Hybrid Electrochemical Hydrogen/Metal Hydride Compressor

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Subrecipients:
- Skyre LLC
- Savannah River National Laboratory

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Overall Objectives

- Combine two novel technologies, an electrochemical hydrogen compressor (EHC) and a metal hydride compressor (MHC), into a new hybrid solid-state hydrogen compressor system.
- Evaluate the hybrid system for hydrogen refueling and other potential commercial hydrogen applications.
- Perform a techno-economic analysis against DOE cost and performance targets.
- Develop modeling tools to guide small-scale experimental testing for both the EHC and the MHC components as well as for the design and testing of a prototype hybrid compressor unit.
- Design, fabricate and test a 1–5 kg/day prototype unit and validate the models for future full-scale application of this technology.

Fiscal Year (FY) 2018 Objectives

- Demonstrate an EHC bench-scale system able to reach the required operating conditions.
- Demonstrate the technical feasibility of the selected hybrid compressor system under partial load and transient conditions.
- Develop a detailed transport model to demonstrate the proposed prototype system for partial load and transient conditions.
- Identify at least one large-scale hybrid compressor system that meets the FOA techno-economic targets under steady state and nominal conditions and design of a prototype.

Technical Barriers

This project addresses the following technical barrier from the Hydrogen Delivery section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan[1]:

(B) Reliability and Costs of Gaseous Hydrogen Compression.

Technical Targets

Hydrogen refueling station compression systems currently have a high capital cost per unit throughput. Today's mechanical compression technology requires frequent maintenance, resulting in the need for redundancy to minimize downtime and leading to high cost. Because of this, DOE is evaluating alternatives to mechanical compressors for refueling station systems up to 100 kg/h. DOE targets for hydrogen compression include achieving output pressures over 875 bar; energy consumption and efficiencies better than today's three-stage mechanical compressors and on a path to approach 1.4 kWh/kg, and a reliability of 80% with a leak rate <0.5%. A preliminary techno-economic model developed during the first half of this fiscal year has shown a hybrid EHC/MHC configuration with good potential of meeting many of DOE's compressor targets.

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

FY 2018 Accomplishments

- High-temperature membranes were selected so that waste heat from the EHC stage can be used to drive the MHC stage.
- Nafion 117 was selected as the baseline membrane and evaluated at high temperature (150°C) and high pressure (100 bar) with promising results for 100 hours.
- HP2 and HP3 metal hydride (MH) materials (TiCrMn type) were selected as the best candidate materials based on their operating conditions, cost, and availability.
- HP3 was down-selected as the first candidate MH.
- The performance of new MH vessel design, showing substantial performance and cost improvement over standard shell and tube designs, was modeled and successfully verified.
- Nafion 117 operating at high temperatures (>120°C) was found to have suitable waste heat to drive the MH stage, identifying a thermally self- sustaining configuration.
- An initial design was identified for the prototype and large-scale configurations.
- The techno-economic analysis of the new hybrid integrated system identified the current techno-economic performance of the system and a viable path to reach the DOE targets.

INTRODUCTION

Various alternatives to traditional mechanical compressor systems have been considered, including metal MHCs and EHCs. Both MHCs and EHCs are solid-state systems that have no moving parts other than valves. Both are quiet and have low maintenance requirements. However, strength and material issues as well as water and heat management issues have challenged EHCs, especially when operated at very high pressures. Similarly, low efficiency, especially when staging is required to attain high pressure ratios, has challenged MHCs and has made them too complex and expensive. Material degradation due to hydrogen impurity effects has also created issues for MHCs.

One novel alternative evaluated here is to combine EHC and MHC technologies in a way to maximize their advantages and to minimize each of their challenges to improve the overall systems performance on a path to meet or exceed current DOE targets. A hybrid EH/MH compressor takes advantage of lower maintenance/operating costs as well as increased reliability associated with both the MHC and EHC technologies over traditional mechanical compressors. Neither the MHC nor the EHC has any moving parts other than valves. The hybrid system also takes advantage of the higher efficiency and lower cost of the EHC by operating at lower delivery pressures combined with the robust and simple operation of a single-stage MH compressor at higher pressures. Both MHC and EHC technologies are scalable and can be used for a variety of hydrogen compression and delivery applications.

