Hybrid Electrochemical Hydrogen/Metal Hydride Compression

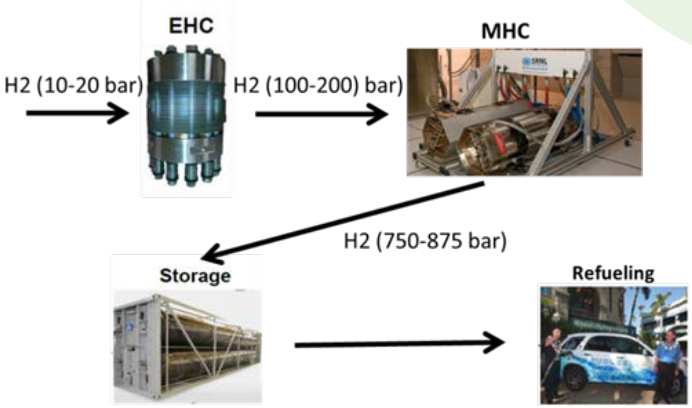
Scott Greenway (PI), Martin Sulic, Aaron Wilber, Ted Motyka (*GWE)*

Bruce Hardy, Anna d'Entremont (*SRNL)*

George Roberts, Phillip Baker, Daryl Ludlow, Trent Molter (*SI)*

Claudio Corgnale *(GWE)* - Presenter

June 14, 2018



Project ID: PD137

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POWERFUL EXPERTS

Overview

Timeline and Budget

- Project Start Date: 10/01/16
- Project End Date: 09/30/19
- Total Project Budget: $3750K
  - Total Recipient Share: $752K
  - Total Federal Share: $2998K
  - Total DOE Funds Phase 1*: $1415K

* Phase 1 (18 months): end date 3/31/18

Barriers

- Hydrogen Delivery barriers
  - Cost of high pressure large scale hydrogen compression systems
  - Efficiency of large scale compression systems
  - Reliability of high pressure large scale compression systems

Partners (funded)

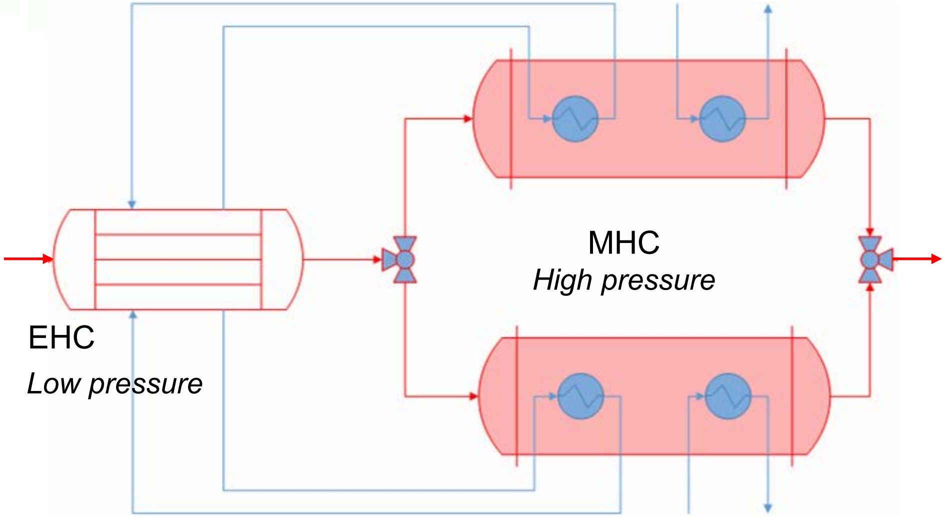
- Savannah River National Laboratory (SRNL)
- Sustainable Innovations (SI)
- Greenway Energy (GWE) - lead

Relevance

Project objective (Phase 1 & 2):

Identify and build a two-stage hybrid thermo-electrochemical compressor to achieve the DOE targets:

- Large scale hydrogen compression
- High operating pressures
- Efficiencies equal to the DOE targets
- Overall costs equal to the DOE targets
- High reliability



Project achievements (Phase 1):

- **EHC configuration** with Nafion® membrane identified with stability demonstrated for 100 hours
- Baseline **MH materials characterized at industrial level** without performance degradation demonstrated (so far) for 20 cycles
- **Novel and effective configuration designs** achieved for prototype and large scale compressor
- EHC-MHC **matching condition** identified, achieving a thermally self sustaining configuration with complete EHC heat recovery in the MHC
- Viable **path toward the DOE techno-economic targets** identified

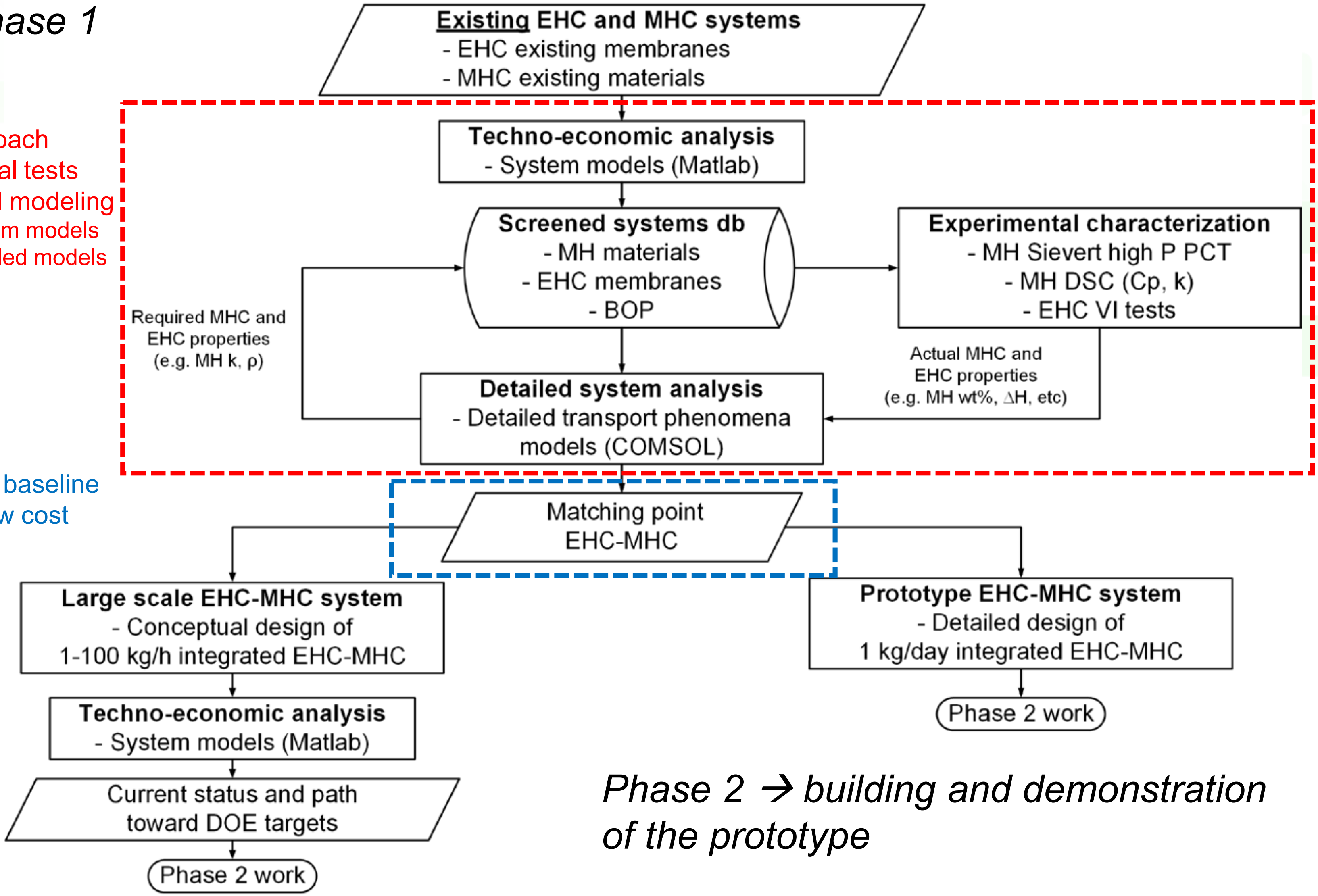
DOE = US Department Of Energy
EHC = Electrochemical Hydrogen Compressor
MHC = Metal hydride Hydrogen Compressor
MH = Metal hydride

Approach

Project Phase 1

Integrated approach
- Experimental tests
- Hierarchical modeling
  - System models
  - Detailed models

Identification of baseline effective and low cost configuration



Phase 2 → building and demonstration of the prototype

db = Database
EHC = Electroch. H_2 Compr.
MHC = MH H_2 Compr.
MH = Metal hydride
BOP = balance of plant
DSC = Differential Scanning Calorimetry
VI = Voltage-Current density
PCT = Pressure-Concentration-Temperature
ρ, Cp, k, ΔH, wt% = Density, specific heat, thermal conductivity, reaction enthalpy, weight capacity

