

III.12 Hybrid Electrochemical Hydrogen/Metal Hydride Compressor

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- Demonstrate an EHC bench-scale system, able to reach required operating conditions.
- Demonstrate the technical feasibility of the selected hybrid compressor system under partial load and transient conditions using a detailed, integrated, system model.

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.

- (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; 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 of <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.

FY 2017 Accomplishments

- A techno-economic modeling framework for evaluating MH and EH compression stages has been completed and a leading candidate system, operating at large scale, based on Ti-based, MH and polybenzimidazole (PBI) membrane, EHC technologies, has been identified.
- Preliminary estimates show that waste heat from a higher temperature PBI EHC system should have enough energy to drive the MHC system.
- A new MHC heat transfer design has been identified that can substantially reduce the heat transfer area, reduces required thermal, and reduces cost associated with heat transfer systems.
- EHC differential pressure tests showed that PBI membrane may be robust enough for compression applications.

Overall Objectives

- Combine two novel technologies, electrochemical hydrogen compressor (EHC) and 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/d prototype unit and validate the models for future full-scale application of this technology.

Fiscal Year (FY) 2017 Objectives

- Develop a techno-economic modeling framework for evaluating metal hydride (MH) and electrochemical hydrogen (EH) compression stages.
- Identify at least one system, operating at large scale, based on MHC and EHC technologies, demonstrating a viable path to reach the techno-economic targets.

- A new material type for EHC stage bipolar plates was shown to have good resistance to phosphoric acid environments.
- Small-scale MH testing and characterization systems have been designed and sample quantities of candidate MH materials have been ordered.
- The availability of larger quantities of MH materials has been identified; cost and shipping details are being pursued for Period 2.
- An integrated hybrid compressor system model is under development, the MHC system has successfully modeled and is currently being integrated with the EHC system.



INTRODUCTION

Various alternatives to traditional mechanical compressor systems have been considered, including MHC and EHC. 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 and 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 have 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

Greenway Energy will integrate an EHC unit with a 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/d and outlet pressures 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

An initial techno-economic model has been completed. The model includes:

- EHC stack and MH vessel and materials;
- Balance of plant equipment (heat exchangers, valves, humidifiers, and dryers), with the main objective of humidify the hydrogen feeding the electrochemical 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 MH compressor system; and
- 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 final pressure of 875 bar.

Preliminary identification of at least one hybrid configuration that has the potential to meet DOE targets is underway. Regarding the EHC system, four membranes have been down selected as the baseline constitutive membranes: Nafion 212 membrane system, PBI film membrane system, Advent® membrane, and a Fumatech® membrane. Regarding the high-pressure MH compressor system, three baseline MH materials working at high pressures have been down-selected: HP1: $\text{TiCr}_{1.9}$; HP2: $(\text{Ti}_{0.97}\text{Zr}_{0.03})_{1.1}\text{Cr}_{1.6}\text{Mn}_{0.4}$; and HP3: $\text{Ti}_{1.1}\text{CrMn}$.

