

Metal Hydride Compression

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Subcontractors: Hawaii Hydrogen Carriers LLC, Honolulu, HI

Project Start Date: October, 2016

Project End Date: September, 2019

Overall Objectives

- Investigate and demonstrate on a laboratory scale a two-stage metal hydride compressor with a feed pressure of approximately 100 bar delivering high purity H₂ gas at outlet pressures ≥ 875 bar
- Demonstrate an increase in the TRL of this technology from 2 to 5 and enable the development of a comprehensive cost analysis for a production system scaled to 100 kg H₂/hr flow rate
- Demonstrate through engineering analysis that the compressor design is capable of an energy efficiency of ≤ 4.0 kWh/kg

Fiscal Year (FY) 2017 Objectives

- Demonstrate through laboratory characterization two metal hydrides for the Low (LP) and High (HP) pressure stages that meet the system level requirements
- Down select compressor bed designs for both stages based on trade studies
- Demonstrate the capability of an energy efficiency of ≤ 4.0 kWh/kg using a system-level dynamic model with realistic metal hydride properties and a baseline system design

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Delivery section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

(B) Reliability and Costs of Gaseous Hydrogen Compression

Technical Targets

This project is developing metal hydride compressor technology that is currently at a TRL of 2. The results of this project will address several of the DOE technical targets for small, forecourt compressors, specifically:

- Specific energy: The 2020 target for 100 bar pipeline delivery is 1.6 kWh/kg. Our project goal is to demonstrate that a metal hydride compressor can achieve a specific energy of less than 4.0 kWh/kg as a first step towards this target.
- Uninstalled Capital Cost: The 2020 target for 100 bar pipeline delivery is \$275,000. A cost analysis for a commercial system in FY19 will address this target.
- Outlet Pressure Capability: The 2020 and Ultimate targets are 950 bar. We plan to demonstrate a prototype compressor capable of > 875 bar pressure with a goal of 950 bar.

FY 2017 Accomplishments

- Developed a dynamic system-level model using Matlab/Simulink for feasibility and design trade studies

- Demonstrated feasibility of 50 - 875 bar H₂ compression and delivery at reasonably achievable temperatures through system-level analysis of a baseline design using literature data for available metal hydrides
- Completed a parameter study using the dynamic system model to probe design space including the effects of cycle time, alloy, feed pressure, and bed geometry on hydrogen flow rate and energy efficiency
- Identified several approaches to achieve energy efficiency and hydrogen compression cost targets including heat recuperation, waste heat utilization, and heat pump options
- Identified five candidate alloys for each compressor stage based on extensive literature research, pared the list down to two for each stage, and engaged vendors to supply the alloys in small quantities for characterization as well as large quantities for our prototype compressor
- Designed, assembled and calibrated a high pressure Sieverts cycling apparatus for characterization of candidate metal hydrides
- Completed pressure-composition-temperature (PCT) measurements of a metal hydride candidate that looks promising for the low pressure stage of the compressor

Introduction

Conventional hydrogen compressors often contribute over half of the cost of hydrogen stations, have poor reliability, and have insufficient flow rates for a mature FCEV market. Fatigue associated with their moving parts including cracking of diaphragms and failure of seal leads to failure in conventional compressors, which is exacerbated by the repeated starts and stops expected at fueling stations. Furthermore, the conventional lubrication of these compressors with oil is generally unacceptable at fueling stations due to potential fuel contamination. Metal hydride (MH) technology offers a very good alternative to both conventional (mechanical) and newly developed (electrochemical, ionic liquid pistons) methods of hydrogen compression. Advantages of MH compression include simplicity in design and operation, absence of moving parts, compactness, safety and reliability, and the possibility to utilize waste industrial heat to power the compressor. Beyond conventional H₂ supplies of pipelines or tanker trucks, another attractive scenario is the on-site generating, pressuring and delivering pure H₂ at pressure (≥ 875 bar) for refueling vehicles at electrolysis, wind, or solar generating production facilities in distributed locations that are too remote or widely distributed for cost effective bulk transport.

