Engineering an Adsorbent-Based Hydrogen Storage System:

What Have We Learned?

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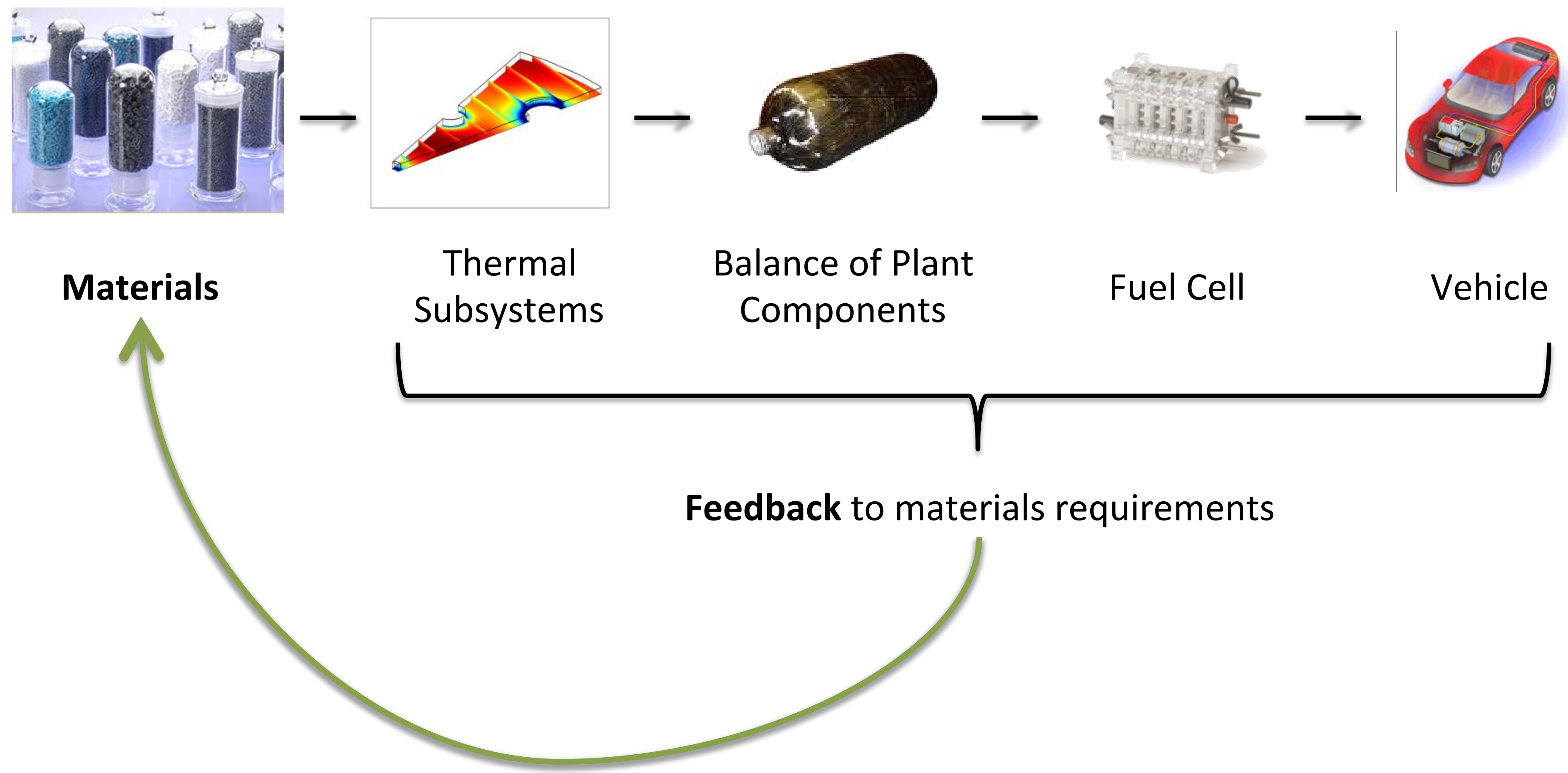
Overview

- For the past 5 years the HSECoE has been developing hydrogen storage systems based on adsorbent, metal hydride, and chemical hydride media
- As we near the Center's conclusion, we seek to translate insight gained from the Center to the materials development community
- This presentation summarizes:
    1. Lessons learned in the development of a MOF-5-based storage system
    2. Materials properties needed to achieve DOE targets (Adsorbent Acceptability Envelope)

Engineering *around* an **imperfect** material can guide development of an optimal material



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HSECoE Goals – Adsorbent System

- Model, design, and construct an adsorbent-based hydrogen storage system that has the potential to meet DOE 2017 targets.
- Reveal design tradeoffs, e.g.:
  - Gravimetric vs. volumetric density
  - Capacity & cost vs. fill time
  - Pros/cons of various HX designs
- Guide materials development by identifying materials properties that most strongly impact system performance.

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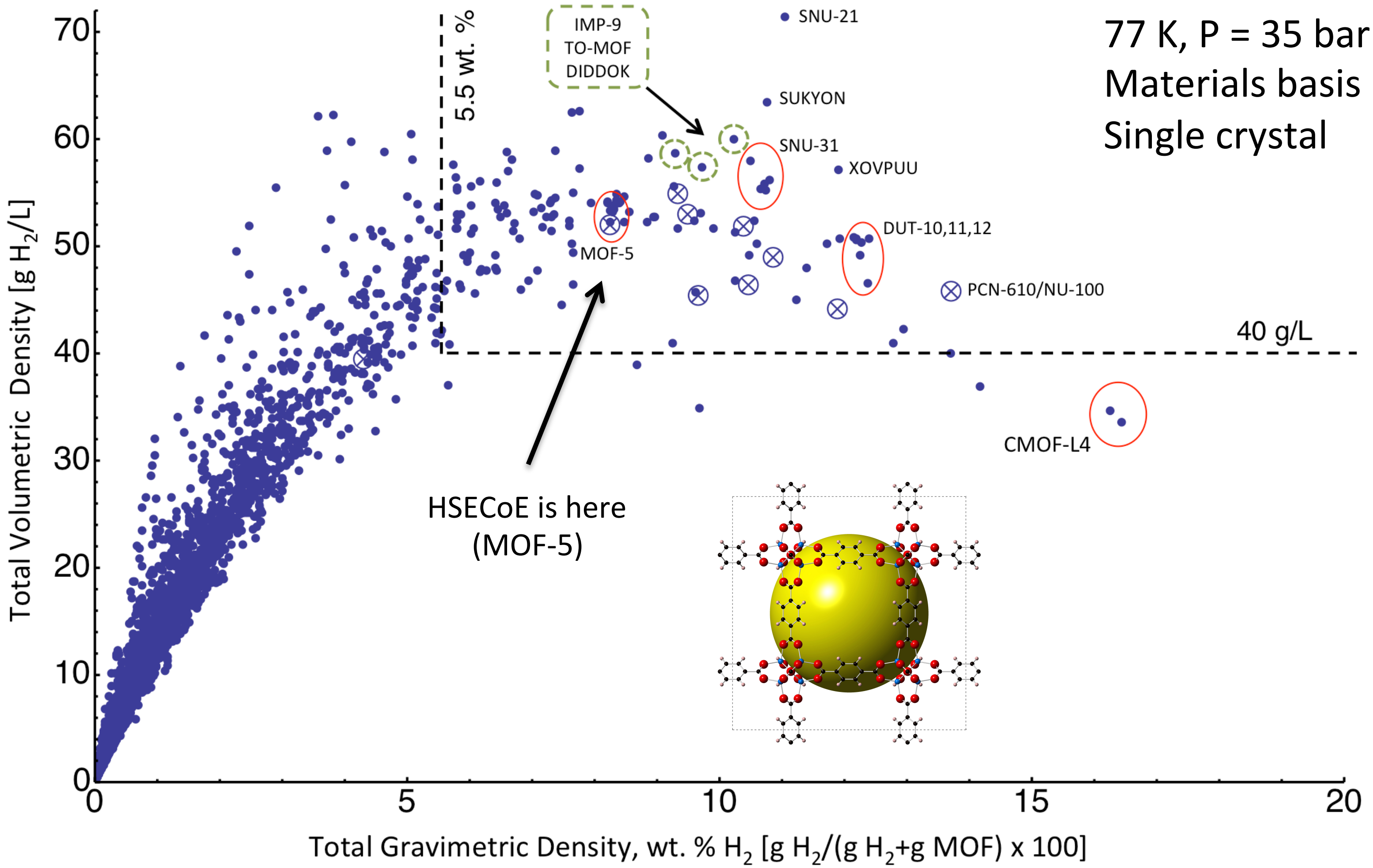
Part 1:

HSECoE Highlights

MOF-5 Selected as Baseline Adsorbent

Good combination of volumetric and gravimetric density;
Available in large quantities (BASF)



Goldsmith, Wong-Foy, Cafarella, and Siegel, *Chem. Mater.*, **25**, 3373 (2013)

System Performance Metric

The Center developed a multivariable approach to measure design tradeoffs.
This model was used to rank various system concepts.

