

Best Practices for Characterizing Engineering Properties of Hydrogen Storage Materials

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contracted with

***National Renewable Energy Laboratory
Contract and Technical Manager: Phil Parilla***

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ST052

This presentation does not contain any proprietary, confidential, or otherwise restricted information

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Engineering Thermal Properties : Daniel Dedrick

Sandia National Laboratories

Engineering Thermal Properties : Ewa Rönnebro

Pacific Northwest National Laboratories

- Overview -

Timeline

- Start – Feb 2007
- End – Continuing
- 90% complete

Budget

- Total project funding
 - DOE \$1,092K
 - Contractor \$218K
- Funding FY10 \$222K
- Funding FY11 \$200K

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
- Authors: University of California Berkeley- California Institute of Technology - Pacific Northwest Laboratories - Texas A&M University - Los Alamos National Laboratory - Université Paris-Sud - VU University Amsterdam and the Delft University of Technology - University of Nevada Reno
- International Energy Agency Hydrogen Implementing Agreement (IEA) Task 22, Dr. Kuriyama AIST, Japan
- Review by experts: IEA Task 22 & others

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- *Relevance* -

- Hydrogen storage materials R&D is a challenging subset of energy storage and environmental materials R&D that also includes analogous activities in areas such as natural gas storage, CO₂ separation and sequestration. The creation of Best Practice standards in this field will certainly be of great value to the materials research community at large.
- 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.
- Accurate measurement methods and metrics are required to determine how new materials compare to all of these targets.
- The initial sections of this document have been made available for public use by pdf download from the DOE website.

- 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*** -

- Accurate measurement metrics are required to determine how new materials compare to all to DOE targets.
- Accurate measurements practices are also required whenever data is generated that will be used for modeling and engineering of scaled-up systems.
- This project's goal is the establishment of uniform practices in the measurement and presentation of hydrogen storage materials performance.
- The project delivers a public resource as an aid:
 - to the DOE hydrogen storage research community,
 - to students, academic and industry researchers world wide (for hydrogen storage and materials development in general), and
 - to improve international communications on these issues between government, university, and industry.

- **Milestones 2010/2011** -

Milestone	Results	%Comp
Finalize Updated Capacity Section	Public input on Spill-over effects were addressed, reviewed by NREL and incorporated into document	100%
Finalize Thermodynamic section	Final review of the Thermodynamic section has been completed and reviewer's edits and comments are currently being addressed.	95%
Draft Cycle-Life Section	Draft version of the Cycle-life section completed.	100%
Review of Cycle-Life Section	Initial review and integration of edits and comments completed, final review near completion.	95%
Draft Thermal Properties Section	Draft version in progress	15%

- **Go/No-Go FY10:** If the deliverables has not been completed or is determined to provide no value to the program the project will be terminated (9/11).

- Approach: Project 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.
- **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 and present new techniques for precisely determining equilibrium thermodynamics.
 - Define protocols to separate true equilibrium conditions from kinetic effects.
- **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.
- **Task 6: Engineering Thermal Properties**
 - Review measurement techniques currently being used for measuring thermal conductivity and heat capacity properties of hydrogen storage materials.
 - This task will include an evaluation of common thermal property measurement methods used in other applied materials fields that may be appropriate for hydrogen storage materials.
- **Task 7: Engineering Mechanical Properties**
 - Examine benefits and limitations of methods for measuring porosity, skeletal, apparent, and packing densities.
 - The validity of translating measurements on small samples to full systems scale performance will be examined.
 - Currently used and alternative methods for measuring material expansion forces will be presented.

- Collaborations -

- Contributions to this project from world experts including written materials, examples, presentation or editorial review of draft documents from:
 - Dr. Phil Parilla (contract manager) and Dr. Thomas Gennett, National Renewable Energy Laboratory, Golden CO, USA. (Introduction, Kinetics, Capacity, Spillover)
 - Dr. Gary Sandrock Consultant to U.S. Department of Energy. (Introduction, Kinetics)
 - Dr. George Thomas Consultant to U.S. Department of Energy. (Introduction, Kinetics)
 - Professor Sam Mao University of California Berkeley. (Introduction, Kinetics, Capacity, Thermodynamics sections)
 - Dr. Michael Miller of Southwest Research Institute®, San Antonio TX. (Kinetics)
 - Dr. Anne Dailly, and Dr. Frederick Pinkerton of General Motors GM R&D Center. (Capacity)
 - Professor Channing Ahn, California Institute of Technology, USA, IEA Task 22. (Capacity, Spillover)
 - Professor Evan Gray, Griffith University, Brisbane, Australia , IEA Task 22. (Capacity)
 - Dr. Ole Martin Løvvik of the Institute for Energy Technology in Kjeller Norway. (Kinetics)
 - Dr. Nobuhiro Kuriyama and Dr. Tetsu Kiyobayashi , AIST, Japan, IEA Task 22. (Introduction, Kinetics sections)
 - Dr. Eric Poirier of NRC Canadian Neutron Beam Centre Chalk River Laboratories, Canada (Capacity section)
 - Dr. Kevin Ott, Dr. Anthony Burrell, and Dr. Troy Semelsberger of Los Alamos National Laboratory (Capacity, Thermodynamics sections)
 - Professor Klaus Yvon, University of Geneva, Switzerland IEA Task 22. (Capacity section)
 - Professor Gavin Walker, University of Nottingham, United Kingdom IEA Task 22. (Thermodynamics Section)
 - Professor Richard Chahine, Université du Québec à Trois-Rivières, Canada, IEA Task 22. (Kinetics, Capacity and Engineering Thermal Properties section)
 - Dr. Martin Dornheim, Helmholtz-Zentrum Geesthacht, Germany, IEA Task 22. (Engineering Thermal and Mechanical Properties sections)
 - Dr. Maximilian Fichtner, Karlsruher Institute for Technology, Germany, IEA Task 22. (Engineering Thermal and Mechanical Properties sections)

- Key Accomplishments -

2007 – 2010:

- **Task 1: Final Introduction section 100% complete.**
- **Task 2: Final Kinetics section 100% complete.**
- **Task 3: Original Capacity section 100% complete.**

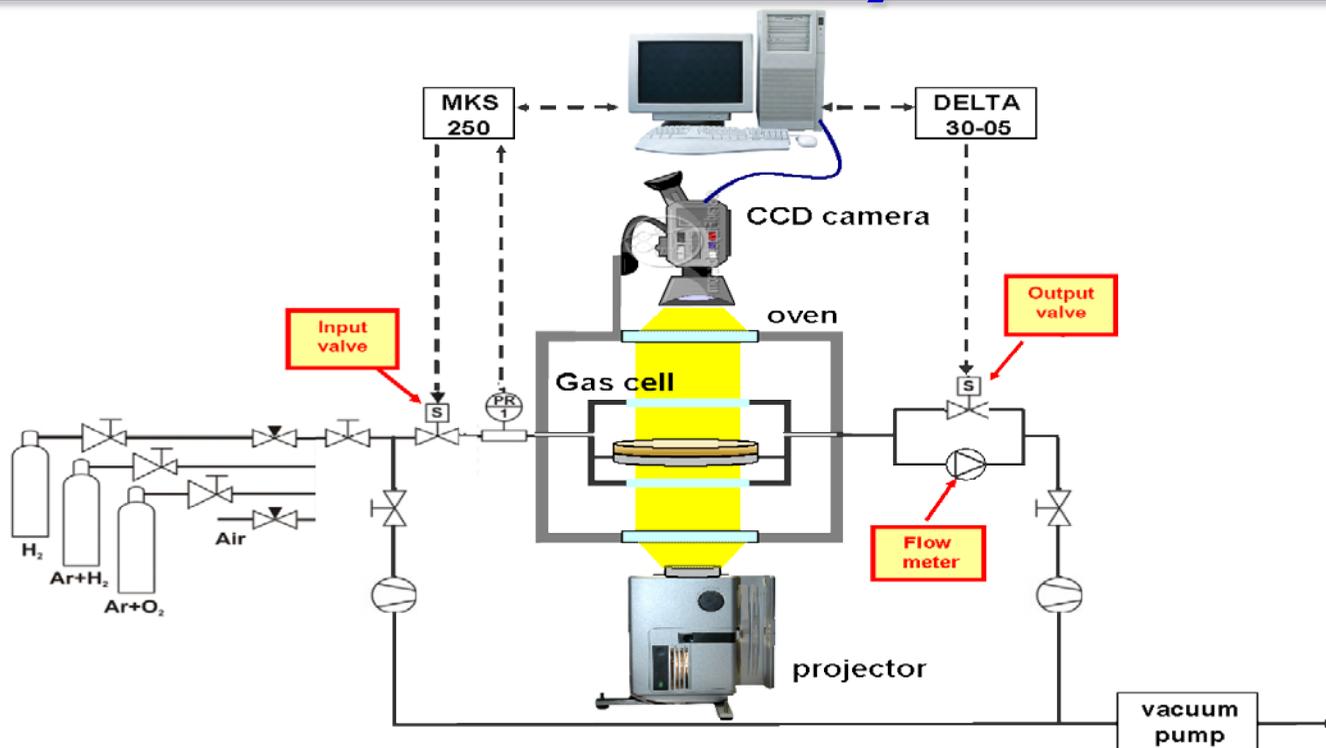
2010 – 2011:

- **Task 3: Updated Capacity section, including review of Spillover section by Tom Gennett and Phil Parilla (NREL) and Channing Ahn (CalTech) 100% complete and available on the web.**
- **Task 4: Final Thermodynamic section reviewed 95% complete.**
- **Task 5: Final version Cycle Life reviewed 95% complete.**
- **Task 6: Engineering Thermal Properties section work in progress.**
Co-authors Daniel Dedrick and Ewa Rönnebro.
- **Reviewed Tasks 1-3 Document Delivered to DOE Dec. 2010.**
- **Public comment received and integrated into document.**
- **Final Tasks 1-3 Document Posted to DOE website for world-wide access.**
- **Review by Hydrogen Storage Tech Team, September 16, 2010**
- **Additional International Co-Authors: Pierre Dantzer, Yevheniy Pivak and Bernard Dam, and Reviewers: Gavin Walker, Richard Chahine, Maximilian Fichtner, and Martin Dornheim contributions developed through collaborations within IEA Task 22.**

Please download the current Best Practices document from:

http://www1.eere.energy.gov/hydrogenandfuelcells/storage/test_analysis.html

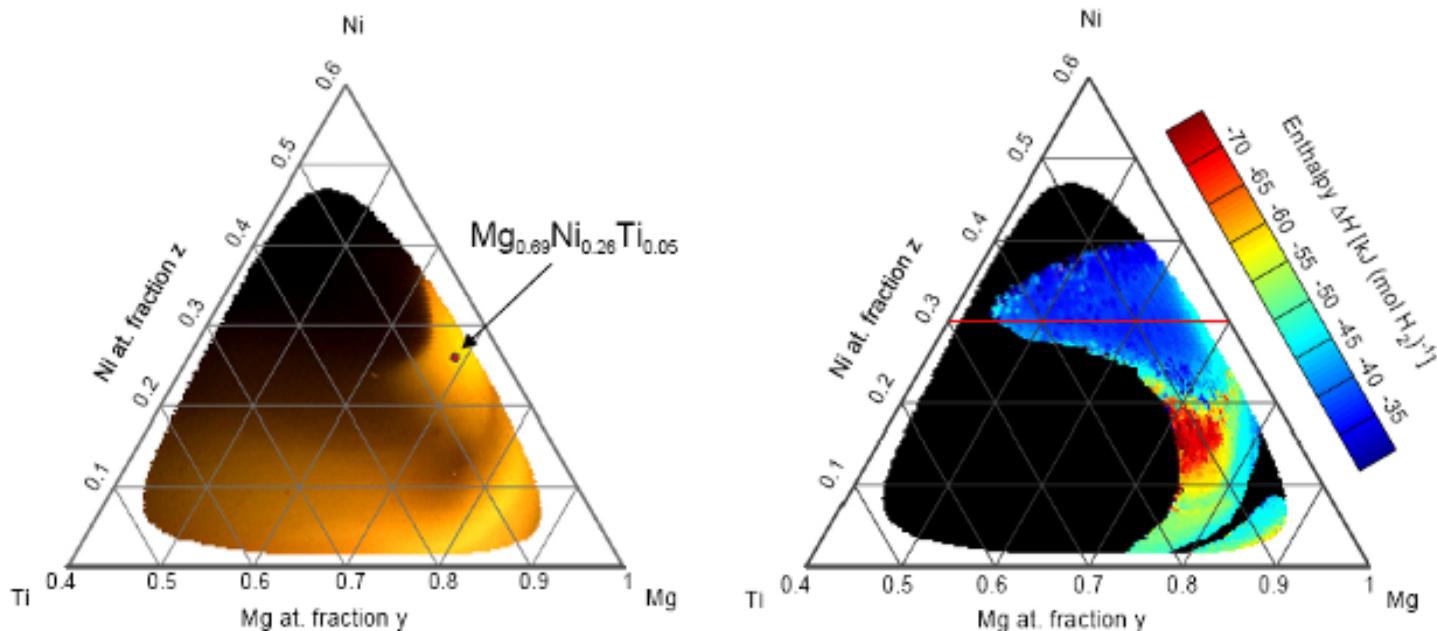
- Technical Accomplishments - Additions to Thermodynamics Section



Schematic representation of a Hydrogenography setup.

- **Thermodynamic measurements possible using Hydrogenography**
- **Hydrogenography:** The log of optical transmission of a thin film is proportional to the local hydrogen concentration of the material in the two phase region. Changes in optical transmission are measured while slowly increasing (or decreasing) hydrogen pressure to produce an isotherm. Thus, plateau pressures can be measured simultaneously at every point on a two dimensional combinatorial film with composition gradients. Repeating the measurement at several temperatures gives a van 't Hoff plot for every composition.

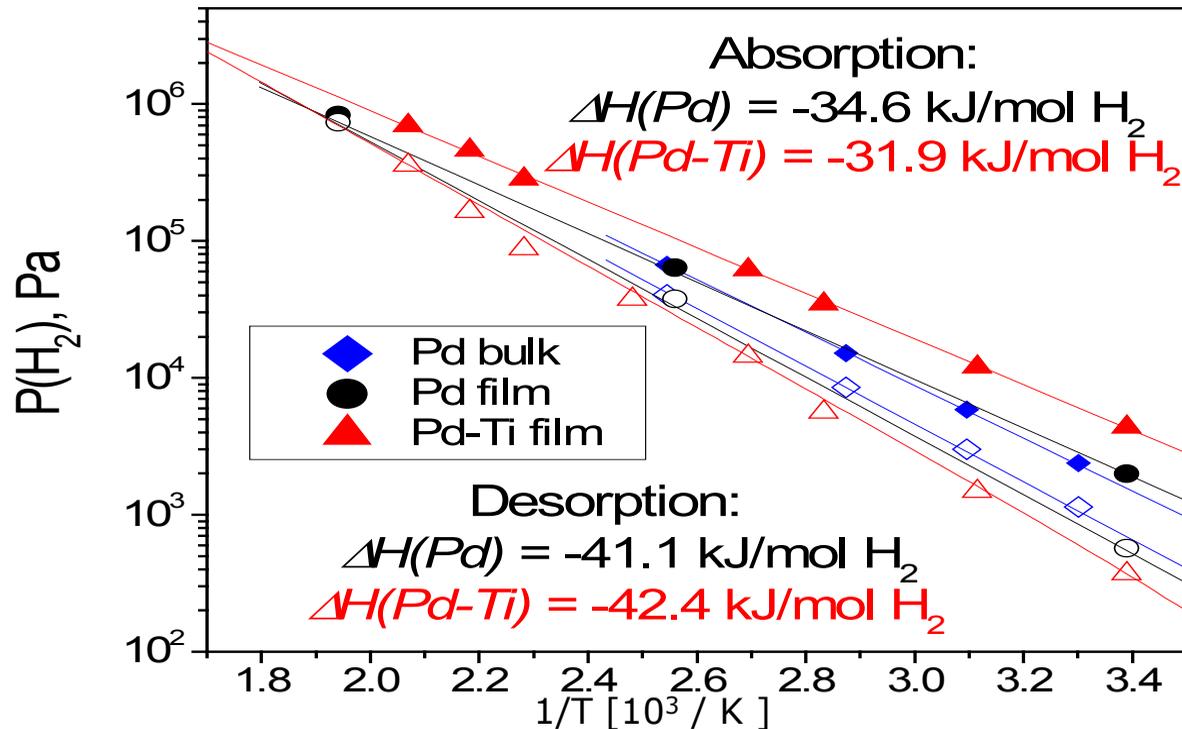
Hydrogenography for Combinatorial Synthesis and Rapid Thermodynamic Scanning



Ternary composition diagram (left) showing the final optical transmission state and the enthalpy map (right) of the Mg-Ni-Ti system, estimated using the optically determined hydrogenation plateaus. Black region on the right-hand picture represents chemical compositions that do not have a well defined plateau on the PTI's.

- **Hydrogenography allows rapid thermodynamic scanning of thousands of compositions simultaneously.**

Hydrogenography for Measuring Nano-scale Thermodynamic Properties



Van 't Hoff plot of bulk Pd (black), free Pd films (blue), and clamped Pd-Ti film (red, Hydrogenography). Solid symbols: absorption and open: desorption.