Approach-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 - Complete**

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 – Complete**

As of April 2017

April 2018

Experimental characterization

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 - Complete**

Task 1.3: MH bench scale experimental tests

Hierarchical modeling

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 - Complete**

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 - Complete**

Prototype design

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 and design of a prototype. **03/31/18 - Complete**

MH = Metal hydride
EC = Electrochemical
EHC = Electrochemical H_2 Compressor

Accomplishments and Progress

EHC membranes	*Pros*	*Cons*
Nafion®	• Commercially available • Reliable and consolidated	• Water handling • Max T physical limit = 190 °C (melting)
PBI®	• Higher T • No water handling	• Compatibility with PA • Unknown long time reliability and stability

MHC materials	*Pros*	*Cons*
HP1 (Ti-Cr)	• Commercially available	• High hysteresis • High slope in the 2phase region • High cost
HP2 (TiZr-Cr-Mn)	• 'Low' cost • Low ΔH • Available	• Actual performance of the industrial material to be verified
HP3 (Ti-Cr-Mn)	• 'Low' cost • Low ΔH • Available	• Operating conditions of the industrial material to be verified

Previous status as of June 2017

- Screening and database population of EHC membranes
  - Both Nafion and PBI membranes selected as possible candidates
- Screening and database population of MHC materials
  - Three Ti-based candidates selected
  - Additional Ti MHs downselected in conjunction with SNL project
- Initial matching point identified

PBI =
MHC = Metal hydride compressor
EHC = Electrochemical H2 Compressor

HP3 = $Ti_{1.1}CrMn$
HP1 = $TiCr_{1.9}$
HP2 = $(Ti_{0.97}Zr_{0.03})_{1.1}Cr_{1.6}Mn_{0.4}$

SNL = Sandia National Lab

High temperature PBI® vs Nafion®

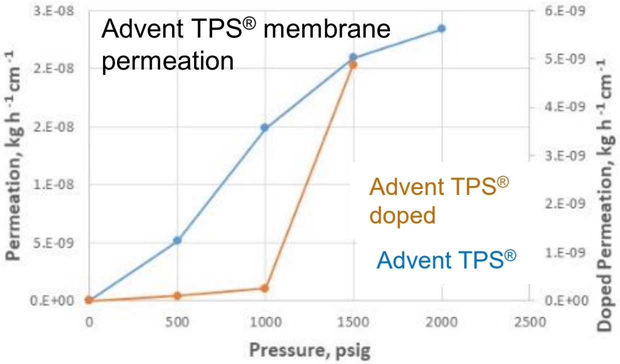
Advent PBI® membrane

- Cost of chemical compatibility
  - SI projected a 4x cost of the current Nafion® hardware
- Material processing
  - Swelling of membrane during doping cased membrane to tear

  - PA likely causes degradation
- Permeability variation
  - Irrecoverable permeation increase at higher differential pressures

Nafion 117® membrane

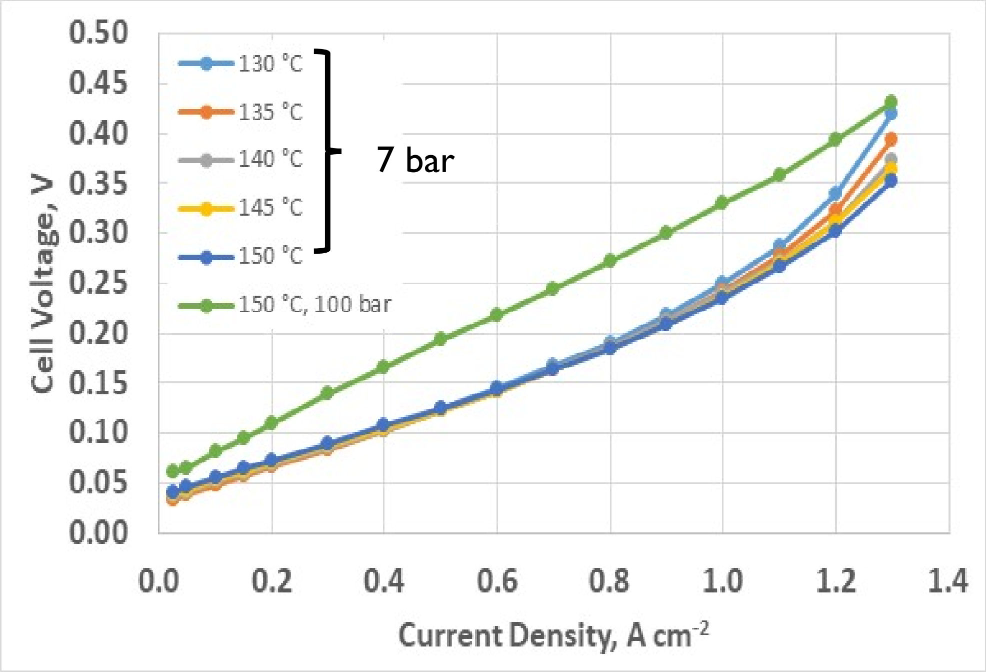
- Known systems suited for pressurized water applications
  - Membrane tests demonstrated high hydration
  - Pressures suppress steam formation
- Material stability and advantages
  - Demonstrated 100 hours operation at 130 °C < T < 190 °C
  - Potential for thickness reduction (so far Nafion 117 adopted)



Advent TPS® membrane permeation

SI = Sustainable Innovations
PBI = Polybenzimidazole
PA = Phosphoric acid

Nafion EHC characteristic



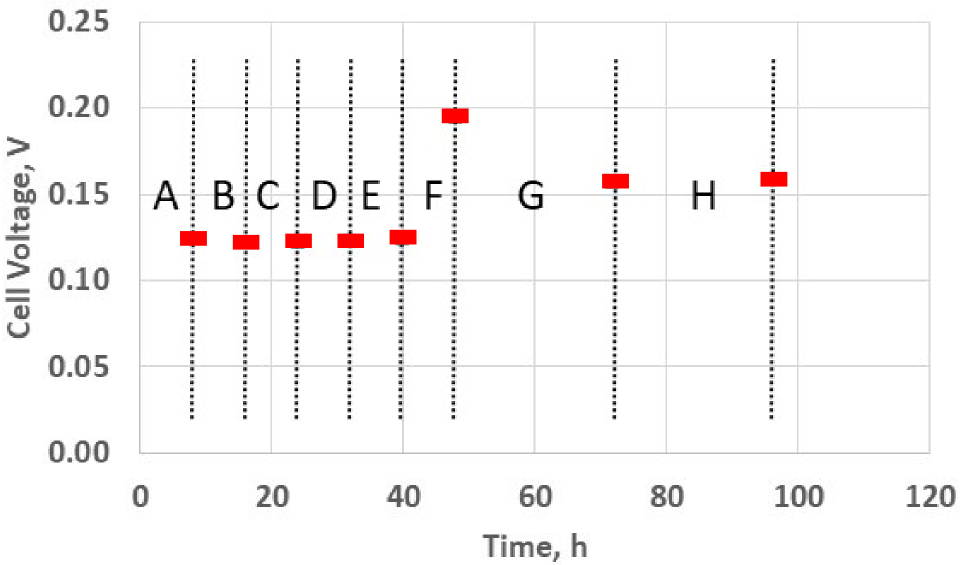
Nafion 117® membrane V-I characteristic

- Tests carried out so far at high temperatures (130-150 °C) and high pressures (up to 100 bar).
- Operating current densities of 400 – 900 mA/cm^2 gives possible matching points with the MHC
- Future actions for performance improvement
  - Thinner membranes
  - Membrane pretreatment at high T for higher water uptake
  - Redesign of the flow field for better gas distribution

The EHC system based on Nafion is technically feasible at 100 bar and 150 °C

MHC = Metal hydride H_2 Compressor
EHC = Electrochemical H_2 Compressor

Nafion EHC stability tests



- Single cell tests for 95 hours at 500 mA/cm^2
  - Temperatures 130-150 °C
  - Pressures 15-101 bar