- System Score = Gravimetric Score + Cost Score + Volumetric Score
- Gravimetric Score
  $= S_{GD\%} (I_{FE} \times C_{GFE} + I_{DR} \times C_{GDR} + I_{VA} \times C_{GVA} + I_{VC} \times C_{GVC})$
- Cost Score
  $= S_{C\%} \times I_{VC} \times C_{CVC}$
- Volumetric Score
  $= S_{VD\%} \times I_{VDR} \times C_{VDR}$

$S_{GD\%}$ = % gravimetric density system target from 2017 target
$S_{C\%}$ = % system cost target from 2017 target
$S_{VD\%}$ = % volumetric density system target from 2017 target

I_{FE} **11.3**= importance rating for fuel economy (vehicle level)
I_{DR} **5.5**= importance rating for driving range (vehicle level)
I_{VA} **3.4**= importance rating for vehicle acceleration (vehicle level)
I_{VC} **19.2**= importance rating for vehicle cost (vehicle level)

C_{GFE} **0.03**= correlation % change in gravimetric density for fuel economy (% system to % vehicle)
C_{GDR} **0.03**= correlation % change in gravimetric density for driving range (% system to % vehicle)
C_{GVA} **0.04**= correlation % change in gravimetric density for vehicle acceleration (% system to % vehicle)
C_{GVC} **0.1**= correlation % change in gravimetric density for vehicle cost (% system to % vehicle)*
C_{CVC} **0.15**= correlation % change in cost for vehicle cost (% system to % vehicle)
C_{VDR} **1**= correlation % change in volumetric density for driving range (% system to % vehicle)

* this correlation value is a placeholder and needs to be confirmed with further analysis

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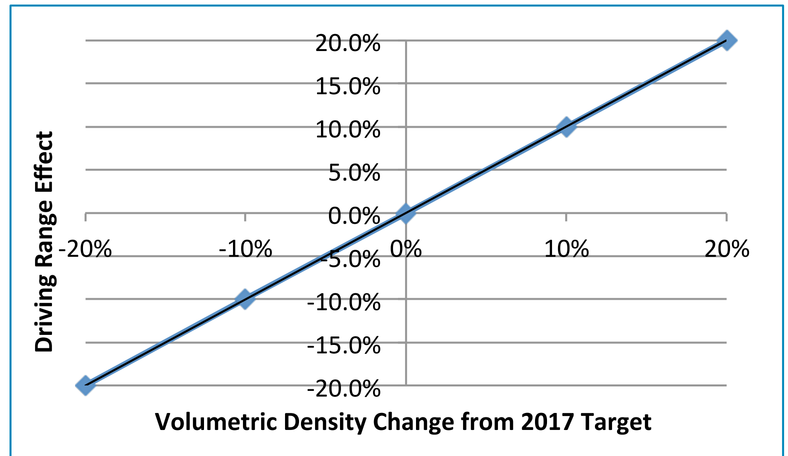

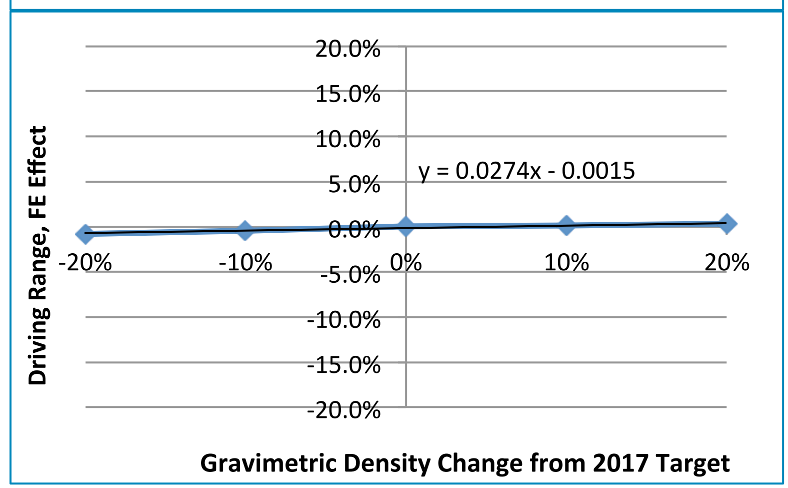

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Rapid System Design Tool

Narrowed space of possible designs to 4 "systems of interest."

Approach – From over ½ Billion combinations… down to 4 Systems

Over ½ Billion Possible System Combinations:

- Internal heat exchangers (all options) **(x45)**
- Tank types **(x6)**
- L-to-D ratios **(x3)**
- LN_2 inner wall chiller **(x2)**
- Hemispherical vs. oblate endcaps **(x2)**
- Pressure vessel only vs. full design **(x2)**
- Material types (with volume-% changes) **(x87)**
- Media packing density **(x10)**
- Full tank pressure **(x12)**
- Full tank temperature **(x7)**
- Empty tank temperature **(x4)**

Eliminate unrealizable system options and combinations of options

62 Million Reasonable Systems Combinations:

- Internal heat exchangers (all options) **(x31)**
- Tank types **(x2)**
- L-to-D ratios **(x3)**
- LN_2 inner wall chiller **(x2)**
- Hemispherical vs. oblate endcaps **(x2)**
- Pressure vessel only vs. full design **(x1)**
- Material types (with volume-% changes) **(x29)**
- Media packing density **(x5)**
- Full tank pressure **(x12)**
- Full tank temperature **(x6)**
- Empty tank temperature **(x8)**

Perform a parametric study

Option #1	Option #2	Option #3	…	Option N
1	1	1	…	1
2	1	1	…	1
⋮	⋮	⋮	⋮	⋮
N_1	1	1	…	1
1	2	1	…	1
2	2	1	…	1
⋮	⋮	⋮	⋮	⋮
N_1	N_2	N_3	…	N_N

Filter the Results

Final 4 Systems:

- Three flow-through cooling with resistance HX options:
  1. HexCell with powder MOF-5
  2. HexCell with 0.32 g/cc compacted MOF-5 pellets
  3. Helical coil with powder MOF-5
- One isolated-LN_2 cooling with isolated-H_2 heating option:
  4. MATI with 0.32 g/cc compacted MOF-5 pucks

David Tamburello, SRNL

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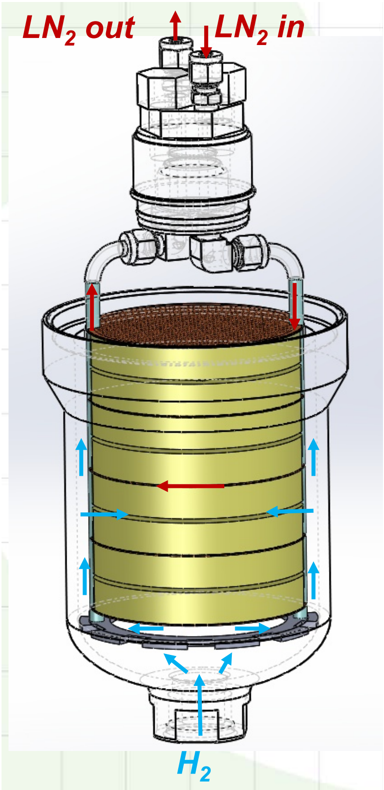
System Prototypes

Two system prototypes are being built and tested in the final phase of the HSECoE

MATI*

Densified media

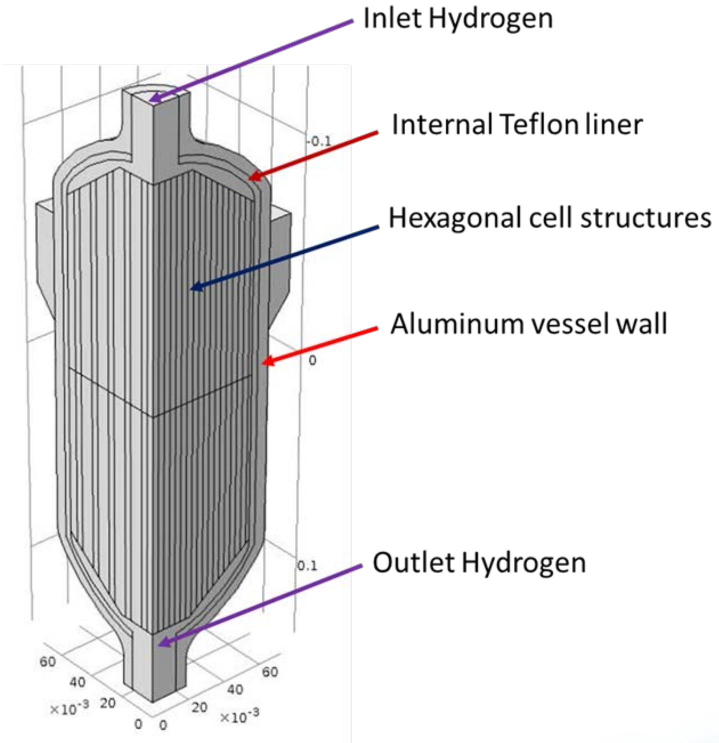
Isolated cooling/heating flow



Hex-Cell

Powder media

Flow-through cooling + resistive heating



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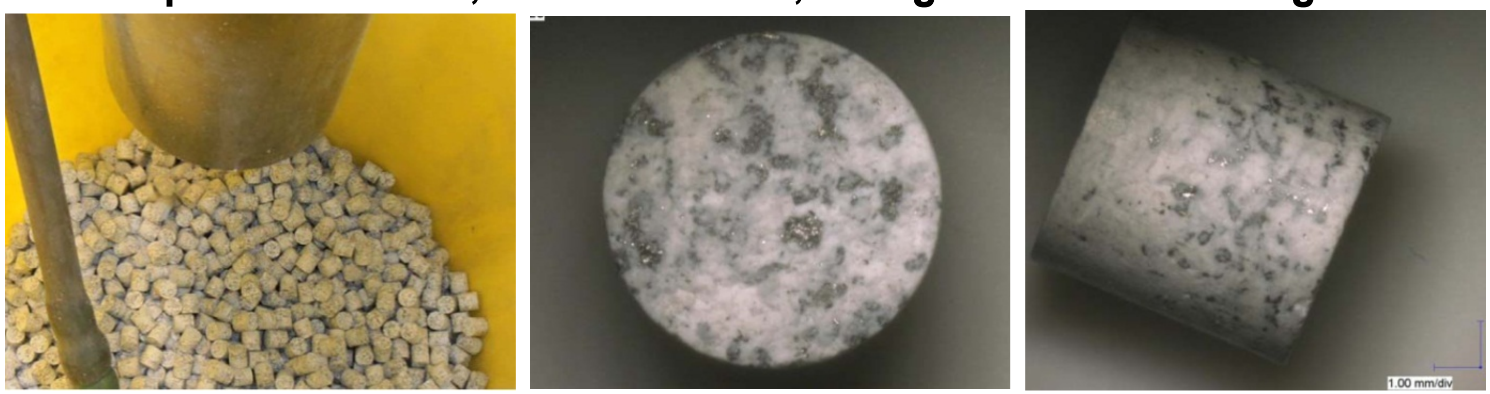
*Modular Adsorption Tank Insert