- Comparison of thin film Sievert's and Hydrogenography measurements of thermodynamics of Pd absorption and desorption.
- Clamped films show modified thermodynamics.

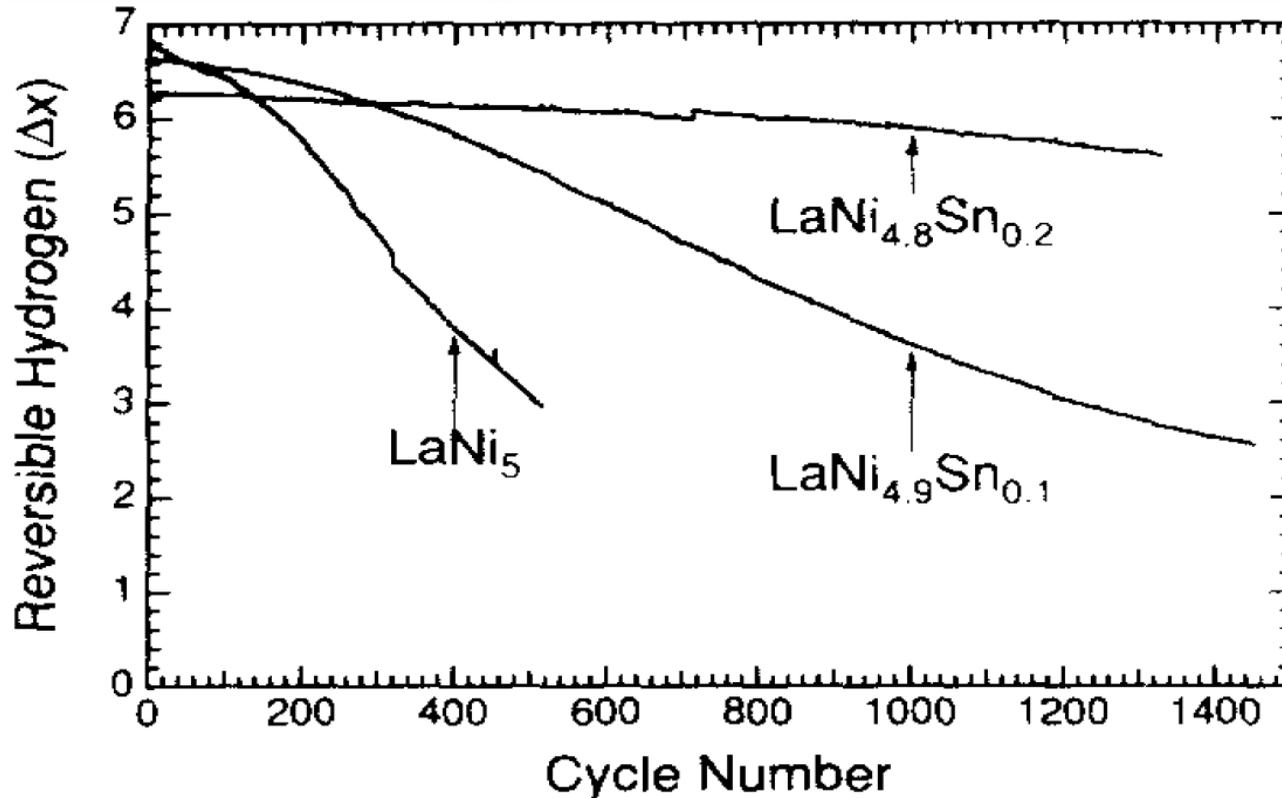
Y. Pivak, H. Schreuders, M. Slaman, R. Griessen, B. Dam, in preparation
Y. Pivak, R. Gremaud, K. Gross, M. Gonzalez-Silveira, A. Walton, D. Book,
H. Schreuders, B. Dam, R. Griessen, Scripta Materialia 60(5) (2009) 348

Cycle Life Measurements Section

Introduction/Definitions: Cycle Life Measurements is key to the study of the performance of **on-board reversible hydrogen storage materials** as they may be used in real applications. (Off-board regenerable on not applicable to these measurements) Typically;

- The first step is to make measurements of the total reversible capacity as hydrogen is charged and released from the material over many cycles.
- Following this, measurements often focus on modifying the storage material itself to improve the ability to retain capacity over many cycles. This may be supported by more fundamental studies of what causes degradation of the material with cycling.
- An important metric of performance besides capacity is the rate of hydrogen uptake and release which is also likely to degrade with cycling. In the later stages, measurements are aimed at evaluating how storage materials perform when cycled under non-ideal conditions (temperature excursions, exposure to air, impurities in the hydrogen gas supply....).
- Finally, thorough testing of the materials and storage system at a scaled up level are necessary to be able to evaluate true application level performance.
- Each level of cycle-life testing may require its own unique experimental setup, procedures and special attention to details that may unexpectedly adversely impact the reliability of the measurements.

Materials Development Goal: Improved Cycle Life Performance

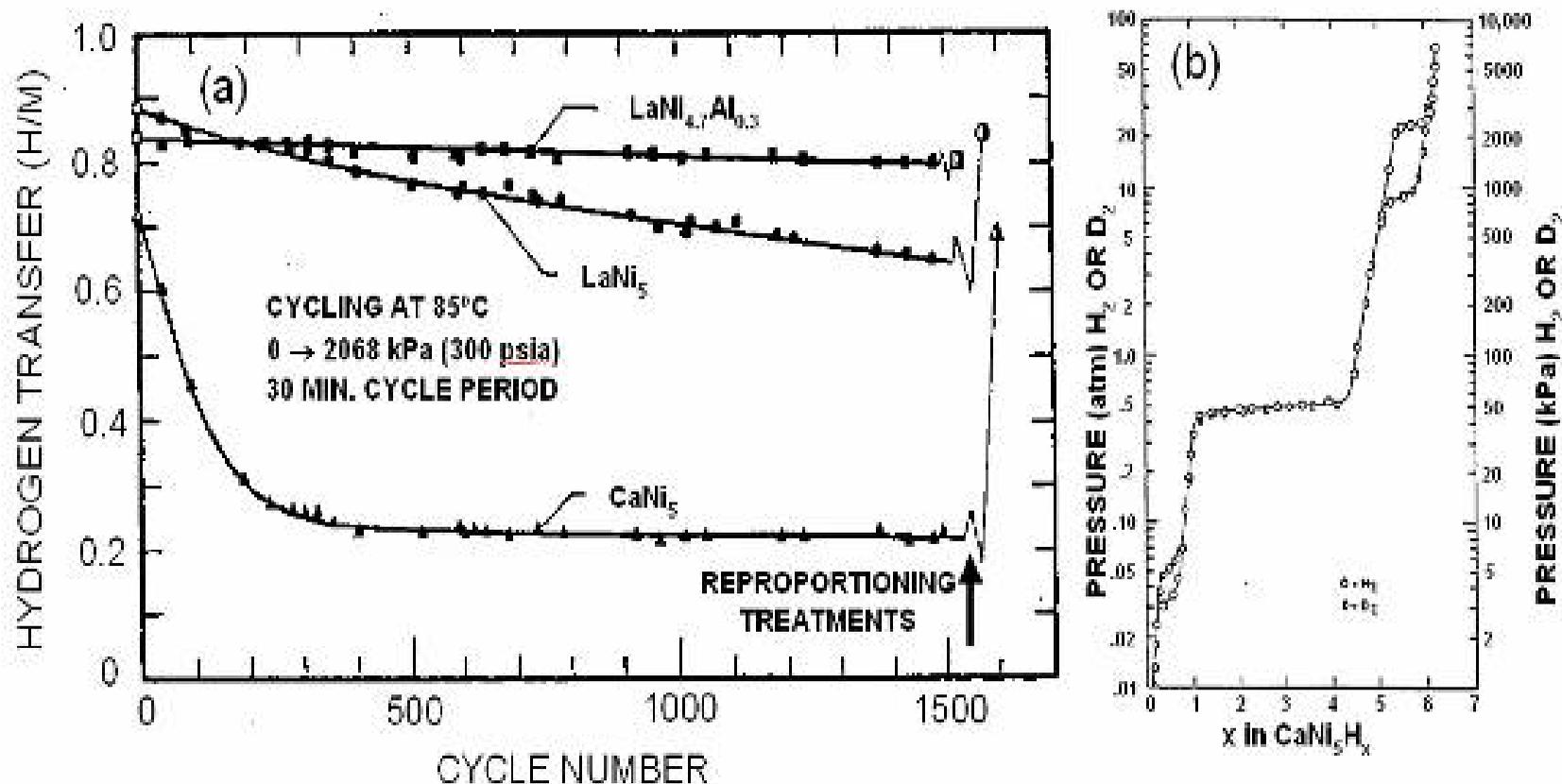


Hydrogen concentration changes Δx for $\text{LaNi}_{5-y}\text{Sn}_y\text{H}_x$ obtained from the maximum and minimum pressures for each cycle.