APPROACH

This project integrates an EHC unit with an MHC system into an overall hybrid compressor system. The hybrid compressor will be designed to compress a hydrogen flow rate of 10 kg/h (scalable to 100 kg/h) with an outlet pressure of 875 bar. A prototype hybrid unit will be designed based on the results obtained from system models and detailed models developed to simulate the overall full-scale hybrid compressor system. During Period 2, a prototype will be built and tested for a hydrogen flow rate of 1–5 kg/day and an outlet pressure of 875 bar. The modeling activities (along with selected experimental tests) will represent the basis to design larger scale (10–100 kg/h) hybrid systems and assess their performance against the DOE techno-economic targets.

RESULTS

Screening Analysis of Candidate Hybrid Compressor Systems

The initial techno-economic model developed during FY 2017 has been refined to include:

- Additional balance-of-plant equipment (heat exchangers, valves, humidifiers, and dryers), with the main objective to humidify the hydrogen feeding the EH compressor and dehumidify the hydrogen flow feeding the MH compressor.
- Enthalpy balance equations to assess the efficiency of the EHC system and consequently the available waste heat to be used to desorb hydrogen from the MHC system.
- Volumetric efficiency of the MH compressor system, identifying the additional MH material to be included in the system to assure the continuity and steady state operation performance of the overall compressor.

A schematic of the two-stage compression system is shown in Figure 1. A humidifier unit is placed before the EHC stage to provide the hydrogen flow with the right water content (especially for the Nafion membrane EHC). Two parallel EHC units compress the hydrogen up to pressures on the order of 100–200 bar. The hydrogen flow is then dehumidified in a dryer unit, and the water is collected, pumped, and reused in the humidifier units. The dried hydrogen feeds the MHC units (two parallel units) that compress the hydrogen up to a final pressure of 875 bar.

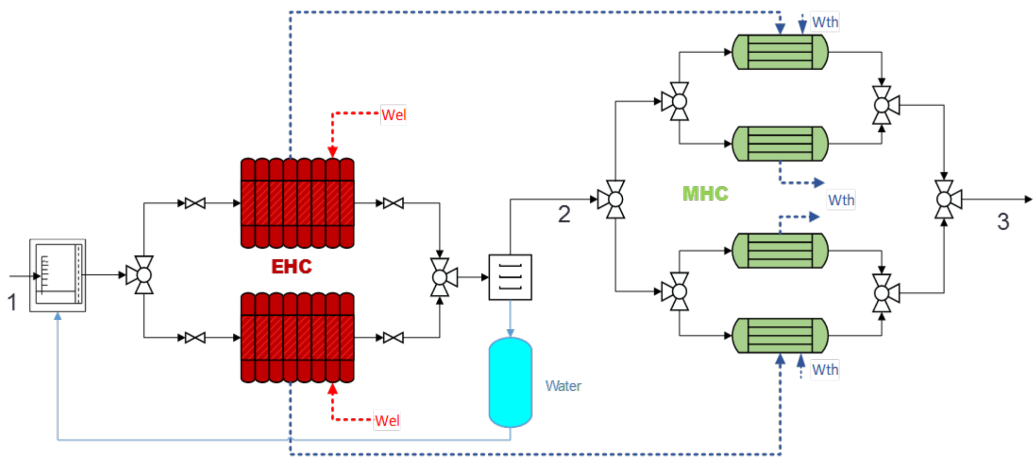

Figure 1. Hybrid compressor schematic (first stage: EHC; second stage: MHC)