Densification of Powders

MOF-5 powders can be formed into pellets & pucks without binder

GW0117 – pellets 6x6 mm, 5 +/- 0.1% ENG, .391 g/cc with σ = .013 g/cc



Pucks: ø5 cm x 1.5 cm

ENG layering +pins

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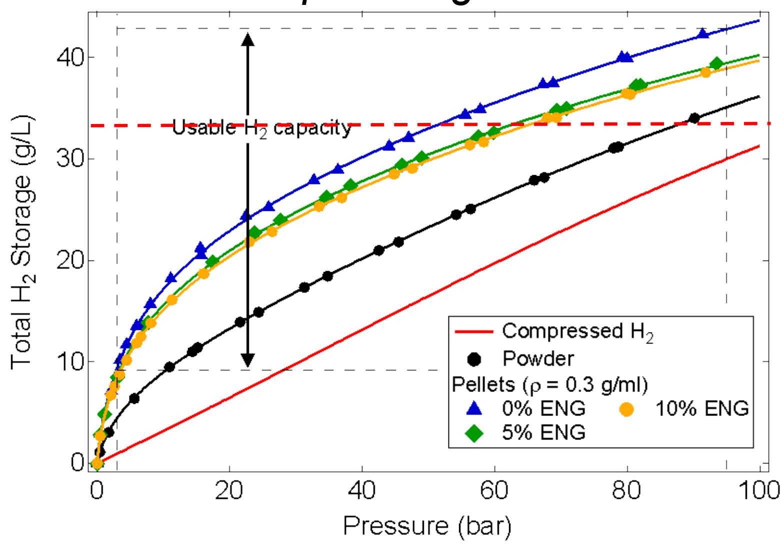
J. Purewal *et al.,* J. Phys. Chem. C 2012, 116, 20199–20212
J. Purewal, *et al.,* International Journal of Hydrogen Energy **37**, 2723 (2012).

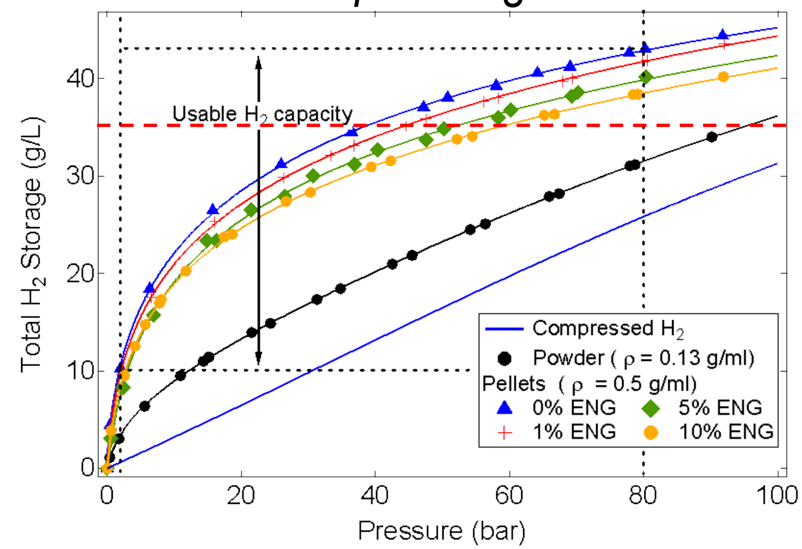
Improved Volumetric Density in MOF-5 Pellets

Monoliths have > 50% improvement in volumetric hydrogen density.
Practical upper limit to density = ~0.5 g/cc (plastic deformation)

ρ = 0.3 g/cc



ρ = 0.5 g/cc



- Note: All curves currently assume skeletal densities of 2 g/cc and 100% packing efficiency.

Powder 5-60 bar & 80 K	0.3 g/cc + 5% ENG 5-60 bar & 80 K	0.3 g/cc + 5% ENG 5-60 bar & 80-160 K	0.5 g/cc + 5% ENG 5-60 bar & 80 K	0.5 g/cc + 5% ENG 5-60 bar & 80-160 K
20 g/l	**22 g/l**	**31 g/l**	**22 g/l**	**34 g/l**
60% packing efficiency:	*20 g/l*	*26 g/l*	*21 g/l*	*27 g/l*

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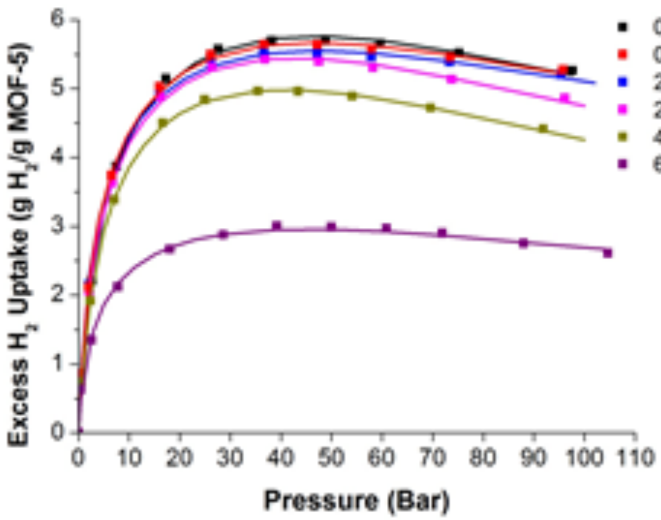
J. Purewal *et al.,* J. Phys. Chem. C 2012, 116, 20199–20212
J. Purewal, *et al.,* International Journal of Hydrogen Energy **37**, 2723 (2012).

Stability: Robustness to Air-Exposure

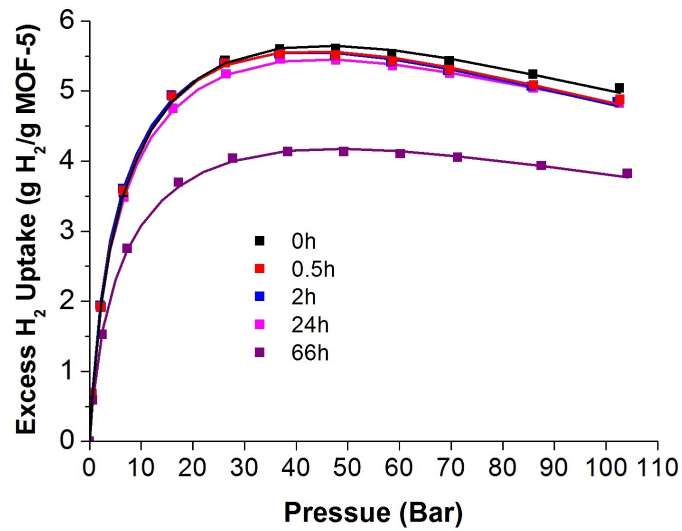
Exposure tests show that MOF-5 undergoes limited capacity degradation in humid environments for exposure times up to 2 hours

Relative humidity = 45 %

Powder, ρ = 0.13 g/cm^3



Pellets, ρ = 0.37 g/cm^3



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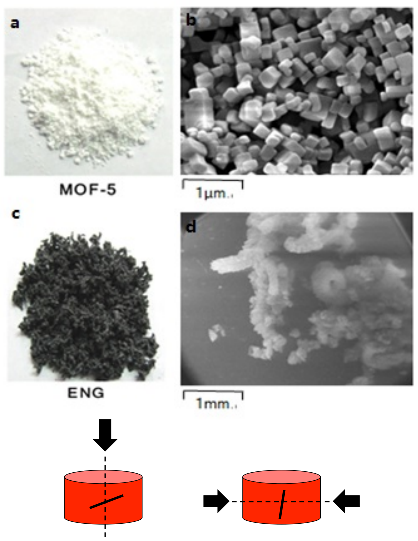
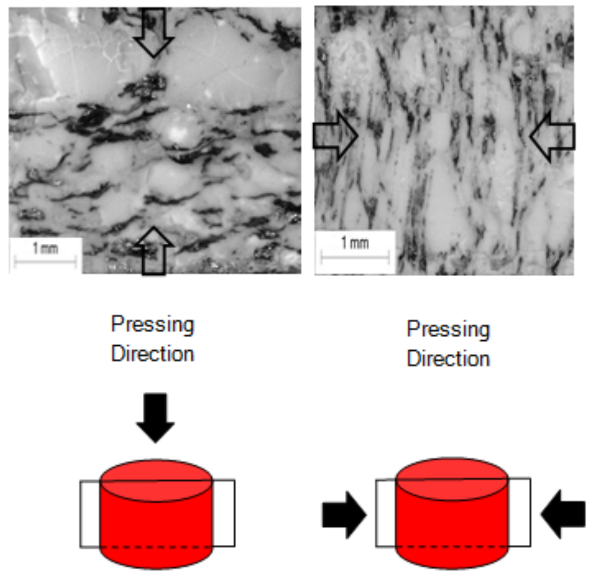
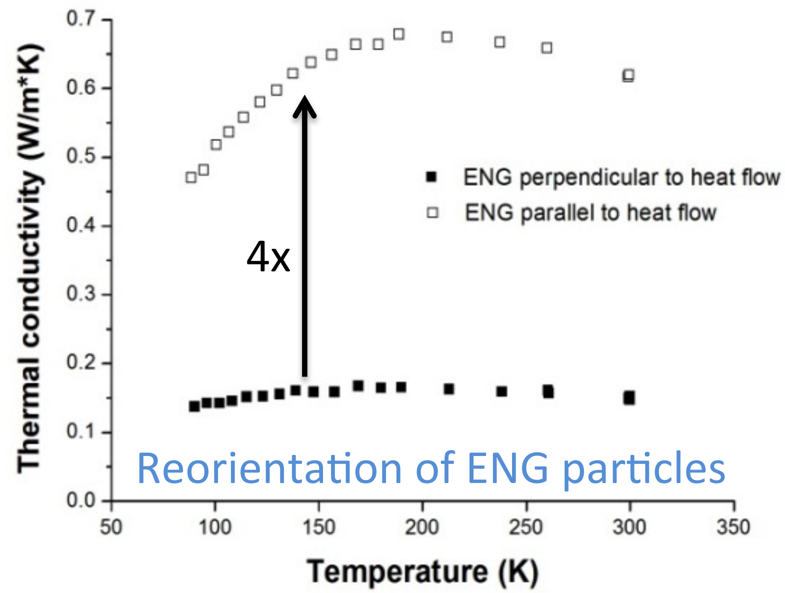
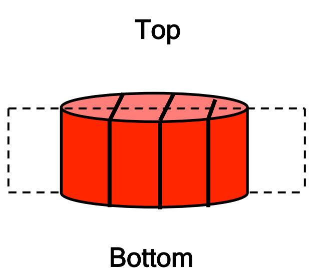
Thermal Conductivity

