Best Practices for Characterizing Hydrogen Storage Properties of Materials

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May 20, 2009

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Co-Authors

DOE Hydrogen Program

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Overview

Timeline

- Start – Feb 2007
- End – Cont.
- 70% complete

Budget

- Total project funding
  - DOE $670K
  - Contractor $134K
- Funding FY08 $220K
- Funding FY09 $270K

Barriers

- Technical Targets: On-Board Hydrogen Storage Systems
- Barriers addressed
  - A. System Weight and Volume.
  - C. Efficiency.
  - D. Durability/Operability.
  - E. Charging/Discharging Rates.
  - J. Thermal Management.
  - Q. Reproducibility of Performance.

Partners

- NREL: Dr. Parilla, Contract Management
- University of California Berkeley
- California Institute of Technology
- Pacific Northwest Laboratories
- IEA Task 22, Dr. Kuriyama AIST, Japan
- Review by experts: IEA Task 22 & others

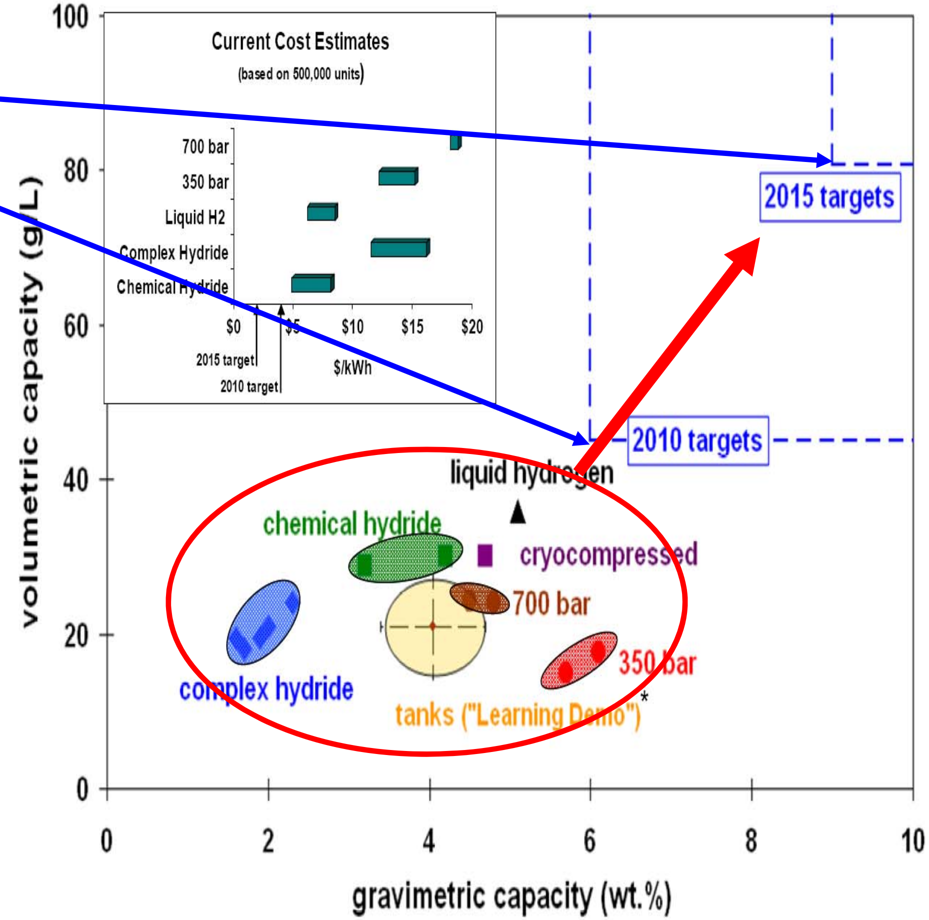
Relevance

- The EERE and Fossil Energy are working to develop innovative materials for reversible hydrogen storage including high surface area adsorbents, metal organic frameworks, and metal hydrides, as well as approaches that are regenerable off-board such as chemical hydrides and liquid carriers.
- There are many challenges in the accurate characterization of the hydrogen storage properties of new materials.
- There is a need for consistent measurement practices and improved communication of technical results.
- This project addresses this need through the creation of a reference document detailing best practices and limitations in measuring hydrogen storage properties of materials.
- The initial sections of this document have been made available for public use by pdf download from the DOE website.
- The project is on schedule for the remaining 3 sections.

Relevance to Program Targets

Table 3.3.2 Technical Targets: On-Board Hydrogen Storage Systems

Storage Parameter	Units	2007	2010	2015
System Gravimetric Capacity				
Usable, specific-energy from H_2	kWh/kg	1.5	2	3
(net useful energy / max system mass) [a]	(kg H_2/kg system)	(0.045)	(0.06)	(0.09)
System Volumetric Capacity				
Usable energy density from H_2	kWh/L	1.2	1.5	2.7
(net useful energy / max system volume)	(kg H_2/L system)	(0.036)	(0.045)	(0.081)
Storage System Cost [b] Fuel cost [c]	\$/kWh net (\$/kg H_2) \$/gge at pump	6 (200) ---	4 (133) 2-3	2 (67) 2-3
Durability / Operability				
Operating ambient temperature [d]	°C	-20/50 (sun)	-30/50 (sun)	-40/60 (sun)
Min/max delivery temperature	°C	-30/85	-40/85	-40/85
Cycle life (1/4 tank to full) [e]	Cycles	500	1000	1500
Cycle life variation [f]	% of mean (min) at % confidence	N/A	90/90	99/90
Min delivery pressure from tank; FC = fuel cell, ICE = internal combustion engine	Atm (abs)	8FC / 10 ICE	4FC / 35 ICE	3FC / 35 ICE
Max delivery pressure from tank [g]	Atm (abs)	100	100	100
Charging / Discharging Rates				
System fill time (for 5 kg)	min	10	3	2.5
Minimum full flow rate	(g/s)/kW	0.02	0.02	0.02
Start time to full flow (20 °C) [h]	s	15	5	5
Start time to full flow (- 20 °C) [h]	s	30	15	15
Transient response 10%-90% and 90% - 0% [i]	s	1.75	0.75	0.75
Fuel Purity (H_2 from storage) [j]	% H_2	99.99 (dry basis) See Appendix C		
Environmental Health & Safety				
Permeation and leakage [k]	Scc/h	Meets or exceeds applicable standards		
Toxicity	-			
Safety	-			
Loss of useable H_2 [L]	(g/h)/kg H_2 stored	1	0.1	0.05



Accurate measurement methods and metrics are required to determine how new materials compare to all of these targets.

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Objectives

What ?

- ***To prepare a reference document detailing best practices and limitations in measuring hydrogen storage properties of materials***
- Document reviewed by experts in the field (IEA, IPHE, Industry)
- Document to be made available to researchers at all levels in the DOE hydrogen storage program

Why ?

- To reduce errors in measurements
- Improve reporting and publication of results
- To improve efficiency in measurements
- Reduce the expenditure of efforts based on incorrect results
- Reduce the need for extensive validation
- To increase the number of US experts in this field (students, etc.)

Benefit to DOE and Researchers

- The transfer the knowledge and experience in making critical performance measurements from experts in this field to the entire DOE hydrogen storage research community.

- Provide a published resource to aid those just entering to this rapidly expanding field.

- Aid in the establishment of uniform measurement practices and presentation of performance data.

- Improve international communications on these issues between government, university, small and large business entities.

Milestones - 2008/2009

Milestone	Results	%Comp
Finalize Kinetics section	Kinetics section reviewed by many experts all contribution integrated into final version.	100%
Prepare draft of the Introduction	Preface and Introduction section draft completed. Sections reviewed and finalized.	100%
Document integration	At the request of the DOE, first three sections were integrated into one document for final review and published on the DOE hydrogen web site.	100%
Prepare draft Capacity Section	Draft completed with contributions from UC Berkeley, Caltech and PNNL	100%
Finalize Capacity section	Final revisions of the capacity section are underway and is in the process of review.	25%
Begin Thermo and Cycle-Life Section	Materials and content being researched, drafts in outline format.	15%

- **Go/No-Go FY09:** If the deliverable has not been completed or is determined to provide no value to the program the project will be terminated (9/09).

Approach - Overview

- **Task 1: General Introduction** * **(Added at request of DOE)**
  - General introduction to hydrogen storage materials R&D.
  - Overview of measurement techniques and best choice related to purpose of study.
  - Overview of common errors and accuracy of these techniques.
- **Task 2: Kinetics**
  - Emphasis on measurement conditions and material properties that strongly influence the results of kinetic measurements
  - Benefits and limitations of applying mechanistic analysis to kinetics data.
- **Task 3: Capacity**
  - Hydrogen capacity has been the key metric for the success and failure of materials to be considered for practical hydrogen storage.
  - The objective of this task is to clarify issues that can impact these measurements.
- **Task 4: Thermodynamic Stability**
  - Review methods for precisely determining equilibrium thermodynamics.
  - Define protocols to separate true equilibrium conditions from kinetic effects.
  - Present new measurement techniques for the rapid thermodynamic analysis.
- **Task 5: Cycle-life Properties**
  - Cycle-life measurements are critical for evaluating the performance of hydrogen storage materials for applications where hundreds of cycles will be required.
  - Define how such tests should be performed, what parameters may impact the results, and what properties are e.g., capacity fade, or degradation in kinetics, are most critical in performance evaluation.

Key Accomplishments

- ***Task 1: Final Introduction section 100% complete.***
- ***Task 2: Final Kinetics section 100% complete.***
- ***Task 3: Capacity section in progress 60% complete.***
  - Compiled examples from the literature and performing example measurements to illustrate key issues associated with Hydrogen Storage Capacity measurements.
- ***Participation as project in IEA Task 22.***
- ***Contributions and editorial reviews by many world experts.***
- ***Reviewed Tasks1&2 Document Delivered to DOE Dec. 2008.***
- ***Posted to DOE website for world-wide access.***

Please download the current Best Practices document from:

http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/bestpractices_h2_storage_materials.pdf

Collaborations

- Contributions to this project from world experts including written materials, examples, presentation or editorial review of draft documents from:
  - Dr. Philip Parilla, National Renewable Energy Laboratory, Golden CO, USA.
  - Dr. Gary Sandrock of the U.S. Department of Energy.
  - Dr. George Thomas of the U.S. Department of Energy.
  - Professor Sam Mao University of California Berkeley.
  - Dr. Michael Miller of Southwest Research Institute®, San Antonio TX.
  - Dr. Anne Dailly, Dr. Eric Poirier, and Dr. Frederick Pinkerton of General Motors GM R&D Center.
  - Professor Channing Ahn, California Institute of Technology, USA, IEA Task 22.
  - Professor Richard Chahine, Université du Québec à Trois-Rivières, Canada, IEA Task 22.
  - Professor Evan Gray, Griffith University, Brisbane, Australia , IEA Task 22.
  - Dr. Ole Martin Løvvik of the Institute for Energy Technology in Kjeller Norway.
  - Dr. Nobuhiro Kuriyama and Dr. Tetsu Kiyobayashi , AIST, Japan, IEA Task 22.

