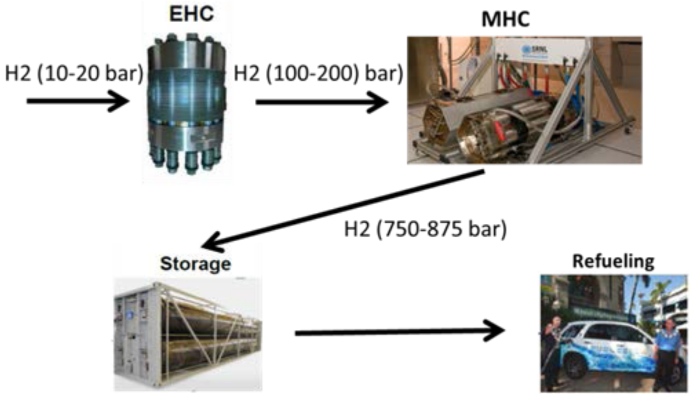
# Hybrid Electrochemical-Metal Hydride Compression



EHC

H2 (10-20 bar)

H2 (100-200) bar)

MHC

H2 (750-875 bar)

Storage

Refueling

Ted Motyka, Claudio Corgnale, Martin Sulic (GWE)
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Bruce Hardy (SRNL)
Presenter: Scott Greenway (GWE)

Project PD137

SRNL™

Sustainable Innovations

GreenWayEnergy®
POWERFUL EXPERTS

# Overview

## Timeline and Budget

Project Start Date: 10/01/2016
Project End Date: 09/30/2019
FY17 DOE Funding: $1,415K*
Cost Share: $360K*

* Period 1 (18 months)

## Partners

Sustainable Innovations, LLC
Savannah River National Laboratory

## Hydrogen Delivery Technical Barriers

- Reliability and Costs of Gaseous Hydrogen Compression
- Challenges: Increase the reliability, reduce the cost, and improve the energy efficiency of gaseous hydrogen compressors

# Relevance
# Traditional and Advanced $H_2$ Compression Technologies

## Mech. $H_2$ Compressors

- Commercial
- Require Frequent Maintenance (High OpEx)
- High energy consumption compared to compression of other gases
- No separation capability
- No ability to use waste heat to perform compression work

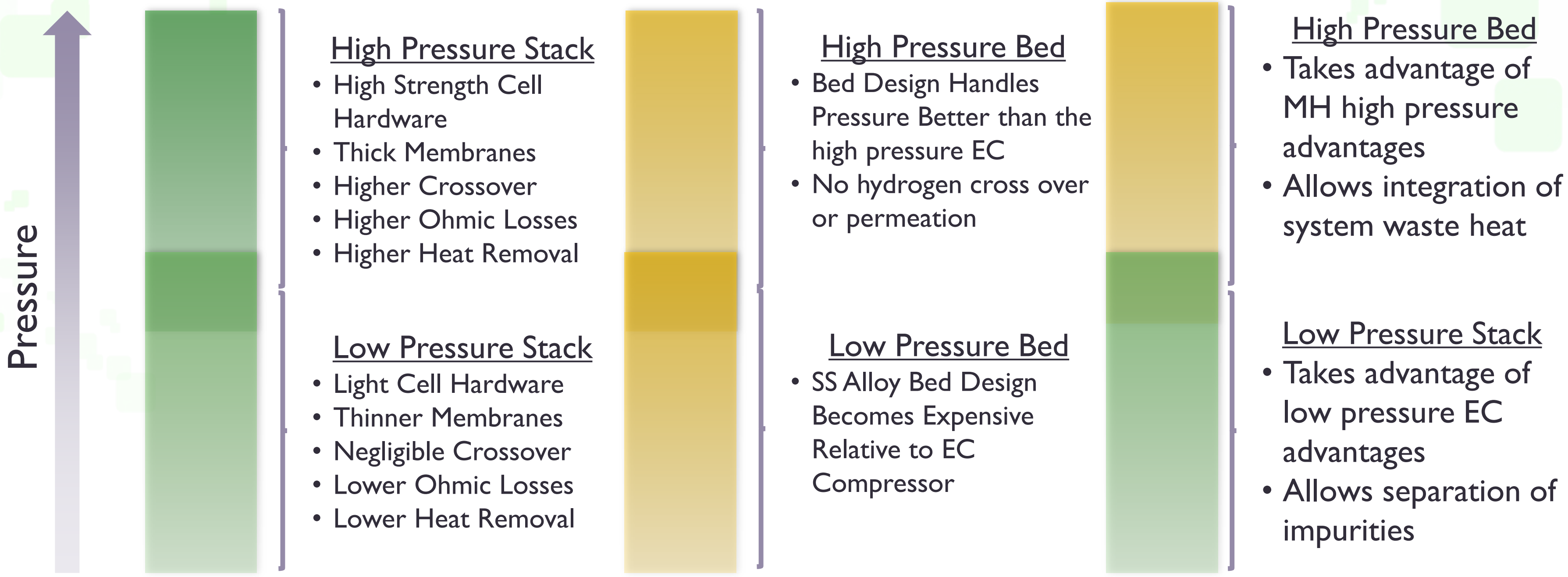
## EC $H_2$ Compressors

- Semi-commercial
- No moving parts
- Theoretically limited only by Gibbs Energy (adiabatic efficiency)
- Compression efficiency mostly determined by membrane conductivity
- Adds separation capability to hydrogen compression
- Can be used in hydrogen recycling applications
- Membranes have problems with $H_2$ crossover

## MH $H_2$ Compressors

- Pre-commercial
- No moving parts
- Requires no electricity input
- Adds ability to utilize waste heat for compression
- Long life-time
- Thermal energy input can be high due to heating/cooling of the MH material
- Metal hydride materials can be expensive (High CapEx)

# Relevance
# Advanced 2-Stage $H_2$ Compression Strategies



## Staged EC Compressor

High Pressure Stack
- High Strength Cell Hardware
- Thick Membranes
- Higher Crossover
- Higher Ohmic Losses
- Higher Heat Removal

Low Pressure Stack
- Light Cell Hardware
- Thinner Membranes
- Negligible Crossover
- Lower Ohmic Losses
- Lower Heat Removal

## Staged MH Compressor

High Pressure Bed
- Bed Design Handles Pressure Better than the high pressure EC
- No hydrogen cross over or permeation

Low Pressure Bed
- SS Alloy Bed Design Becomes Expensive Relative to EC Compressor

## Hybrid EC/MH Compressor

High Pressure Bed
- Takes advantage of MH high pressure advantages
- Allows integration of system waste heat

Low Pressure Stack
- Takes advantage of low pressure EC advantages
- Allows separation of impurities

# Major Phase I Tasks and Milestones

*Task 1.1: Screening analysis of candidate, hybrid compressor systems*

Milestone 1.1.1: Development of a techno-economic modeling framework for evaluating MH and EC compression stages **12/31/16**

Milestone 1.1.2: Successful identification of at least one system, operating at large scale, based on MH and EC technologies, demonstrating a viable path to reach the techno-economic targets reported in the DOE FOA **3/31/17**

*Task 1.2: EHC bench scale experimental tests*

Milestone 1.2.1: Successful demonstration of the EHC bench scale system, being able to reach the required operating conditions **9/30/17**

*Task 1.3: MH bench scale experimental tests*

*Task 1.4: Hybrid compressor system model development and application*

Milestone 1.4.1: Successful demonstration of the technical feasibility of the selected hybrid compressor system under partial load and transient conditions **6/30/17**

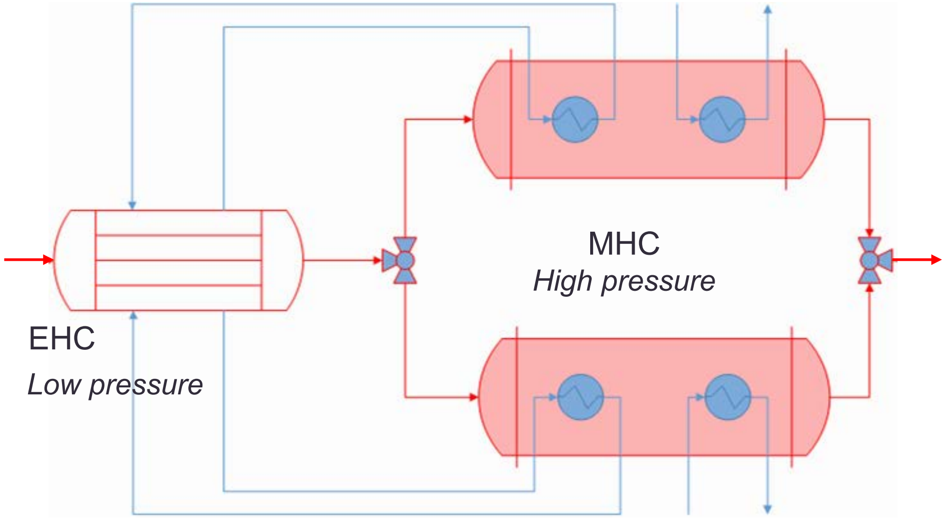
*Task 1.5: MH tank detailed model development*

Milestone 1.5.1: Detailed transport model results need to demonstrate that the proposed prototype system for partial load and transient conditions to be compared with experimental data during Phase 2 **12/31/17**

*Task 1.6: Hybrid Compressor prototype design*

Milestone 1.6.1 (Go/No-Go): Identification of at least one large-scale hybrid compressor system that meets the FOA techno-economic targets under steady state and nominal conditions. **3/31/18**