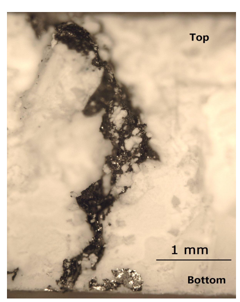
Reorientation and layering of ENG additions can dramatically improve the low conductivity of MOF-5

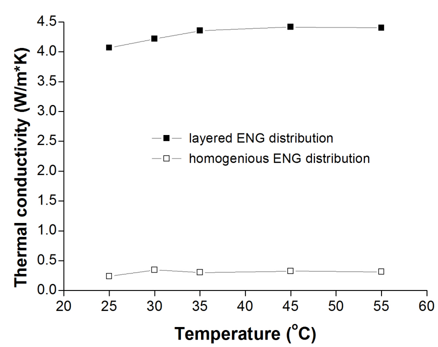












Layering increases conductivity 20x

Y. Ming, *et al.*, International Journal of Heat and Mass Transfer, **82**, 250 (2015).
D. Liu, International Journal of Hydrogen Energy **37**, 6109 (2012).

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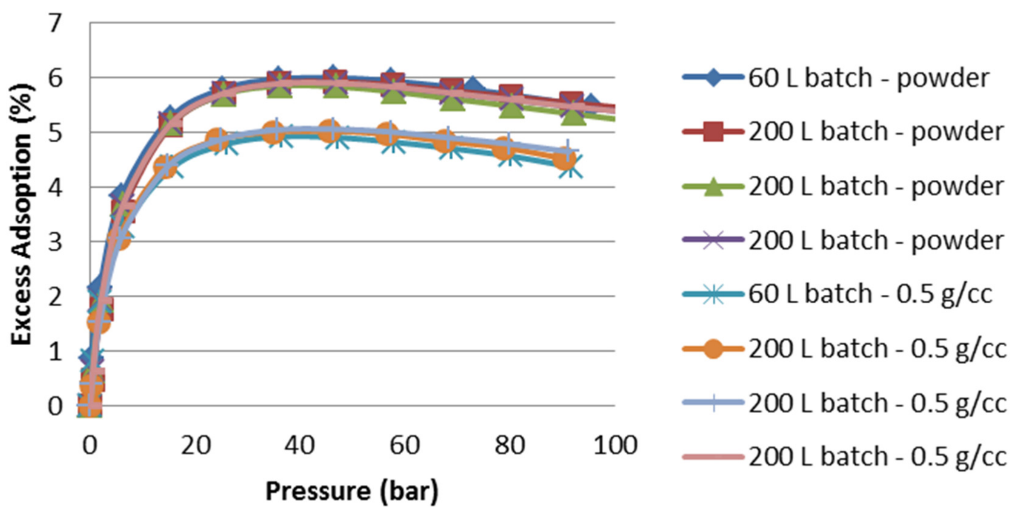
Scale-up of MOF-5

MOF-5 manufacturing process has delivered ~9.3 kg of material.
Performance confirmed to be within 10% of lab-scale material



Batch Code	Reactor Size [L]	Amount [kg]	BET [m²/g]	LSA [m²/g]	Zn [wt%]	C [wt%]	Crystal size* [µm]	Particle size** [mm]
GP0372	200	3.1	2937	3838	32	37	0.2-2.0	
GP0374	200	3.5	2870	3794	34	37	0.2-2.0	
GP0375	200	3.2	2955	3896	34	37	0.2-2.0	
GP0378	Mix	9.3	2937	3877	30	37	0.2-2.6	0.1-1.3
GP0326	60	1	2905	3891	34	37	0.2-3.0	0.1-1.4
Scale-Up Difference:			1%	.4%				7%
Reference GW0116	7	.14	2680	3547			0.2-2.0	

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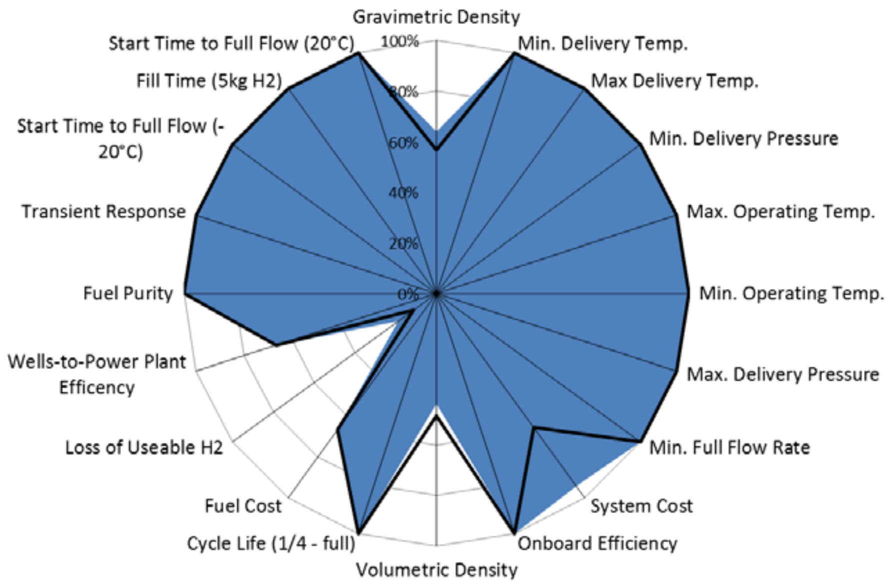
System Design Improvements

The center has identified lower cost designs, but limitations in capacity and loss of usable hydrogen remain

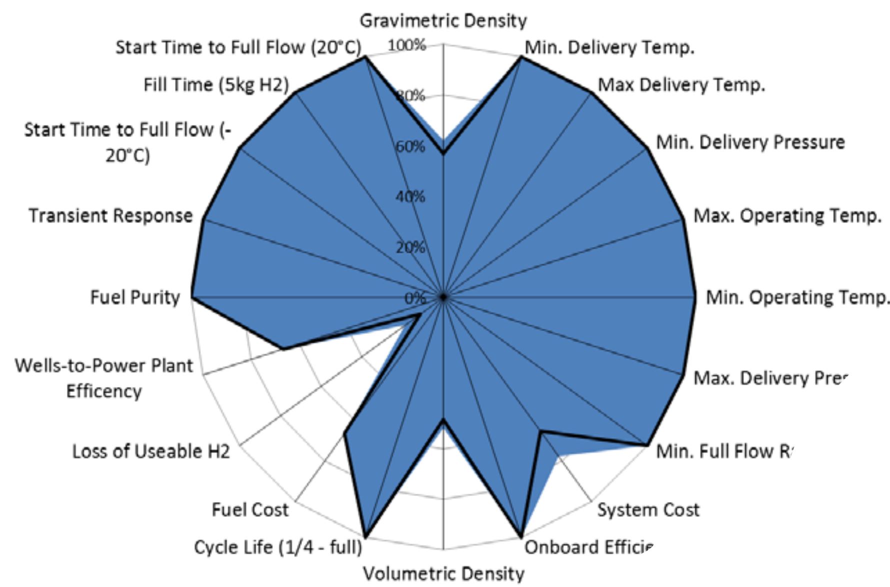
Phase 2

End of Phase 1 Baseline

Hex-Cell System



MATI System



Phase 1 system: AX-21 powder, **Type 3 CF tank, 200 bar**, 80 K

Lower pressure → lower cost,
heavier tank → comparable capacity!