Previous techno-economic analyses of the Nafion membrane and PBI membrane systems showed potential cost advantages for a higher temperature PBI system over Nafion. However, further exploration into materials compatibility has revealed potential cost challenges with the phosphoric acid used in PBI systems. Alternatively, recent experimental results indicate an expanded temperature window for Nafion to 150°C, thus maintaining the availability of high-quality waste heat to power the MH cycle. A final membrane down-selection was made in favor of Nafion over PBI membranes due to several disadvantages over Nafion, which include a 4x increase in cell hardware cost to make the hardware compatible with the PBI membranes and swelling of the membrane during doping causing membranes to tear. Nafion was also found to offer the following benefits over PBI membranes for this application:

- Significant experience with Nafion.
- Cell hardware rated for 6,000 psi.
- Application is suited for pressurized water operation.
- Anode and cathode pressure suppress steam.
- Membrane remains hydrated.
- Material stability (below Tm ~ 190°C).
- Demonstrated 100 hours of cell operation at 150°C.

A final decision was made to down-select Nafion 117 for the membrane system for the reasons described above and based on testing described below. The opportunity exists to evaluate Nafion 115 (thinner membranes) in the future as a further cost reduction

EHC Bench-Scale Experimental Tests

Previous testing of Nafion at 150°C was limited to a maximum output pressure of 200 psig. During FY 2018, a high-pressure pump was installed on the test stand to allow testing up to 1,750 psig (120 bar). Figure 2 shows a range of test conditions tested on a single cell stack operating at 500 mA/cm^2 over a period of 95 run hours. Voltage remained constant at fixed conditions. During the high-temperature testing with Nafion reaching 150°C and 120 bar output pressure, the team leveraged a proprietary hydration and thermal management approach. Future actions for performance improvement include investigation of thinner membranes, membrane pretreatment at high temperature for higher water uptake, and redesign of the flow field for better gas distribution.

Test Point	Temperature	Anode Pressure	Cathode Pressure
	(°C)	(psig)	(psig)
A	130	75	200
B	135	75	200
C	140	75	200
D	145	75	200
E	150	75	200
F	150	75	1750
G	150	100	1450
H	150	100	1450

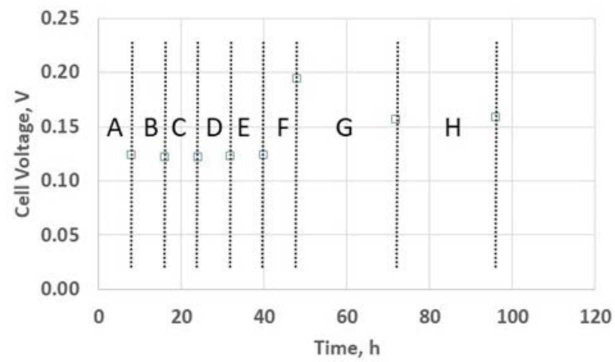

Figure 2. Nafion 117 cell test results during 95-hour operation at elevated temperatures

MH Bench-Scale Experimental Tests

An automated Sieverts apparatus was designed and fabricated for this project during FY 2017. This apparatus, which can operate at pressures greater than 875 bar and temperatures greater than 170°C, has been used to evaluate several high-pressure MH candidates identified last year (TiCr, TiCrMn, TiCrMnFe) as well as several identified in collaboration with the Sandia National Laboratories project team investigating similar high-pressure materials (TiCrMnFeV). Figure 3 shows the results for the characterization of one of our candidate MH materials, HP3 (TiCrMn). Figure 3a shows absorption and desorption isotherms from 22°C to 170°C, while Figure 3b shows van't Hoff plots for the same material, which is used to determine the enthalpy (ΔH) and entropy (ΔS) for the material. HP3 was selected as our best candidate MHC material thus far but additional testing to evaluate alternative annealing methods for this alloy are underway to improve its performance at higher pressures and lower temperatures.