# Accomplishments
# Task 1.1: Screening Model



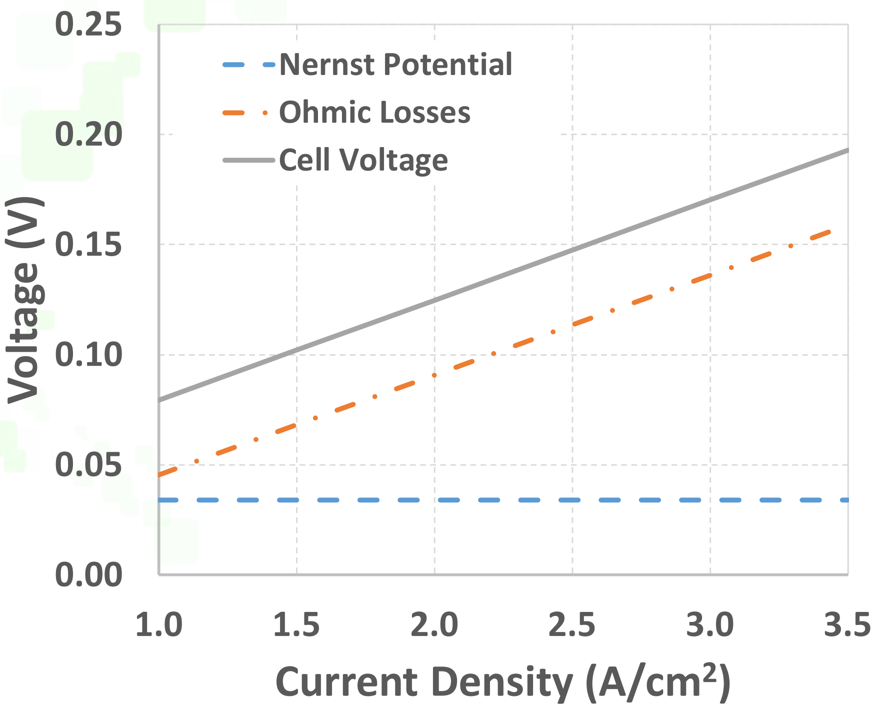
High-level model to screen system configurations/materials against the DOE targets

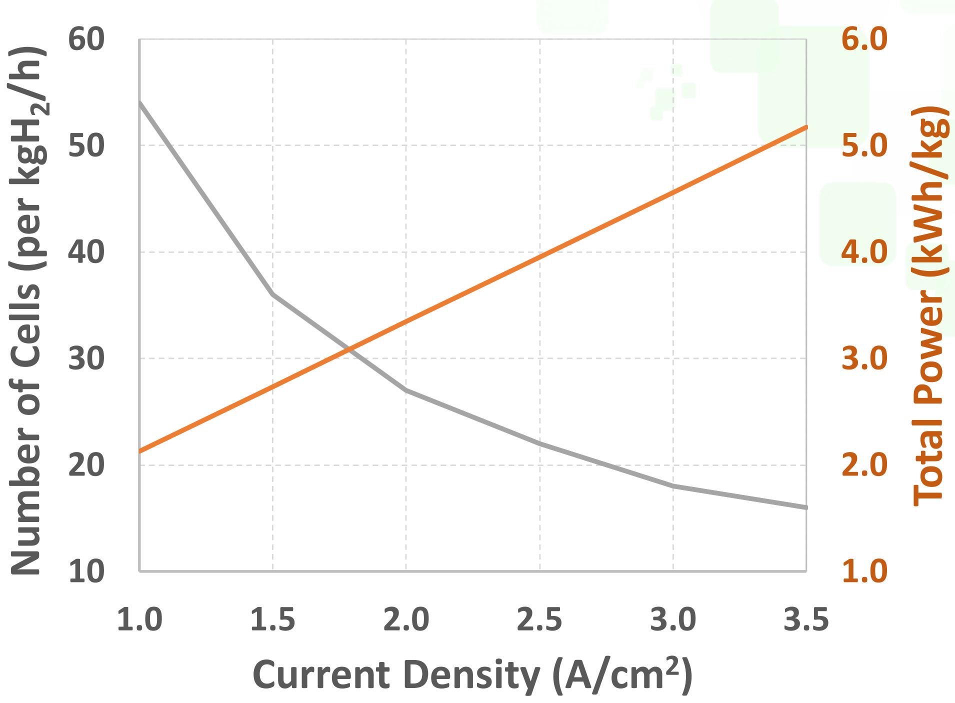
- Global steady-state mass and energy balances for the EC and MH stages
- Evaluates design and operating conditions (i.e. system configurations, EC properties):
  - Techno-economic design optimization
  - Material selection to meet technical targets

# Accomplishments
# Task1.1: EC Stage Materials Screening

| ***Metric*** | **Nafion** | **PBI Film** | **Advent** | **Fumatech** | Comments |
|---|---|---|---|---|---|
| Operating T (°C) | < 100C | 120-180 | 120-200 | 160-180 | Higher EHC temp provides better compatibility and possible recovery in the MH |
| Membrane thickness (um) | N212 = 50<br>N211 = 25<br>N115 = 125 | 70um | | 53um | Thicker can help with back diffusion of H2, but leads to increased power consumption. |
| Membrane area (cm2) | 500 | 500 | | 500 | Function of conductivity and target energy consumption. |
| Range of current density (A/cm2) | 1-4 | 1-4 | 1-4 | 1-4 | Function of conductivity and target energy consumption. |
| Membrane conductivity (Ohm-cm$^{-1}$) | 0.5 - 0.11<br>[ 0.02 – 0.05 in hardware typ. ] | 0.1<br>[ 0.05 in hardware typ. ] | 0.08<br>[ lower in hardware] | 0.1<br>[lower in hardware] | [ typical performance in hardware deviates from material conductivity due to interfacial losses ] |
| Electrolyte | PFSA | PA | PA | PA | |
| Water crossover ($kg_{H20}/kg_{H2}/h$) | 28.5 | Negligible | Negligible | Negligible | Used the relationship in reference * |
| Research focus / performance limitations | Investigate upper temperature limit with high pressure | PA compatibility, strength, conductivity | PA compatibility, strength, conductivity | PA compatibility, strength, conductivity | |

# Accomplishments
# Task 1.1: Projected Results for Nafion EC Stage





***Single cell***

Inlet pressure = 10 bar

Outlet pressure = 100 bar

$H_2$ flow rate = 0.0466 kg/h at 2.5 A/cm$^2$

***Overall system***

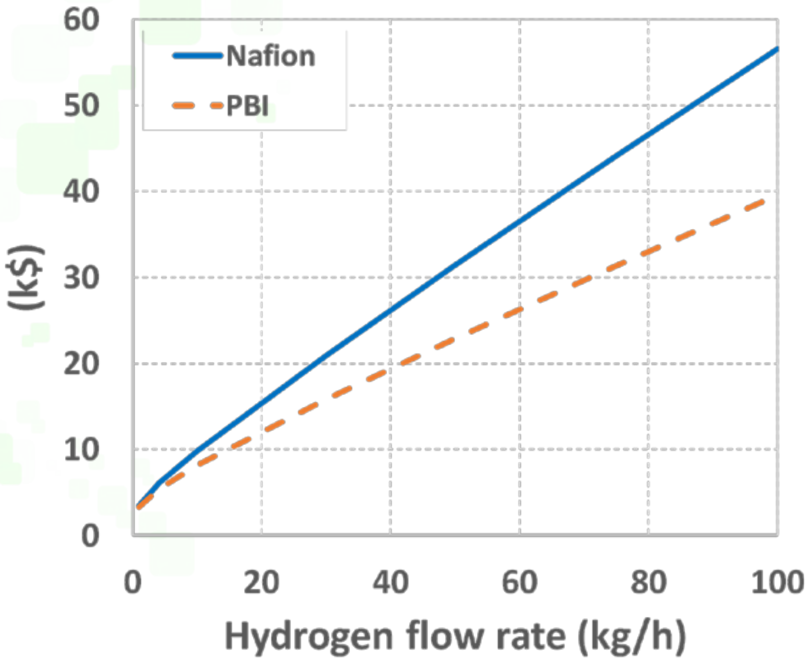
Inlet pressure = 10 bar

Outlet pressure = 100 bar

DOE target (100 – 875 bar) = 1.6 kWh/kg

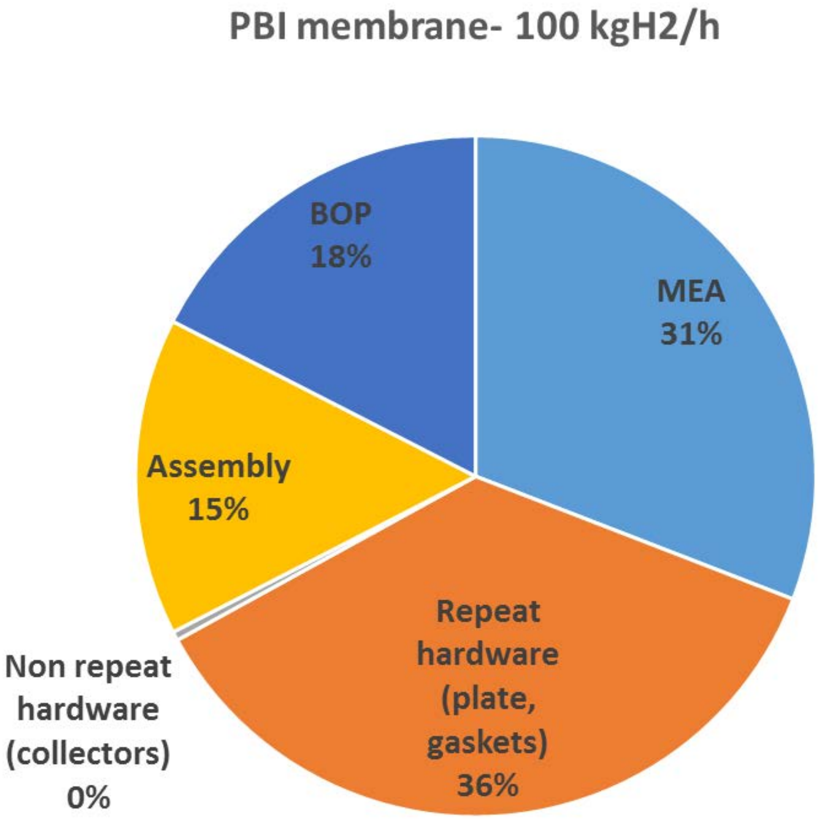
# Accomplishments
# Task 1.1: Projected Economic Results for PBI Membrane