Final system: MOF-5, **Type 1 Al tank, 100 bar**, 80K

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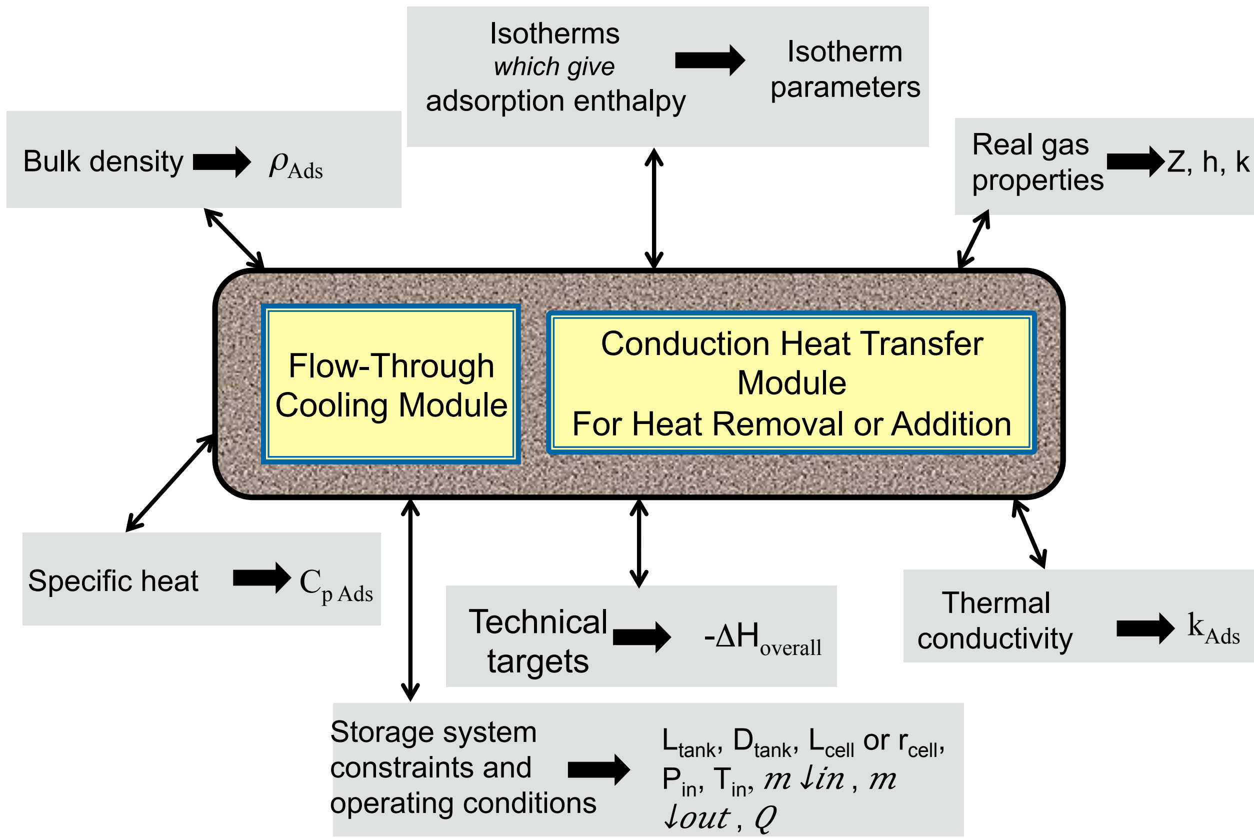
Part 2:

Adsorbent Acceptability Envelope

Adsorbent Acceptability Envelope

Leverages knowledge gained by HSECoE in modeling, characterization, and construction of adsorbent system



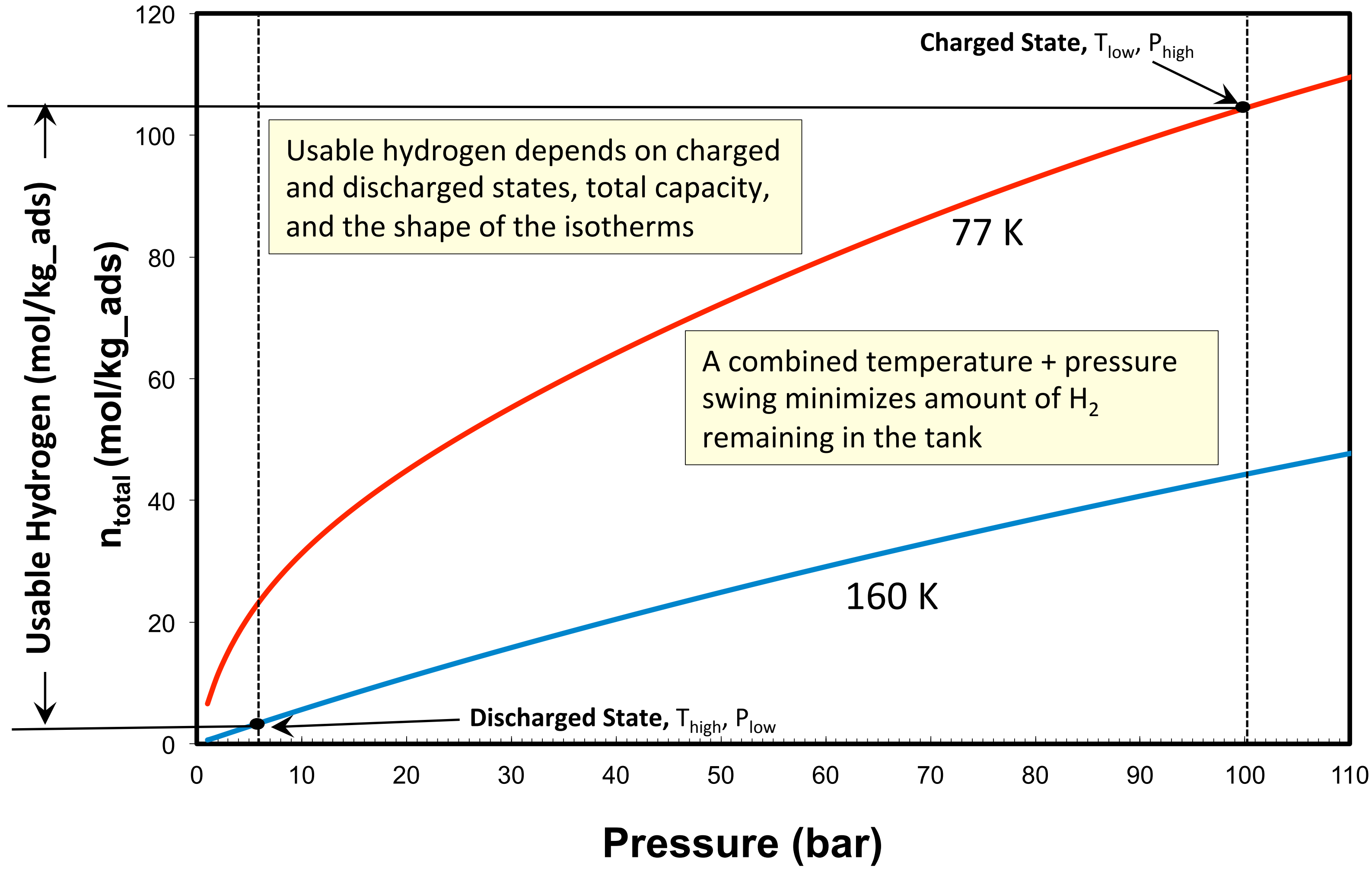
Overview

Goal: Identify coupled adsorbent and storage vessel properties that can meet 700 bar and DOE targets

- Accomplished by:
  - Use of isotherms that yield necessary amount of **usable** hydrogen (not just total)
    - Depends on final (empty) and initial (full) states
    - Determined through numerical variation of isotherm parameters
    - Can also determine parameters that **optimize** usable hydrogen
    - Isotherms also determine enthalpy of adsorption
  - Requires knowledge of bulk, crystal, and skeletal densities
    - OR bulk density, inter-particle porosity, and intra-particle porosity

Definition: Usable Hydrogen

Determined using a temperature + pressure swing from T_{low}, P_{high} to T_{high}, P_{low} = 5 bar



UNILAN Isotherm

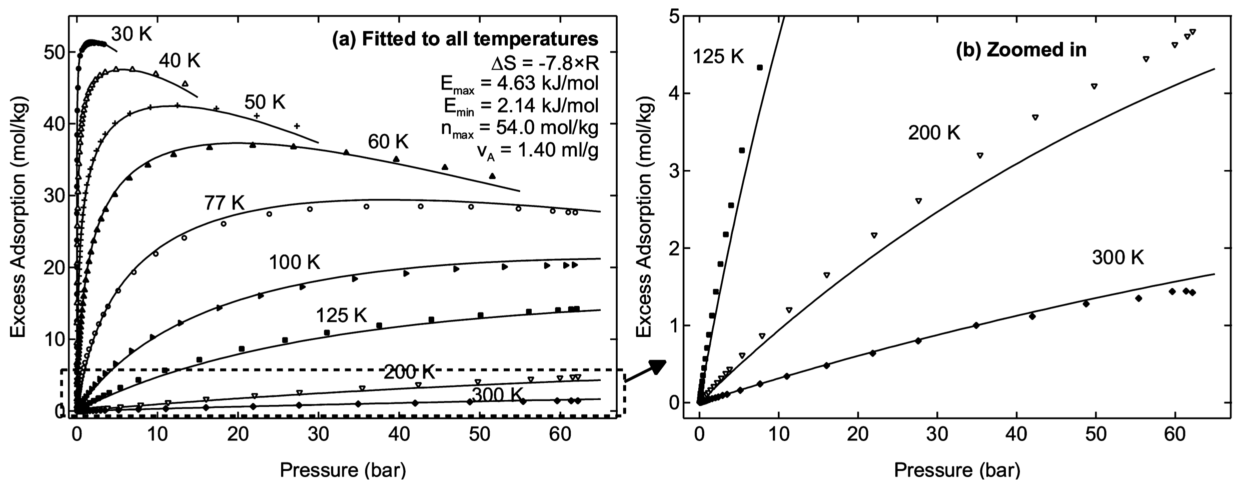
UNILAN model provides an accurate description of the MOF-5 experimental data, requiring only five parameters to predict uptake across a wide temperature range

$$n_a = \frac{n_{max}RT}{(E_{max} - E_{min})} ln\left(\frac{e^{-\Delta S_0/R} + \frac{P}{P_0}e^{E_{max}/RT}}{e^{-\Delta S_0/R} + \frac{P}{P_0}e^{E_{min}/RT}}\right)$$

$$n_{Total} = n_a + c(V_v - V_p)$$

$$n_{Usable} = n_{Total}(T_{chg}, P_{chg}) - n_{Total}(T_{disch}, P_{disch})$$

E_{max} and E_{min} = The maximum and minimum values of $-\Delta H_0$ ($|\Delta H_0|$ is the isosteric heat) [J/mol]. $-\Delta H_0$ is uniformly distributed between E_{min} and E_{max}.