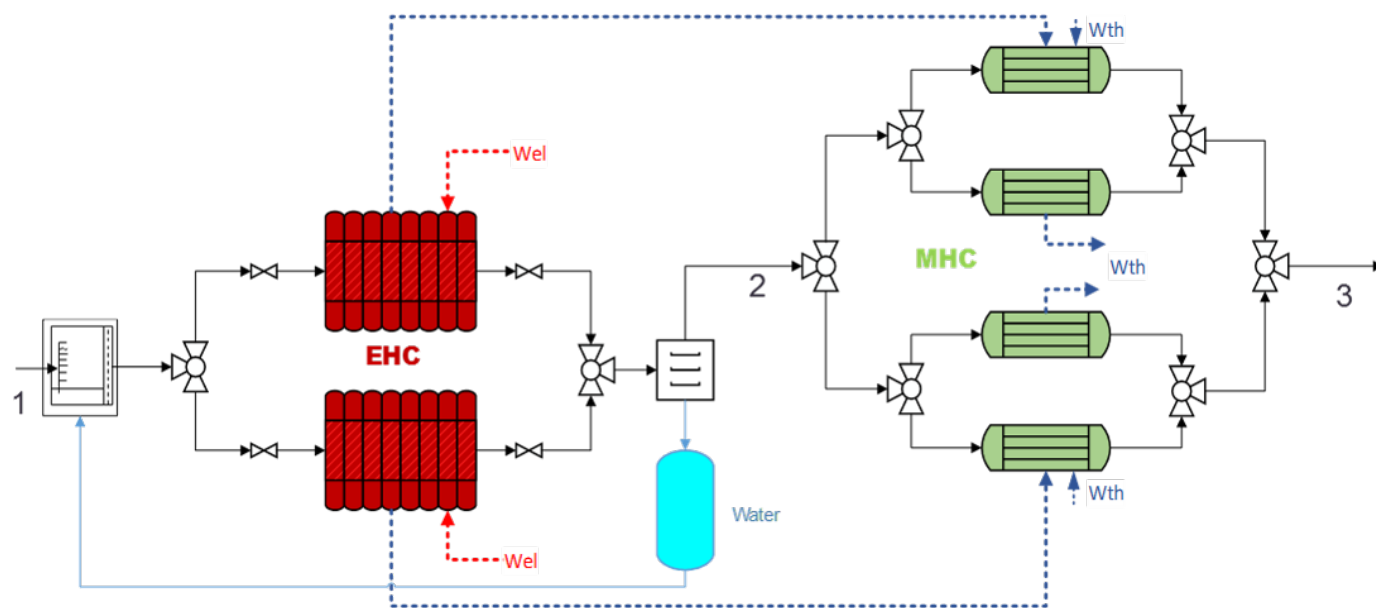


FIGURE 1. Hybrid compressor schematic (first stage: EHC; second stage: MHC)

A comparison of the Nafion 212 and PBI systems is shown in Figure 2. Figure 2 shows that the Nafion 212 EHC system has a slightly lower cell voltage than the PBI systems but it does not offer any heat recovery opportunity with the MHC, due to the low operating temperature of the Nafion system. In addition, an economic comparison between the two proposed membrane systems shows that the PBI system achieves an installed cost reduction of about 27% compared to the corresponding Nafion system.

As with the EHC system, a techno-economic analysis has been applied to the three down-selected materials for the MH system (HP1, HP2, and HP3). A new heat transfer design has been developed and modeled (an invention disclosure

is being filed for the new design). Preliminary conceptual design and performance of the new vessel design for the three selected metal hydrides show that hydride materials HP2 and HP3 appear to give the best technical performance. A summary of the results from the economic analysis is shown in Figure 3. Figure 3 shows a comparison between the new conceptual design and the more traditional shell and tube (S&T) design. A less pure Ti-Fe material has been assumed for this case with a Ti cost of \$3.8/kg for the HP1, HP2, and HP3 alloys highlighting the contribution of both the material cost and the vessel and heat exchanger cost. A reduction of the heat exchanger and pressure vessel cost of almost 70% has been achieved from the S&T to the new design.

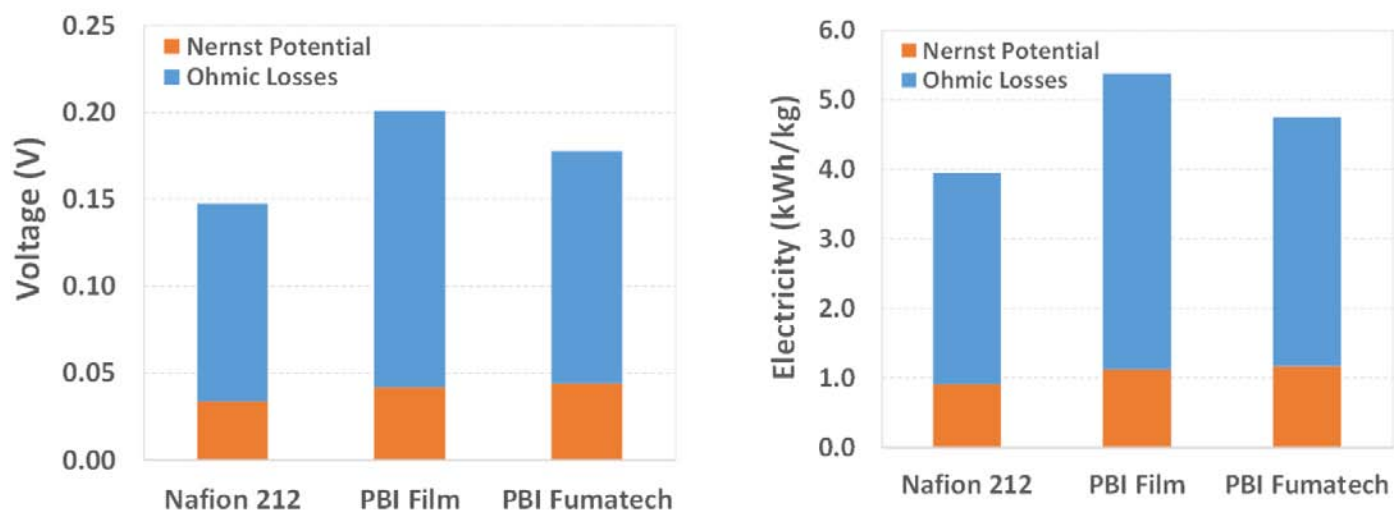
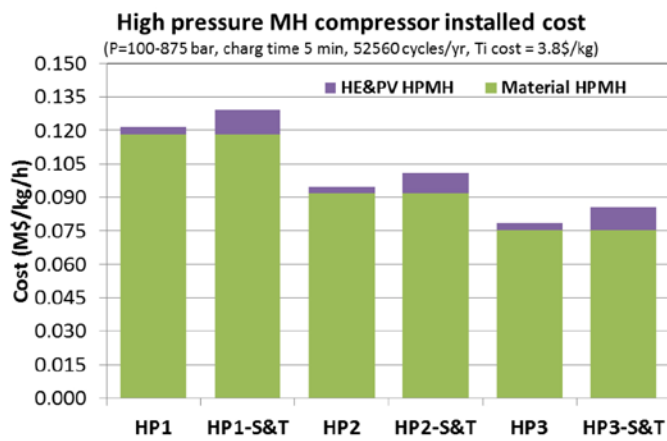