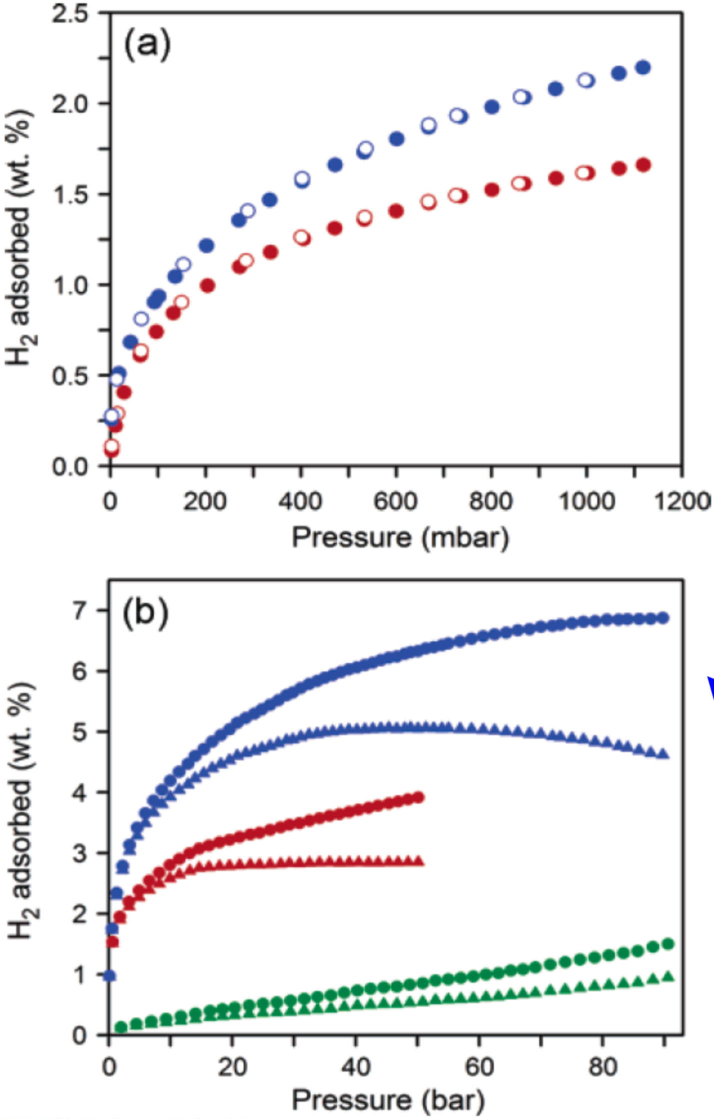
Response to 2008 Reviewers Comments

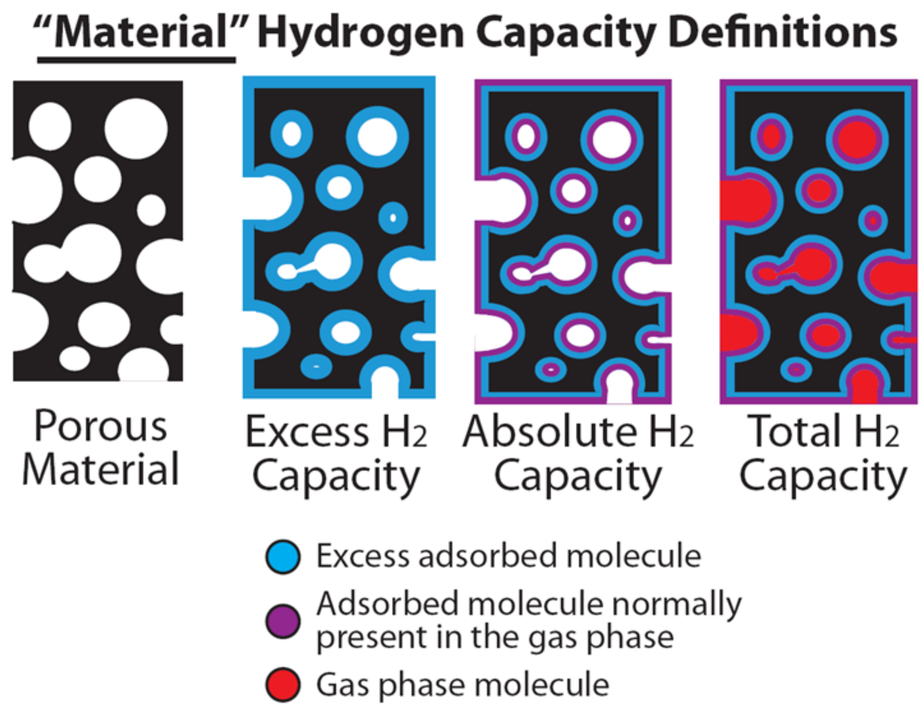
- ***Relevance:*** “The project is important to the overall subprogram and clearly of vale for its advancement”. Our objective is to focus on key issues that are most relevant to the program.
- ***Approach:*** ”Quite useful is the latest restructuring of the project”, The document restructuring has been completed. ”Care should be taken to ensure broad applicability rather than too much focus on one technical field (e.g. metal hydrides)”. We have added authors with a expertise to address the other two critical areas of hydrogen storage materials development: physisorption and off-board regenerable chemical hydrides.
- ***Accomplishments:*** “It is definitely useful to have this data in one source rather than having to interpret information that otherwise needs to be gleaned from textbooks or papers”. It is our intent that this one document will serve as a complete resource for researchers at all levels. At the same time, we have added a list of recommended reading for each topic (textbooks) and have referenced over 100 papers.
- ***Collaborations:*** ”The PI has obtained guidance from a broad group of knowledgeable scientists in the field”. IEA HIA task 22 is providing a great venue to present information and to establish the participation of experts in this project. We have also setup an open web-based system to receive input from the entire international community.
- ***Future Work:*** “There may be some value in addressing measurement instrument stability...”. This issue is being addressed at this time. Issues concerning “...comparing excess densities between, physisorption materials and metal hydrides…” at a systems level. The current work is addressing the issues of capacity definitions and metrics on both a materials and systems level, with important distinctions being made between physisorption, reversible, and off-board regenerable chemisorption materials as well as those materials that overlap categories.

Section 3: Capacity

Examples: Task 3 Capacity

Capacity Definitions: Adsorption Materials





H2 adsorption isotherms (a) below 1.2 bar and (b) up to 90 bar MOF's 1′ (red) and 1m′ (blue) at 77 K, and 1m′ at 298 K (green).
Triangles = Material Excess Capacity
Circles = Total Material Capacity

M. Dinca *et al.* "Hydrogen Storage in a Microporous Metal-Organic Framework with Exposed Mn2+ Coordination Sites", J. Am. Chem. Soc. 2006 *128*, 16876-16883

Capacity Definitions: Adsorption Materials

Maximum Material Excess H_2 Capacity

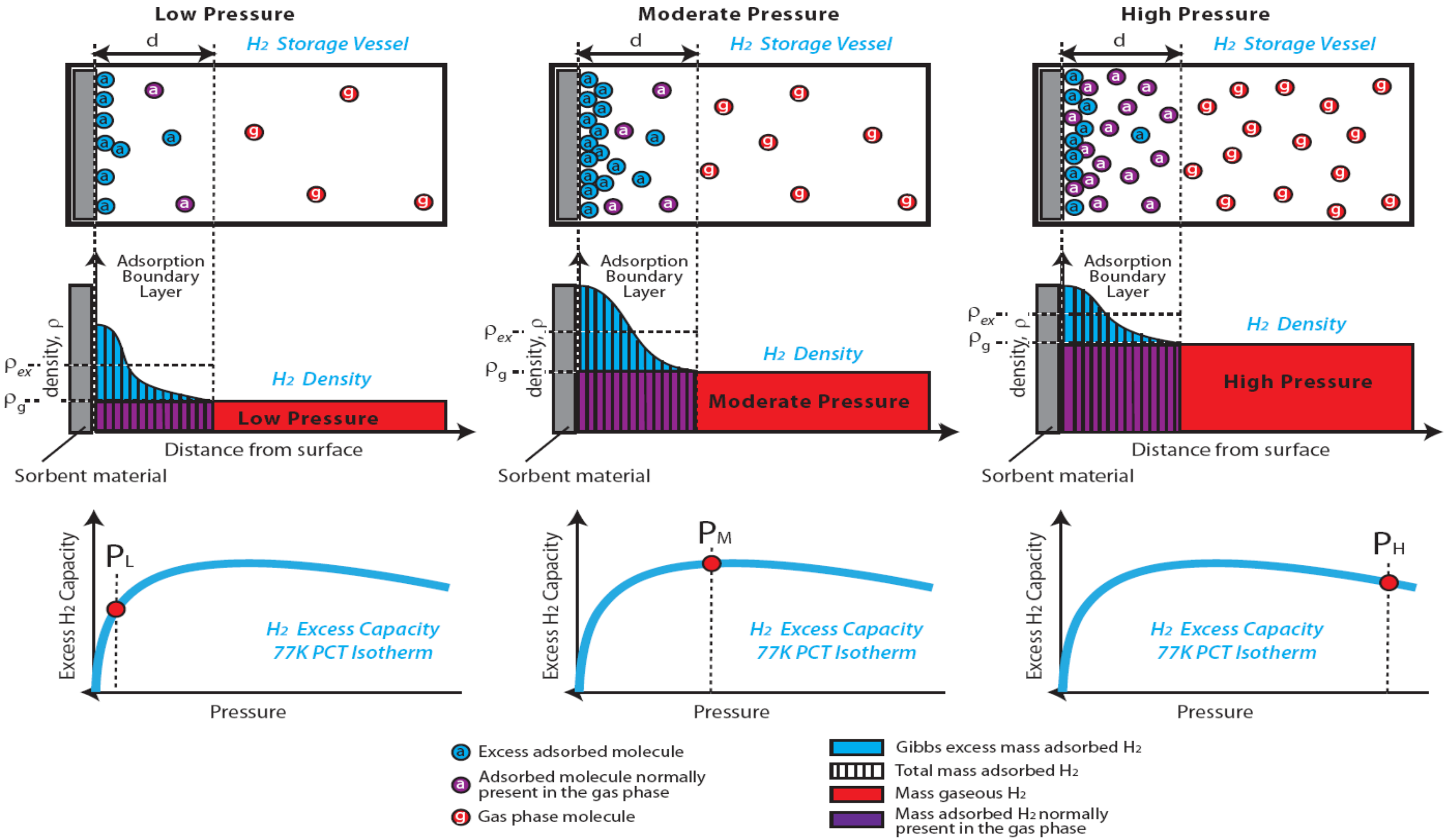


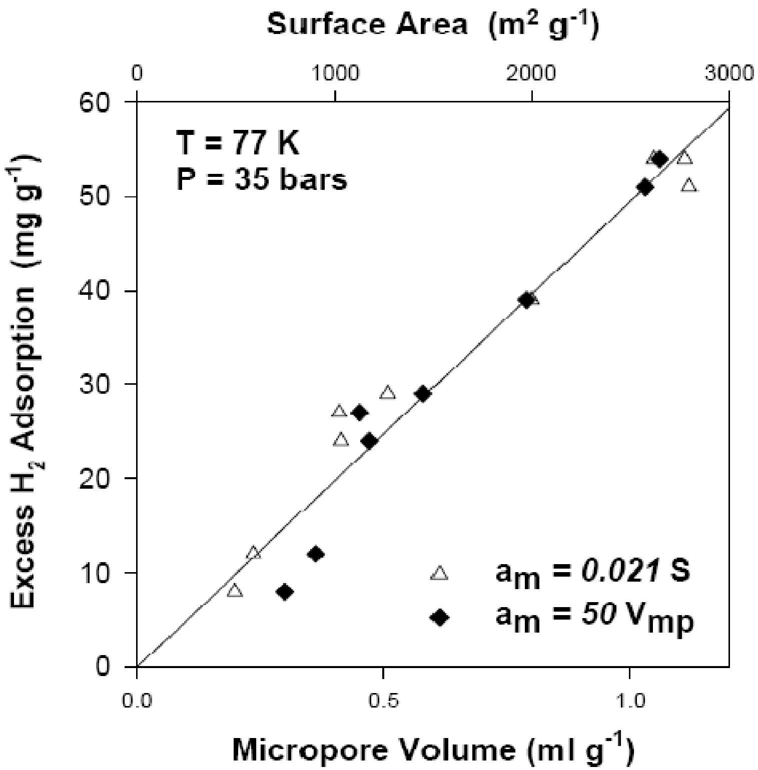
Illustration of the shape of excess capacity curve and the point of maximum excess capacity for physisorption material at 77K.