<u>Installed costs</u>

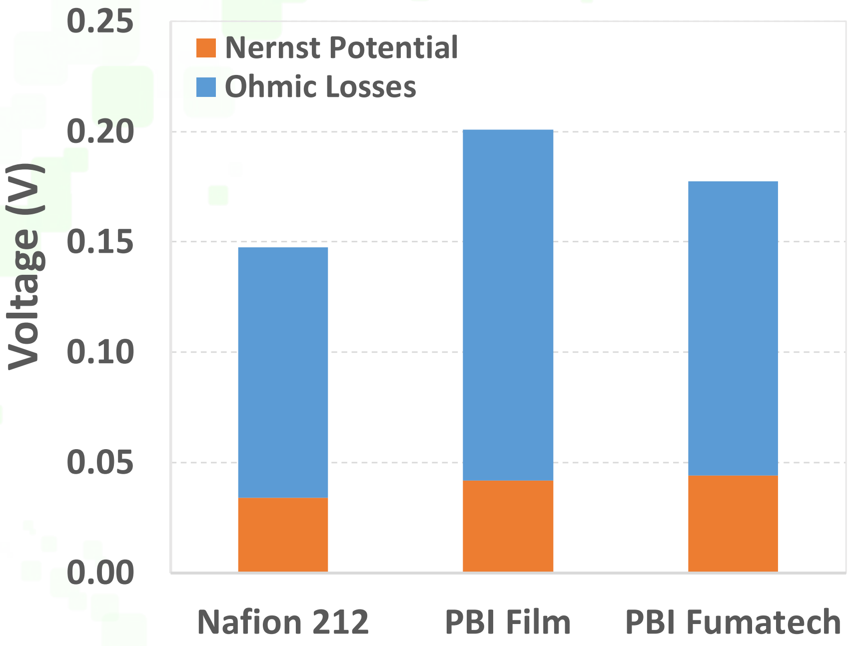


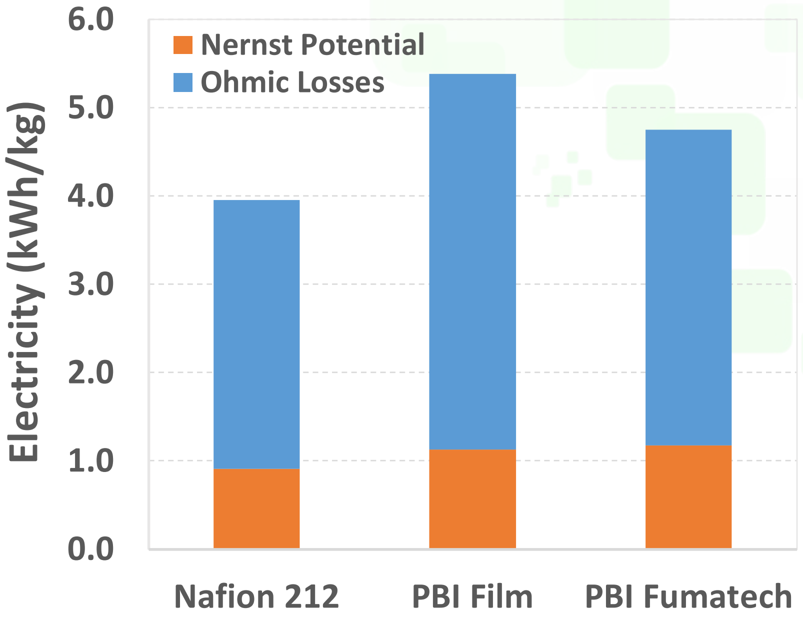
<u>PBI membrane EC stage</u>
Inlet pressure = 10 bar
Outle pressure = 100 bar
Current density 2.5 A/cm$^2$
Cell Voltage ≈ 0.18 V
Compression Work ≈ 4.7 kWh/kg

<u>Installed cost breakdown</u>



# Accomplishments
# Task 1.1: Techno-Economic Model Results for EC stage





- Nafion 212 has slightly lower cell voltage than PBI membranes but does not offer heat recovery with the MH stage due to its lower temperature
- PBI membrane seems to be the better option

# Accomplishments
# Task 1.1: MH Stage Material Screening

## Metal Hydride Materials

| High Pressure MHs (HP) | DH (kJ/mol) | wt% | Bulk density (kg/m$^3$) | Operating P (bar)/T (°C) |
|---|---|---|---|---|
| HP1: $TiCr_{1.9}$ | 26.2 | 1.3 | 3130 | 100/40<br>875/125 |
| HP2:<br>$(Ti_{0.97}Zr_{0.03})_{1.1}Cr_{1.6}Mn_{0.4}$ | 23.4 | 1.7 | 3170 | 100/32<br>875/125 |
| HP3:<br>$Ti_{1.1}CrMn$ | 22.9 | 1.5 | 3160 | 100/27<br>875/119 |

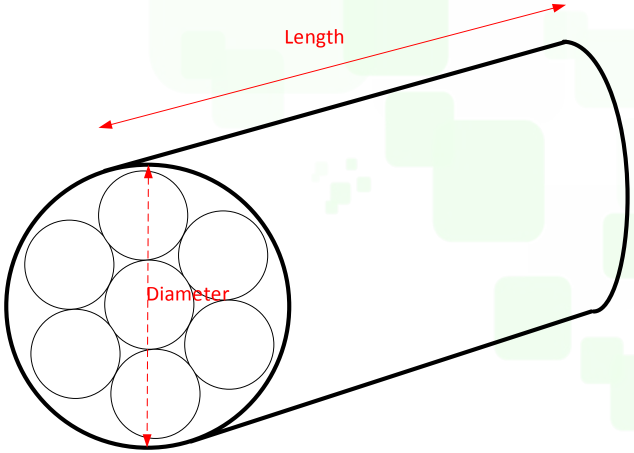
## Assumptions and Constraints

- Inlet hydrogen pressure = 100 bar after ECH compression
- Outlet hydrogen pressure = 875 bar (compression ratio about 9)
- Hydrogen flow rate = 1-100 kg/h
- Heating fluid maximum temperature = 150 °C (it matches with EHC waste heat temperature)
- Cooling fluid min temperature = 10 °C
- Gaseous hydrogen mass in the HPMH assumed negligible (at 100 bar)
- Relevant contribution of the gas hydrogen at 875 bar, due to void space of the MH system and to the MH expansion-contraction during charging-discharging process

# Accomplishments

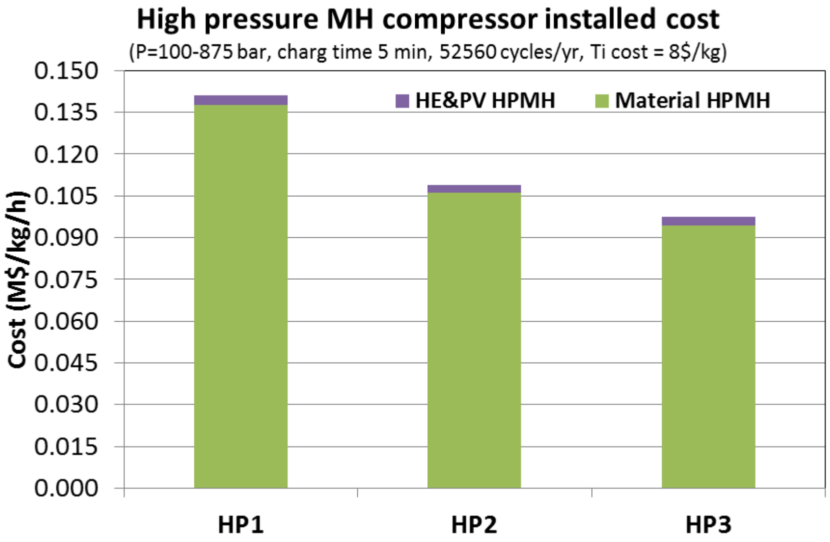
# Task 1.1: High Pressure MH Stage Properties