MH hydrogen compression utilizes a reversible heat-driven interaction of a hydride-forming metal alloy with hydrogen gas to form the MH phase and is a promising process for hydrogen energy applications [1,2]. To deliver hydrogen continuously, each stage of the compressor must consist of multiple MH beds with synchronized hydrogenation & dehydrogenation cycles. Multistage pressurization allows achievement of greater compression ratios using reduced temperature swings compared to single stage compressors. The objectives of this project are to investigate and demonstrate on a laboratory scale a two-stage MH hydrogen (H₂) gas compressor with a feed pressure of >50 bar and a delivery pressure ≥ 875 bar of high purity H₂ gas using the scheme shown in Figure 1. Progress to date includes the selection of two candidate metal hydrides for each compressor stage, supplier engagement and synthesis of small samples, and the beginning of in-depth characterization of their thermodynamics, kinetics, and hydrogen capacities for optimal performance with respect to energy requirements and efficiency. Additionally, bed design trade studies are underway and will be finalized in FY18. Subsequently, the prototype two-stage compressor will be fabricated, assembled and experimentally evaluated in FY19.

Approach

The approach for this project is split into three phases to meet the project objectives: 1) feasibility assessment and system design, 2) hydride degradation assessment and prototype fabrication, and 3) prototype performance evaluation. In the first phase, candidate hydride materials are selected based on literature review and team experience. Absorption and desorption isotherms of selected hydrides are then measured and compared to system level requirements to demonstrate feasibility. In parallel, trade studies are performed on different design configurations for the prototype compressor beds and a down selection made. Finally, a system-level compressor model is developed and used for feasibility assessment of the hydride materials and bed designs. In the second phase, accelerated cycling tests (~1000 cycles) on candidate hydrides are performed to determine degradation rate, if any, and assess regeneration potential. In parallel, component fabrication and assembly drawings for compressor beds are developed based on the down selected designs. Procurement of hydride alloys and fabrication of bed components follows. Once received, the integrated prototype compressor is assembled. In the third and final phase of the project, the prototype compressor is integrated with the test facility and performance testing of the prototype is conducted. This testing will assess the impact of heating rates, state of charge, and temperature ranges on compressor performance as well as degradation behavior. This will include up to 300 hours of operation. Results of the prototype characterization will be documented and used for the conceptual design and cost analysis for a 100 kg H₂/hr commercial system in a final report to DOE.

Results

Metal hydride selection and characterization

Candidate low and high pressure alloys were identified in Q1 based on extensive literature review and design requirements. In Q2, these alloys were down-selected to two alloys for each stage. Seven different suppliers were then contacted to determine a reliable source for the selected hydride alloys. Of these suppliers, the list was pared down to Ames Lab and Japan Metals and Chemicals (JMC) for their ability to produce any of the candidate alloys of interest. In addition, it was determined that Sandia had possession of ~100kg of GfE Hydralloy C5 from a previous project. Because AMES is only capable of relatively small batches and the cost is thus relatively expensive, JMC was selected for procurement of test quantities (i.e., ~ 50 grams) of the three AB₂ alloys not already in possession by the team.

Characterization of these alloys is underway using PCT (pressure, composition, temperature) apparatus to provide/confirm material absorption and desorption isotherms. The low pressure alloys are being characterized at HHC using a Suzuki Shokan 2 channel thermo-volumetric analyzer with medium (≥ 150 atm) pressure capability. Figure 2 shows isotherms of the Hydralloy C5 alloy recently measured with this system. This result is consistent with literature data for the alloy at up to 50 °C, but provides higher temperature and pressure data not previously measured. The isotherms indicate that Hydralloy C5 is a viable candidate for the low pressure stage of the compressor and the measured data will be used in the system level model for confirmation.

The high pressure alloys will be characterized at ORNL using a custom designed test apparatus capable of accurate isotherm measurements up to 1000 bar and 150 C. This high-pressure Sievert's system design was completed in early Q2 incorporating ideas/practices from similar high-pressure cycling stations at both JPL and SNL (HyMARC). The design will make use of existing infrastructure at ORNL as much as possible. A safety review was completed and the design was approved in January. Assembly and system testing will be completed by the end of August. First measurements of a high-pressure hydride are set to be completed in August with full characterization of both alloys to be completed in Q1FY18. A picture of the assembled system is shown in Figure 3.