Example Measurements: Adsorption Materials

Physisorption materials development:

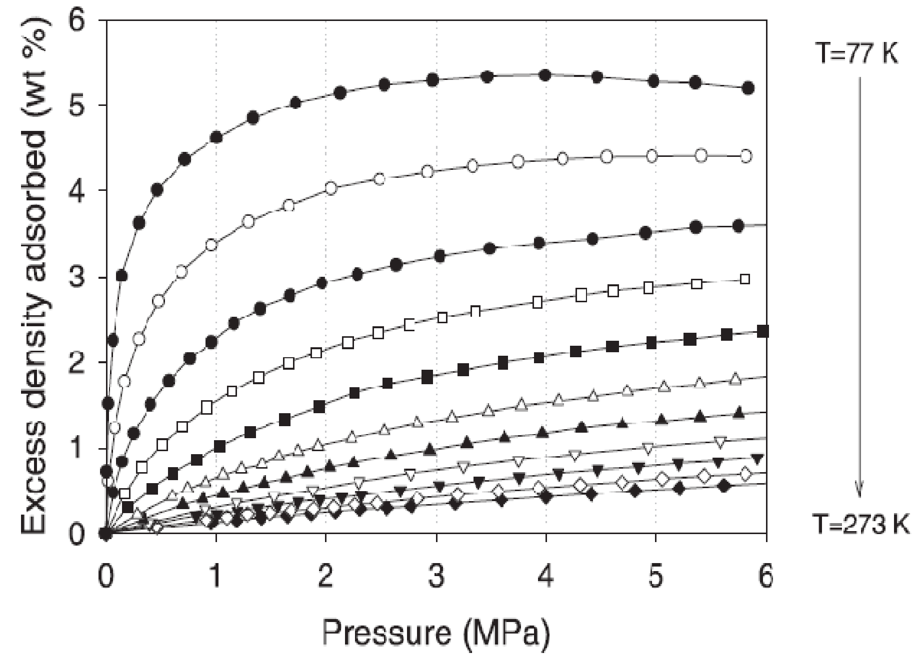
1) Increasing the specific surface area.

2) Increasing the adsorption enthalpy.



Data demonstrating the "Chahine Rule" excess H_2 adsorption capacity is proportional to micropore volume.

Chahine, R., Bose, T.K. Hydrogen Energy Progress XI,, 1996, Vol.2, 1259-1263



H_2 adsorption excess capacity measurements on superactivated carbon AX-21TM as a function of temperature.

E. Poirier et al. Applied Physics A 2004 78, 961-967.

Capacity Definitions: Adsorption System

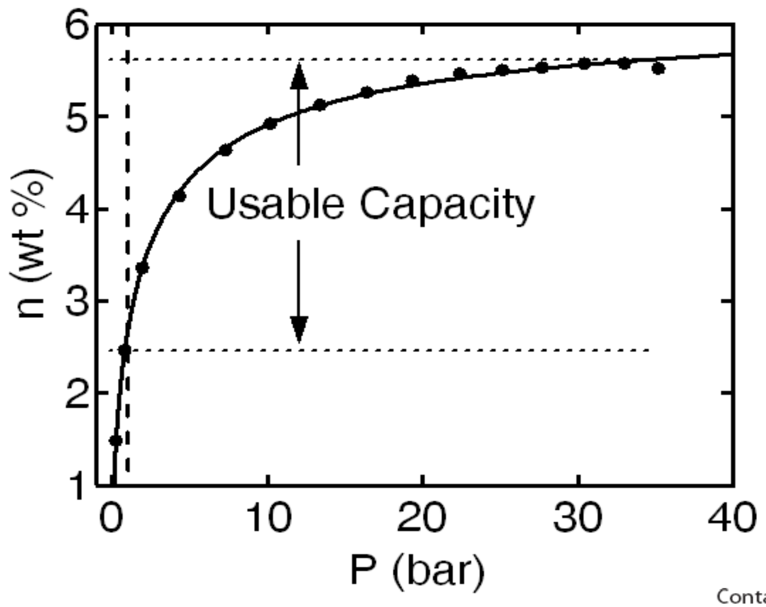


Illustration of the "usable capacity" above 1 bar pressure.

To utilize full stored hydrogen capacity requires increasing temperature of cryo-storage materials (with energy storage penalty of re-cooling on each fill).

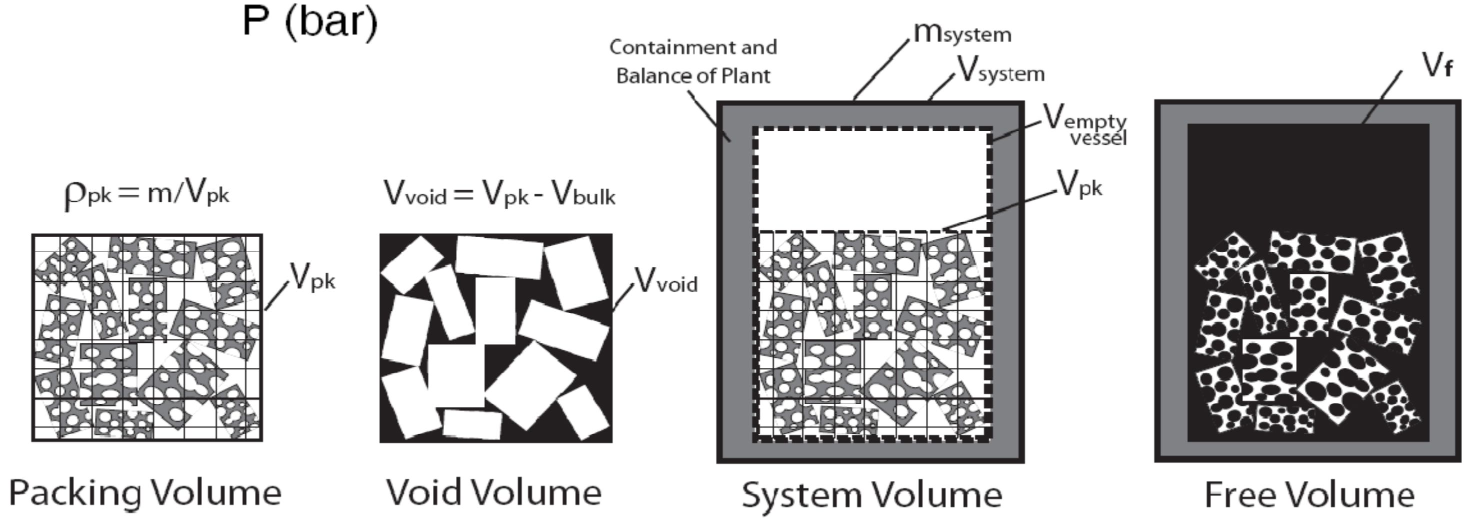
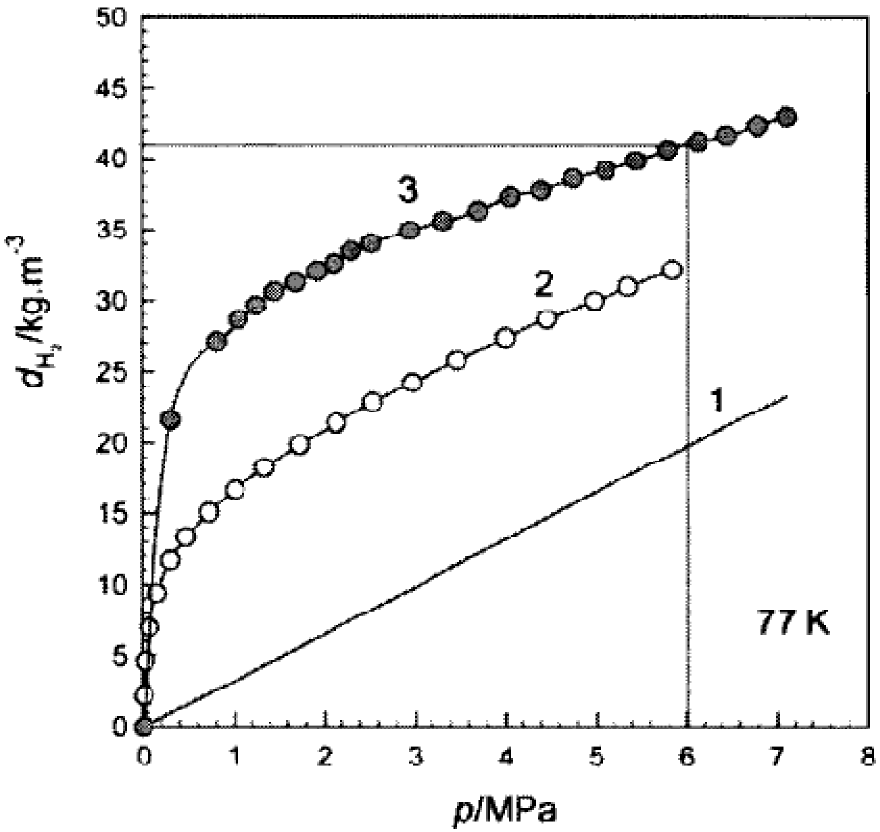


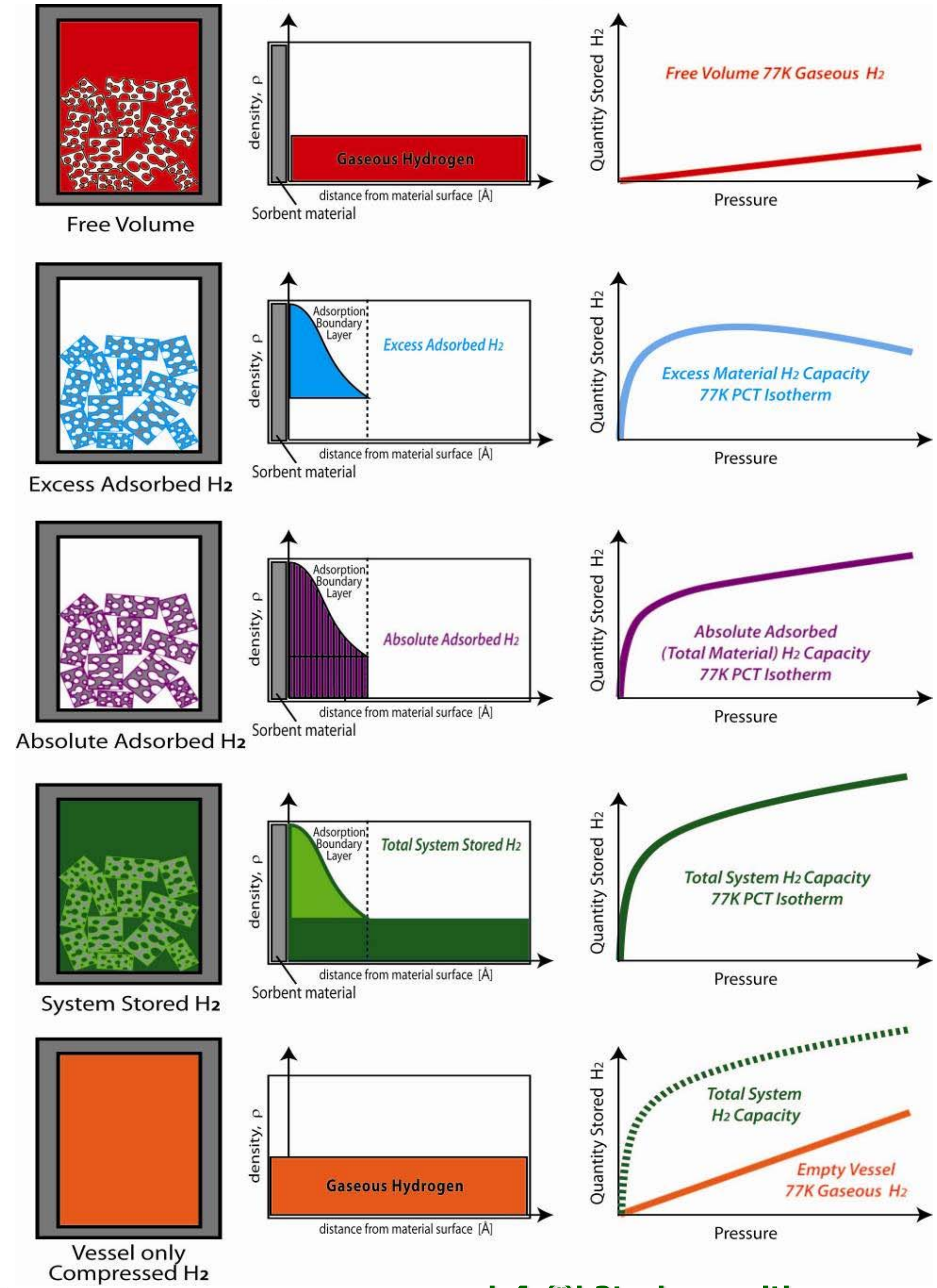
Illustration of volume and density definitions relevant to hydrogen storage capacities at a system level.