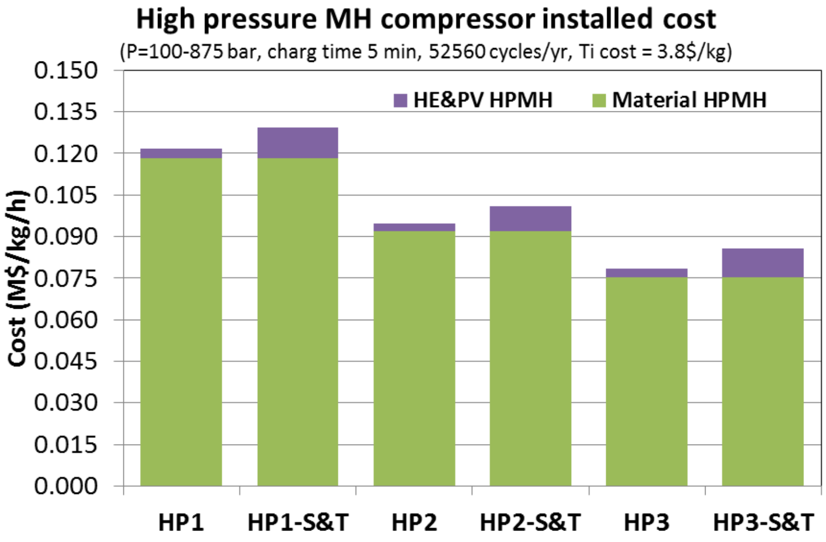
| High Pressure MHs (HPMH) | DH chem reaction (kW/100kg/h) | DH sensible (kW/100kg/h) | DH total (kW/100 kg/h) | Number of units | Diameter of each unit (m) | Length each unit (m) |
|---|---|---|---|---|---|---|
| HP1: $TiCr_{1.9}$ | **366.8** | 122.9 | 489.7 | 4 (2 charging mode + 2 discharging mode) | 0.35 | 4.5 |
| HP2: $(Ti_{0.97}Zr_{0.03})_{1.1}Cr_{1.6}Mn_{0.4}$ | **327.6** | 110.3 | 437.9 | 4 (2 charging mode + 2 discharging mode) | 0.30 | 5.0 |
| HP3: $Ti_{1.1}CrMn$ | **320.6** | 125.3 | 445.9 | 4 (2 charging mode + 2 discharging mode) | 0.42 | 2.8 |



Initial screening of Ti-MHs based on the material coupled system techno-economic properties and current constraints and assumptions

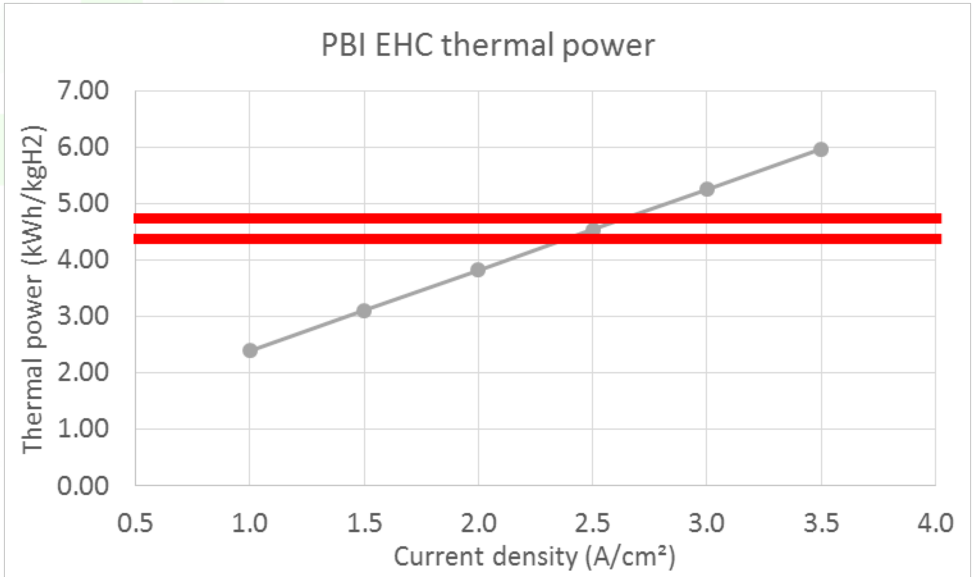
# Accomplishment
# Task 1.1: Techno-economic results for MH system





- Based on new heat transfer design
  - Reduces heat transfer area
  - Reduces required thermal power (sensible heat)
  - Reduces cost associated with heat transfer system
  - Traditional shell & tube solution (S&T) cost ≈ $550k/100kg/h
  - New heat transfer solution cost ≈ $170k/100kg/h
- Variation of the costs based on Ti-impurities (Pure Ti = 8 $/kg; Ti-Fe material = 3.8 $/kg)
- HP2 or HP3 down selected as most attractive candidates

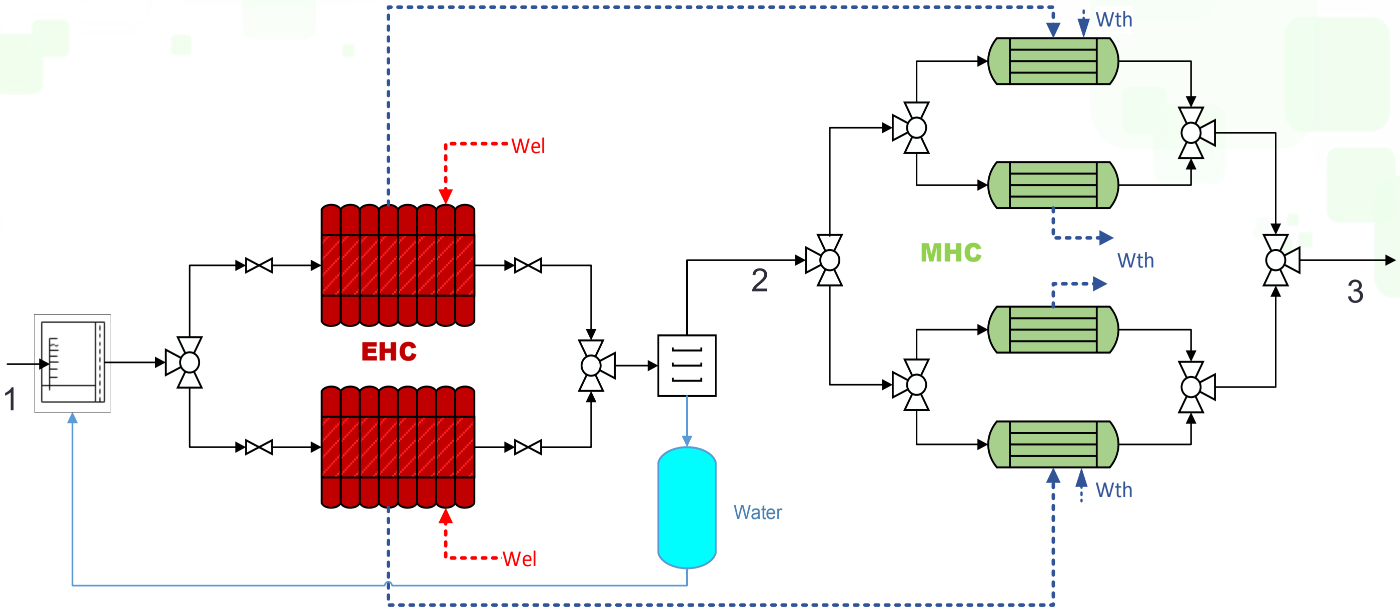
# Accomplishments
# Task 1.1: Internal heat recovery from EC Stage to MH Stage



Electrochemical system waste heat can be used to power the MH system

- Hydrogen desorption thermal power required by the MH system (at 170 °C) = 4.3-4.9 kWh/kg
- Matching temperatures between the EC stage and the operating conditions of the MH stage requires an EC stage current density for total heat recovery of about 2.5 A/cm$^2$

# Accomplishments
# Task 1.1: Proposed Baseline Hybrid Compressor System PID



- Waste heat from the PBI EC stage (~180 °C) recoverable to the MH stage for $H_2$ desorption
- Possible internal heat exchange in MH stage to recover part of the heat available from $H_2$ adsorption
- No additional input thermal energy required
- Internal heat recovery heat exchanger design in progress

## State Points

| Point | Temperature (°C) | Pressure (bar) | Flow rate (kg/s) |
|---|---|---|---|
| 1 | 20 | 10-20 | 10-100 |
| 2 | 50 | 100-200 | 10-100 |
| 3 | 150 | 875 | 10-100 |