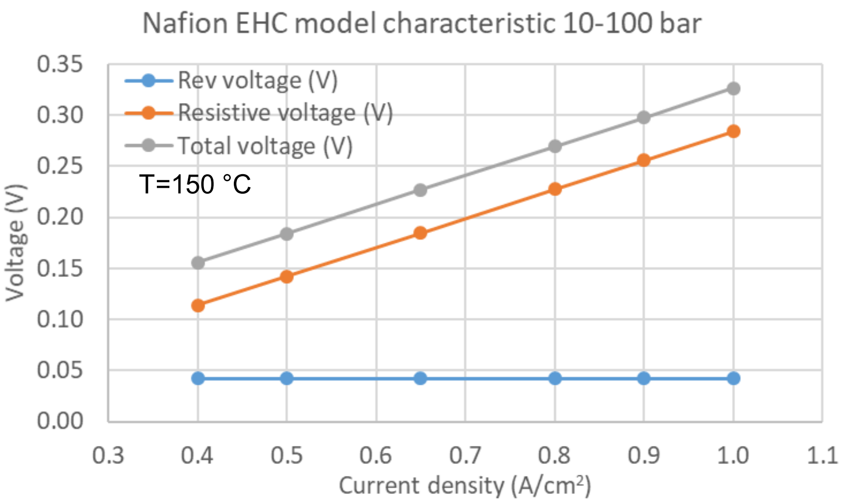
Test Point	Temperature	Anode Pressure	Cathode Pressure
	(°C)	(bar)	(bar)
A	130	6.2	14.8
B	135	6.2	14.8
C	140	6.2	14.8
D	145	6.2	14.8
E	150	6.2	14.8
F	150	6.2	121.7
G	**150**	**7.9**	**101.0**
H	**150**	**7.9**	**101.0**

No performance degradation observed

- Constant voltage at low pressure for > 40 hours
- Constant voltage at high pressure for > 25 hours

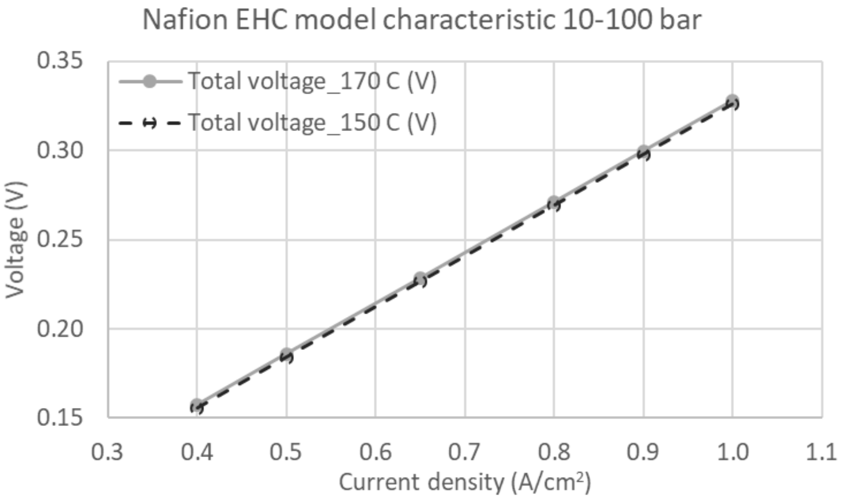
EHC = Electrochemical H_2 Compressor

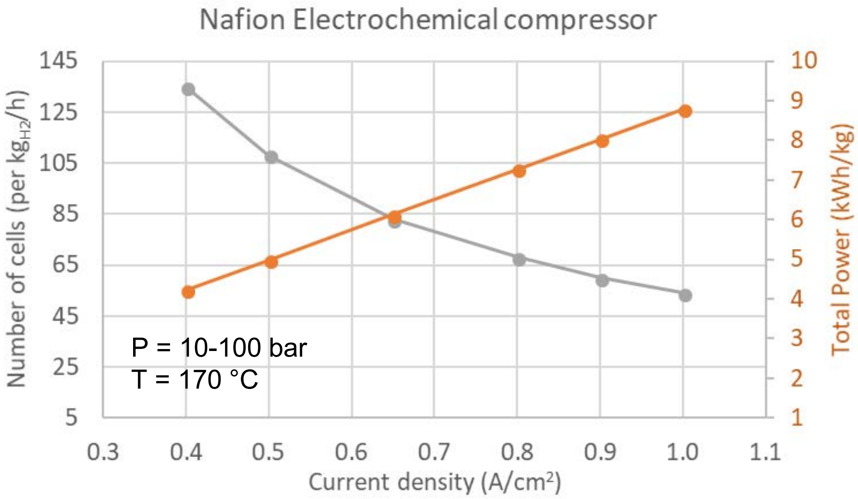
Nafion EHC model high T predictions


Nafion EHC model characteristic 10-100 bar

Current Nafion 117® membrane V-I model characteristic

- Model from Springer et al.* fitting the 10-100 bar data
- Tests in progress for 170 °C (may be required by the MHC) and lower thickness membranes
- Model predictions for 170 °C show feasibility and not appreciable efficiency variation

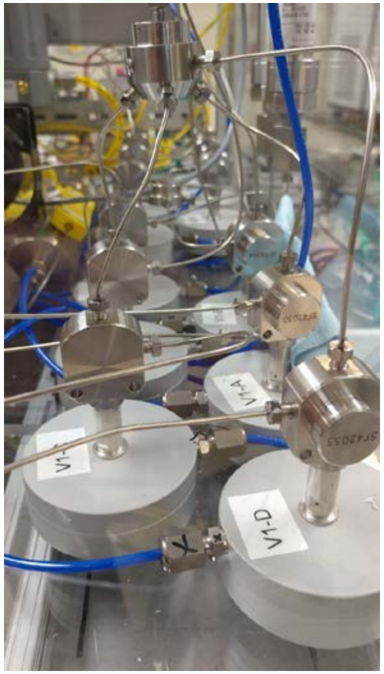

Nafion EHC model characteristic 10-100 bar

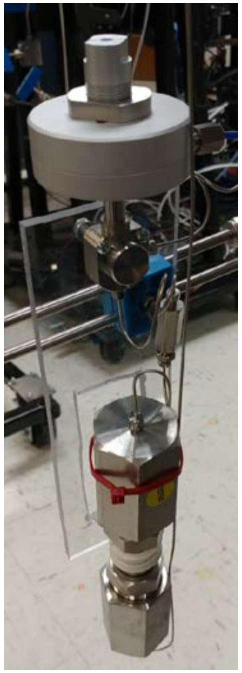

Nafion Electrochemical compressor

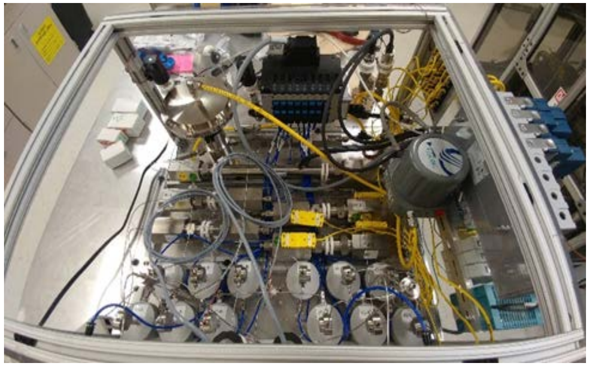
MHC = Metal hydride H_2 Compressor
EHC = Electrochemical H_2 Compressor

* Springer et al. JES, Vol. 138, No. 8, August 1991

MHC experimental apparatus





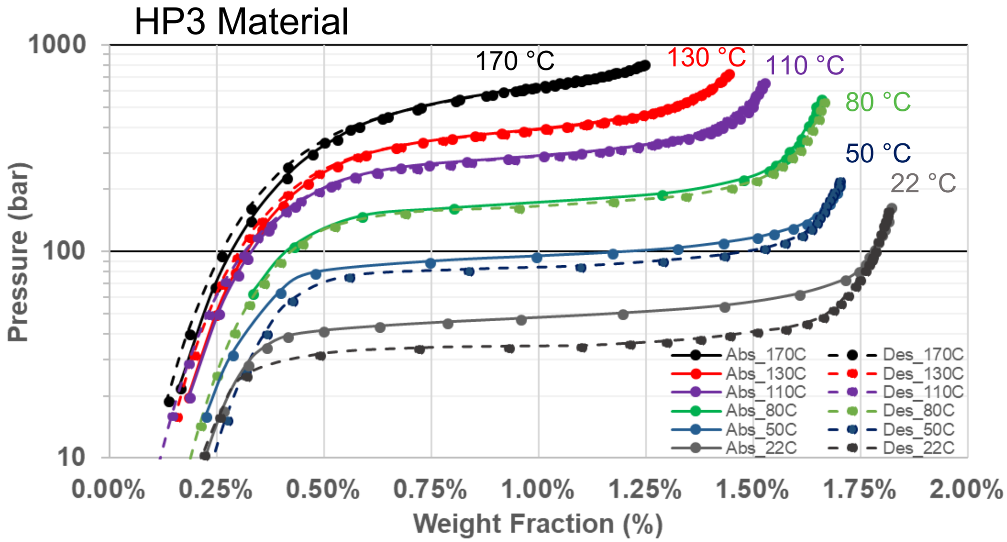


- Small scale high pressure Sieverts' for material PCT
  - Operating conditions
    - grams of MH
    - T up to ≈ 170 °C
    - P > 875 bar
  - Leak proofed
  - 2 channels in parallel
  - Results validated against $LaNi_5$ experimental low P data (provided by ORNL)
  - Automated operation
    - Programmable regulator (1020 bar/15,000 psi max rating)
    - High-precision pressure transducers (0.01% FS; ±0.01 bar)
    - Pneumatic valves with negligible internal volume (40,000 psi rating)