FIGURE 2. Technical performance comparison between Nafion and PBI membrane systems



HPMH – high pressure metal hydride; HE&PV – heat exchangers and pressure vessels

FIGURE 3. Economic comparison between traditional S&T and new design with low cost Ti

The techno-analysis performed took advantage of the waste heat from the EHC system to power the MHC system. It was determined that the hydrogen desorption from the MHC system requires thermal 4.3–4.9 kWh/kg at about 170°C depending on the MH alloy. The potential electrochemical system waste heat that can be recovered using a PBI membrane EHC system is shown in Figure 4. This figure shows that a high temperature PBI membrane operating at a current density of about 2.5 A/cm² has the required heat to desorb the hydrogen from the metal hydride system. More analyses are in progress on specific EHC and MHC configurations to arrive at an optimized hybrid compressor system taking into account not only installed costs but long-term operating cost as well as overall system performance and reliability.

EHC Bench Scale Experimental Tests

Sustainable Innovation carried out testing on a bench scale EHC system aimed at (1) developing appropriate membrane electrode assemblies for operating at high temperatures, (2) evaluation of high temperature and high-pressure membranes, and (3) identifying appropriate design modifications to the cell stack to accommodate (1) and (2).

Membrane material compatibility testing for 150–120°C operation at 90–120 bar differential pressure was begun. While Nafion and similar membranes have been demonstrated to operate at high differential pressures and with high proton conductivity, operating temperature is typically limited to less than 100°C. To date, membranes capable of higher temperature operation at 150–200°C have not demonstrated sufficient strength to withstand 90–120 bar differential pressure. Additionally, these high temperature compatible membranes utilize phosphoric acid as the electrolyte, leading to potential materials compatibility conflicts due to corrosion.

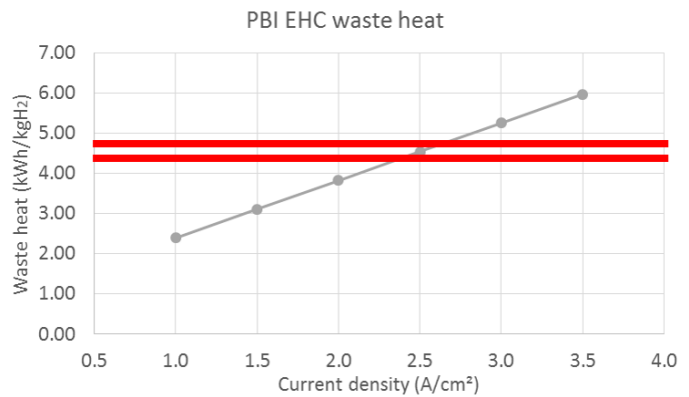


FIGURE 4. PBI EHC system waste heat (red lines represent the MHC heat required to desorb the stored hydrogen)

Material samples of high pressure EHC components have been exposed to phosphoric acid at operating temperature. Initial results indicate that alternate materials and/or protective coatings must be employed to maximize lifetime performance. Base materials were found to completely dissolve within 24 hours. Two material options have been identified that provide corrosion resistance. Sustainable Innovation has received quotes on replacement parts for the existing compressor hardware and is purchasing samples.

Multiple PBI film options have been tested within Sustainable Innovation's high pressure EHC hardware at low and high temperature. Initial testing indicates that dry and imbibed PBI membrane can withstand 100 bar at 160°C. Properly supported PBI membrane seems to be capable of supporting high pressure differentials. Electrochemical testing of PBI membranes at pressure is scheduled for the second half of FY 2017. In addition, Nafion, which is typically limited to operation at less than 100°C, will be evaluated at higher operating ranges between 120°C and 140°C.