# Accomplishments
# Task 1.2: EC Stage Bench-Scale Studies

***Electrochemical Compressor Technical Requirements***

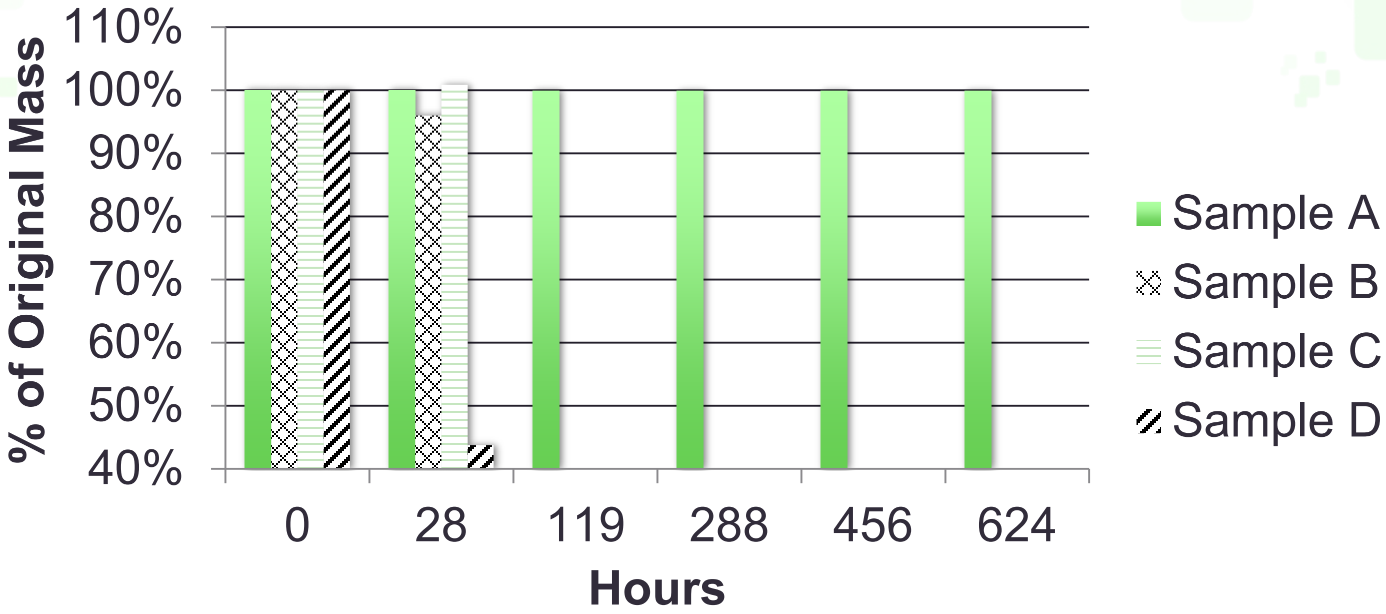
| ***Requirement*** | ***Value*** | ***Unit*** |
|---|---|---|
| *Inlet Pressure* | *1-30* | *bar* |
| *Outlet Pressure* | *120* | *Bar* |
| *Operating Temp* | *150-200* | *°C* |
| *Current Density* | *0-1.5* | *A/cm$^2$* |
| *Active Area* | *82* | *cm$^2$* |
| *Cells per stack* | *Up to 100* | |

Performed experimental tests on a bench scale EHC system based on the technical requirements listed above. The tests are aimed at:

1. developing appropriate MEAs for operating at high temperatures
2. evaluating high temperature and high-pressure membranes at laboratory scale
3. down selecting material sets and operating regime, and
4. making appropriate design modification to cell stacks.

# Accomplishments
# Task 1.2: EC Stage Material Compatibility Studies

- Phosphoric acid materials compatibility is critical to high temperature operation
  - Exposure to 160C 85% PA

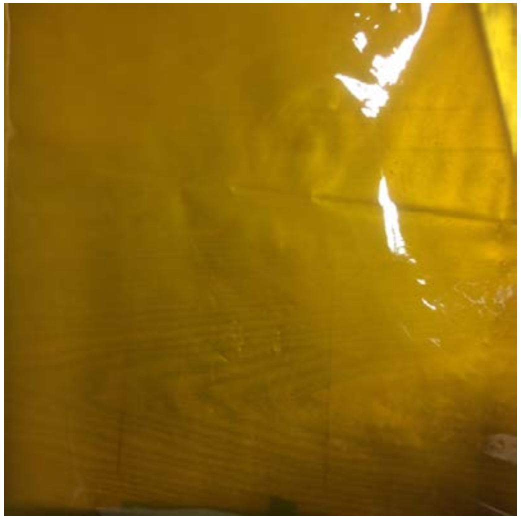


<u>Note</u>: Sample B and D tests were stopped after 1 day due to substantial mass loss. Sample E fully dissolved in 1 day (not shown). Sample C was selected for further testing as a coating in Sample A.

- Samples A & C demonstrated high performance
- Sample A has been selected for functional testing in the electrochemical hydrogen compressor

# Accomplishments
# Task 1.2: Differential Pressure Studies

- PBI film was assembled in Sustainable Innovation's compressor hardware for static differential pressure testing.
- Room temperature @ 1500 psid, 160°C
  - Dry membrane: no failure
  - Acid imbibed membrane: no failure
- Result: Properly supported PBI film may be robust enough for compression
- Next Steps:
  - Repeat tests with PA treated PBI
  - Repeat tests with Advent, Fumatech and other samples (samples have been requested)



# Accomplishments
# Task 1.3: MH Stage Bench-Scale Studies

Perform bench scale metal hydride tests based on results of best candidate materials from screening analyses to:

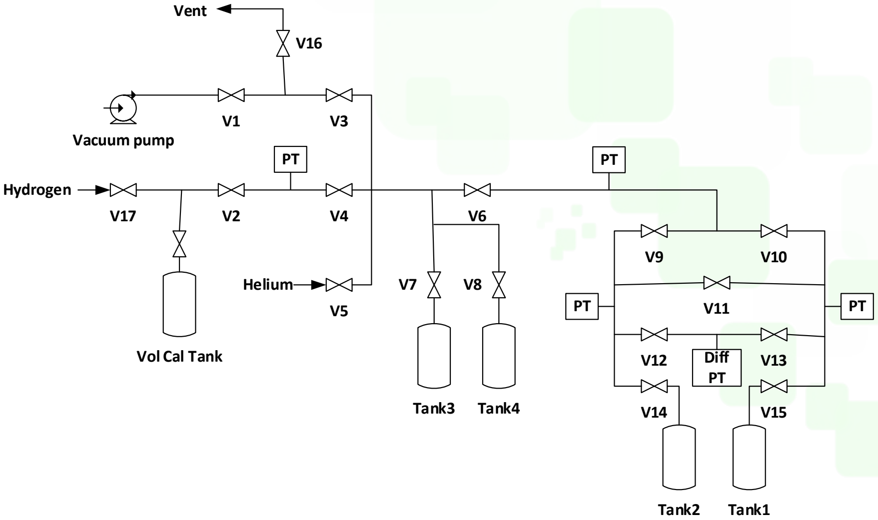
1. evaluate the thermodynamic data needed to model the MH system (i.e. reaction enthalpy, entropy, etc.)
2. evaluate the kinetics of the selected material, with charging and discharging profiles at different temperatures and pressures
3. evaluate the chemical and physical properties of the material (i.e. density, thermal conductivity, specific heat, etc.).

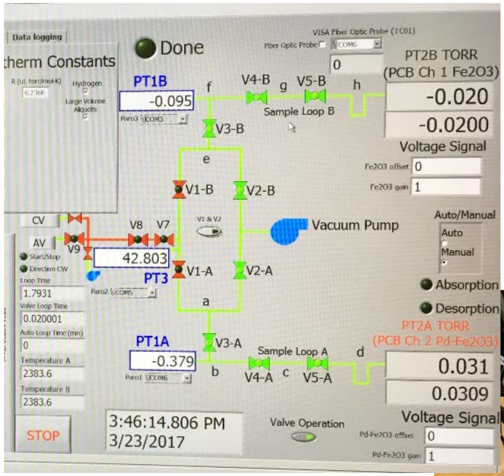
All the MH system tests will be carried out under the selected operating conditions to reach outlet pressures of 875 bar.

- Vendors have been identified to provide small samples of MH materials for laboratory testing and characterization and samples are being procured.
- Quotes for larger volumes of materials for large-scale testing during Phase 2 are also being evaluated and material will be procured after selection of a final candidate material is made.

# Accomplishments
# Task 1.3: MH Stage Bench and Large-scale Studies

- Assembly of small scale system for material characterization near completion
- Small-scale allows for testing material in microgram level
- Large-scale system being retrofitted for high pressures




Data logging

therm Constants

R (uL·torr/mol·K) 6.236E

Hydrogen ☑

Large Volume Aliquots ☑

● Done

PT1B -0.095

Paro3 COM3

PT3 42.803

Paro2 COM5

PT1A -0.379

Paro1 COM6

● Start/Stop

● Direction CW

Loop Time 1.7931

Valve Loop Time 0.020001

Auto Loop Time (min) 0

Temperature A 2383.6

Temperature B 2383.6

3:46:14.806 PM 3/23/2017

VISA Fiber Optic Probe (TC01)

Fiber Optic Probe ☐ COM6

0

PT2B TORR (PCB Ch 1 Fe2O3) -0.020 -0.0200

Voltage Signal

Fe2O3 offset 0

Fe2O3 gain 1

Auto/Manual: Auto ○ Manual ●

● Absorption

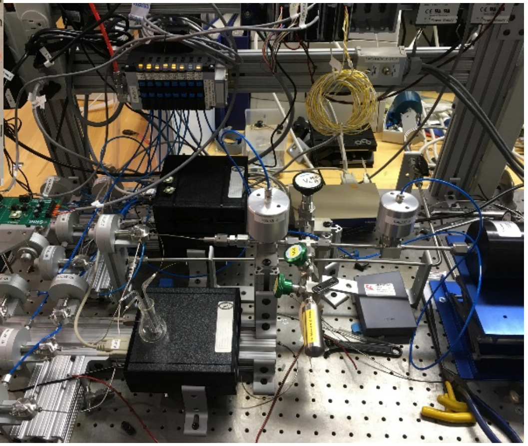
● Desorption

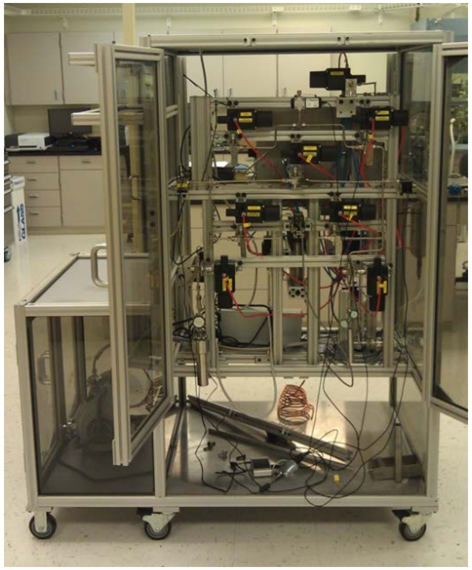
PT2A TORR (PCB Ch 2 Pd-Fe2O3) 0.031 0.0309

