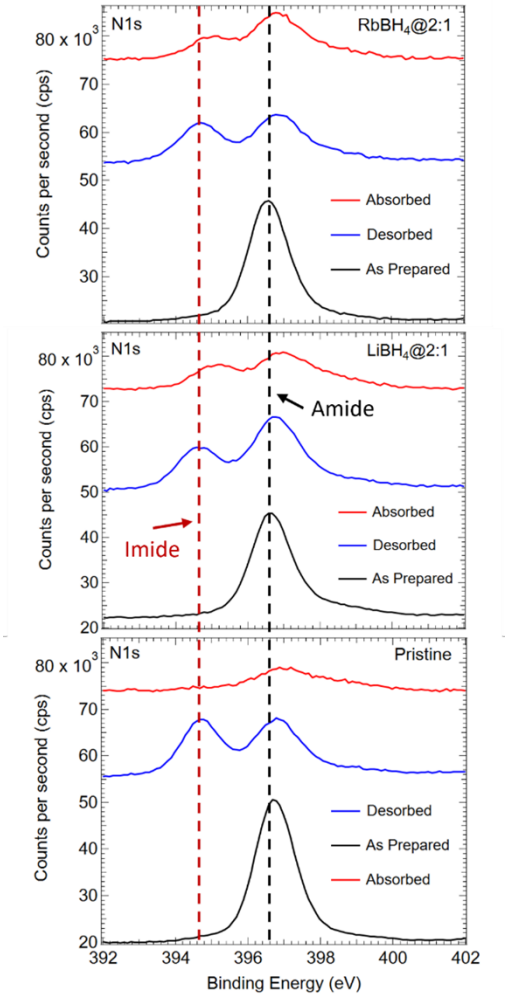

Figure SNL-4. N 1s XPS spectra for the pristine material (below), $LiBH_4$@2:1 (middle), and $RbBH_4$@2:1 (top) showing the surface and near-surface regions contain a mix of amide and imide in the desorbed and reabsorbed states.

Focus Area 2E: Liquid Organic Hydrogen Carriers (LOHC)

Sandia Contact: Mark Allendorf, (925)294-2895, mdallen@sandia.gov

Ru and Mn catalyst assessment for 1,4 butanediol and dehydrogenation. From an industrial standpoint, solvent-free reaction conditions are advantageous due to decreased reaction time, lower energy consumption, and an increased hydrogen capacity of the system. Consequently, we investigated the kinetics and hydrogen storage capacity for the dehydrogenation of 1,4 butanediol at 165 ˚ C under neat conditions using both **Ru-MACHO** and **2-BH_4**. These kinetic measurements were performed using Sieverts technique (**Figure SNL-5**). These studies demonstrate that under neat conditions, **Ru-MACHO** features a higher hydrogen storage capacity than **2-BH_4** with the given values of 3.9 and 3.2 wt%, respectively. Given the high performance of these Ru and earth-abundant catalysts reported in Q4. A manuscript is currently underway titled: “Ru, Mn, and Fe catalyzed (De)hydrogenation of 1,4 butanediol.”

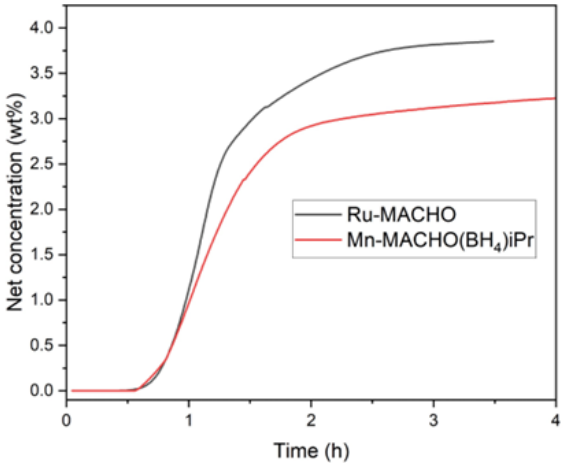

Figure SNL-5. Sieverts plot displaying H_2 release as a function of time for 1,4 butanediol dehydrogenation.

Industrial Advisory Board (IAB)

During the past quarter, we held a planning discussion about the IAB. The IAB was formed two years ago with the intent to provide real-world experience and guidance to HyMARC. However, the mission of HyMARC has shifted to emphasize near-term demonstrations and deployments. This shift, as well as a sense that additional benefit could be gained from the IAB, motivated us to review :1) the relationship of the IAB to HyMARC; 2) the IAB institutional composition; and 3) how we can best interact with the IAB to assist HyMARC in its evolving mission. Toward these ends, Lennie Klebanoff assumed leadership HyMARC IAB effort to optimize the IAB/HyMARC interactions. This activity will begin next quarter (FY25/Q2).

Publications and Presentations

Publications

1. X. Wang, P. Peng, M. Witman, V. Stavila, M. Allendorf, H. Breunig "Technoeconomic Insights into Metal Hydrides for Stationary Hydrogen Storage" submitted, 10.26434/chemrxiv-2024-gwrzq
2. L. Way, M. Witman. et al. "Efficient pressure-composition-temperature diagram predictions to discover and optimize metal hydrides" in preparation.
3. Fadonougbo, Witman, et al. "On the design of room temperature TiZrMnCrFeNi-based high entropy hydrides" in preparation.
4. N. Torquato, V. Stavila, M. Allendorf et al. "Ru, Mn, and Fe catalyzed (De)hydrogenation of 1,4 butanediol" in preparation.

Presentations

1. Witman M. *Data-driven discovery and modeling of hydrogen energy materials*. University of Missouri, Invited Seminar for NSF Research Traineeship in Data Science. December **2024**.
2. V. Stavila, M. Shivanna, W. Taylor, N. Torquato, M. Allendorf "Nanoconfined Metal Hydrides As Alternatives to Lithium Ion Battery Energy Storage" PRiME 2024, Oct. 5 – 11, 2024, Honolulu, HA. *Meet. Abstr.* **MA2024-02** 2543, **DOI** 10.1149/MA2024-02372543mtgabs