Hybrid Compressor System Model Development and Application

A system model for the hybrid compressor has been developed. The model includes both the ECH system as well as the MHC system. The initial results have the EHC operating at steady state providing hydrogen at 100 bar and a maximum of 100 kg/h to the MHC. The metal hydride volume is ~12 m³ and assumes material expansion of 15% (crystal volume) on hydrogen uptake with a bed porosity of 10% when fully expanded (fully charged). Figures 5a and 5b show the operation of the metal hydride beds during four-hour cycles.

During the first three cycles, more hydrogen enters the compressor than exits. This is due to hydrogen discharge from the metal hydride during the heating phase and unavoidable re-uptake of hydrogen by the MH bed upon cooling to initial state at 314 K. This causes the amount of

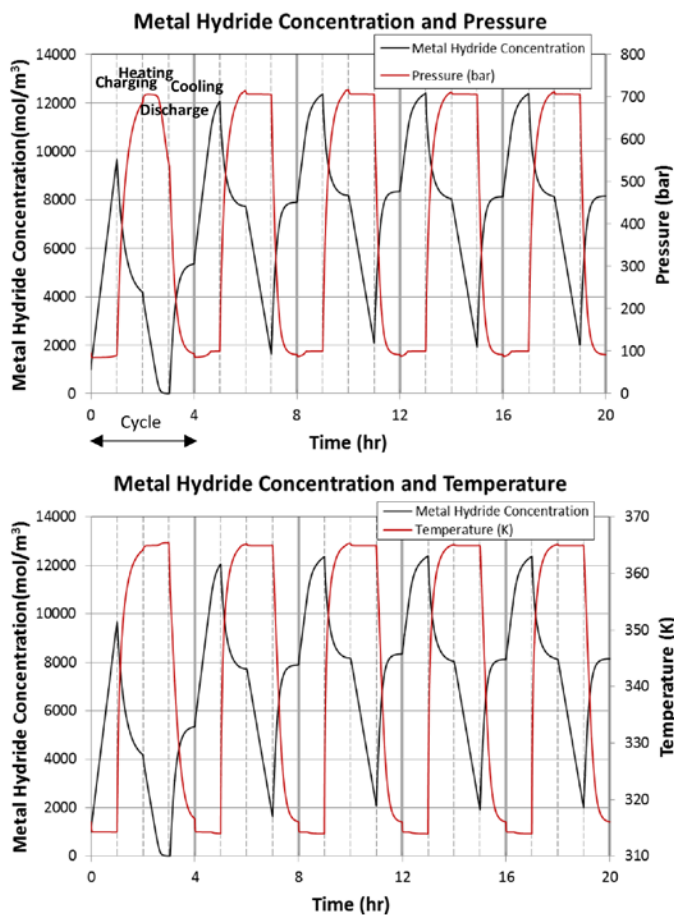


FIGURE 5. Hybrid compressor system model showing MHC performance versus pressure and temperature, respectively

hydrogen retained in solid phase, prior to charging, to rise for the first three cycles, then stabilize.

For the postulated MH properties and bed volume, delivery is ~50 kg/h at 700 bar. The current model is being updated to include the more specific information on the electrochemical and metal hydride materials obtained from the techno-economic screening analysis as well as to include other operating conditions and system configurations.

CONCLUSIONS AND UPCOMING ACTIVITIES

A techno-economic modeling framework for evaluating MHC and EHC stages has been completed and a leading candidate system, operating at large scale, based on Ti-based metal hydride and PBI membrane electrochemical technologies, has been identified. Preliminary estimates show that waste heat from a higher temperature PBI EHC system should have enough energy to drive the MHC system. A new MHC heat transfer design has been identified that can substantially reduce the heat transfer area, reduce the required thermal energy, and reduces cost associated with heat transfer systems. EHC differential pressure tests showed that PBI membrane may be robust enough for compression applications. A new material type for EHC stage bipolar plates was shown to have good resistance to phosphoric acid environments.

Upcoming Period 1 activities include fabrication and operation of a high-pressure, small-scale, MH testing and characterization system; evaluation of alternate compressor internal materials for electrochemical testing of PBI compressors; exploration of maximum temperature limitations of Nafion while under high pressure operating conditions; finalization of compressor material set (PBI or Nafion); completion of integrated hybrid compressor system; and design of an integrated hybrid EH–MH compressor prototype system by the end of Period 1 (March 31, 2018).

FY 2017 PUBLICATIONS/PRESENTATIONS

1. Greenway, S. et al., “Tech Team Project Review,” National Renewable Energy Laboratory, Golden, CO, November 2, 2016.