MHC = Metal hydride H_2 Compressor
PCT = Pressure-Composition-Temperature
MH = Metal hydride

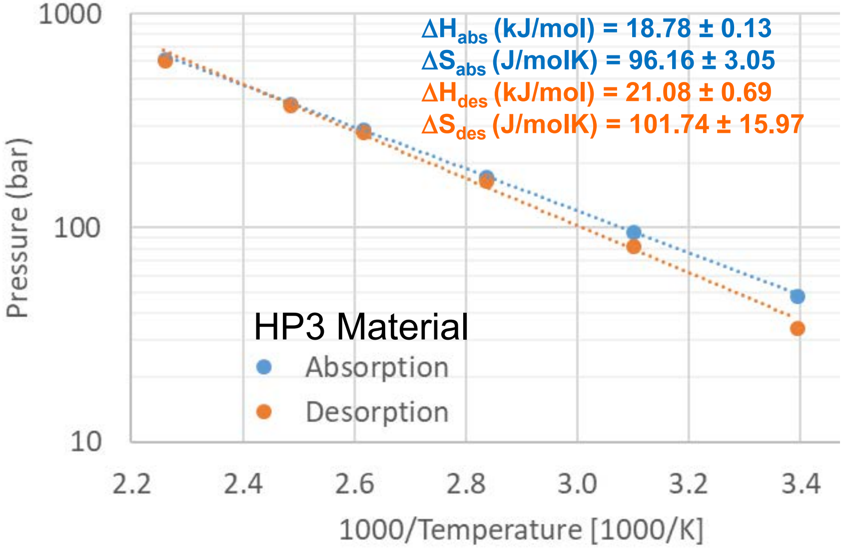
FS = Full scale
ORNL = Oak Ridge National Lab

MH experimental PCT data



Material (from JMC)	Pros	Cons	Comment
HP3 (‘TiCrMn’)	Hysteresis; Plateau	Low P	Similar behavior for HP2;
New HP4 (‘TiCrMnFe’)	Hysteresis; High P	Plateau; Low wt%	Alternative MH to HP2 and HP3

MHs characterization (XRD, SEM, etc) and treatment in progress

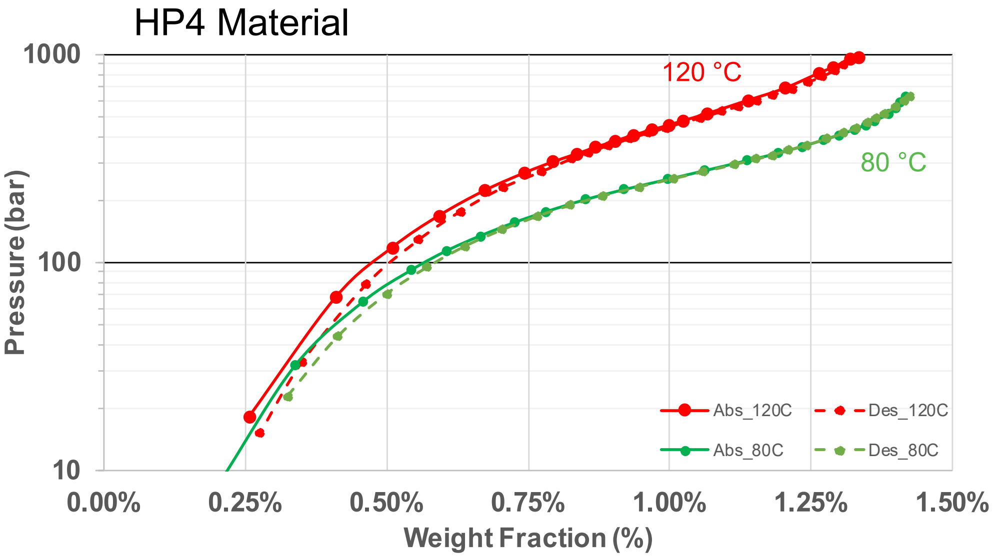


ΔH_{abs} (kJ/mol) = 18.78 ± 0.13

ΔS_{abs} (J/molK) = 96.16 ± 3.05

ΔH_{des} (kJ/mol) = 21.08 ± 0.69

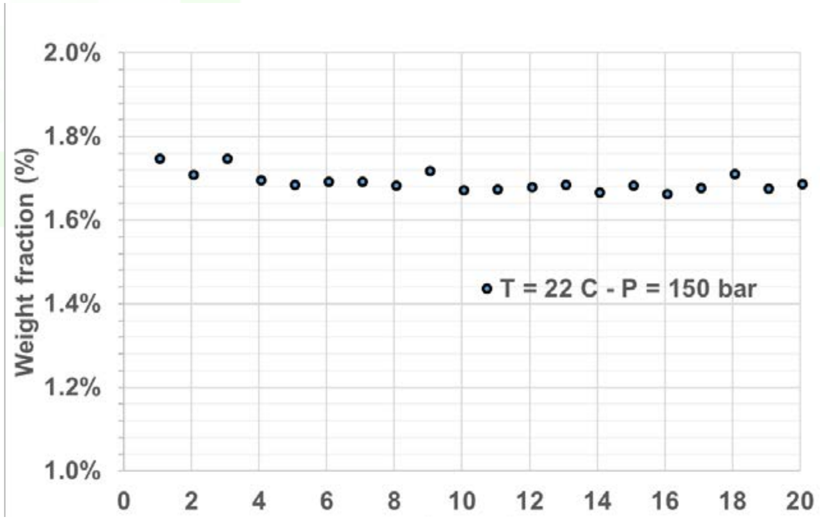
ΔS_{des} (J/molK) = 101.74 ± 15.97

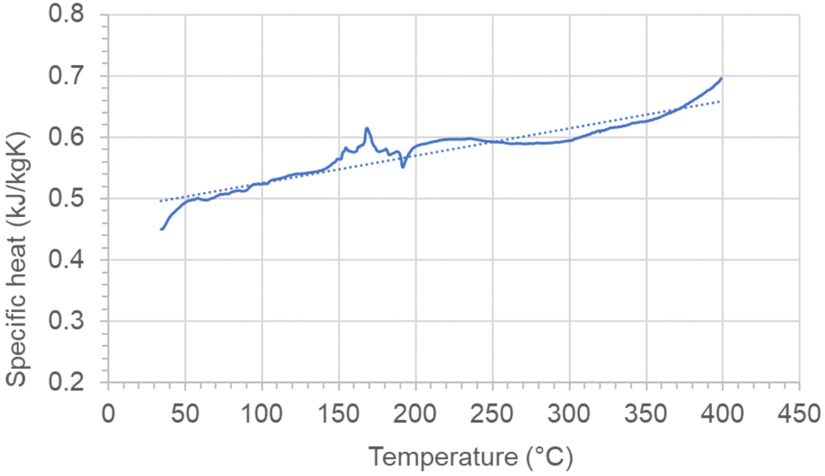


PCT = Pressure-Composition-Temperature
MH = Metal hydride
HP3 = High Pressure MH 3 ($Ti_{1.1}CrMn$)
JMC = Japan Metal Co.

XRD = X-Ray Diffraction
SEM = Scanning Electron Microscope
HP2 = $(Ti_{0.97}Zr_{0.03})_{1.1}Cr_{1.6}Mn_{0.4}$
HP4 = $TiCr_{1.55}Mn_{0.2}Fe_{0.2}$