- **Good cycling performance is critical for practical hydrogen storage.**
- **Small modifications to materials can have a great impact on Cycle Life performance.**

Bowman, R. C., Jr., Luo, C. H., Ahn, C. C., Witham, C. K., and Fultz, B. "The effect of tin on the degradation of $\text{LaNi}_{5-y}\text{Sn}_y$ metal hydride during thermal cycling". J of Alloys and Comps 217 (1995) 185-192.

INTRINSIC: Degradation by Disproportionation of Hydrides



a) Comparison of hydrogen capacity loss vs. cycles for $\text{LaNi}_{4.7}\text{Al}_{0.3}$, $\text{LaNi}_{5.2}$, and CaNi_5 , before and after pressure cycling at 85°C between 0 and 2068 kPa (300psi). This shows a significant loss in CaNi_5 but this loss is recovered after repositioning. (b) A reference isotherm of CaNi_5 (taken at 25°C) showing three different plateaus due to Ca isotopes.

Sandrock, G.D., et al., Hydrides and Deuterides of CaNi_5 . Materials Res. Bull., 1982. 17: p. 887-894.

EXTRINSIC: Gaseous Impurity Effects on Classic Hydrides

Definitions: There are four classic types of alloy-impurity interactions:

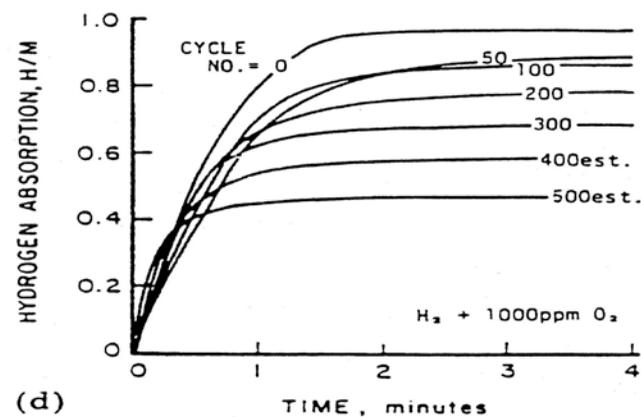
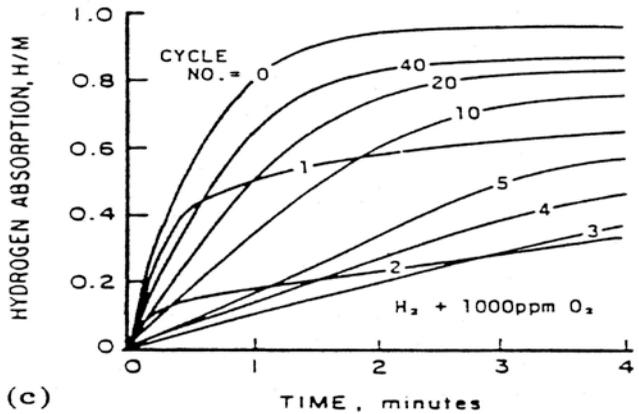
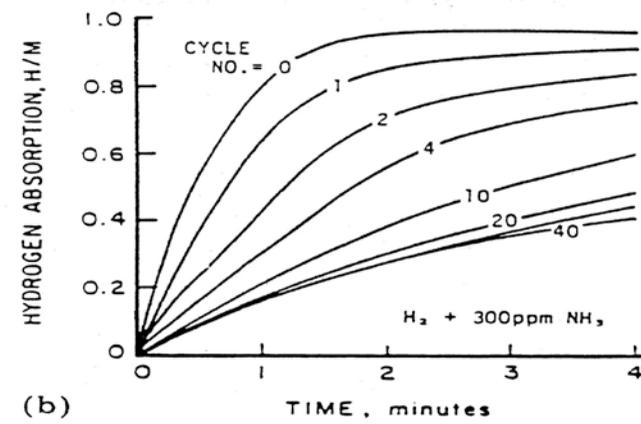
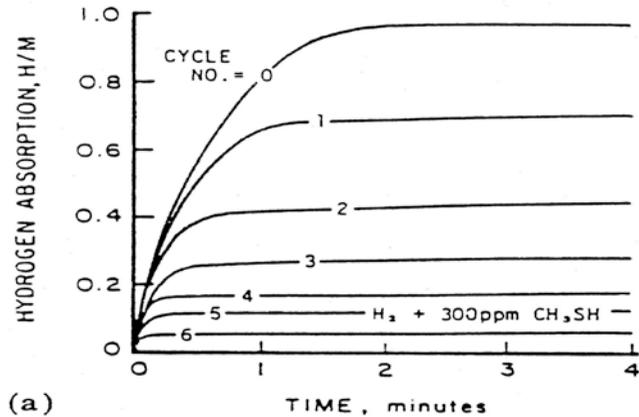
Innocuous: is observed as essentially no cyclic effect on rate or capacity, i.e., inert. Examples include N_2 and CH_4 interactions with AB₅ intermetallics at room temperature. However, innocuous impurities at high levels (<1%) can exhibit what appears to be retardation during absorption. This is simple "inert gas blanketing" where the innocuous impurity gas simply collects and concentrates in the cracks and interparticle voids, resulting in a type of H₂ diffusion barrier. Inert gas blanketing is asymmetric and is not seen on desorption as the impurity gas is quickly swept away.

Poisoning: results in a severe and rapid loss of H-capacity with cycling. The impurity is able to virtually stop hydriding with only a monolayer of surface coverage, suggesting that dissociative chemisorption is deactivated. Typical poisons include CO (near room temperature) and the S-containing gases (e.g., CH_3SH methyl mercaptan).

Retardation: is characterized by losses of absorption/desorption reaction rates without significant loss in ultimate H-capacity. Retardants include NH_3 , CO_2 on the AB₅ alloys or CO at temperatures above 100°C.

Reaction: is the effect of bulk corrosion loss of alloy resulting in irreversible capacity loss. Although O_2 exhibits a short-term retardation-recovery behavior (on alloys such as LaNi₅), its long term behavior is as a reactant by oxidizing the alloy. The alloy damage caused by a reactant generally cannot be recovered without complete metallurgical reprocessing.

Example: Gaseous Impurity Effects on LaNi_5



Effects of impurity interactions with LaNi_5 on the absorption profiles during cycling. (a) Poisoning, (b) Retardation, (c) Retardation-Recovery, (d) Reaction. Curves measured at 25°C and 3.4 atm

- **Extrinsic gas impurity effects can be significant with cycling and should be examined for all potential reversible storage materials.**

Sandrock, G. and P.D. Goodell, Cyclic life of metal hydrides with impure hydrogen: Overview and engineering considerations. Journal of the Less Common Metals, 1984. 104: p. 159-173.