Purewal *et al.*, J. Phys. Chem. C 2012, 116, 20199–20212

Assumptions and Operating Scenarios

The approach uses an assumed set of operating conditions and system architecture

System Architecture

- Flow through (Hex-cell)

- Type 1 Al vessel
- 5:1 Length:diameter
- Internal HX = 20% mass
- 5.6 kg usable H_2 stored
- 1” MLVI
- LN_2 jacket
- MOF-5 like adsorbent
- 181 kg/m^3 powder

Scenario 1: Cryo System

T_{low} = 77 K
P_{high} = 100 bar
T_{high} = 160 K
P_{low} = 5 bar

Scenario 2: Ambient System

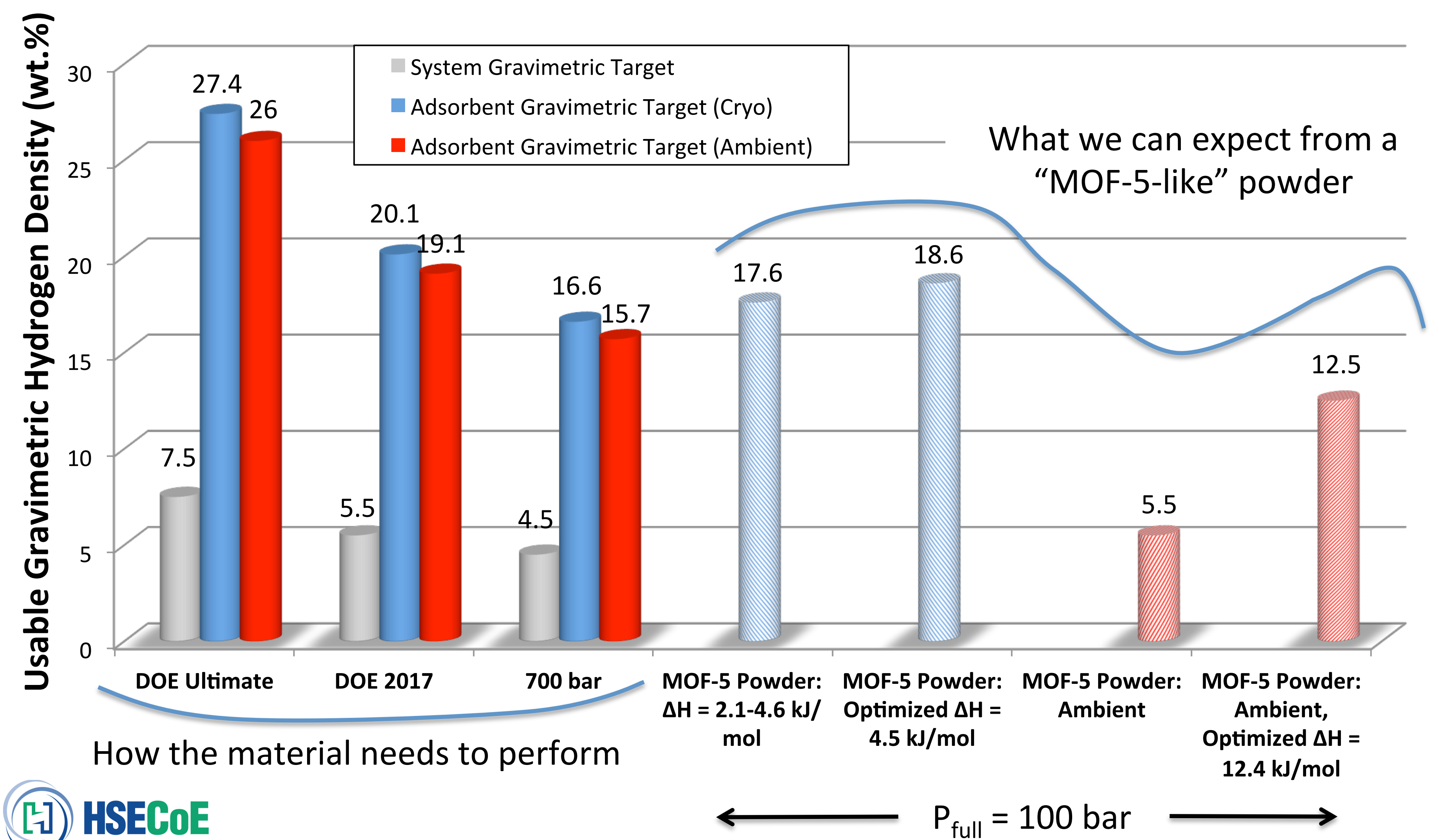
T_{low} = 230 K
P_{high} = 100 bar
T_{high} = 400 K
P_{low} = 5 bar

Procedure

1. Set initial (full) and final (empty) T, P conditions
2. Fix entropy change, ΔS, to nominal value for MOF-5
3. Set value for bulk density of adsorbent, ρ_{bulk} (181 kg/m^3 MOF-5 powder)
4. Back-calculate materials capacity targets based on system targets & system mass + volume
5. Numerically determine required isotherm parameters with respect to usable hydrogen
   - Optimize n_{max}, E_{max}, and E_{min} in UNILAN model to meet target values (at adsorbent level)
   - Convert isotherm parameters to gravimetric and volumetric H_2 densities (at adsorbent level)
6. Repeat steps 3-5 for different operating scenarios and materials densities

Materials Capacity Targets – Gravimetric

A powder MOF-5-like system can surpass 700 bar in gravimetric density at low-T



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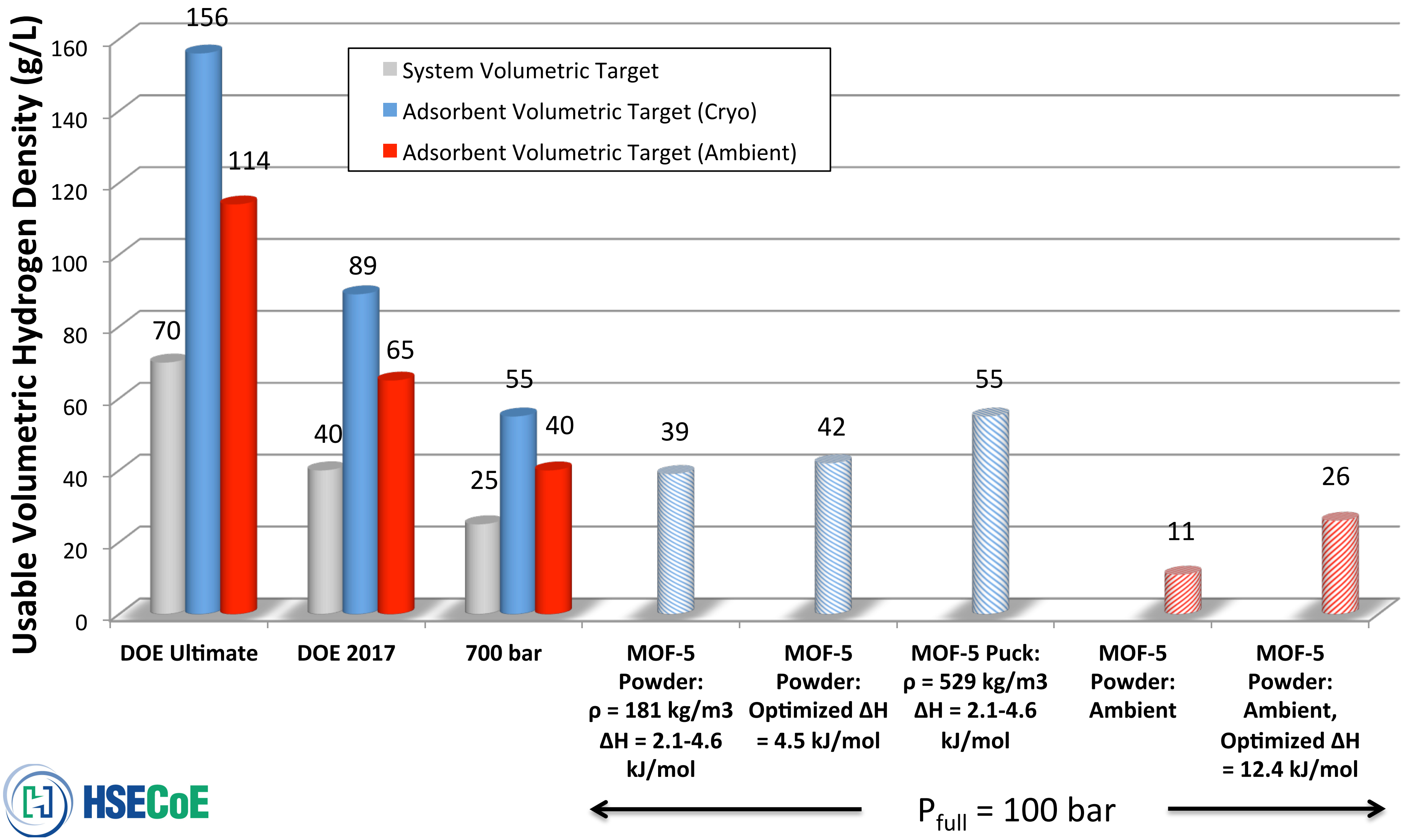
Materials Capacity Targets – Volumetric