Capacity Definitions: Adsorption System



Volumetric Total System H_2 Capacity of (1) an empty sample cell, (2) cell filled with superactivated carbon powder, and (3) a sample cell filled with superactivated carbon granules.

L. Zhou. Renewable and Sustainable Energy Reviews 2005 9, 395-408.



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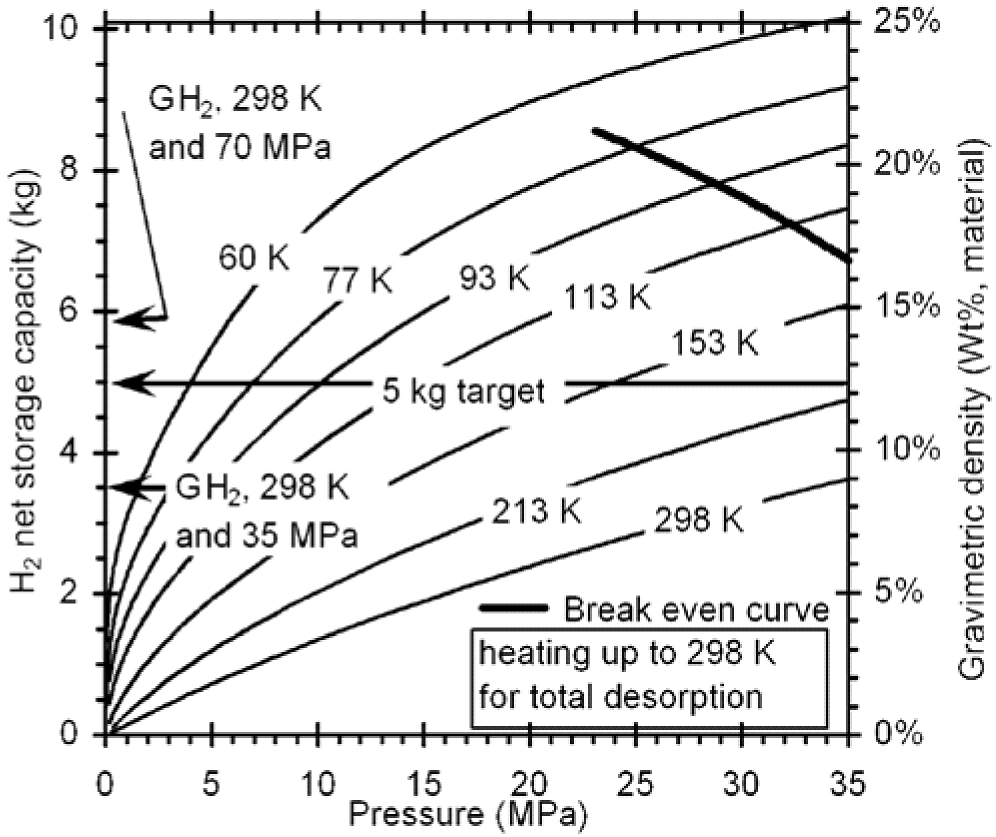
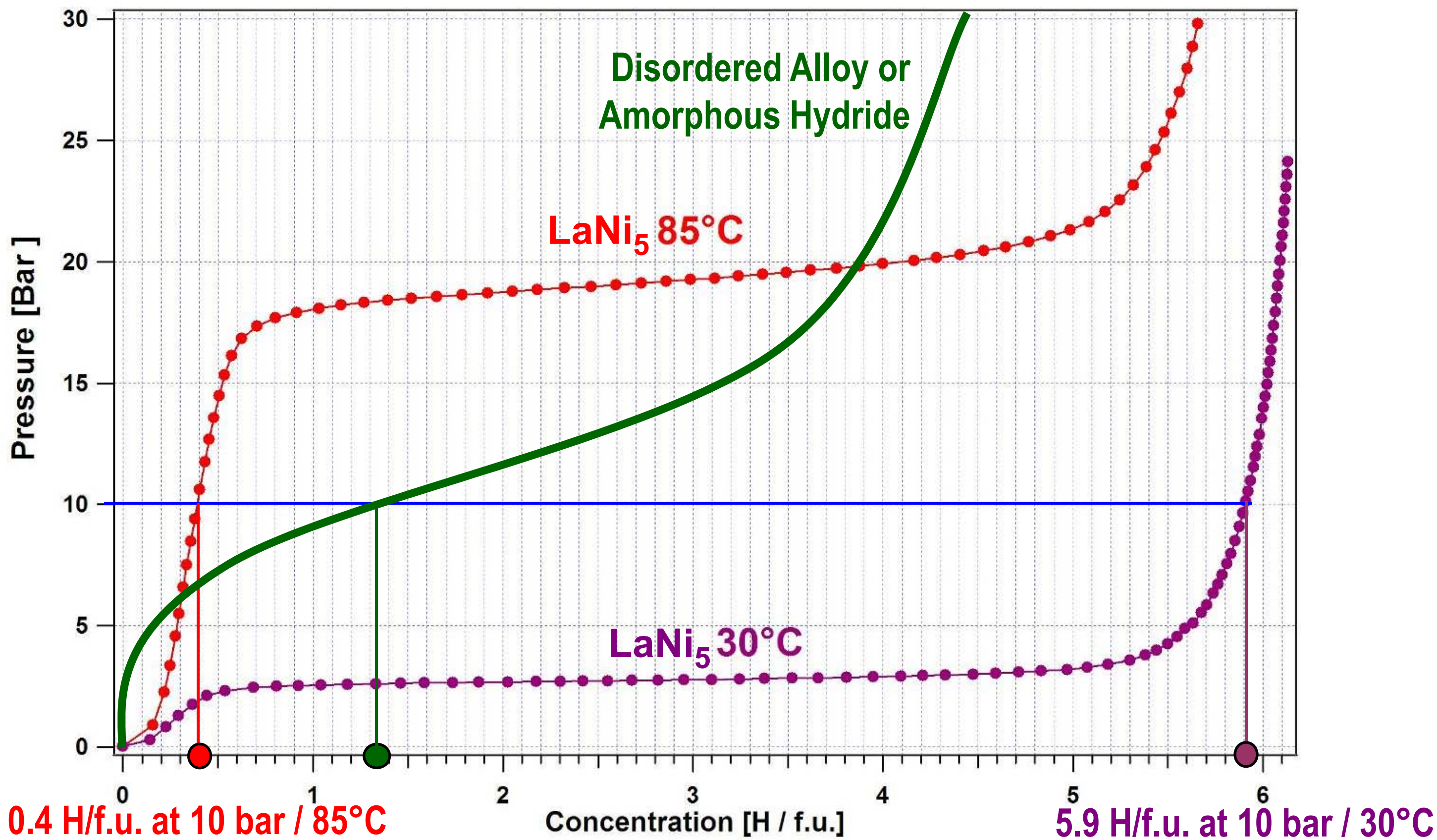
Example: Adsorption System



Calculated Net H_2 storage capacity of a 150 L tank filled with Maxsorb MSC-30™ activated carbon (heating to 298 K for discharge, outlet pressure 0.25 MPa). The "break even curve" compares cryogenic compressed gas that gives the same storage capacity. Room temperature compressed gas at 35 and 70 MPa also noted.

M.-A. Richard, D. Cossement, P.A. Chandonia, R. Chahine, D. Mori, and K. Hirose, "Preliminary evaluation of the performance of an adsorption-based hydrogen storage system", accepted 2008, AIChE Journal.

Capacity Definitions: Reversible Hydride Materials



- **Example: Equilibrium PCT measurements of $LaNi_5$ → Flat Plateau.**
- **Capacity is dependent on Temperature and Pressure.**
- **"Usable Capacity" effected by, Thermodynamics, Kinetics and homogeneity of hydrogen bonding sites.**