Cycle-Life Measurement Methods

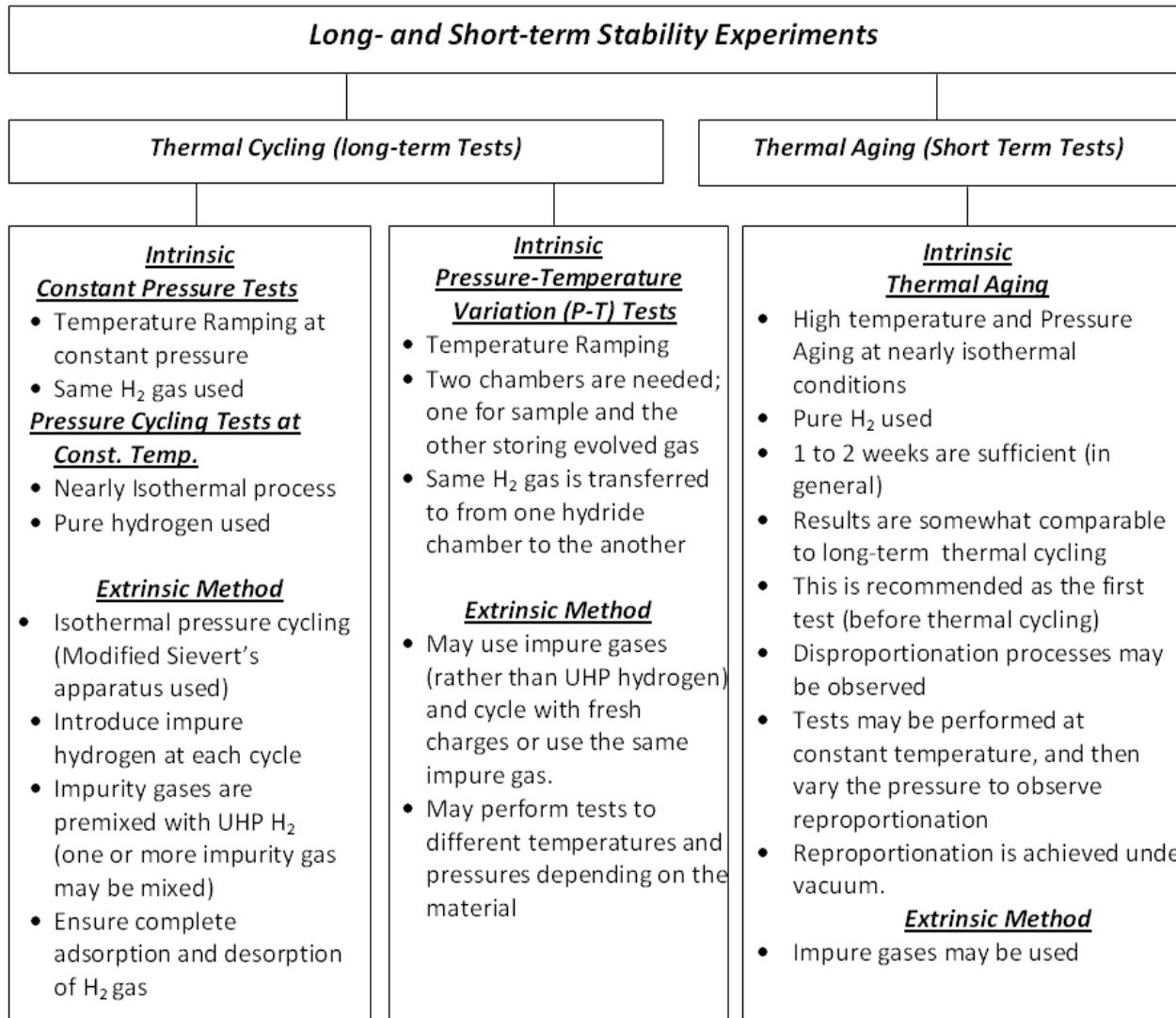
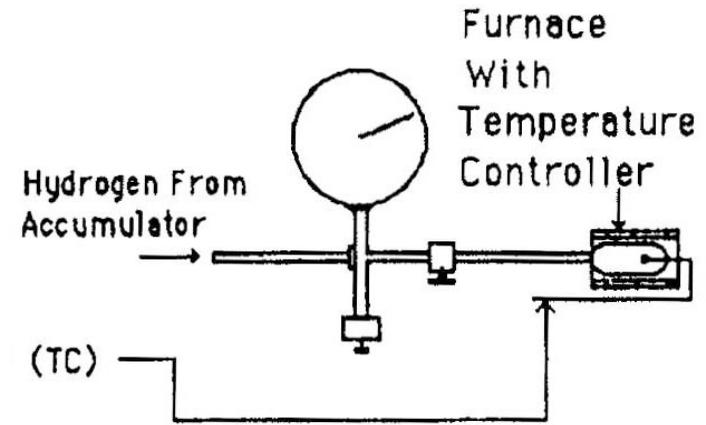
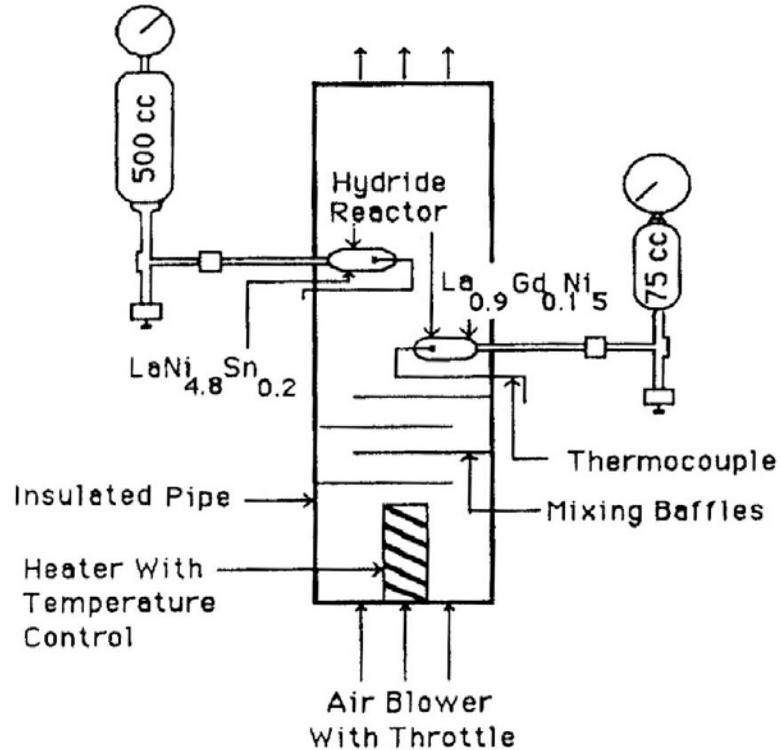


Chart of hydrogen storage materials stability testing methods.

Chandra, D., "Intermetallics for hydrogen storage", in the book "Solid-state hydrogen storage, Materials and chemistry", edited by Gavin Walker, (2008) Woodhead Publishing Limited, Cambridge England, CRC Press, 327.

Thermal Testing Measurement Apparatus



(A) Thermal Cycling Apparatus

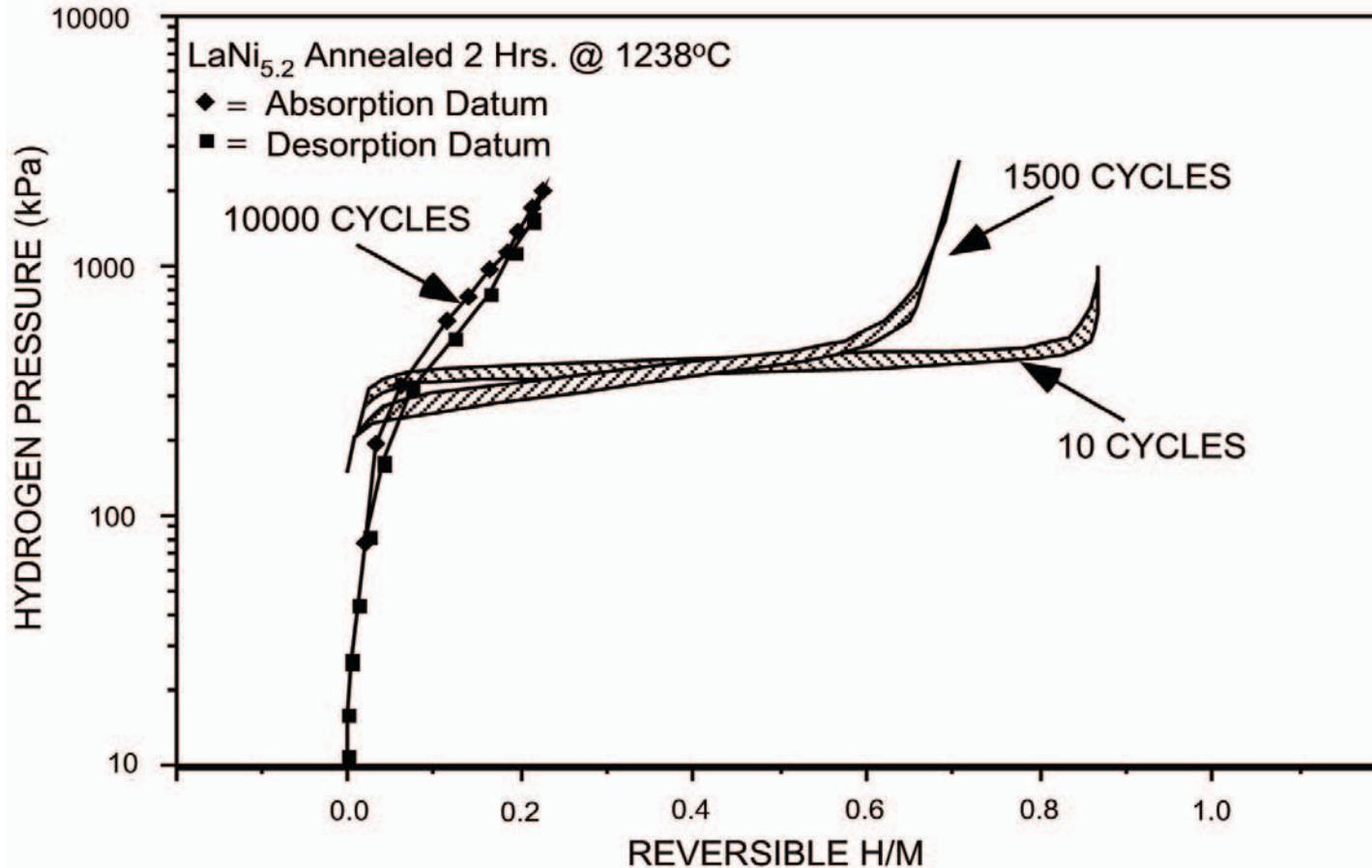
(B) Thermal Aging Apparatus

Closed (recycled) gas systems for intrinsic Thermal Cycling:
(A) Heating/Cooling apparatus for long-term thermal cycling
(B) High pressure apparatus for rapid thermal aging.