Voltage Signal

Pd-Fe2O3 offset 0

Pd-Fe2O3 gain 1

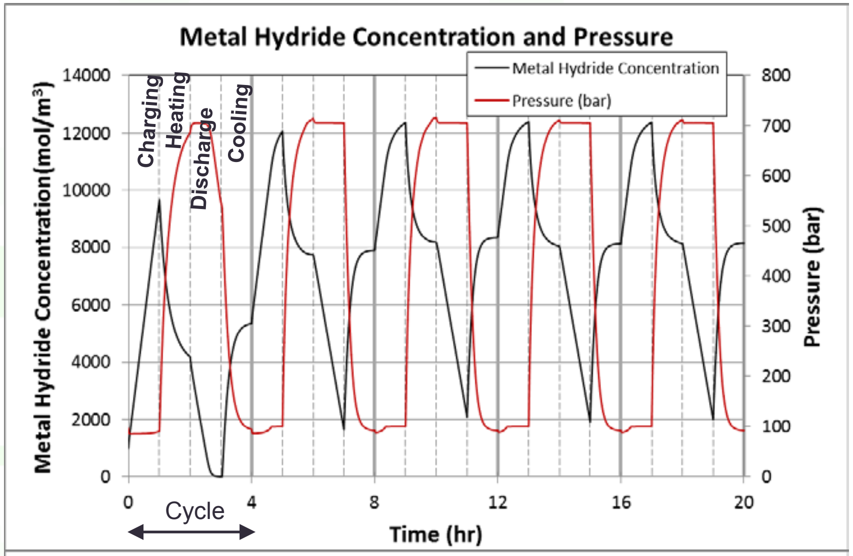


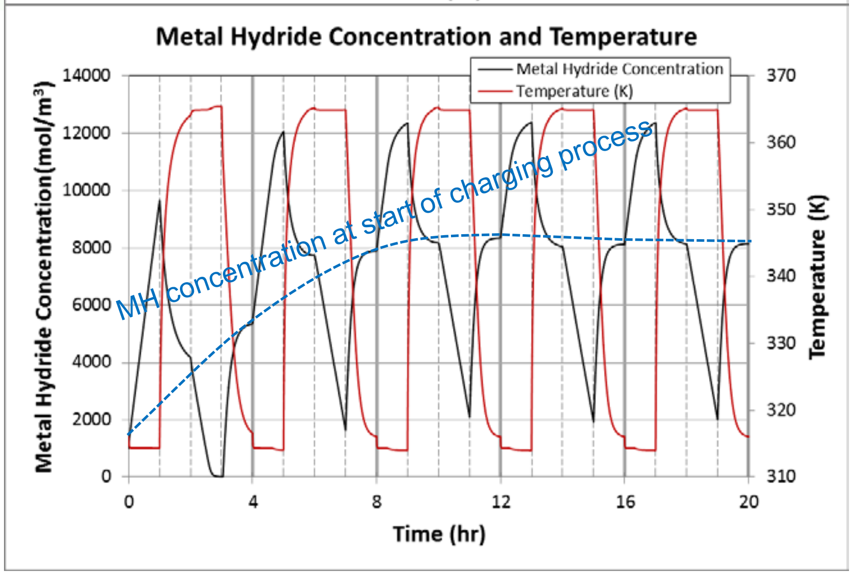


# Accomplishments
# Task 1.4 Hybrid Compressor System Model Development

- A system model is being developed, for the proposed hybrid system.
- The model will include transient lumped parameter based energy and mass balance equations.
- Suitable kinetics expressions will be included in the model for both the EHC and the thermal MH system.
- The model will evaluate the hybrid compressor, system performance for a range of operating conditions, configurations, electrochemical compressor properties, etc.
- The models will be applied with the aim of:
  1. characterizing the behavior of screened systems under steady state and transient (under start and shut down) conditions;
  2. verifying the behavior of the proposed system under partial load conditions;
  3. analyzing the performance of the system for different MH and EHC configurations.

# Accomplishments
# Task 1.4: Operating Characteristics of MH Compressor Stage





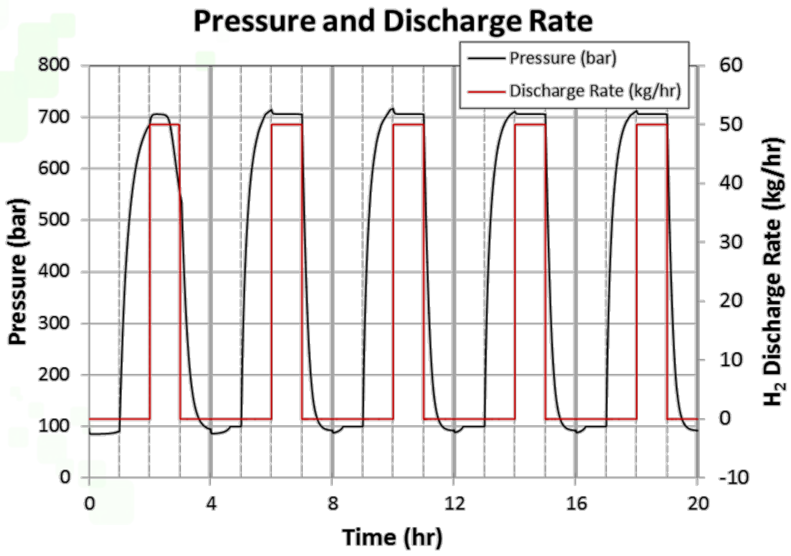
$H_2$ inflow from ECC at 100 bar & maximum of 100 kg/hr
Metal hydride volume is ~12 $m^3$
Assumes MH expansion of 15% (crystal volume) on $H_2$ uptake
Expanded (fully charged) bed porosity of 10%

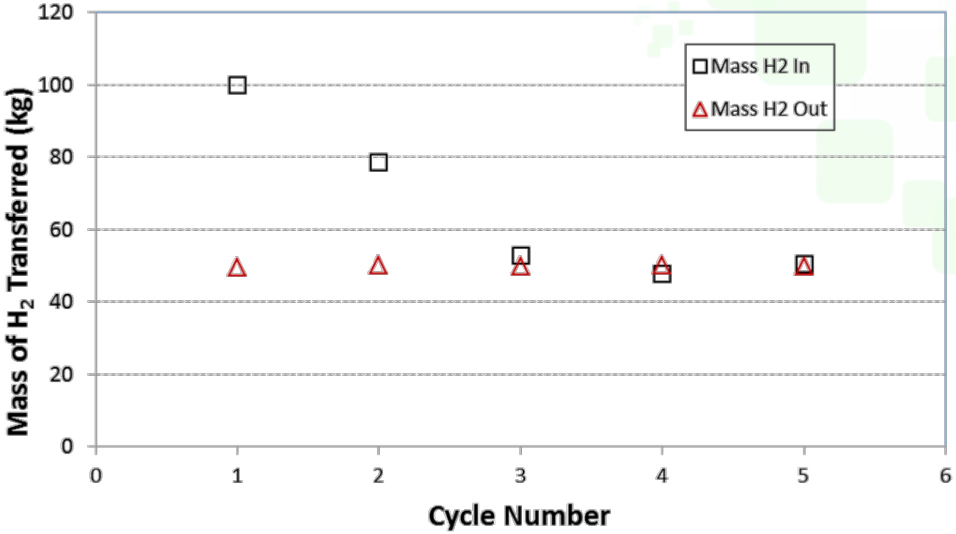
Operating Scheme
4 hour cycles, each consisting of 4 parts:
- 1 hour charging – heat removal to keep P≤ 83bar ($T_{eq}$=314K)
- 1 hour heating – heat addition to raise P to 700 bar
- 1 hour discharge – heat addition to maintain P at 700 bar
- 1 hour cooling – heat removal to return P to 96 bar and/or T to 314K

For first 3 cycles more $H_2$ enters the compressor than exits. This is due to $H_2$ discharge from MH during heating phase & unavoidable re-uptake of $H_2$ by the MH bed upon cooling to initial state at 314K. This causes the amount of hydrogen retained in solid phase, prior to charging, to rise for first 3 cycles then stabilize.