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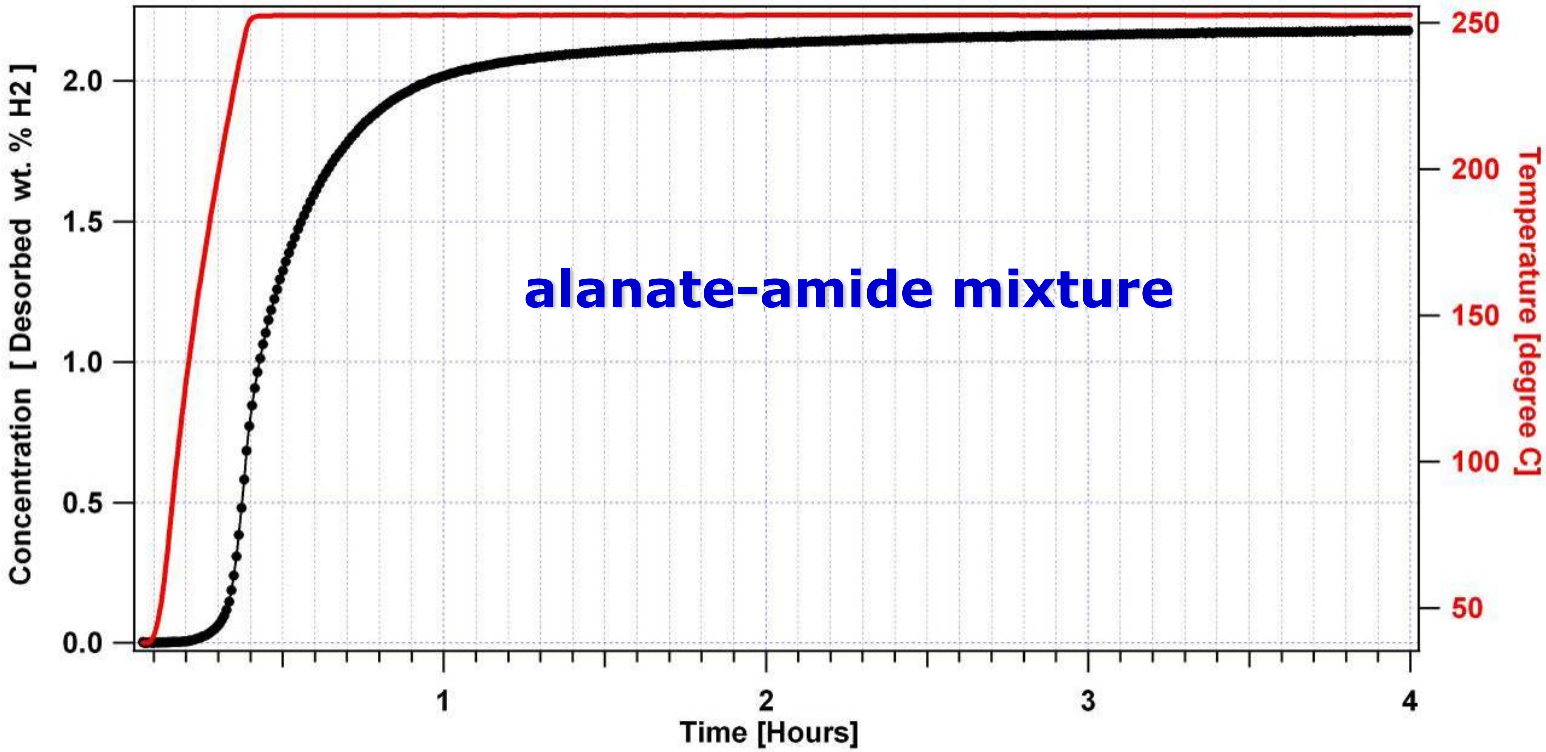
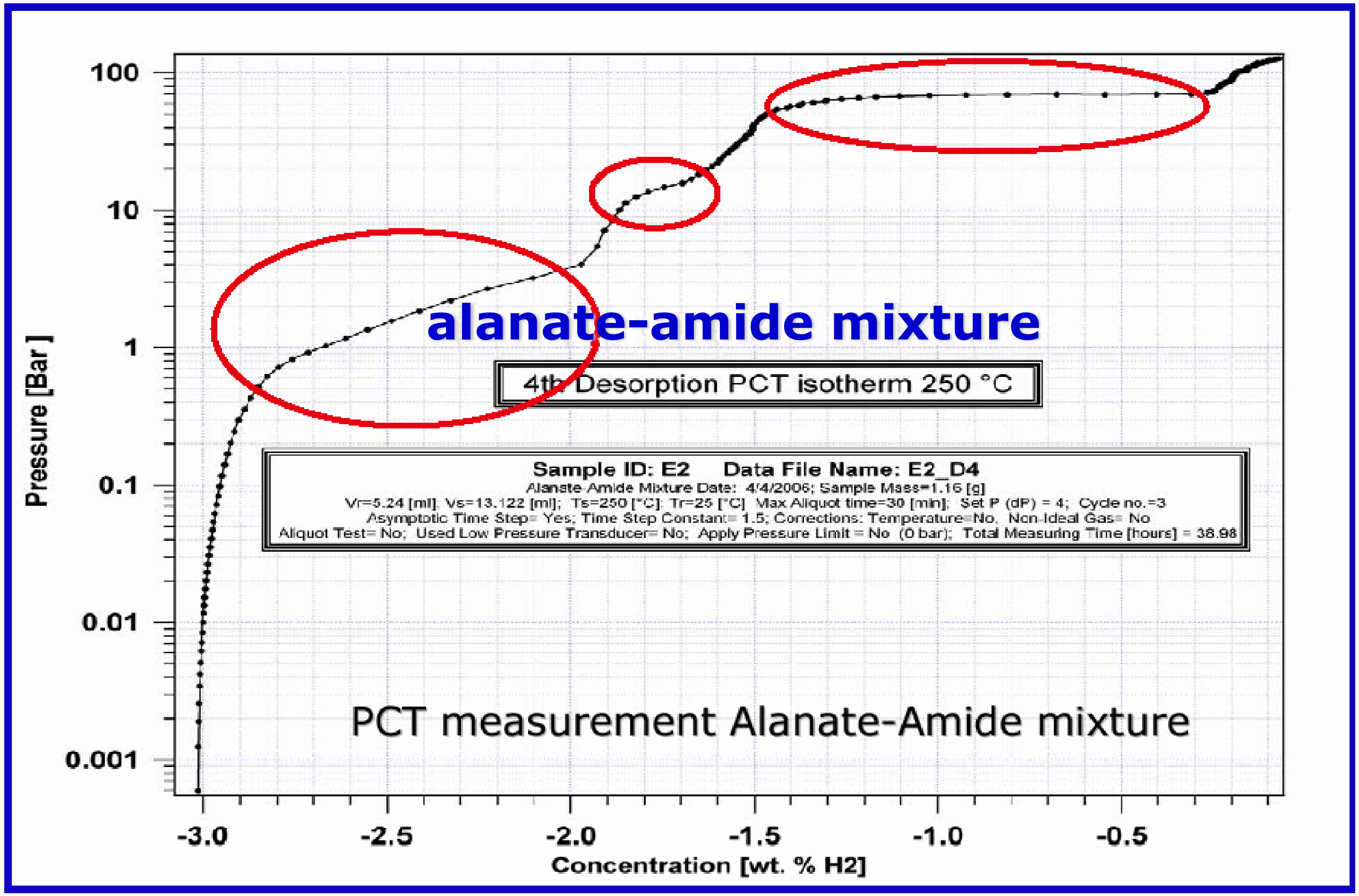
Example: TPD Measurements Reversible Chemisorption Materials



- TPD measurement: 2.2 wt.% desorbed up to 250°C.
- Is this one or multiple reactions ?
- Is Hydrogen only released, or is some of the capacity Ammonia ?

Gross, K.J. MRS Spring 2006 Hydrogen Tutorial

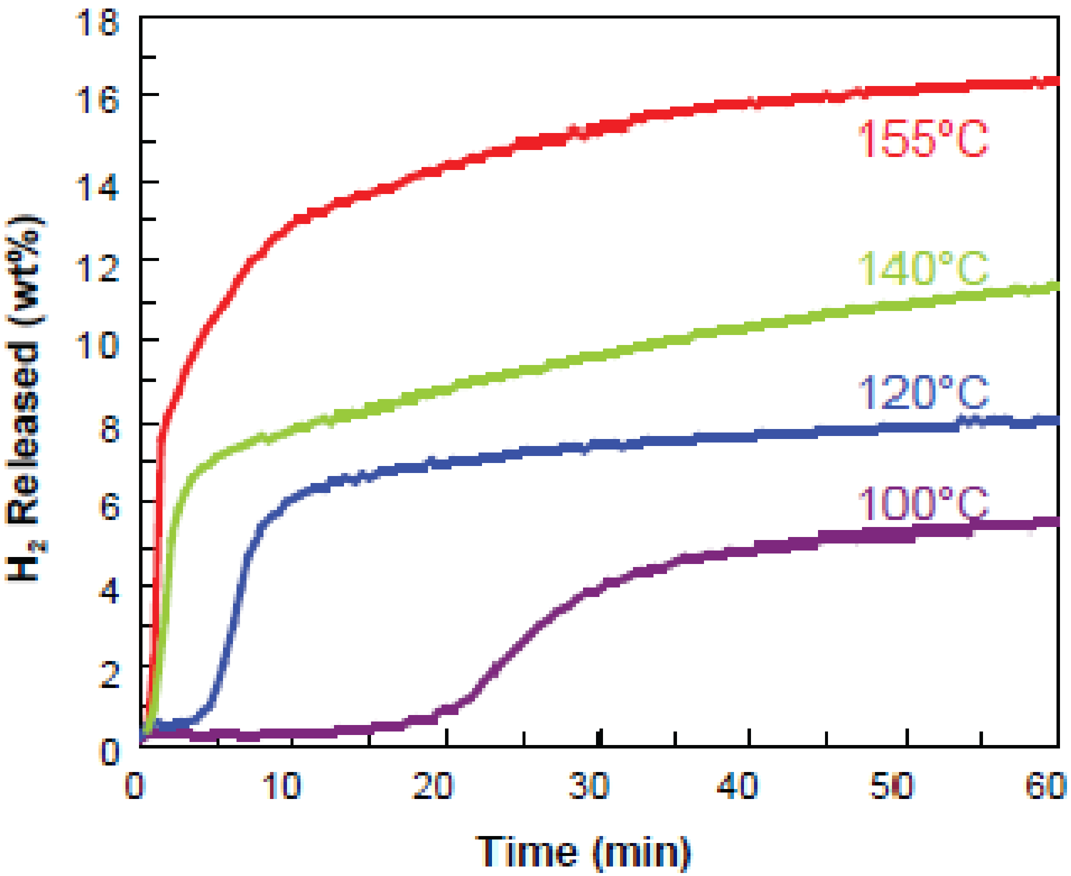
Example: PCT Measurements Reversible Chemisorption Materials



- **Three separate reactions: Sample total capacity 3 wt.%.**
- **However, the capacity of any one reaction may be higher .**

Gross, K.J. MRS Spring 2006 Hydrogen Tutorial

Off-board Regenerable Chemical Hydrides Capacity and Kinetics of Ammonia Borane



- Change in induction period as a function of temperature
- Initial rates and peak rates significantly altered
- Measured rates and capacities are a function of Temperature
- Different process pathways occur at different temperatures
- Steps in dehydrogenation of AB

$nNH_3BH_3 \rightarrow (NH_2BH_2)_n + (n\text{-}1)H_2$ (<120 °C) (Intramolecular)

$(NH_2BH_2)_n \rightarrow (NHBH)_n + H_2$ (> 150 °C) (Intermolecular)

$2(NHBH)_n \rightarrow (NHB\text{—}NBH)_n + H_2$ (< 150 °C) (Cross linkin

$(NHBH)_n \rightarrow BN + H_2$ (> 500 °C) (boron nitride)

- Impact of higher temperature on release of ammonia borane.
- Greater than 16% wt% H2 can be achieved at 155°C.
- However, Hydrogen release is exothermic, Therefore:
- Heat management required to prevent runaway reactions at system level

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http://www.hydrogen.energy.gov/annual_progress07_storage.html#b

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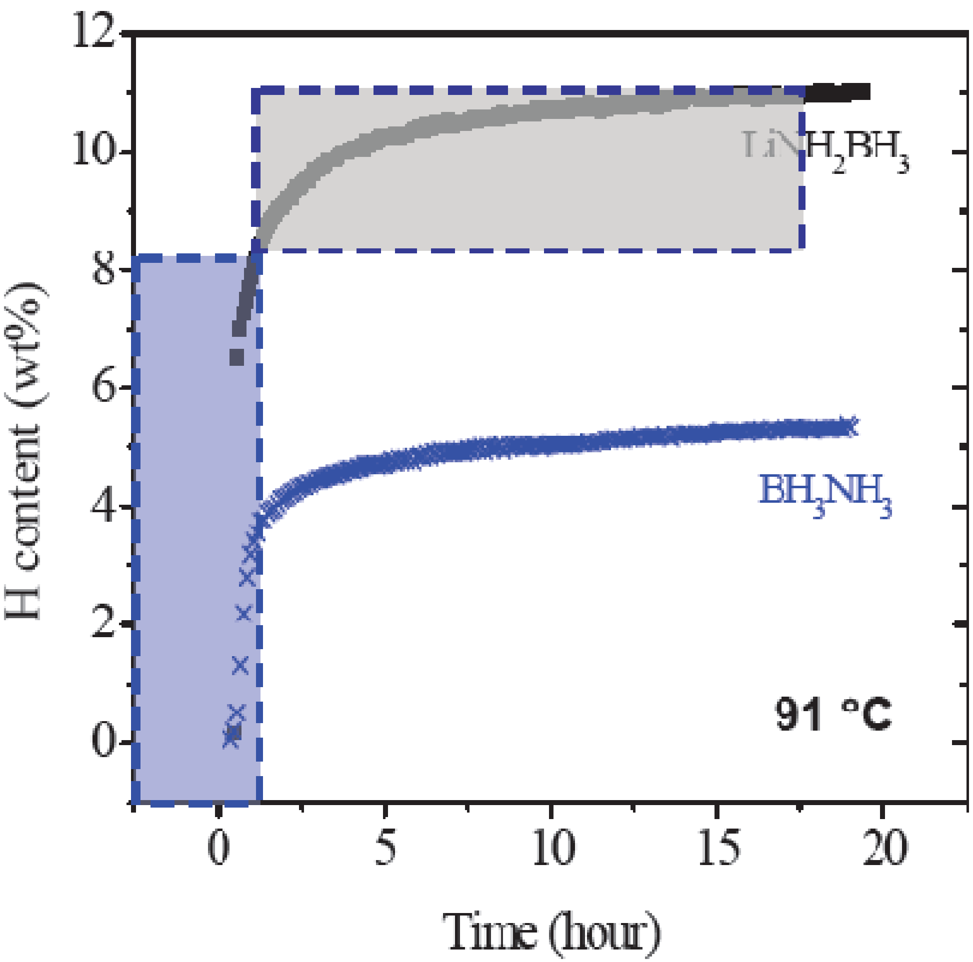
Example Measurements: Regenerable Chemical Hydrides
Chemical modification to enhance kinetics of H2 release