- **Effective methods for testing intrinsic material Cycle Life degradation.**

Lambert, S.W., Chandra, D., Cathey, W.N., Lynch, F.E. and Bowman, R.C. Jr.,
"Investigation of hydriding properties of $\text{LaNi}_{4.8}\text{Sn}_{0.2}$, $\text{LaNi}_{4.27}\text{Sn}_{0.24}$ and $\text{La}_{0.9}\text{Gd}_{0.1}\text{Ni}_5$
after thermal cycling and aging", J. Alloys Compd., 1992. 187: p. 113-135.

Example: P/T Intrinsic Thermal Cycling Tests

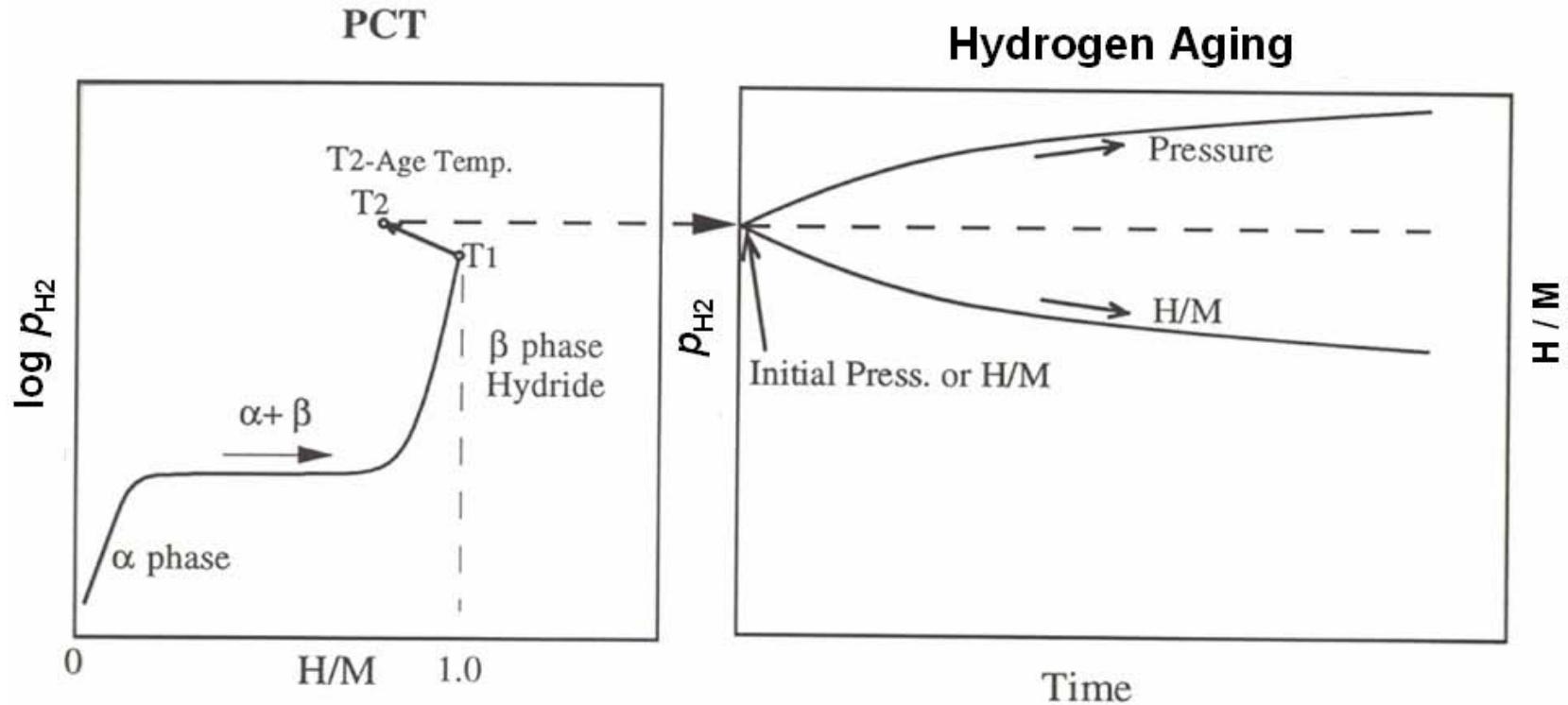


Isotherm of LaNi_{5.2} taken at 25°C after intrinsic P-T 10 (activation), 1500, 10,000 cycles, showing severe degradation of this hydride.

- **P/T closed system thermal cycling is used to test intrinsic materials long-term cycling degradation.**

Chandra, D., "Intermetallics for hydrogen storage", in the book "Solid-state hydrogen storage, Materials and chemistry", edited by Gavin Walker, (2008) Woodhead Publishing Limited, Cambridge England, CRC Press, 327.

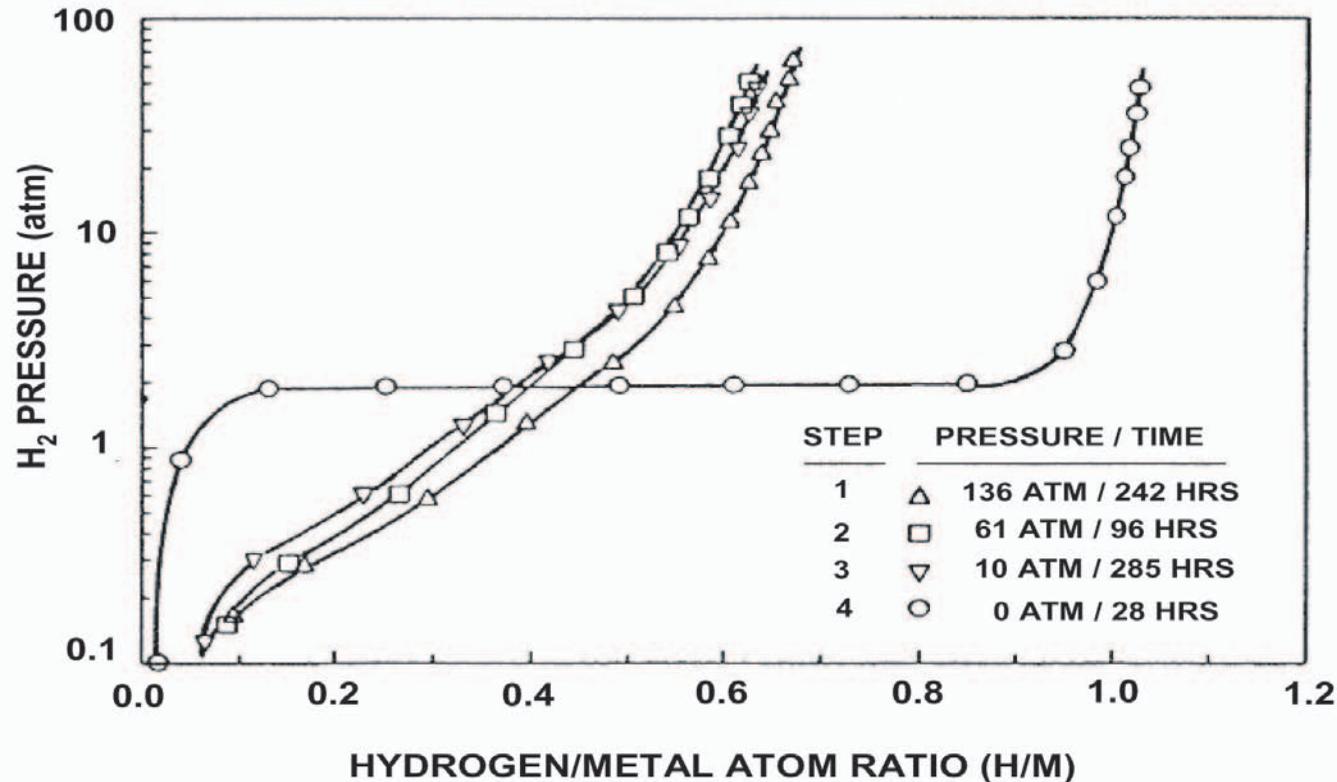
Thermal Aging Method



Schematic of Thermal Aging method. (Left) An isotherm is generated at a temperature T1 until fully saturated in the β phase (above the plateau pressure). The sample holder is sealed and the sample heated to the aging temperature T2. Once the temperature is stabilized, the sample is aged for a certain period of time (Right). If there is disproportionation, then the pressure rises and H/M decreases as function of time.