MH experimental properties and cycling



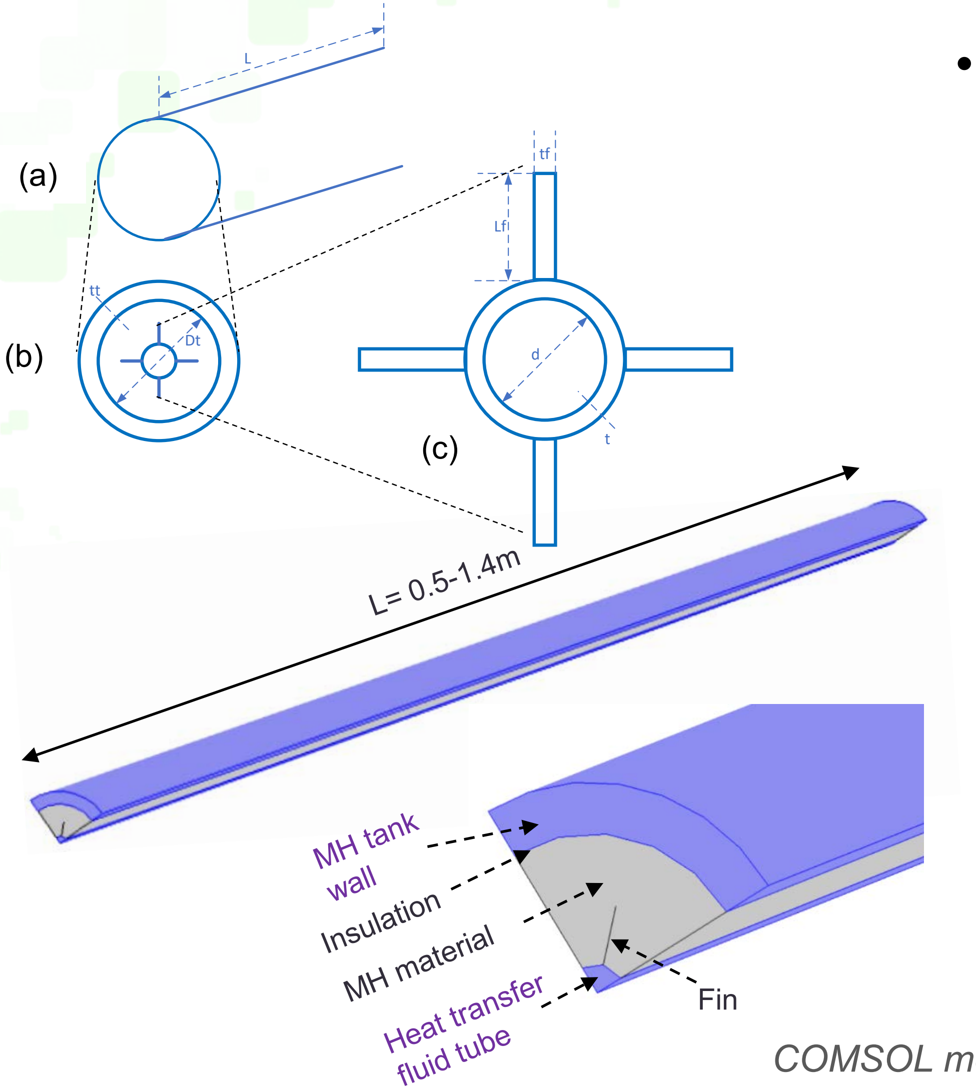


- Complete cycling of commercial HP3 MH
  - Room temperature and pressures between vacuum and 150 bar
  - No observable performance degradation confirming literature data for AB2 MHs
- Material physical and chemical properties measured experimentally

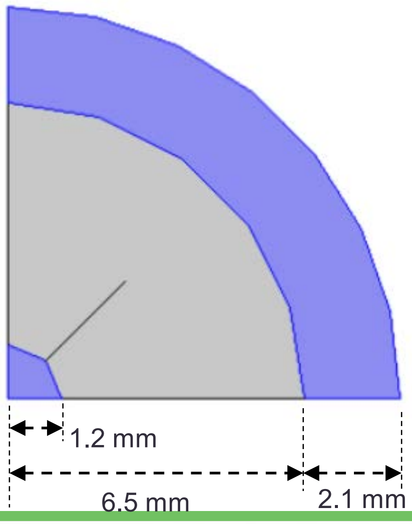
	HP3	Comment
ρ_{Bulk} (kg/m^3)	3300	Measured value, void fraction about 50%
k (W/mK)	0.75 – 3.50	Powder MH value without enhancers (literature data, tests in progress)
C_p (J/kgK)	500	Average value between RT and ≈100 °C

MH = Metal hydride
HP3 = High pressure MH 3 ($Ti_{1.1}CrMn$)
ρ, Cp, k = Density, specific heat, thermal conductivity
RT = Room temperature

MH system novel configuration



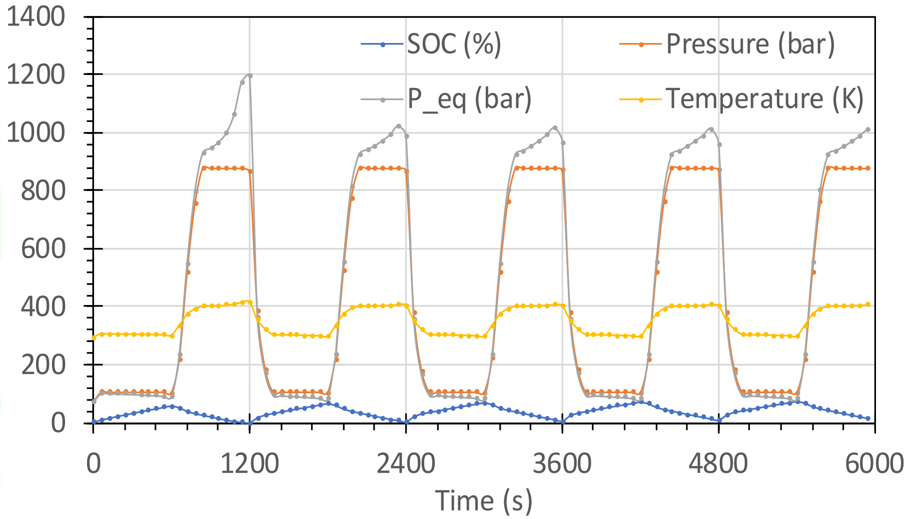
- Novel finned mini-channel heat exchanger configuration
  - Heat provided internally
    - (a) single overall tube
    - (b) front view of MH tube internally heated by finned mini-channel heat transfer tube
    - (c) front view of finned mini-channel heat transfer tube
  - Higher heat exchanger effectiveness
  - Reduction of HE cost of about 50% (2017 AMR presentation)



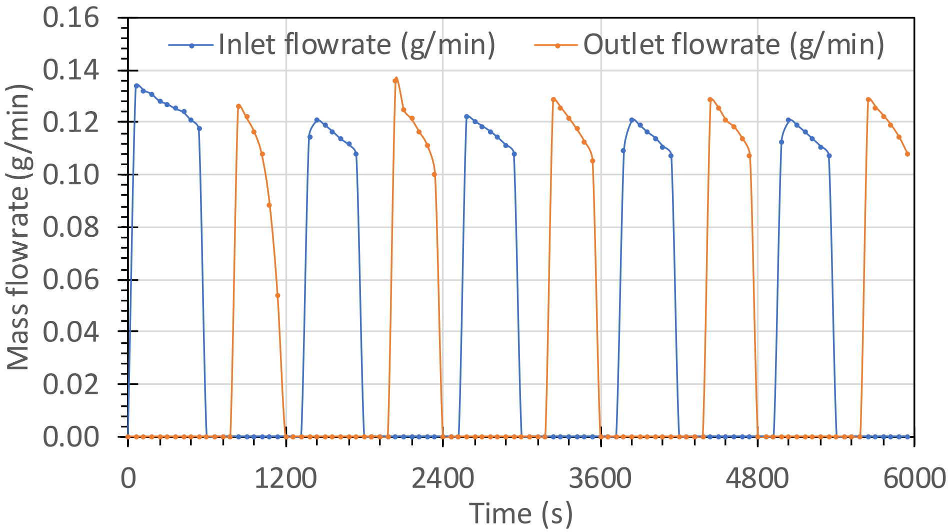
COMSOL model geometry

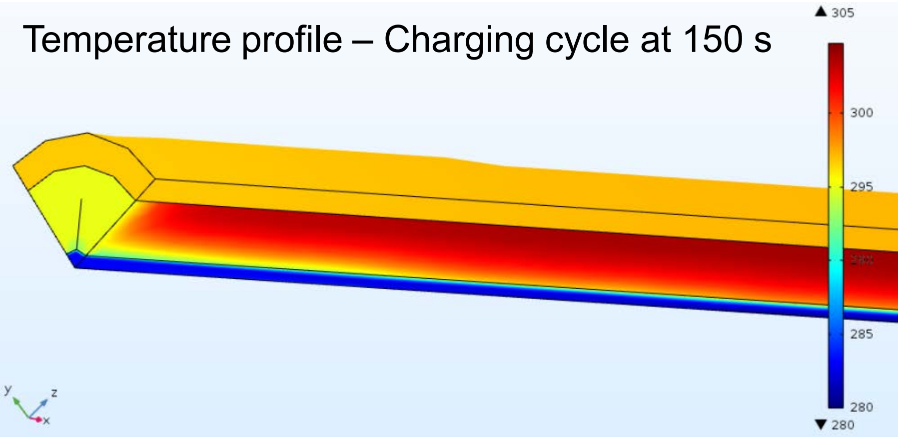
MH = Metal hydride

MH modeling results



- Excellent performance with insulation between the external wall and the MH material
- Almost steady state operating conditions after 5 cycles
- Required additional optimization (fins configuration and heat transfer fluid flow management)