A powder-based system falls short in volumetric H_2 density



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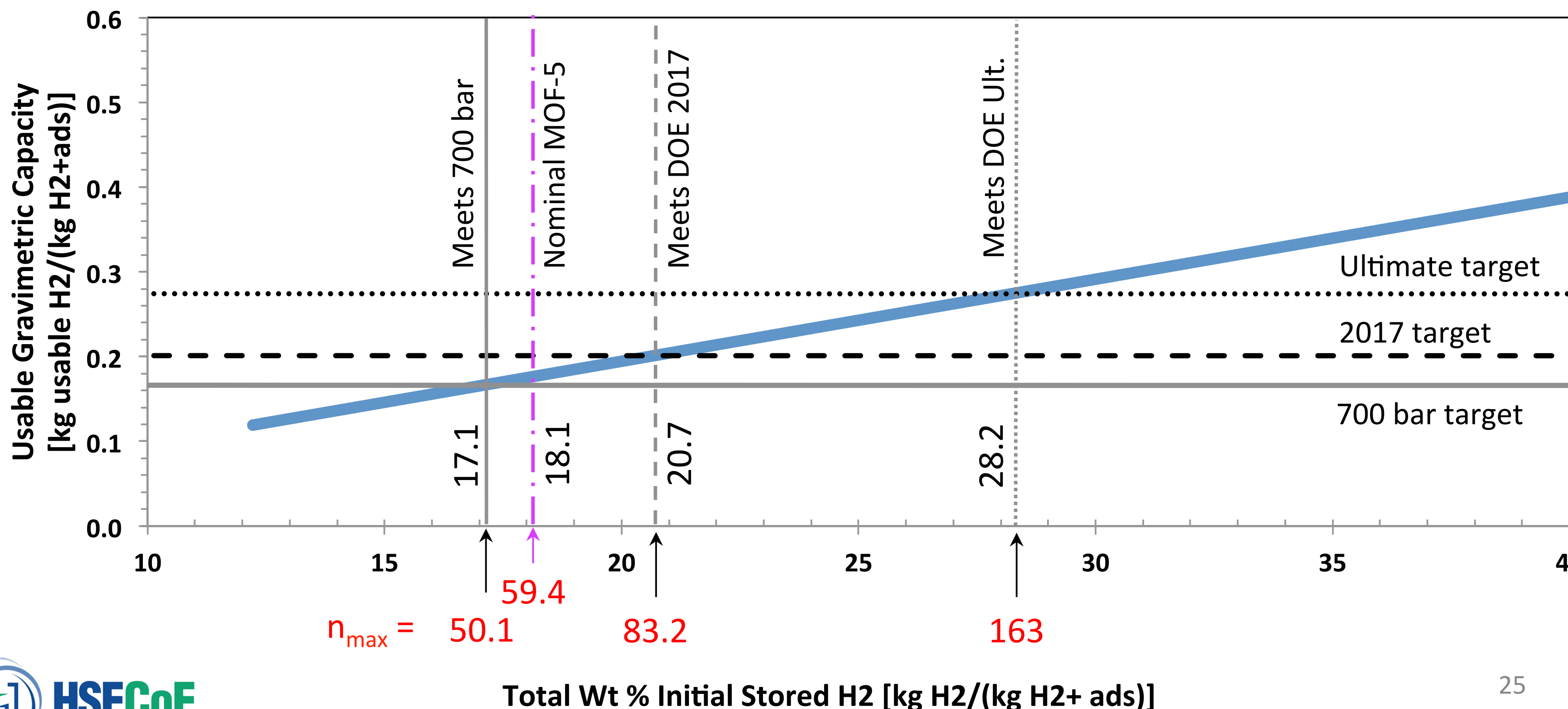
Parametric Dependence on Number of Adsorption Sites

Vary number of adsorption sites (n_{max}) while keeping all other adsorbent properties constant

MOF-5 can surpass 700 bar on a gravimetric basis at cryogenic conditions.
However, reaching the DOE 2017 target will require a 14% improvement in capacity.



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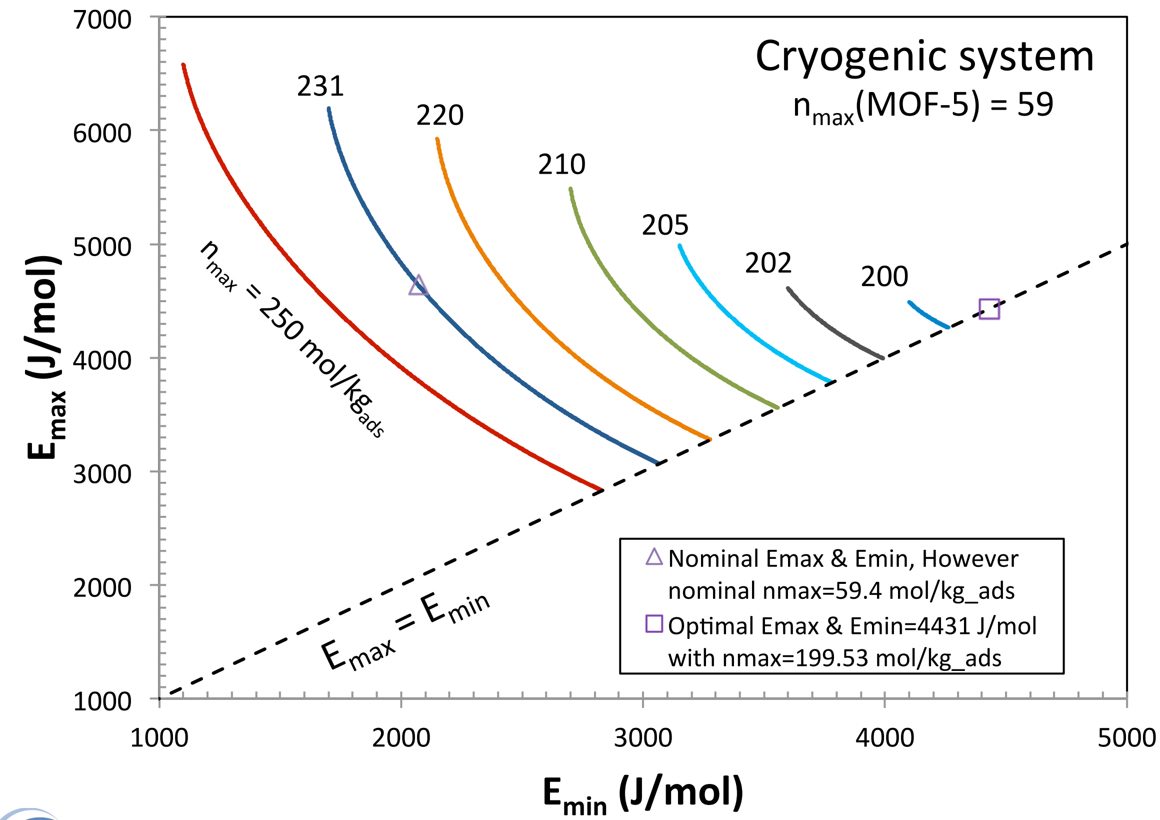
Parametric Dependence on Adsorption Sites *and* ΔH

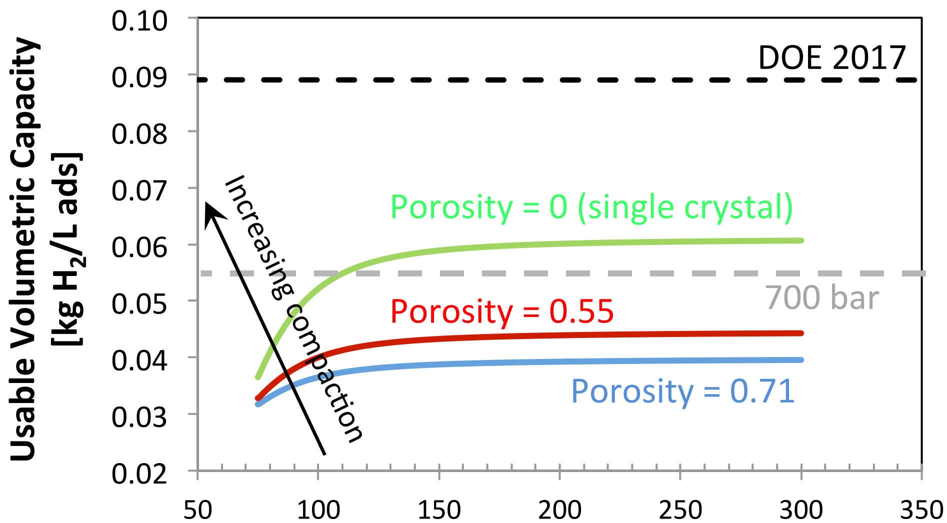
Many combinations of ΔH and n_{max} can in principle satisfy targets
However, meeting volumetric targets with a powder system requires very large n_{max}