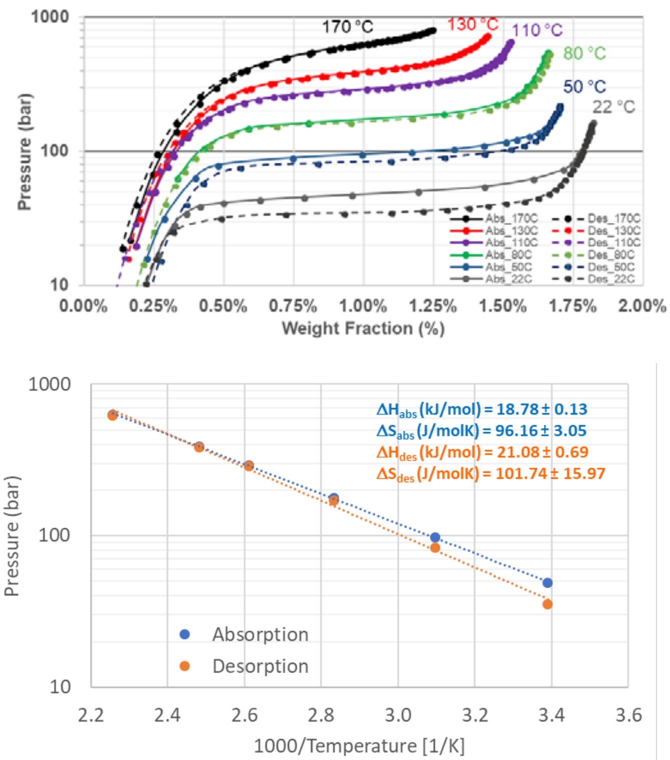

Figure 3. Characterization of MHC candidate HP3 (TiCrMn): (top) absorption and desorption isotherms; (bottom) van't Hoff plot

Hybrid Compressor System Model Development and Application

Global models were developed for the hybrid compressor system. The models are capable of both transient and steady-state calculations and consist of mass and energy equations that are coupled to equations for the thermodynamics of the EHC and the kinetics and thermodynamics of the MHC. Real gas properties were obtained by interfacing dynamically with the National Institute of Standards and Technology REFPROP [1] software. Characteristic parameters for the compressor are based on available data and MH properties that are similar to those anticipated for the actual material. The model for the MHC applies to a transient start-up from an initial MH concentration of 1,000 mol/m^3 and an initial discharged metal concentration of 12,000 mol/m^3 at the start of the first cycle.

In summary, the models demonstrated the capability of the hybrid compressor system to meet the performance targets for hydrogen flow and pressure at nominal conditions and its ability to rapidly recover from an off-normal state. Additionally, it was shown that the hybrid system can operate under partial feed conditions, as well as partial load, and could exceed 80% of the targets for the compressed gas. Based on model calculations, the 1-hour time allotted for certain stages of the MHC cycle can be significantly reduced provided the size of the MH bed is properly adjusted. The current model was used with our most recent material and system results to predict the performance of our final proposed hybrid compressor system configuration for our go/no-go milestone at the end of the period.

MH Tank Detailed Model Development

A detailed model was developed in Comsol and predicts temperature, pressure, hydrogen flowrate, chemical kinetics, and state of charge for the MH bed. Energy consumption, efficiency, and exergy can be computed from the model. Moreover, the model has the flexibility to be applied to a number of system designs and to various MHs with their accompanying kinetics. The EHC stage couples with the MH stage through boundary conditions on the inlet hydrogen stream and on the heat transfer fluid for the MH stage. An application of the MHC model to a single tube in an MHC stage is provided as a demonstration of the model. The tube wall, MH bed, and adjacent heat transfer fluid are a representative periodic region within the MHC. In the model, the temperature of the MH was controlled by changing the inlet temperature of the heat transfer fluid.

Figure 4 shows the initial design simulated. It consisted of a cylindrical MH bed at the center of the compressor tube, contained by a stainless-steel tube wall with four short fins protruding radially inward from the tube into the MH to promote effective heat transfer. The analysis showed excellent performance with insulation between the external wall and the MH material. Steady state was obtained after three cycles. Additional tests with enhanced finned structure and sensitivity analysis on the insulation are in progress.