$LiNH_2BH_3 \rightarrow [LiNBH] + 2\ H_2$ = 10.9 wt% ~ 90C°



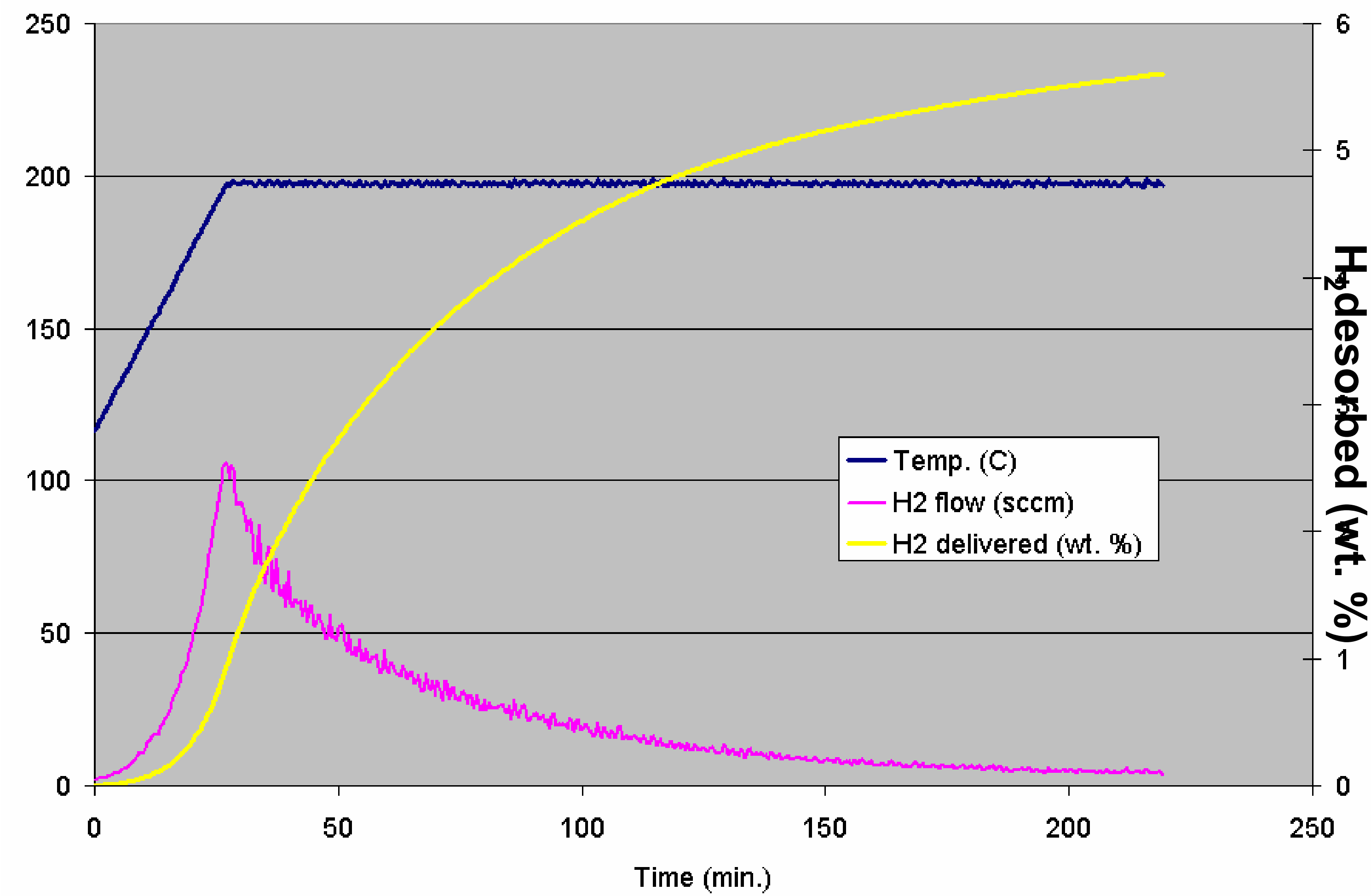
Impact of Kinetics on Capacity

- Initial kinetics are fast
- Capacity ~ 8 wt% in 1st hour
- Final Capacity > 10 wt% by 17 hrs.
- Material Capacity > Usable Capacity
- Thus improvements in kinetics have a great impact on usable capacity.

Nature Mater 7 (2008) 138

Example Measurements: Regenerable Chemical Hydrides

Flow Measurement of Hydrogen Generation from N-ethylcarbazole achieved by thermal methods



- **Capacity vs. time determined from integration of flow data.**

www.hydrogen.energy.gov/pdfs/review06/st_9_cooper.pdf

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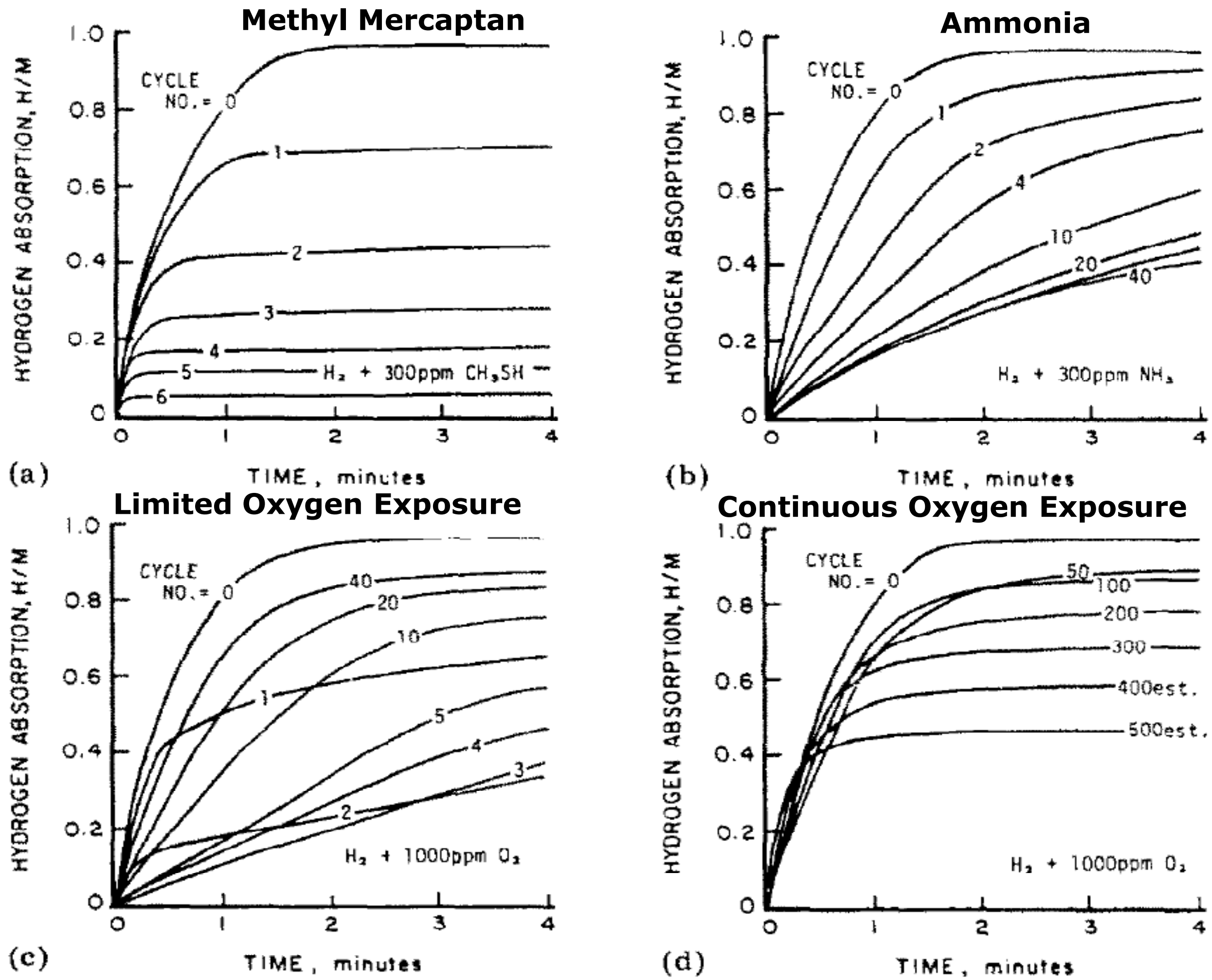
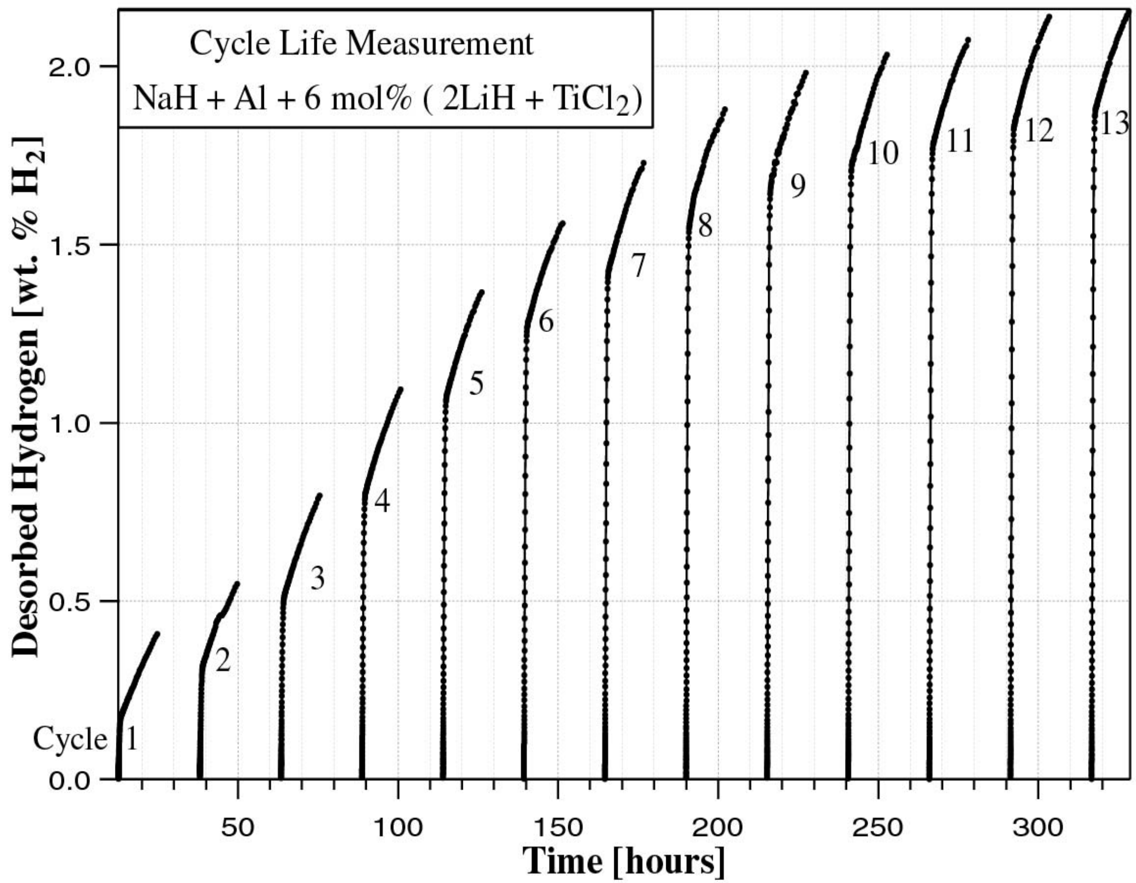
Example: Materials Handling Effect on Capacity



- Effects of different gaseous impurities on Capacity and Kinetics of $LaNi_5$ during cycling: (a) poisoning; (b) retardation; (c) retardation-recovery; (d) reaction.
- Recommendations: Ar Glove box (<1ppm O_2 and H_20), UHP (99.999%) H_2 / He.