Chandra, D., "Intermetallics for hydrogen storage", in the book "Solid-state hydrogen storage, Materials and chemistry", edited by Gavin Walker, (2008) Woodhead Publishing Limited, Cambridge England, CRC Press, 327.

Example: Thermal Aging Tests of LaNi_5

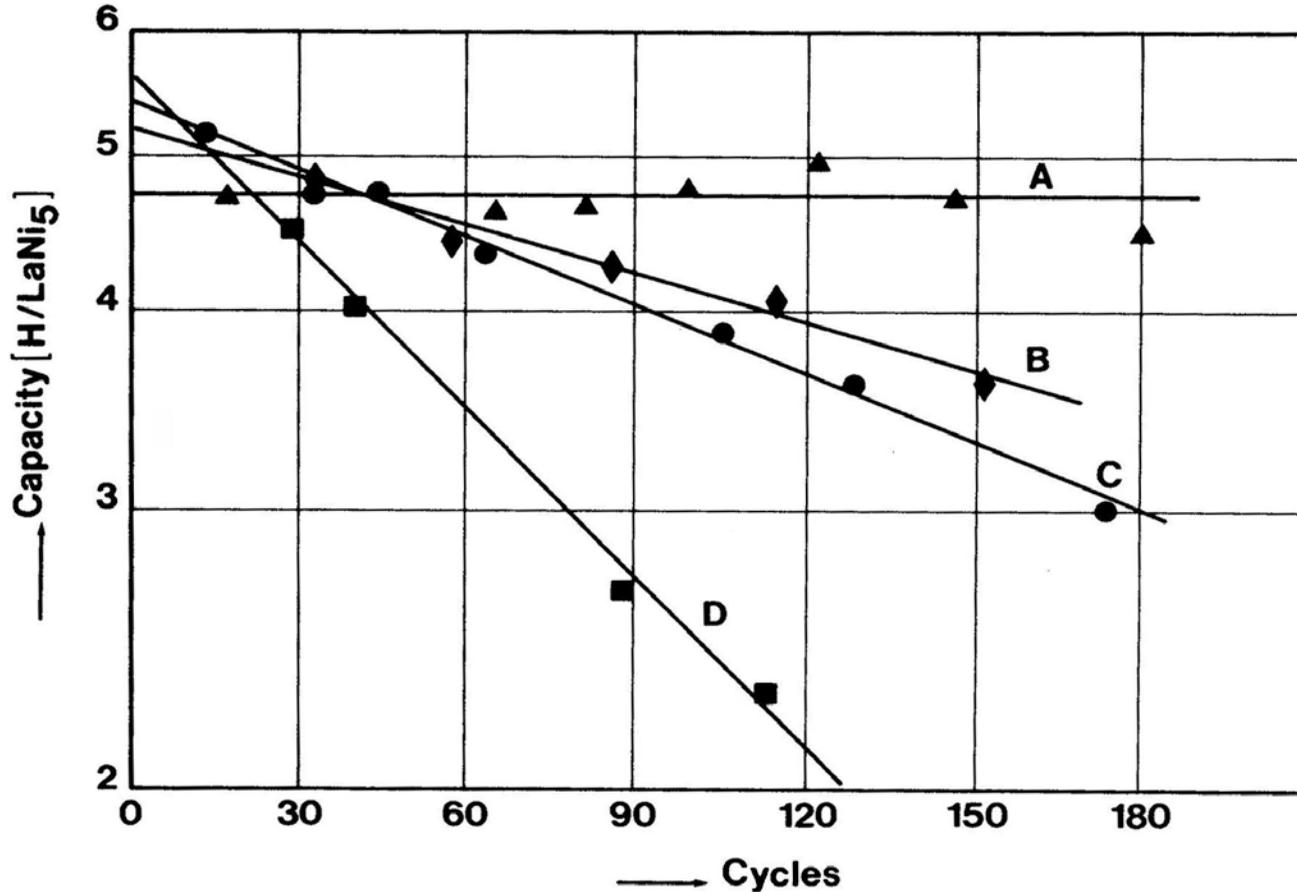


Isotherms of LaNi_5 taken at 25°C after subjecting to aging at high and low hydrogen pressures. Note that the isotherm (4) after vacuum aging the sample at 180°C is nearly the same as before aging indicating full reproporationation of the LaNi_5 hydride.

- Thermal aging may be used on hydrides to rapidly simulate long-term Cycle Life degradation.

Sandrock, G.D., et al., ON THE DISPROPORTIONATION OF INTERMETALLIC HYDRIDES. Zeitschrift Fur Physikalische Chemie Neue Folge, 1989. 164: p. 1285-1290.

Effect of Sample Preparation on Cycle Life

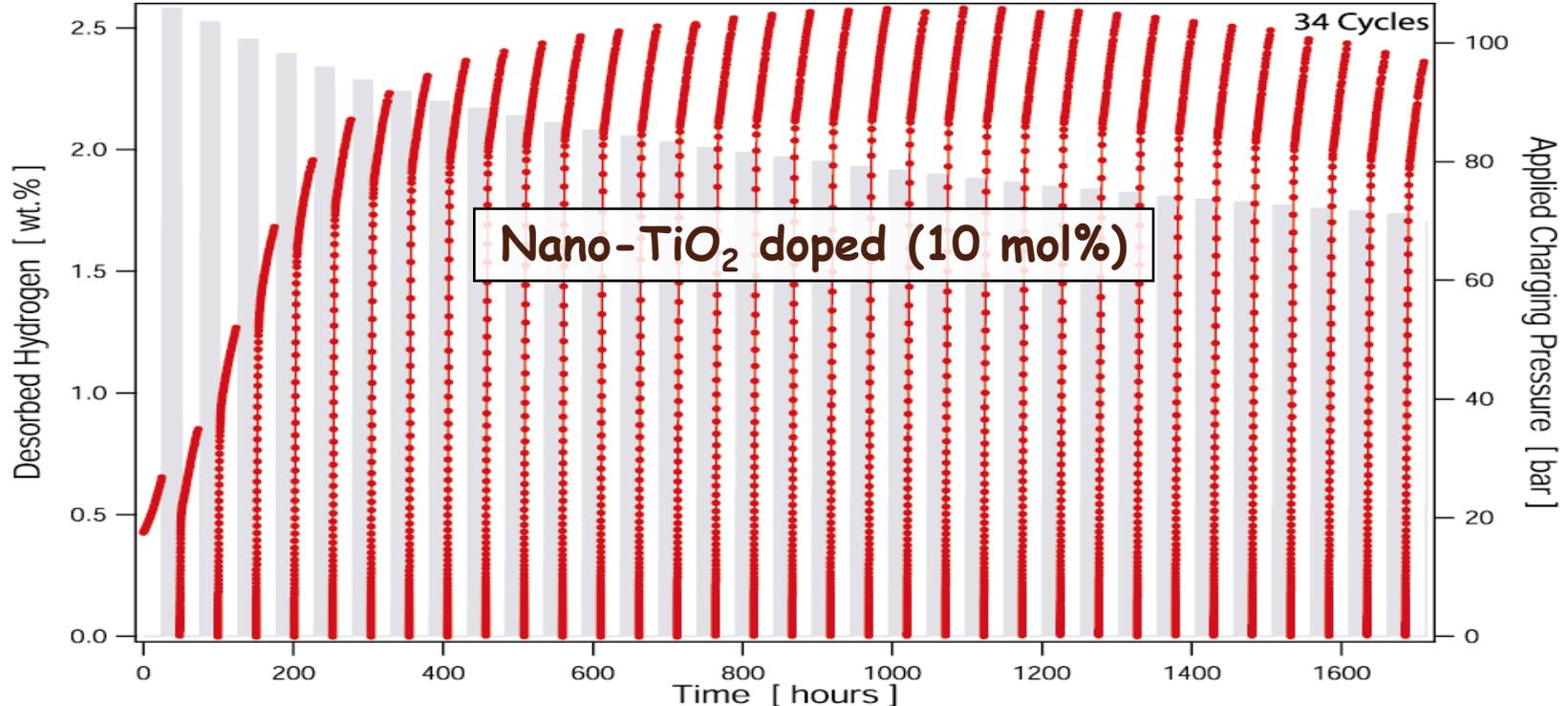


Hydrogen storage capacities of LaNi₅ samples from various suppliers during absorption cycling: (A) Research Chemicals sample, Ergenics (C) Research Chemicals; (D) Molycorp samples are cycled in 12 atm.