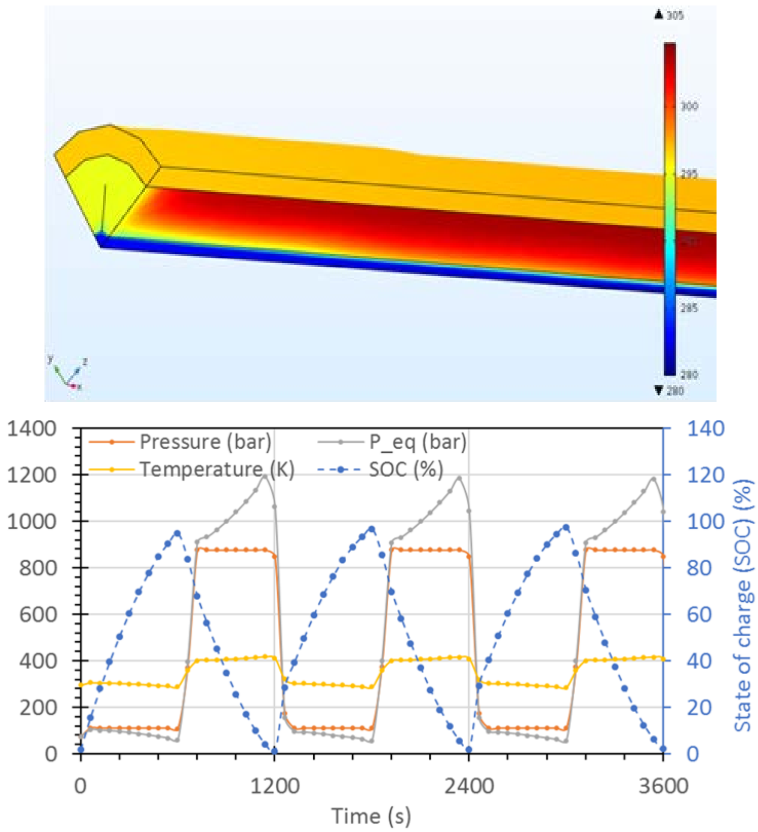

Figure 4. Detailed MH tank simulation: (top) temperature profile—charging cycle at 150 s; (bottom) pressure, temperature, and state of charge plots for three 20-minute cycles

Hybrid Compressor Prototype Design

A prototype, hybrid compressor system (for 1–5 kg/day) was designed and modeled. Several MH compositions (including amendments to enhance thermal conductivity), bed geometries, and heat exchange surface configurations were examined and compared to select the best MH tank format in terms of techno-economic performance. Skyre provided the required details for the EHC system based on the current or advanced high-temperature EHC technology. Figure 5 shows the overall system high level piping and instrumentation diagram schematic. The waste heat available from the electrochemical system membrane electrode assembly is recovered to provide the required heating power to the MH high pressure system. Initial calculations carried out demonstrated the technical feasibility of the integrated approach. The fluid flow rates required to discharge the thermal power produced in the electrochemical system match the flow rates required to transfer the heating thermal power to the MH system. The MH system comprises two parallel units, working in opposite mode (one unit is charging hydrogen and the other unit is discharging hydrogen) to assure continuity. The cooling power is provided through water, operating at about room temperature. The hydrogen processed by the electrochemical unit is stored in a small buffer tank at 100 bar. A three-way valve directs the hydrogen flow to the MH unit working in charging mode. The hydrogen is compressed up to 875 bar through the thermal MH system.