System design

A system-level compressor model was developed using Matlab/Simulink, as shown in Figure 4. The model includes hydride properties (thermal, thermodynamic and kinetics) and heat and mass flow in a two-stage configuration. These properties are literature values based on experimental measurements of candidate materials. The baseline design uses two beds per stage, but the model only simulates one bed for each stage taking advantage of symmetry such that the results from the single bed pair can be used to estimate the performance of the full system. The model allows for time-dependent simulations to determine appropriate cycle times and staging to achieve quasi-continuous hydrogen compression. Simulations of a baseline compressor configuration with 12 min half cycles show the feasibility of the design. With 25 kg of metal hydride per bed, a quasi-continuous flow of hydrogen was achieved, compressed from 100 bar to 875 bar, with an average flow rate of 1.07 kg/hr and a heating requirement of 12.5 kWh/kg. This flow rate is directly proportional to the size of the MH beds, so producing 100 kg/hr, as an ultimate performance goal, would simply require appropriately scaled beds.

Following the baseline predictions, the model was used to simulate a number of additional configurations to look at the effect on flow rate as well as energy consumption and bed utilization. Two different low pressure alloys, three different cycle times, one different bed geometry, and a lower feed pressure were considered. A number of insights were gained from the system simulations. Firstly, energy efficiency can be improved with optimized cycle times, including the use of asymmetric cycle times (longer duration for desorption half cycles). Alloy properties can have a large impact on performance. For example, changing to a lower pressure AB5 alloy for the low pressure stage negatively impacted performance. However, changing to smaller tube diameter to improve heat transfer and using asymmetric half cycles allowed the AB5 performance to approach that of the AB2 alloys. Finally, the results show that 50 bar feed pressure can be used with good performance.

Because the baseline energy use of 12.5 kWh/kg greatly exceeds the desired level, several pathways for achieving energy efficiency were pursued in Q2. While waste heat sources for the metal hydride compressor have been identified, they are not likely to exist in the forecourt but at centralized hydrogen production facilities such as SMR plants and waste-to-energy systems. With a goal of using the compressor at hydrogen stations, other configurations have been investigated. Firstly, a heat recuperator design has been conceptually identified that could reduce the sensible heat requirement of the system by ~40% bringing required heat down to ~10 kWh/kg for the baseline system. If this heat was provided by a natural gas burner (assuming natural gas costs \$0.065/mm-btu, and burners are about 85% efficient) the operating cost would be \$ 0.25/kg. This would be comparable to a conventional compressor using 2.3 kWh/kg at \$0.11/kWh electricity cost.

Another option would be to couple the compressor to an energy efficient heat pump. Two heat pump options were considered: a vapor compression cycle (VCC) and an absorption heat pump (AHP) cycle. A simple analysis of an ideal heat pump cycle shows that a VCC with R21 operating between 25C and 125C has a coefficient of performance of 2.7 that would result in a compressor energy requirement 3.7 kWh/kg. A VCC system with methanol as the refrigerant might further reduce the energy use to 3.1 kWh/kg. With compressor cooling it is possible these COP values could be improved somewhat. For AHP cycles there is the possibility of driving the cycle with heat rather than electricity. This is favorable because it is less expensive to provide heat than electricity. Therefore, a natural gas-fired AHP system might be advantageous. However, an AHP cycle operating over this temperature lift is not likely to produce a COP of > 1.4. At a

COP of 1.4, the heat required for the compressor would be 7.1 kWh/kg. If this heat was provided by burning natural gas, then the cost would be \$0.18/kg.

Conclusions and Upcoming Activities¹

Work in FY17 has demonstrated the feasibility of a two-stage metal hydride compressor to compress hydrogen from 100 bar to > 875 bar over an achievable temperature range with sufficient flow rate. This has been demonstrated primarily through simulations with a dynamic system model that incorporates a baseline design for the compressor beds and literature properties for metal hydride thermodynamic and kinetic properties. The model includes a realistic representation of the heating/cooling system that would be required to drive the process as well as hydrogen flow through a manifold of connected check valves. While the hydride properties used are taken from experimental data, they have been extrapolated to higher temperature and pressure. PCT measurements of selected hydrides at actual expected operating conditions will provide further feasibility evidence.

The team has completed one such set of measurements in FY17 thus far. The commercial material Hydralloy C5 was cycled on a medium pressure Sievert's apparatus over six temperatures from 25 °C to 95 °C demonstrating desorption at over 100 bar. These results indicate that the material is suitable for the low pressure stage of the compressor. Further PCT measurements will be made on ORNL's high pressure apparatus to demonstrate performance at up to 150 °C.