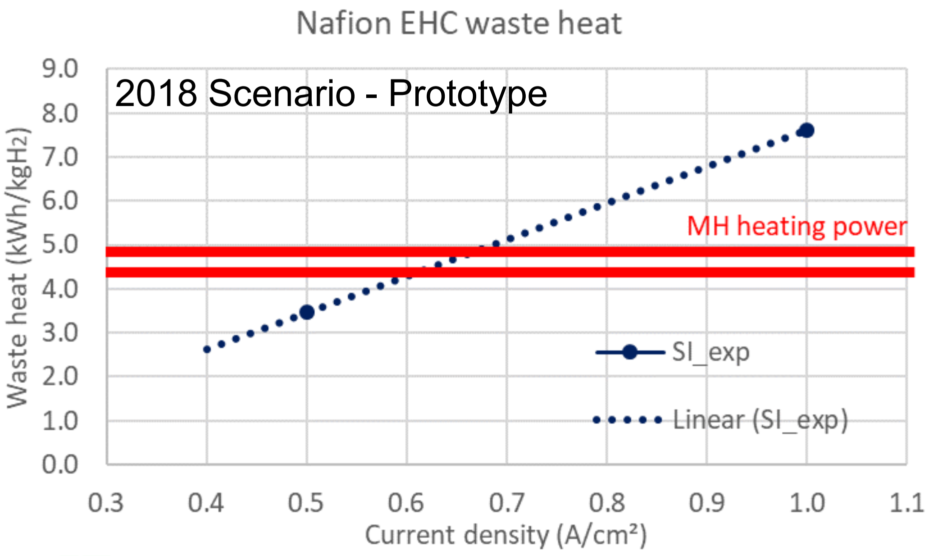




Temperature profile – Charging cycle at 150 s

SOC = State of charge in the MH
P_eq = Equilibrium pressure in the MH
ρ, Cp, k = Density, specific heat, thermal conductivity
RT = Room temperature

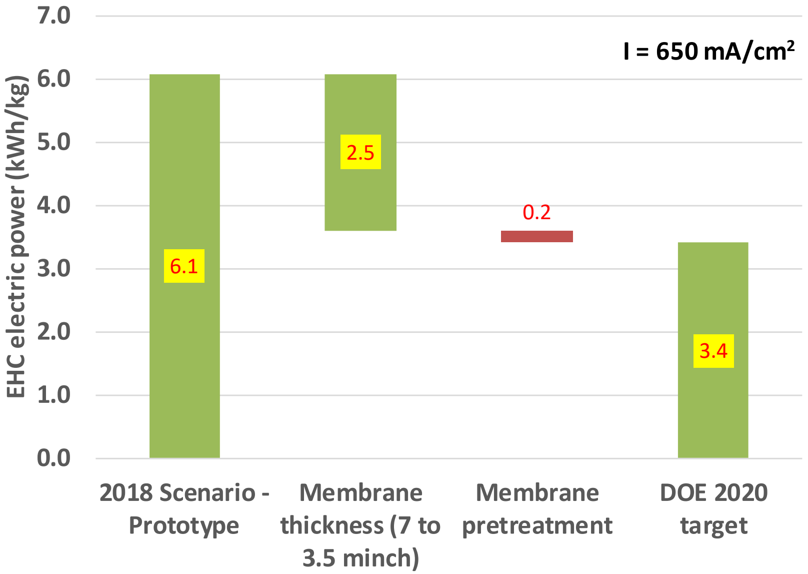
EHC-MHC matching point



Matching point feasible

The electrochemical system waste heat can be used to power the thermal system

- Hydrogen desorption by the MHC system (current status)
  - T = 140 – 160 °C
  - W = 4.3 – 4.9 kWh/kg
- Waste heat available from the EHC system (at 650 mA/cm^2)
  - T = 150 – 170 °C
  - W = 4.3 – 4.9 kWh/kg



MHC = Metal hydride hydrogen compressor
EHC = Electrochemical hydrogen compressor

EHC-MHC design

GWE MHC – single tube, large scale bundle, prototype bundle (3 tubes)

MHC system Mini-channel HE	*Large scale (100 kg/h)*	*Prototype (1 kg/day)*
Charging/discharging time (s)	600 / 600	600 / 600
Units	4	2
Tubes per unit	1194	3
Tube length / diameter (m)	1.40 / 0.024	0.55 / 0.024
Heat transfer enhancer	Al fins or ENG or Al foam	Al fins or Al foam

EHC system Nafion 117	*Large scale (100 kg/h)*	*Prototype (1 kg/day)*
Number of cells	8500	22
Cell area (cm^2)	500	82 at 650 mA/cm^2

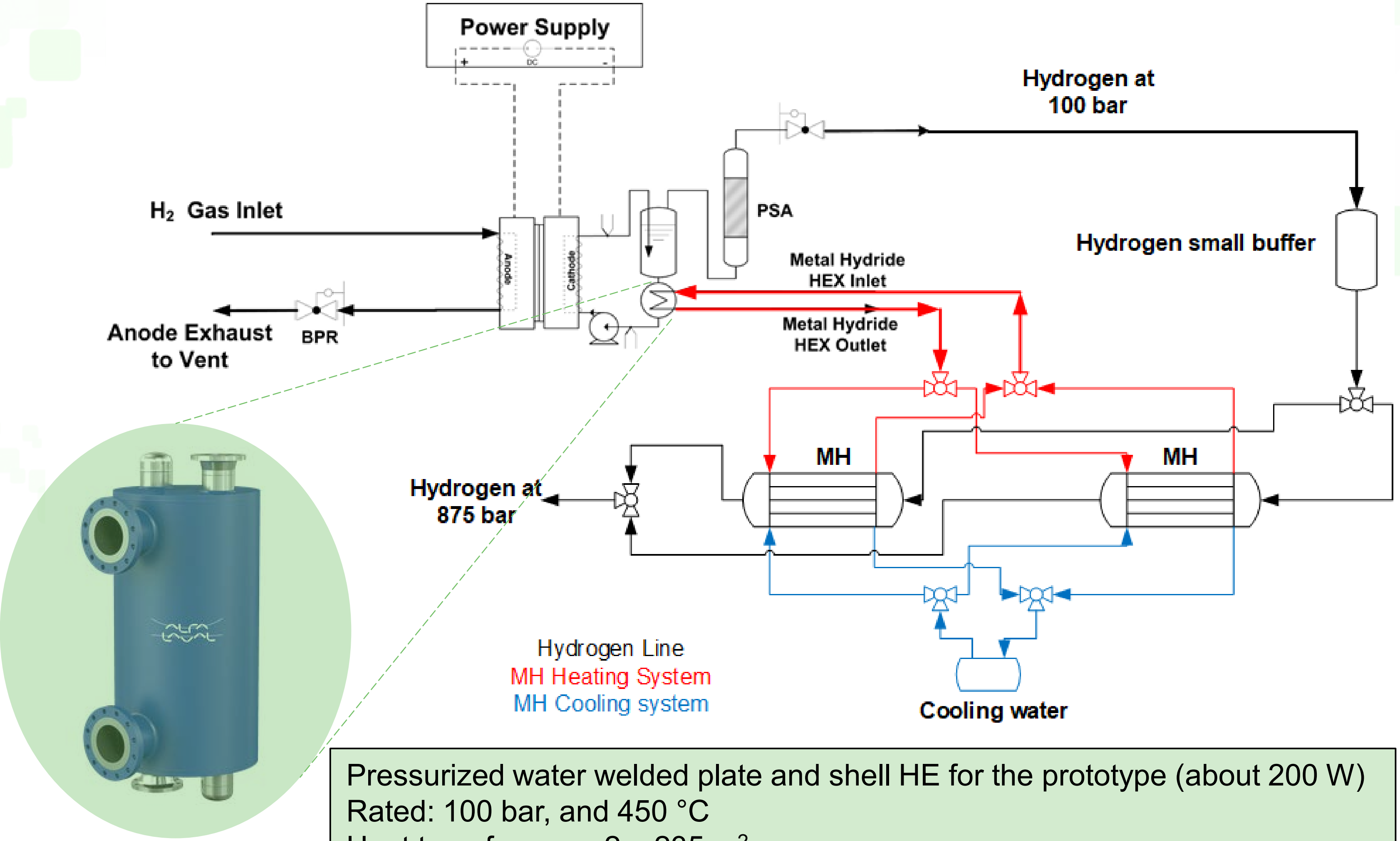
SI EHC – Prototype unit

System matching Plate and shell HE	*Large scale (100 kg/h)*	*Prototype (1 kg/day)*
Water flow rate (L/min)	401,000	30-130
Thermal power (kW)	436	0.183

MHC = Metal hydride hydrogen compressor
EHC = Electrochemical hydrogen compressor
HE = Heat exchanger
MH = Metal Hydride

ENG = Expanded Natural Graphite
GWE = Greenway Energy
SI = Sustainable Innovations