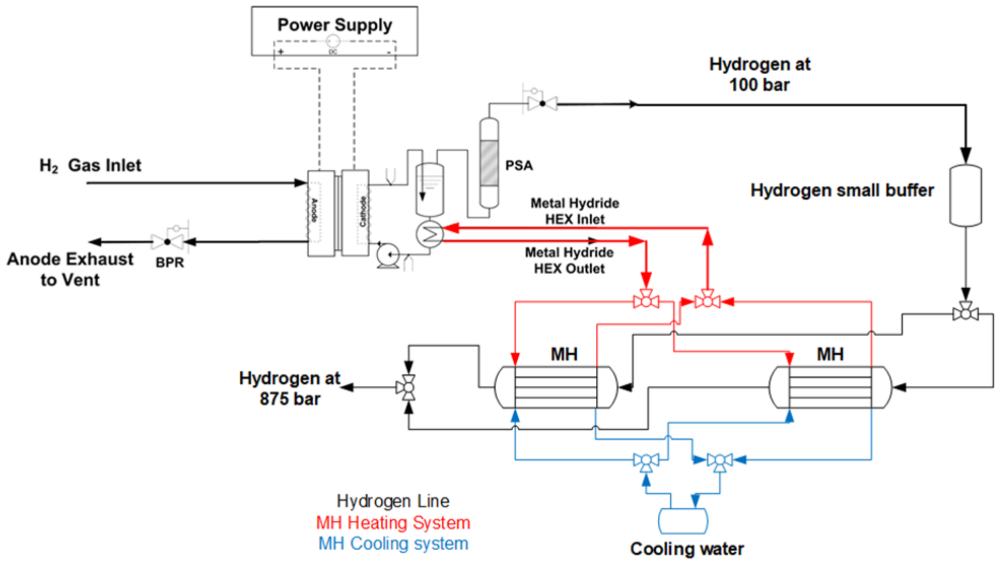

Figure 5. High-level schematic of the integrated electrochemical-thermal compression system for the bench-scale testing

CONCLUSIONS AND UPCOMING ACTIVITIES

EHC Stage

- Nafion 117 was selected as the baseline membrane and evaluated at high temperature (150°C) and high pressure (100 bar) with promising results for 100 hours.
- Long-term operating history of Nafion and issues with component degradation with PBI systems led to the current selection of Nafion as the most cost-effective option.

MHC Stage

- MH candidate materials were evaluated and characterized. A new high-pressure (>875 bar) Sievert apparatus was designed and operated to provide thermodynamic information on the materials at high pressures.
- HP2 and HP3 MH materials (TiCrMn type) were selected as the best candidate materials based on their operating conditions, cost, and availability.
- HP3 was down selected as the first candidate MH
- The performance of the new MH vessel design, showing substantial performance and cost improvement over standard shell and tube designs, was modeled and successfully verified.

EHC-MHC Matching

- Nafion 117 operating at high temperatures (>120°C) was found to have suitable waste heat to drive the MH stage, identifying a thermally self-sustaining configuration

Large-Scale and Prototype-Scale EHC and MHC

- Initial designs were identified for the prototype-scale and large-scale configurations.
- Both an integrated EHC/MHC system model and a detailed heat/mass transfer MHC model have been developed and will be used to finalize the design of the prototype hybrid compressor. Both models will

be validated during prototype testing in Phase 2 and used to provide a preliminary design for a full-scale hybrid compressor system.

EHC-MHC Techno-Economic Analysis

- The techno-economic analysis for the new hybrid integrated system identified the current cost and performance of the system and a viable path to reach the DOE targets.

Upcoming activities during Phase 2 include assembling and demonstration of the prototype hybrid compressor system, detailed model update and validation against the prototype data, and optimization of the hybrid compressor system to reach DOE targets.

FY 2018 PUBLICATIONS/PRESENTATIONS

1. C. Corgnale, et al. "Technical Performance of a Hybrid Thermo-Electrochemical System for High Pressure Hydrogen Compression." *ECS Transactions* 80, no. 10 (2017): 41–54.
2. C. Corgnale, et al. Abstract submitted to the ECS AIMES meeting (September 2018).
3. C. Corgnale, et al. "Techno-Economic Analysis of High-Pressure Metal Hydride Compression Systems." *Metals* 8, no. 6 (2018): 469.

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1. National Institute of Standards and Technology Standard Reference Database 23, Version 9.0. E.W. Lemmon, M.L. Huber, M.O. Mc Linden. Thermophysical Properties Division (Copyright 2010).