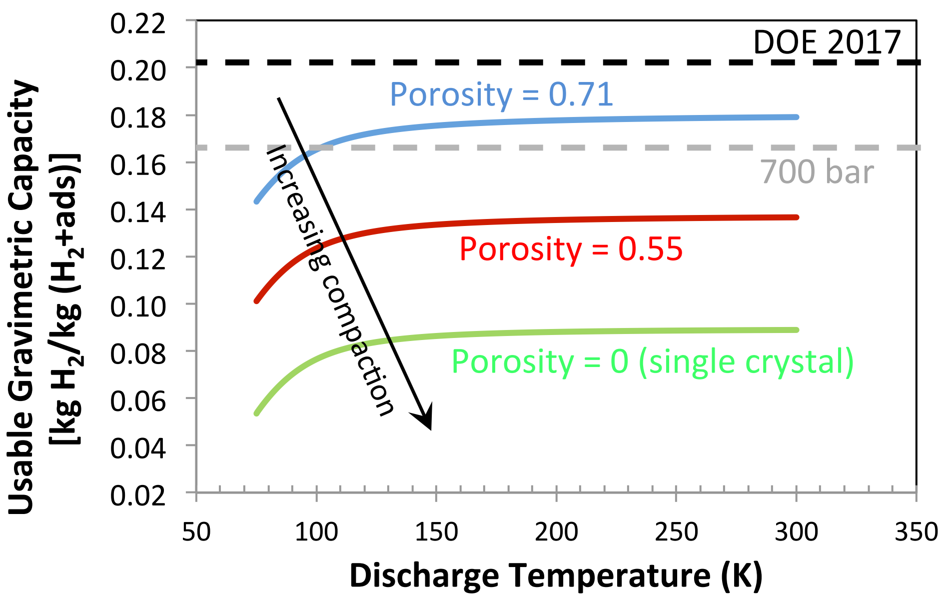
Combinations Which Meet DOE 2017 Volumetric Targets



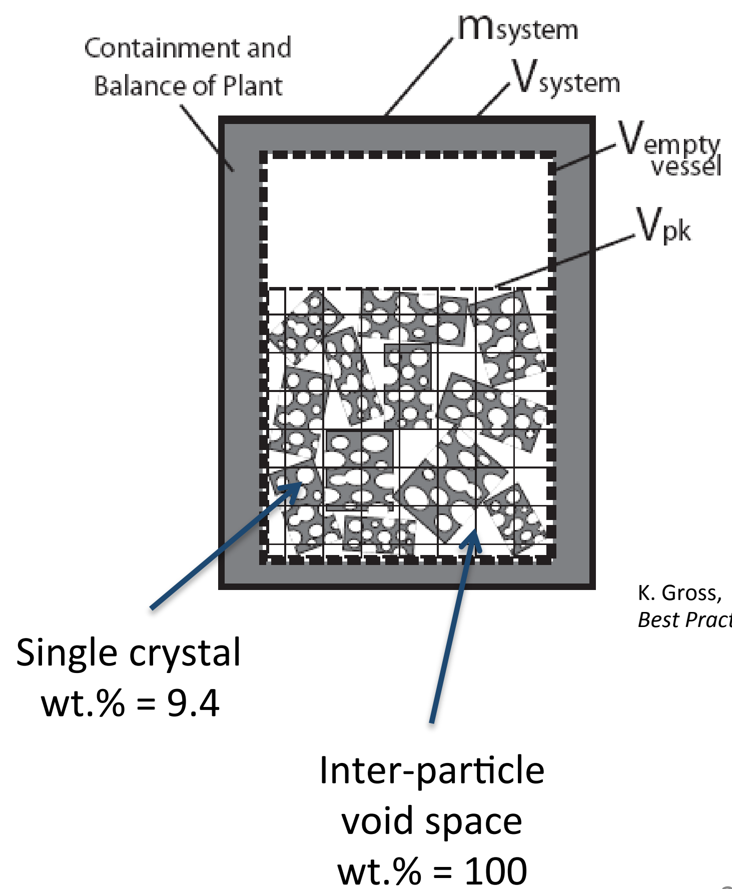
- Each curve represents an adsorbent having a combination of binding sites (n_{max}) and ΔH which would meet the DOE 2017 volumetric target
- Adsorbents having adsorption site heterogeneity ($E_{min} \neq E_{max}$) generally require more adsorption sites to meet target
- Large $E_{max} = E_{min}$ can meet target with smaller n_{max}

Gravimetric/Volumetric Tradeoff





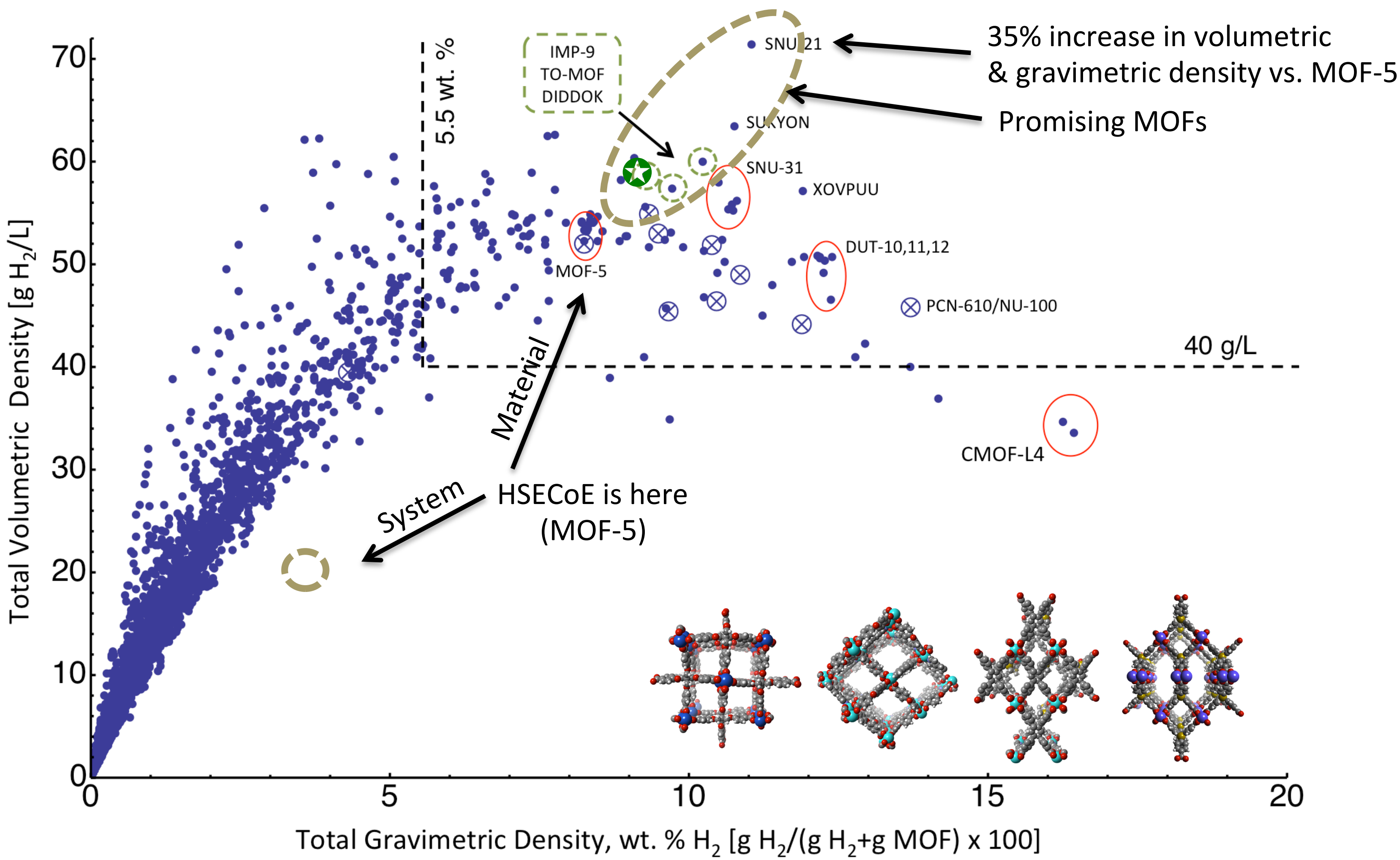
Compaction can be used to increase volumetric density; however, it will come at a loss to gravimetric density arising from closure of inter-particle voids



K. Gross, *Best Practices…*

Alternative Adsorbents?

MOF-5 is a good baseline, but higher-performing alternatives exist



Goldsmith, Wong-Foy, Cafarella, and Siegel, *Chem. Mater.*, **25**, 3373 (2013)

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Summary of Materials Requirements

…for a powder-based adsorbent, P_{max} = 100 bar

System	System-level Targets		Materials-level targets		Notes
	Usable Gravimetric (wt.%)	Usable Volumetric (g/L)	Usable Gravimetric (wt.%)	Usable Volumetric (g/L)	
DOE Ultimate	7.5	70	27.4	156	Cryo-system
			26.0	114	Ambient system
DOE 2017	5.5	40	20.1	89	Cryo-system
			19.1	65	Ambient system
700 Bar	4.5	25	16.6	55	Cryo-system
			15.7	40	Ambient system

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Concluding Remarks (1)

- The Adsorbent Acceptability Envelope has been developed to assess viability of hypothetical hydrogen adsorbents
  - Quantifies the amount of usable hydrogen stored
  - Formulated in terms of isotherm parameters and materials density
  - Applied to a powder-based, flow-through system designed by HSECoE
  - Cryogenic and ambient operating conditions explored
  - Extensions: Additional analysis of ambient-T and densified systems
- An advanced adsorbent may be able to surpass the performance of 700 bar compressed systems
  - Such a system could be attractive from an efficiency (low-P, 100 bar) and cost standpoint (metal tank) even though it would not meet DOE targets
- Achieving the DOE 2017 or Ultimate targets remains a daunting challenge

Concluding Remarks (2)

- Trade-off between volumetric and gravimetric density
  - Densification of powders can be helpful, but should be balanced with losses is gravimetric density and plastic deformation (pore collapse)
  - Achieving high surface area alone is insufficient
  - Materials research should focus on adsorbents that circumvent this tradeoff; high gravimetric and volumetric densities must be achieved *simultaneously*
- Adsorbent stability is important, but should be assessed based on likely/moderate failure modes:
  - E.g.: Withstand limited exposure to humid environments during assembly
- Low thermal conductivity of adsorbents can be overcome with engineering approaches

Acknowledgements

HSECoE Team

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Don Anton (SRNL)

Manuela Gaab (BASF)

Justin Purewal (formerly UM, now Ford)

Jesse Adams and Bob Bowman (DOE)

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