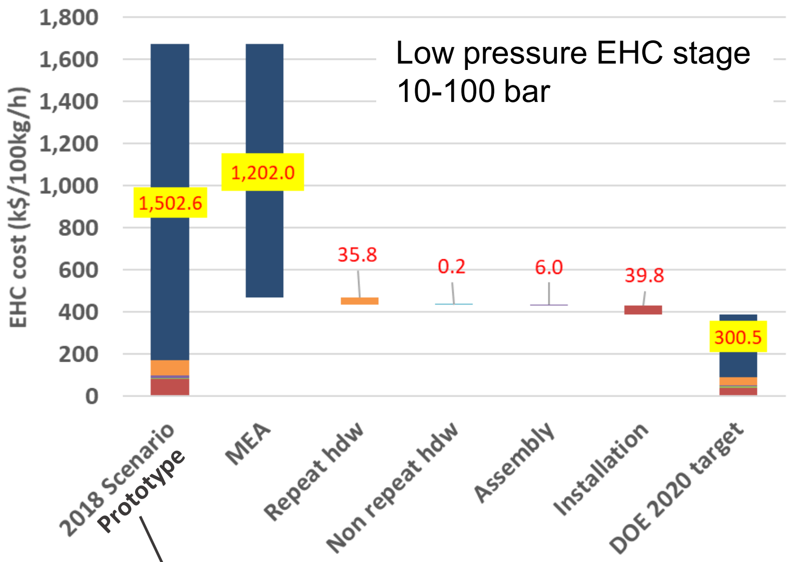
EHC-MHC Prototype schematic

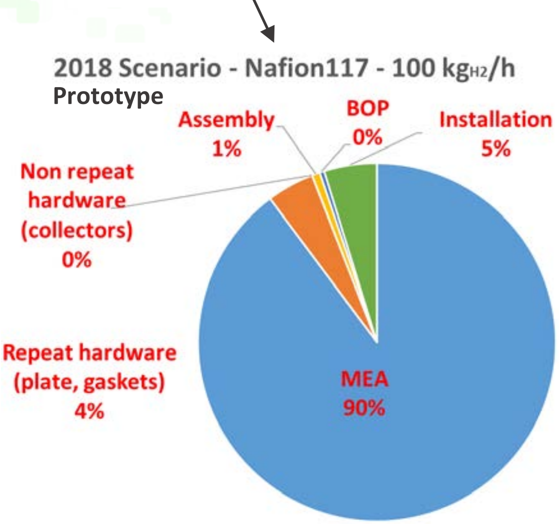


Pressurized water welded plate and shell HE for the prototype (about 200 W)
Rated: 100 bar, and 450 °C
Heat transfer area: 2 – 235 m^2

MHC = Metal hydride hydrogen compressor
EHC = Electrochemical hydrogen compressor
HEX = Heat exchanger
MH = Metal Hydride
PSA = Hydrogen dehydration adsorption unit

Large scale compressor TEA

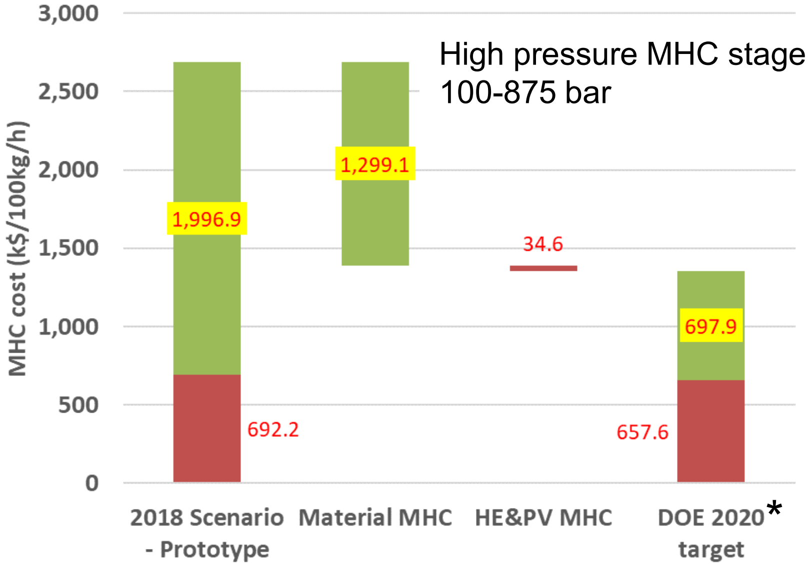

Low pressure EHC stage
10-100 bar

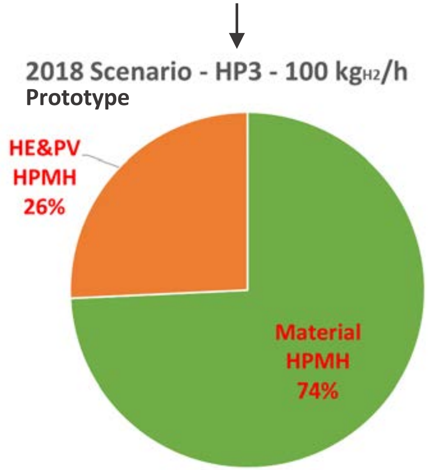


Main need: MEA cost reduction

DOE 2020 scenario

- Large scale production
- Reduction of PtNi loading = 0.142 mg/cm^2 (DOE Fuel Cell target)
- Membrane thickness reduction
- *<u>Required specific MEA cost = 900 $/m^2</u> (current prototype cost 5 times higher)*


High pressure MHC stage
100-875 bar



Main need: MH material cost reduction

DOE 2020 scenario

- Large scale production
- Reduction of expensive elements (e.g. Ti, Zr, etc)
- *<u>Required specific raw material cost = 1.7 $/kg</u> (current Ti-MH prototype material cost 3-4 times higher)*

* Value calculated based on the Net Present Value analysis of the MHC system, see Hattrick-Simpers J, Corgnale C. et al. *Mol Syst Design & Eng*, 2018, DOI: 10.1039/C8ME00005K

TEA = techno-economic analysis
MHC = Metal hydride hydrogen compressor
EHC = Electrochemical hydrogen compressor
MEA = Membrane Electrode Assembly

HE&PV = Heat exchanger and pressure vessel (in the MHC)
MH = Metal hydride

Accomplishments and Progress: Responses to Previous Year Reviewers' Comments

Approach
"excellent approach combining EC and MH compression to reduce investment cost and reduce operating cost and avoid the risk of membrane failure at high pressure"

Accomplishments and Progress
"consider accelerating efforts using good system models"
- Additional emphasis and effort on system and HSECOE detailed models have been carried out.

Collaboration

"accelerate progress by teaming/collaborating with other projects"
- Collaboration with Sandia MH Compressor Group has been expanded

Relevance/Potential Impact
"researchers should compare project costs to mechanical compression and include maintenance, downtime, etc."
- *Additional cost and performance comparisons were performed this past year versus mechanical compressor systems and more are planned during Phase 2.*

Future Work
"focus more on demonstration and model validation and make more use of existing EC and MH expertise"
- Demonstration and model validation are planned for Period 2 once a promising EC and MH system was identified. Only existing EC membranes and MH materials were considered and evaluated during this project in collaboration with our project and other project experts. In agreement with the reviewer comment, a Nafion® based membrane was selected for the EHC system, due to demonstrated reliability.

Collaboration & Coordination

- Ongoing coordination with SNL-HHC-ORNL MH Compressor group for past 18 months with periodic teleconferences.
- Shared results, knowledge of metal hydrides, instrumentation and measurement techniques.
- Agreed to provide shared testing capabilities
- Plan to exchange metal hydrides to provide independent experimental validation for both groups

- ***Collaborations***
  - ***SNL***
  - ***HHC***
  - ***ORNL***
  - ***JMC***
  - ***AMES***
  - ***Purdue Univ***

<u>Issues and solutions/discussions shared between SNL and GWE groups</u>:

1. High-pressure instrumentation components
   - SNL-HHC-ORNL group provided vendors to purchase large reactors and pressure transducers that meet pressure requirements.
   - GWE provided companies used to purchase “micro” high-pressure valves and components used in system.
2. Performance of the alloys received from JMC
   - At least one material received by the SNL/GWE groups does not match literature data
   - Potential improper annealing
   - Contact provided at AMES Laboratory for re-annealing, if needed.
   - Purdue University collaboration to receive their $Ti_{1.1}CrMn$ material (≈100 g)
3. Instrumentation leaks
   - Shared experience of high-pressure with small fittings and potential issues.
   - Discussed risk of fine particle alloy getting into system and causing valve issues.