Sandrock, G.D., Goodell, P.D. , Journal of the Less-Common Metals, 104 (1984) 159-173.

Important: Activation Effects and Capacity

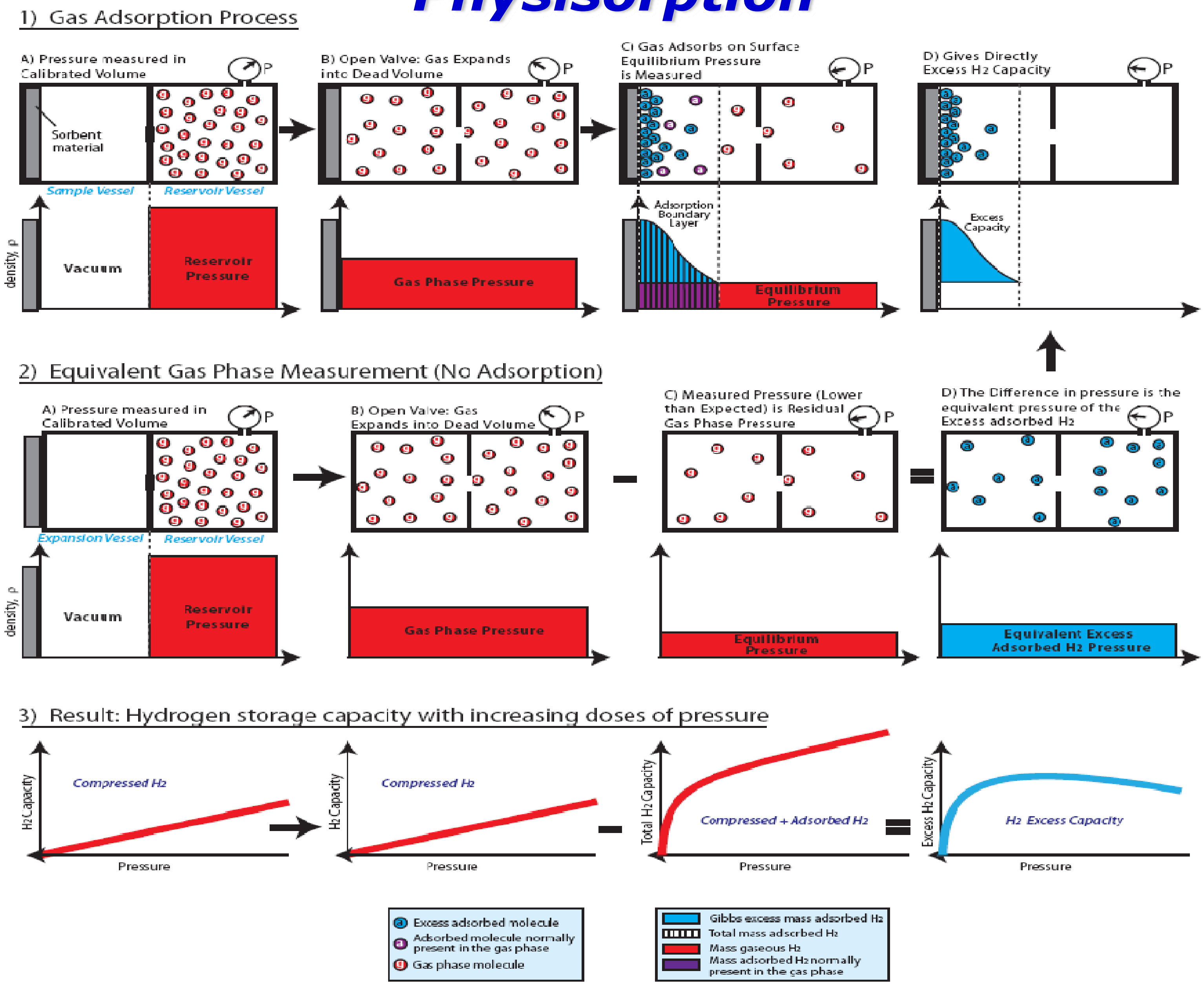


Alanate: with pre-reacted additive

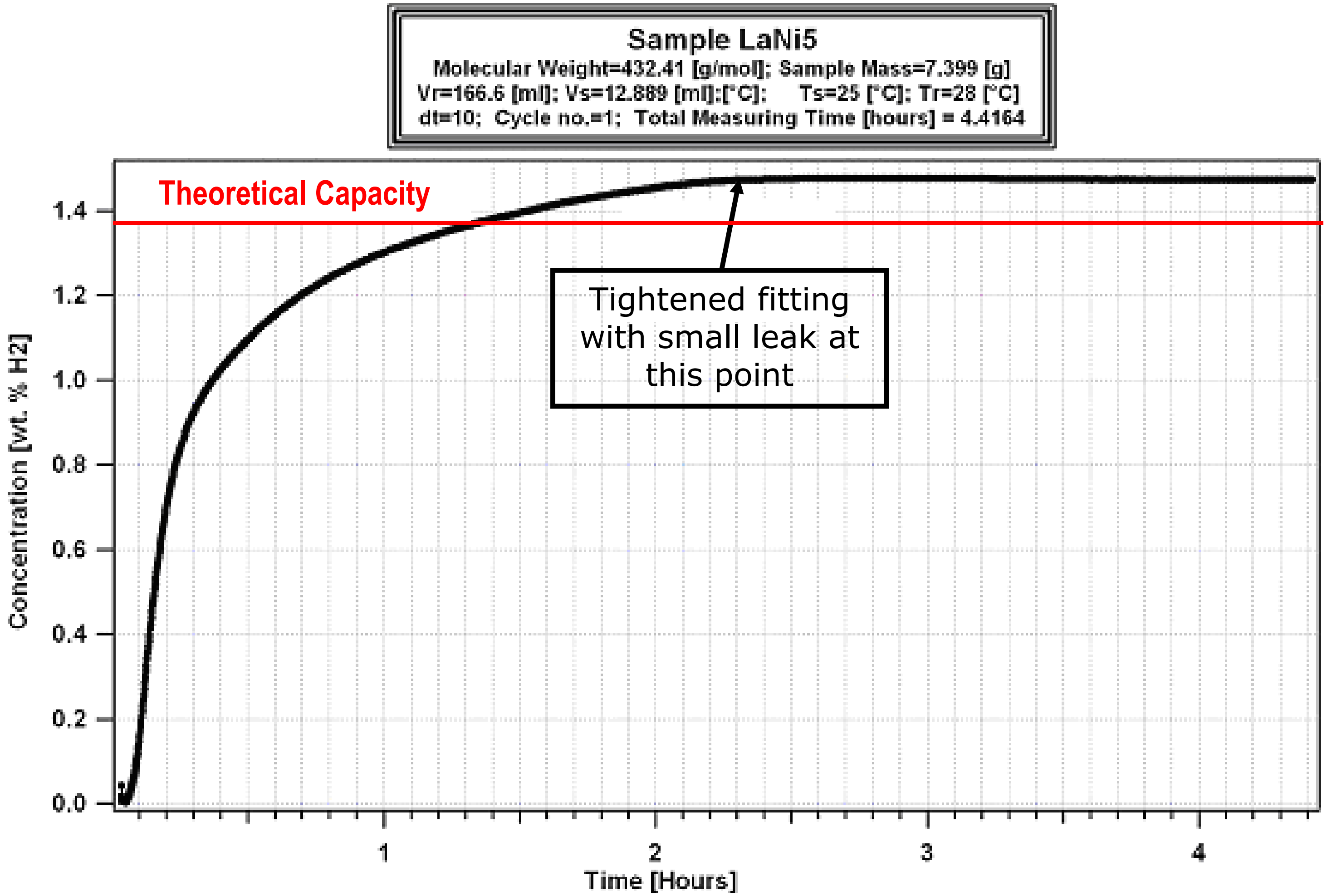
- **Several cycles may be required to achieve representative capacity**
- **New materials should not be disregarded on only one or two cycles**

K.J., Gross, E.H., Majzoub, S.W. Spangler, J. Alloys and Compounds, 356-357 (2003) 423.

Measurements: Volumetric PCT Method Physisorption

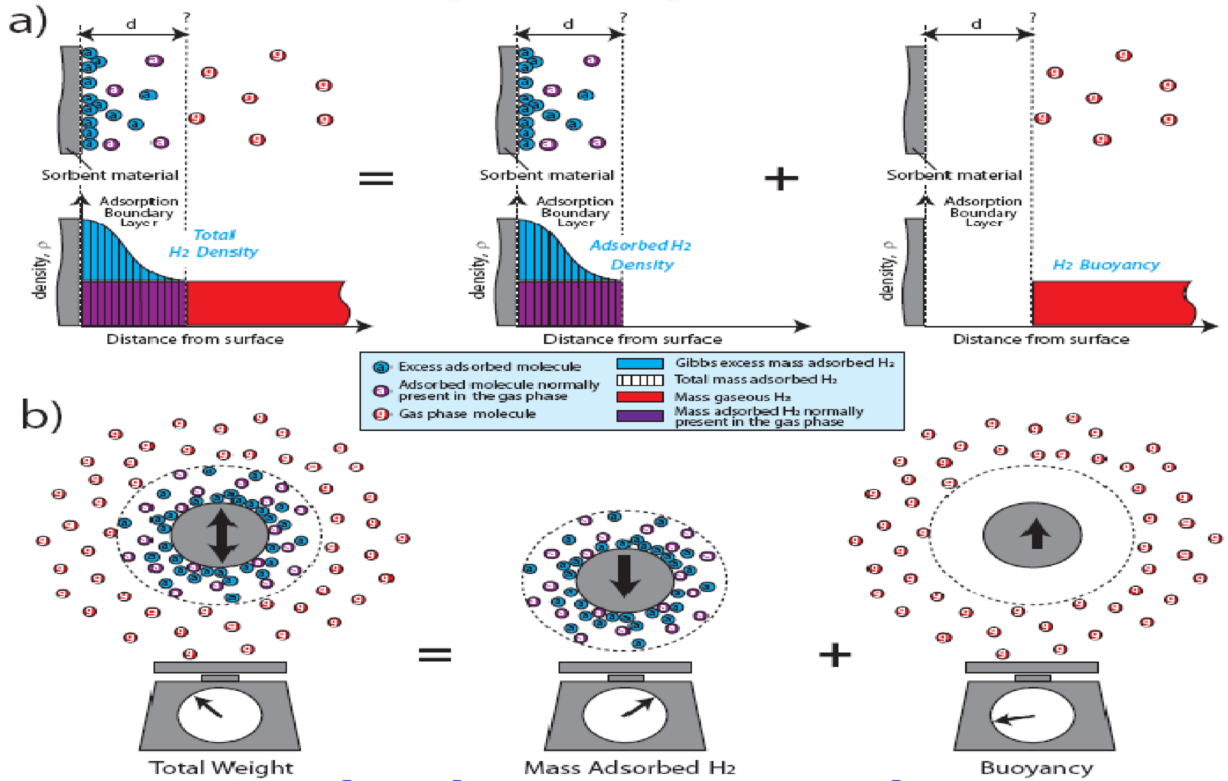


Volumetric Measurement Considerations

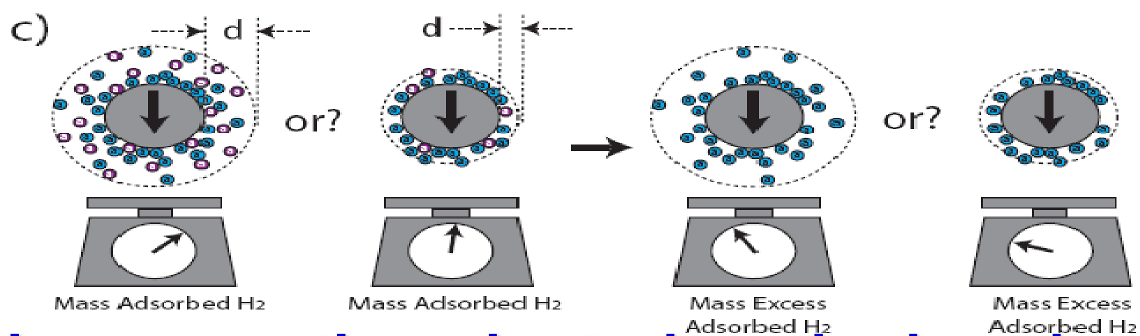


- **Must ensure absolutely leak-free system.**

Measurements: Gravimetric PCT Method Physisorption



Requires buoyancy corrections.