For the postulated MH properties and bed volume, delivery is ~50 kg/hr at 700 bar

# Accomplishments
# Task 1.4: Operating Characteristics of MH Compressor Stage





Current system modeling activities include integrating EC system with MH system

# Response to Previous Year Reviewer's Comments

- New Project – This project was not reviewed last year

# Collaborations and Technology Transfer Activities

- MH Compressor Project Team
  - Material property information collaboration with Bob Bowman (ORNL) and Craig Jensen (U. of Hawaii)
  - MH system modeling collaboration with Terry Johnson (SNL)
- EHC Compressor
  - Membrane material collaboration with Advent Energy

# Remaining Challenges and Barriers

*EC Stage*

- Final EC membrane selection will require a tradeoff between cost, performance and reliability.
- Potential advantages for using high temperature membranes: higher efficiency, higher tolerance to contaminants (CO), simpler water management, and a higher waste heat source for the MH stage.
- Potential disadvantages: more costly, reduced reliability and less application experience.

*MH Stage*

- Material tradeoffs between cost, cycling stability, operating temperatures and pressures, and thermodynamic and physical properties.
- Design considerations to increase heat transfer and minimize vessel weight/heat capacity while maintaining low cost, high reliability and safety.

*Hybrid Unit*

- Optimization of initial, final and intermediate temperatures, pressures and $H_2$ flowrates to meet cost and performance targets.
- Water and heat management between both stages.
- System operation and control.
- Identification and selection of required BOP components.
- Staging designs/layouts to meet long-term targets and future market needs.

# Technology Transfer Activities

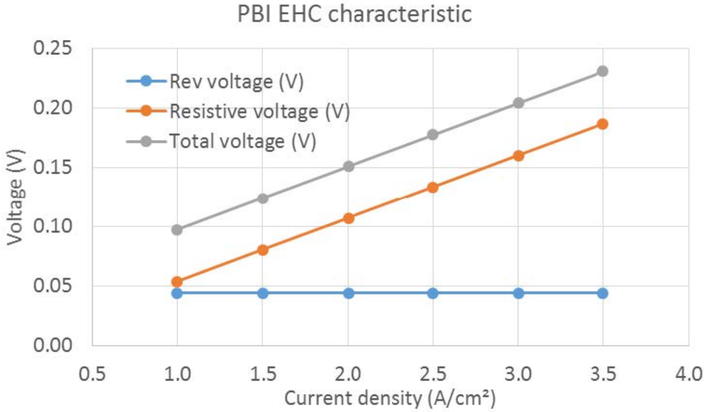
- Invention Disclosure Filed for new MH vessel design

# Summary and Path Forward

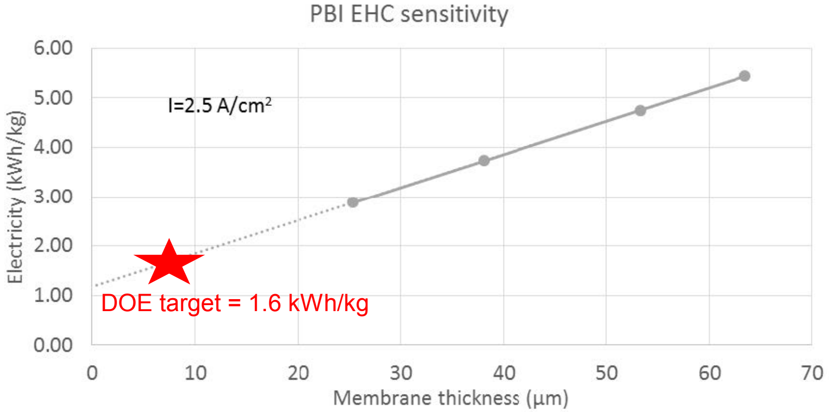
- A techno-economic modeling framework for evaluating MH and EH compression stages has been completed and a leading candidate system, operating at large scale, based on Ti-based, MH and PBI membrane, EHC technologies, has been identified. (note – Nafion is still considered an alternative material following the results of additional bench-scale testing).
- 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 reduces heat transfer area, reduces required thermal and reduces cost associated with heat transfer systems.
- EC differential pressure tests showed that PBI membrane may be robust enough for compression applications.
- A new material type was shown to have good resistance to phosphoric acid environments.
- Small-scale MH testing and characterization systems have been completed and sample quantities of candidate MH materials have been ordered.
- The availability of larger quantities of MH materials have been identified, cost & shipping details are being pursued for Phase 2.
- An integrated hybrid compressor system model is under development, the MH system has successfully modeled and is currently being integrated with the EC system.
- Detailed MH models have been initiated and on schedule to be completed early next fiscal year.
- Design of an integrated hybrid EC-MH Compressor prototype system is planned for the end of Period 1 (3/31/18).

# Technical Backup Slides

# PBI techno-economic analysis



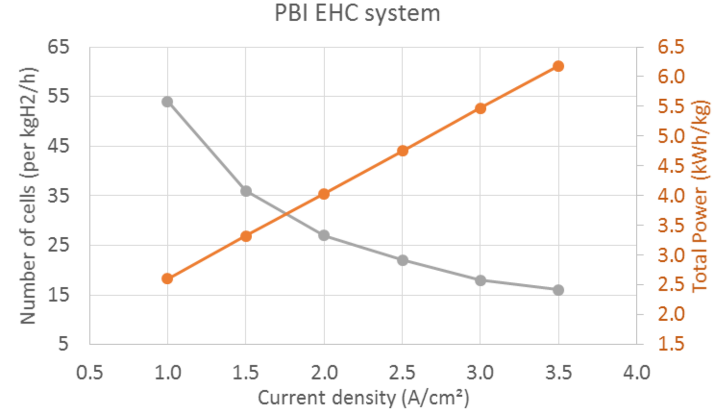
PBI EHC characteristic



PBI EHC sensitivity

I=2.5 A/cm$^2$

DOE target = 1.6 kWh/kg

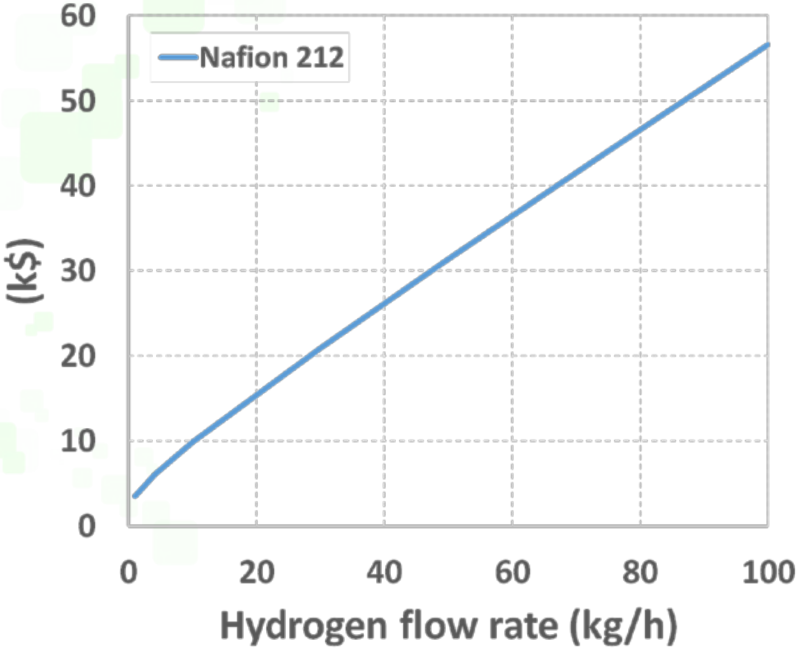


PBI EHC system

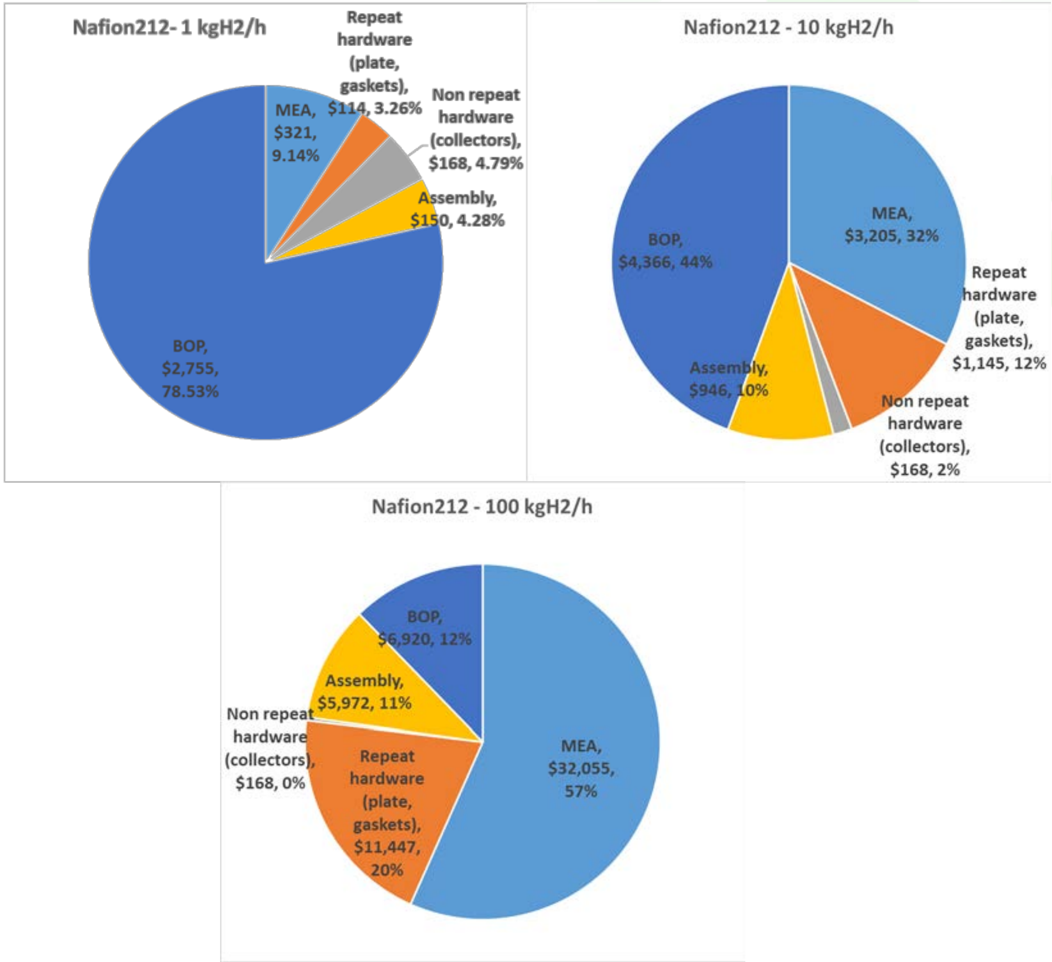
- The DOE target is not an unfeasible targets at current density of 2.5 A/cm$^2$