SNL = Sandia National Laboratory
EHC = Hawaii Hydrogen Carriers
ORNL = Oak Ridge National Lab

JMC = Japan Metals Co.
MH = Metal hydride
GWE = Greenway Energy

Remaining Challenges and Barriers

- EHC system
  - Demonstration of Nafion MEA performance at T > 150°C (possibly required by the MHC system)
  - Enhanced MEA configuration demonstration (reduced thickness, reduced Pt loading, etc)
- MHC system
  - MH material demonstration, showing proper hydrogen desorption at 875 bar and 130-150 °C at feasible material weight capacities
- Interfaced plate and shell heat exchanger
  - Demonstration of proper heat transfer between the EHC and the heat transfer fluid at the required conditions
- Prototype BOP design (e.g. water management equipment, buffer tanks)
- Prototype assembling and demonstration
- Transport model validation against prototype experimental data
- System optimization and enhancement to meet the DOE techno-economic targets

MHC = Metal Hydride Compressor
EHC = Electrochemical Hydrogen Compressor
MEA = Membrane Electrode Assembly
BOP = Balance of Plant
MH = Metal hydride
GWE = Greenway Energy

Proposed Future Work

- ***Assembling and demonstration of the prototype, hybrid compressor system***
  - *Tasks 2.1 and 2.2 – Milestone (3/30/19)*: Successful demonstration of the prototype hybrid compressor system, showing a performance being at least equal to 60% of the efficiency targets (compression work ≤ 2.3 kWh/kg) reported in the FOA for steady state nominal conditions and 40% of the efficiency targets (compression work ≤ 3.5 kWh/kg) for transient conditions.
- ***Detailed model update and validation against the prototype data***
  - *Tasks 2.3 and 2.4 – Milestone (6/30/19)*: Successful validation of the detailed MH tank model. Temperature, pressure and concentration numerical data will be compared with the corresponding experimental data for at least 3 points inside each MH material with a maximum difference of 10%. The data will be compared for full load conditions and for one partial load case, both under steady state conditions and start up and shut down operation.
- ***Optimization of the hybrid compressor system***
  - *Task 2.5 – Milestone (9/30/19)*: Successful identification of an improved performance full-scale system (integrating the ECH, MH and internal heat recovery system) that can achieve all the FOA requirements, except the compression specific work, which will be equal to the isothermal compression work, at the same operating temperatures and pressures. Thus, the improved full scale system will meet: (1) capacity of hydrogen flow rates of at least 100 kg/h; (2) outlet pressures ≥875 bar; (3) compression work and capital costs ≤ to that described in the DOE Hydrogen Delivery MYRD&D; (4) reliability of 80%.

Any proposed future work is subject to change based on funding levels

Technology Transfer Activities

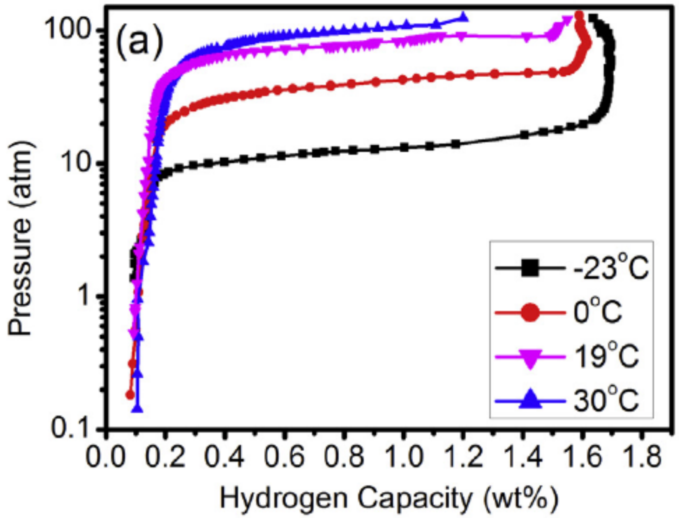
- Invention disclosure and patent opportunities being considered for detailed design of metal hydride heat exchange configuration.
- Additional partnering and funding opportunities being pursued for the development of a small-scale hybrid compressor system for possible near-term hydrogen and fuel cell applications.

Summary

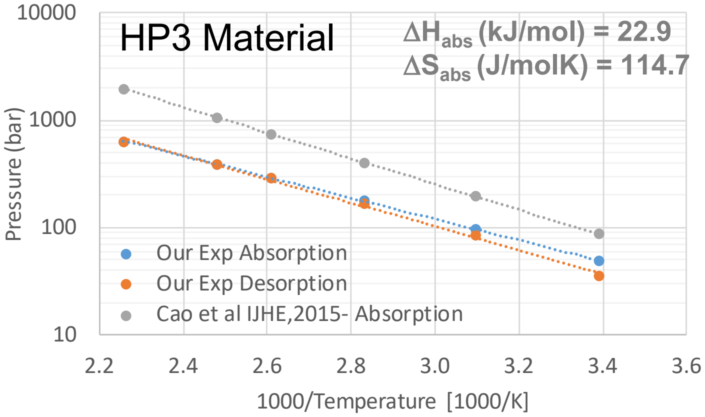
- ***EHC stage***
  - High temperature membranes were selected so that waste heat from the EHC stage can be used to drive the MHC stage.
  - Nafion 117 was selected as the baseline membrane and evaluated at high T (150 °C) & high P (100 bar) with promising results for 100 hours.
- ***MHC stage***
  - HP2 and HP3 MH materials (TiCrMn type) were selected as the best candidate materials based on their operating conditions, cost and availability.
  - HP3 was downselected 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.
- ***EHC-MHC matching***
  - Nafion 117 operating at high temperatures (>120 °C) 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 design identified for the prototype and large scale configurations
- ***EHC-MHC TEA***
  - The TEA of the new hybrid integrated system identified the current techno-economic performance of the system and a viable path to reach the DOE targets

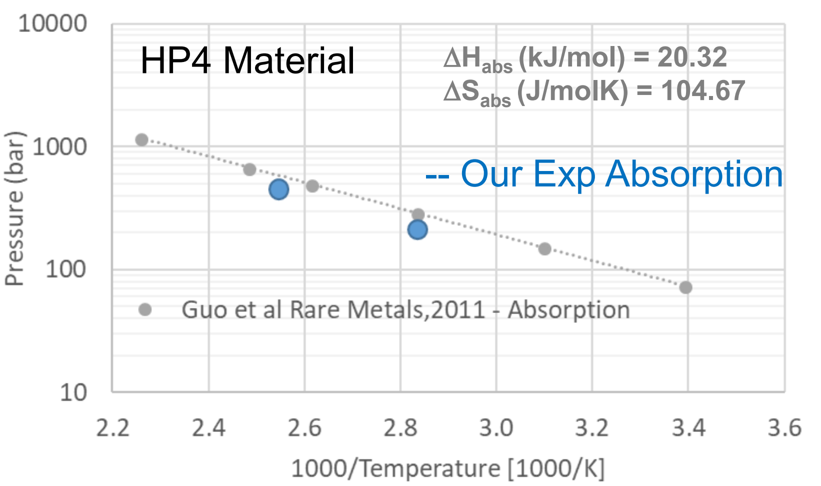
Technical Back-Up Slides

MH literature PCT data – slide 12



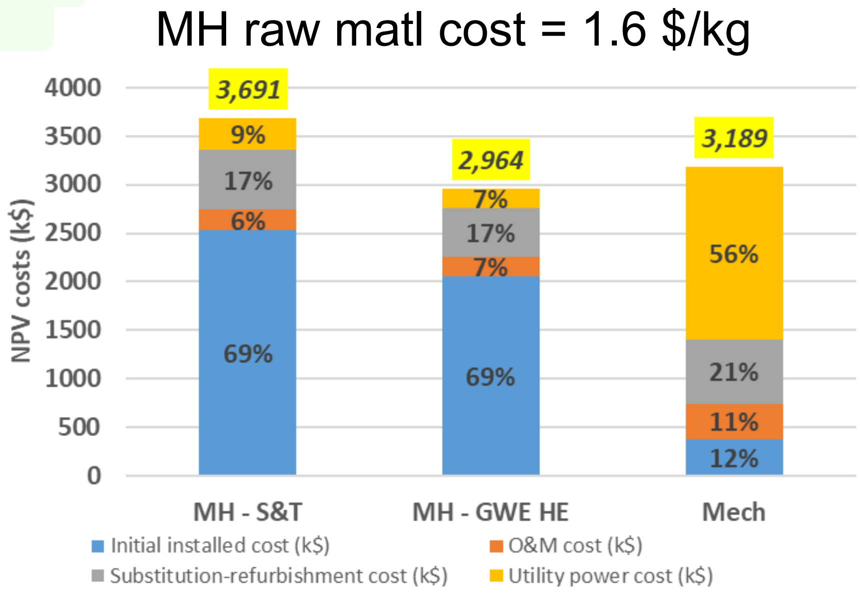
HP3 PCT data from Cao et al. IJHE, 2015





HP3 = High Pressure MH 3 ($Ti_{1.1}CrMn$)
HP4 = $TiCr_{1.55}Mn_{0.2}Fe_{0.2}$

MHC cost NPV values – slide 19



MH raw matl cost = 1.6 $/kg

- NPV cost analysis for DOE target systems (100-875 bar, 100 kg/h)
- Results
  - A MHC with a raw MH material cost $\underline{C_{M^*} = 1.6}$ $\underline{\$/\text{kg}}$ reaches the NPV cost obtained for a mechanical compressor system meeting the DOE targets