Requires assumptions about adsorption boundary layer.

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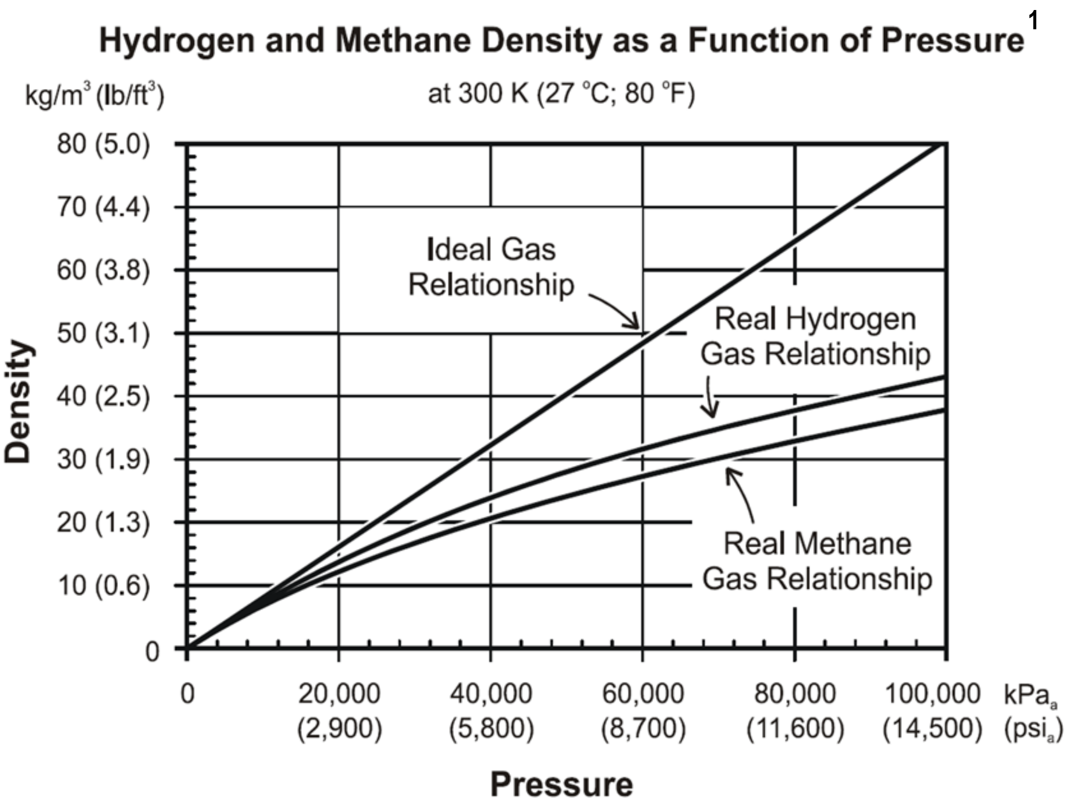
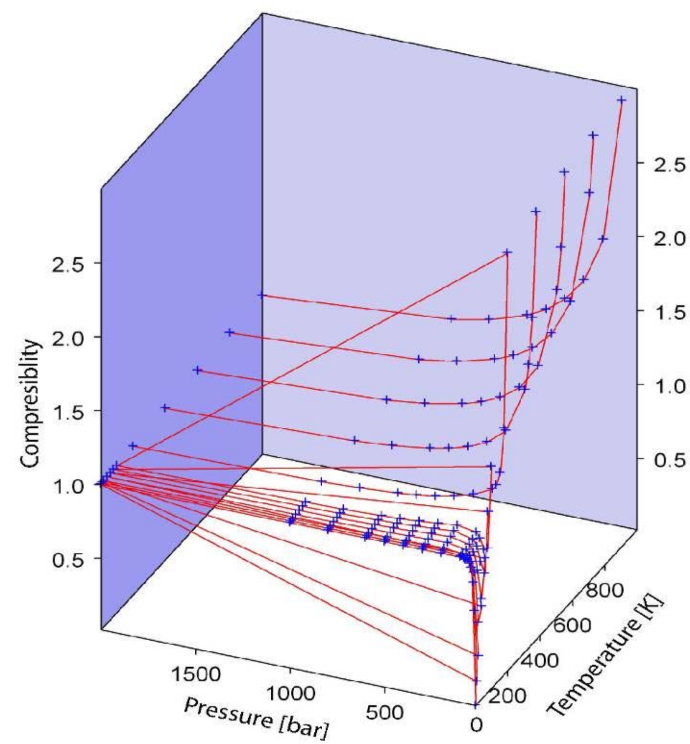
Non-Ideal Gas Considerations
Gravimetric & Volumetric



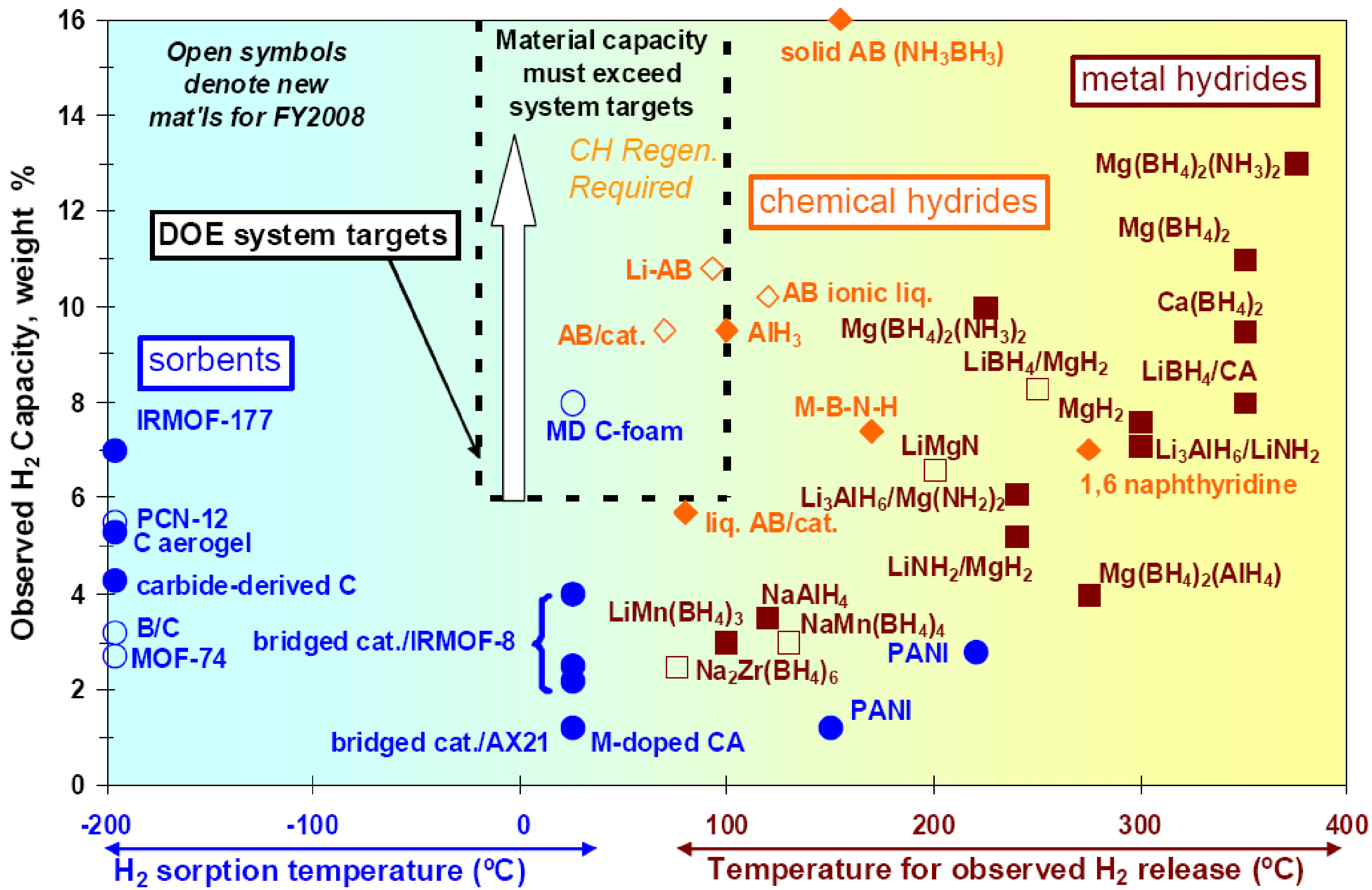


- **The non-ideality of H_2 can effect Capacity measurements.**

1) "Hydrogen Properties", College of the Desert, Hydrogen Fuel Cell Engines and Related Technologies: Rev 0, December 2001

2) The compressibility factor for hydrogen taken from the NIST12 database for fluid properties: Lemmon E.W., Peskin A.P., McLinden M.O., Friend D.G. NIST12 Thermodynamic and Transport Properties of Pure Fluids - NIST Standard Reference Database 23, Version 8.0; U.S. Secretary of Commerce: Washington DC 2007.

Measured Capacities: All Material types



- **Current state of the art material H_2 storage capacity vs. temperature.**
- **Accurate measurements critical for these comparisons.**

Presentation "Hydrogen Storage" by Sunita Satyapal, 2008 DOE Hydrogen Program Merit Review and Peer Evaluation Meeting June 9, 2008 Figures by DOE: G. Thomas, G. Sandrock

Future Work

- ***Capacity***
  - Hydrogen storage capacity is key metric for practical hydrogen storage.
  - It is critical that capacity measurements are performed with a clear understanding of commonly encountered caveats and pitfalls.
  - We will integrate feedback and content from experts on the draft version into the final version to be submitted to the DOE.
- ***Thermodynamics***
  - The objective of this task is to establish methodologies for determining equilibrium thermodynamics of hydrogen storage materials.
  - We will define protocols to separate true equilibrium conditions from kinetic effects.
  - We will examine details of new techniques for rapid determination of thermodynamic stabilities.
- ***Cycle-life Properties***
  - This task will focus on developing better definitions of how such tests should be performed.
  - We will detail what parameters may impact results, and
  - what properties are the most critical in performance evaluation (e.g.. capacity fade, or degradation in kinetics…).

Project Summary

- ***Relevance:*** To fill the need for a best practices guide for the measurement of critical performance properties of advanced hydrogen storage materials.
- ***Approach:*** Create a reference resource of best methods and caveats in measuring Target-based properties: General Introduction to Hydrogen Storage Materials and Measurements, Kinetics, Capacity, Thermodynamic and Cycle Life Measurements.
- ***Accomplishments:*** Task 1 and Task 2 completed. Task 3 in progress.

  Achieving a high-level of participation from experts in the field.
- ***Collaborations:*** Official collaboration with NREL, the University of California Berkeley, Caltech University, PNL and International collaboration through IEA task 22 with AIST Japan as well as industry.
- ***Future Work:*** Complete Task 3 (Capacity) and create drafts for Task 4 (Thermodynamic) and Task 5 (Cycle Life measurements).
- ***Document:***

http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/bestpractices_h2_storage_materials.pdf

Thank You!

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