# Accomplishments
# Task 1.1: Projected Economic Results for Nafion EC Stage

## Installed costs



## Installed cost breakdown



Nafion membrane EC stage

Inlet pressure = 10 bar

Outlet pressure = 100 bar

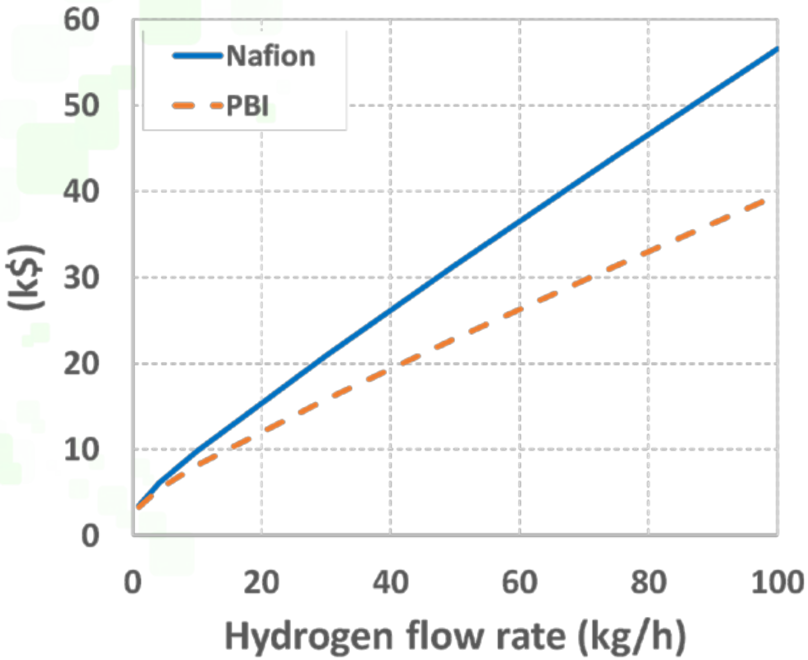
Current Density = 2.5 A/cm$^2$

Cell Voltage = 0.15 V

Compression Work = 4.0 kWh/kg

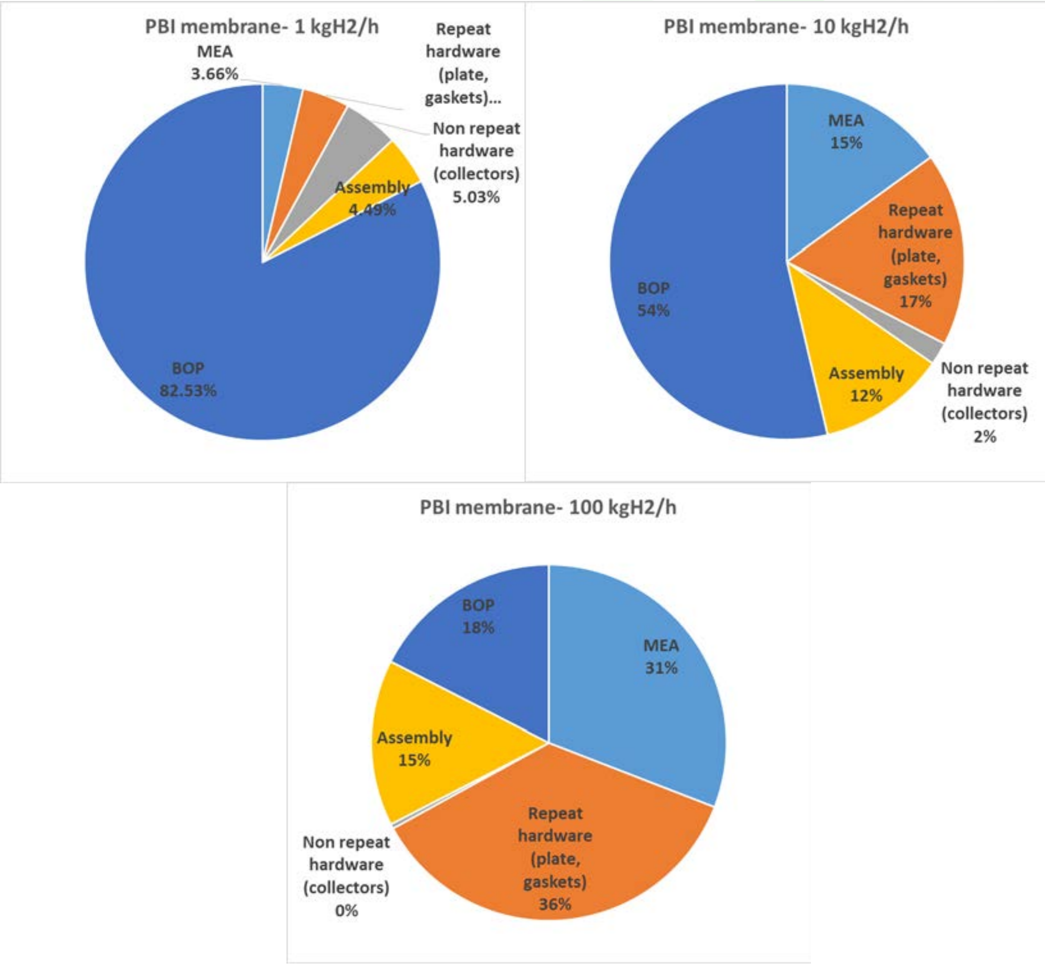
# Accomplishments
# Task 1.1: Projected Economic Results for PBI Membrane

## Installed costs



PBI membrane EC stage
Inlet pressure = 10 bar
Outle pressure = 100 bar
Current density 2.5 A/cm$^2$
Cell Voltage ≈ 0.18 V
Compression Work ≈ 4.7 kWh/kg

## Installed cost breakdown



# Economic data for the EC Stage – Nafion membrane

| ***NAFION 212 membrane – each cell*** | Specific cost SI value) | Total cost (assumed/SI value) @ 100 kgd capacity | Comment |
|---|---|---|---|
| MEA (N212, PtNi, 0.142 mg/cm2 loading - DOE) | $299/m$^2$ | $2201 | Cost estimates will be a function of flux<br>Value derived from 2015 DOE FC cost model w/ modifier for increased membrane thickness to support differential pressures.<br>• MEA cost, including gasket region and trimming waste, 2x multiplier for increased thickness. |
| Repeat non-MEA cell hardware (plate, gaskets) | $106.78/m$^2$ | $786 | Value derived from DOE FC cost model w/ modifier for increased strength requirement<br>• BPP cost, 2x multiplier for heavier material stock for high internal pressures. |
| Non-Repeat Hardware (current collectors, ends, etc) | | $168 | Derived from DOE FC cost model w/ modifier for strength requirement<br>• 2x multiplier for higher internal pressures. |
| Cell assembly cost | | 100-150 $ | Based on previous analyses for electrochemical processes for hydrogen production |
| System – balance of plant | | $3665 | Based on existing SI system balance of plant to pump stack cost ratio projected onto the future pump stack cost predictions (above). |

# Economic data for the EC stage - PBI membranes

| ***Film/Fumatech*** | Specific cost SI value) | Total cost (assumed/SI value) @ 100 kgd capacity | Comment |
|---|---|---|---|
| MEA (PBI, 0.142 Pt mg/cm2  loading) | $70/m$^2$ of membrane + $40.22/m$^2$ of catalyst | | Cathode loading reduced compared to anode loading |
| Repeat non-MEA cell hardware (plate, gaskets) | $106.78/m$^2$ | $786 | Value derived from DOE FC cost model w/ modifier for increased strength requirement<br>• BPP cost, 2x multiplier for heavier material stock for high internal pressures. |
| Non-Repeat Hardware (current collectors, ends, etc) | | $168 | Derived from DOE FC cost model w/ modifier for strength requirement<br>• 2x multiplier for higher internal pressures. |
| Cell assembly cost | | 100-150 $ | Based on previous analyses for electrochemical processes for hydrogen production |
| System – balance of plant | | $3665 | Based on existing SI system balance of plant to pump stack cost ratio projected onto the future pump stack cost predictions (above). |