The specific energy of the baseline configuration of the MH compressor exceeds DOE's goals for this project. Simulations predict 12.5 kWh/kg H₂ for the baseline system modeled. To move this value closer to the ultimate target, several options have been investigated. Through a combination of heat recuperation and heat pump coupling, the specific energy could be reduced to 3-4 kWh/kg H₂. This level has been deemed sufficient for a low TRL technology in the beginning stages of development that has many promising advantages over current technology.

Moving forward, work through FY17 will include down selecting bed designs and carrying out hydride PCT measurements. In FY18, we will perform accelerated cycling tests, complete component fabrication and assembly drawings, procure hydride alloys, fabricate bed component and assemble the prototype compressor, and configure the test facility to enable performance testing. In FY19, we will install the compressor in the high-pressure test facility, conduct performance testing of the prototype, and develop a conceptual design and cost analysis for a 100 kg H₂/hr system.

Special Recognitions & Awards/Patents Issued

FY 2017 Publications/Presentations

1. Johnson, T., "Metal Hydride Compressor for High-Pressure (\geq 875 bar) Hydrogen Delivery," Presentation at the Joint HDTT-CSTT Meeting, Golden, CO, Nov. 2, 2016.
2. Bowman, R., Oral Presentation at Joint HSTT-HDTT Meeting, "Metal Hydride Compressor for High-Pressure (\geq 875 bar) Hydrogen Delivery," Southfield, MI, Feb. 16, 2017
3. Bowman, R., Oral Presentation at 11th International Symposium on Hydrogen & Energy,

¹ Projects that are awarded by FCTO through competitive Funding Opportunity Announcement (FOA) selections are fully funded for the project's full period of performance (subject to go/no-go decisions) in the year the project is awarded. Future direct-funded work at the national laboratories is subject to change based on annual appropriations.

“Status of High-Pressure Metal Hydride Compressors for Applications Exceeding 700 Bar,”
Waikoloa, HI, Feb. 28, 2017

4. Johnson, T. “Metal Hydride Compression,” presented at the 2017 DOE Hydrogen and Fuel Cells Program and Vehicle Technologies Office Annual Merit Review and Peer Evaluation Meeting, June 2017.

References

1. M.V. Lototskyy, Y.A. Yartys, B.G. Pollet, R.C. Bowman Jr., “Metal hydride hydrogen compressors: A review.” *Int J. Hydrogen Energy* 39 (2014) 5818.
2. V.A. Yartys, M.V. Lototskyy, V. Linkov, D. Grant, A. Stuart, J. Eriksen, R. Denys, R.C. Bowman, Jr., “Metal hydride hydrogen compressors: Recent advances & future prospects” *Appl. Phys. A* 122 (2016) 415.

Acronyms

MH	metal hydride
TRL	technology readiness level
SNL	Sandia National Laboratories
ORNL	Oak Ridge National Laboratory
HHC	Hawaii Hydrogen Carriers
LP	low pressure
HP	high pressure
PCT	pressure, composition, temperature
VCC	vapor compression cycle
AHP	absorption heat pump
DOE	Department of Energy
JPL	Jet Propulsion Laboratory
HyMARC	Hydrogen Materials Advanced Research Consortium
FCEV	fuel cell electric vehicle
JMC	Japan Metals and Chemicals

Figure Captions

Figure 1. van't Hoff plots illustrating the operation of a two-stage Metal Hydride Hydrogen Compression system from the low temperature T_L to the high temperature T_H . The black lines represent the van't Hoff plot for the hydrogenation process for stage 1 (lower black line) and for stage 2 (upper black line). The dashed red line represents the coupling between stage 1 and stage 2. The compression cycle is summarized as follows: Step A: A low-pressure H_2 supply (e.g., an electrolyzer or pipeline) is attached to the first stage, at pressure P_s . The temperature of stage 1 is maintained at T_L , during hydrogenation. Step B-C: A sensible heating process raises the bed temperature to T_H , increasing the pressure of the stage 1 vessel. Step D-E: Coupling between stage 1 (dehydrogenation at T_H) and stage 2 (hydrogenation at T_L) occurs. Step F-G: Stage 2 hydride bed undergoes sensible heating in order to achieve the delivery pressure of P_d . Step H: During dehydrogenation of stage 2 high pressure hydrogen is released from the compressor at P_d .

Figure 2. Isotherms of the low pressure candidate Hydralloy C5 measured at HHC

Figure 3. Picture of the high pressure Sievert's apparatus designed and assembled by ORNL

Figure 4. Simulink dynamic system model of the two-stage metal hydride compressor developed at SNL