- **Sample preparation can have a large impact on Cycle Life properties.**

Holleck, G.L., Driscoll, J.R., Paul, B.E., *J. Less-Common Met.* 74, (1980) 379.

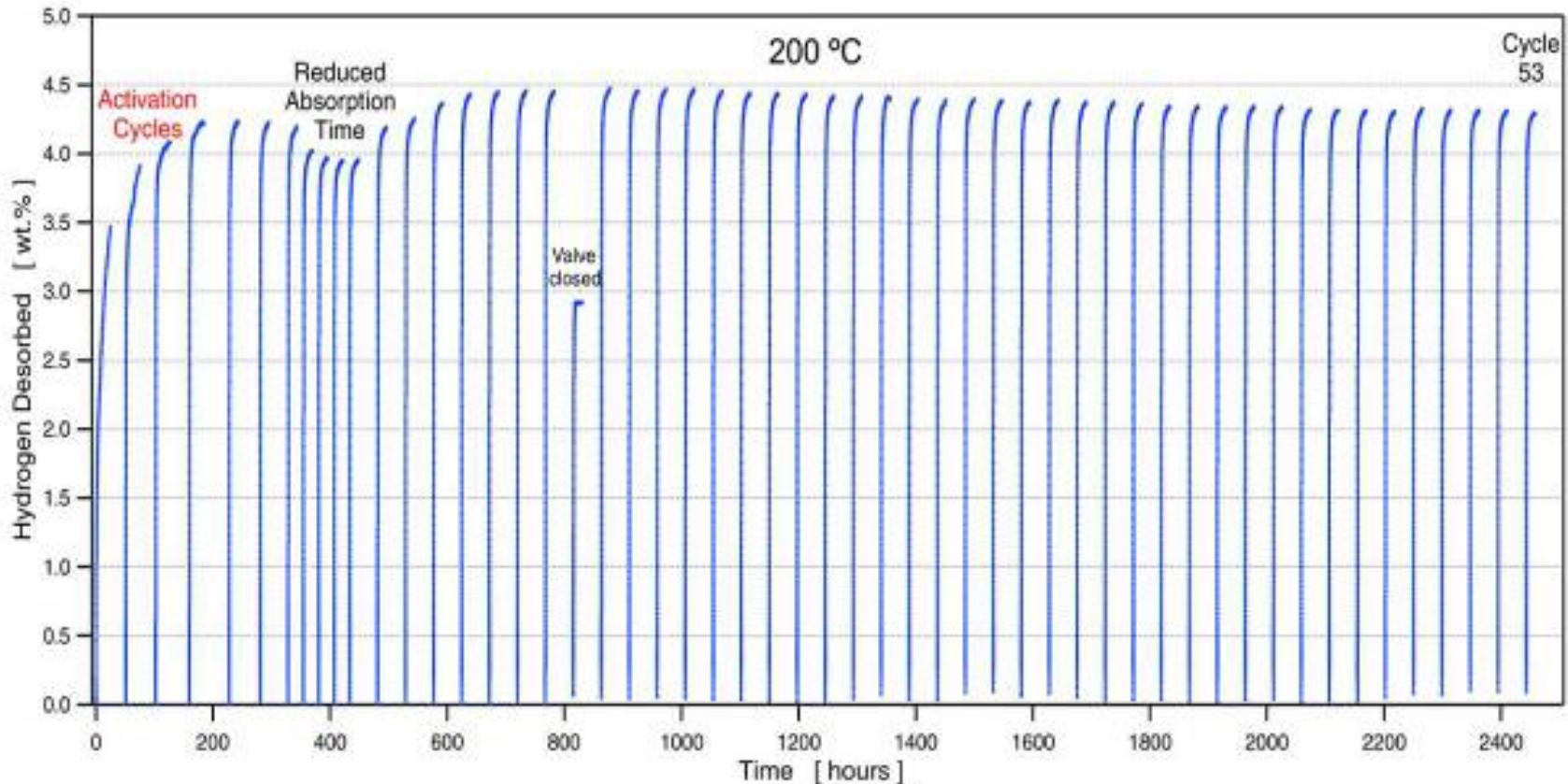
Considerations: Pretreatment / Activation



Hydrogen cycling of NaAlH₄ (NaH + Al starting material) doped with 10 mol% nanoparticle TiO₂. An activation process is observed in the first 20 cycles. Red: hydrogen desorption capacity, Gray: hydrogen charging pressure at each cycle.

- **Pretreatment or Activation may be required prior to (and distinguished from) long-term cycling and other storage property measurements.**

Consideration: Measurement Parameters

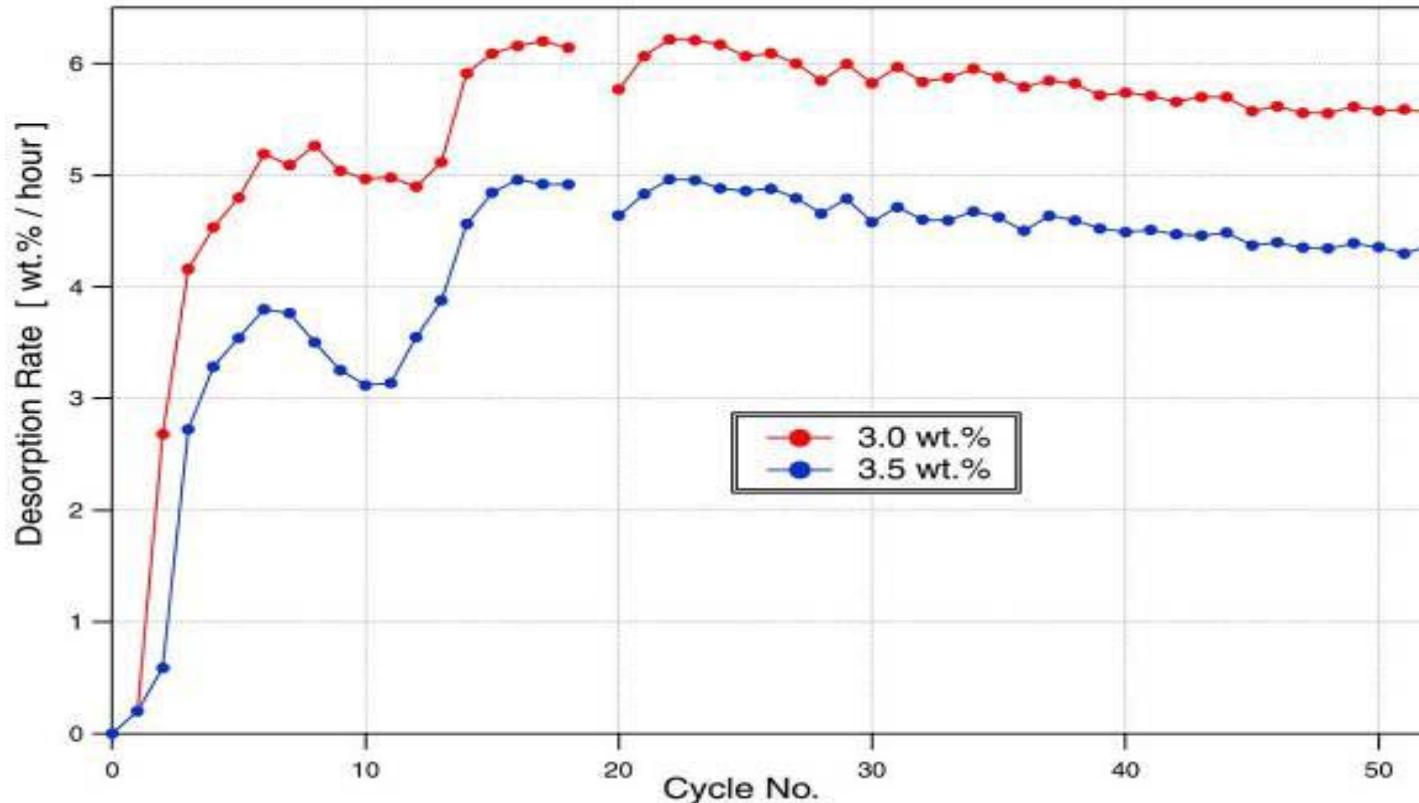


Hydrogen desorption capacity vs. cycles for Li-Mg-Amide/Imide (charging constant pressure 69-83 bar, discharge to 0.5 bar, 200°C).

- **The selection of experimental parameters can change the apparent outcome of the measurement.**
- **Note the change in capacity with reduced cycle time.**

J.J. Vajo, S.L. Skeith, F. Mertens, „Reversible Storage of Hydrogen in Destabilized LiBH₄“ J. Phys Chem. B 109 (2005) 3719-3722

Rate Degradation: Impact on Cycle Life Properties

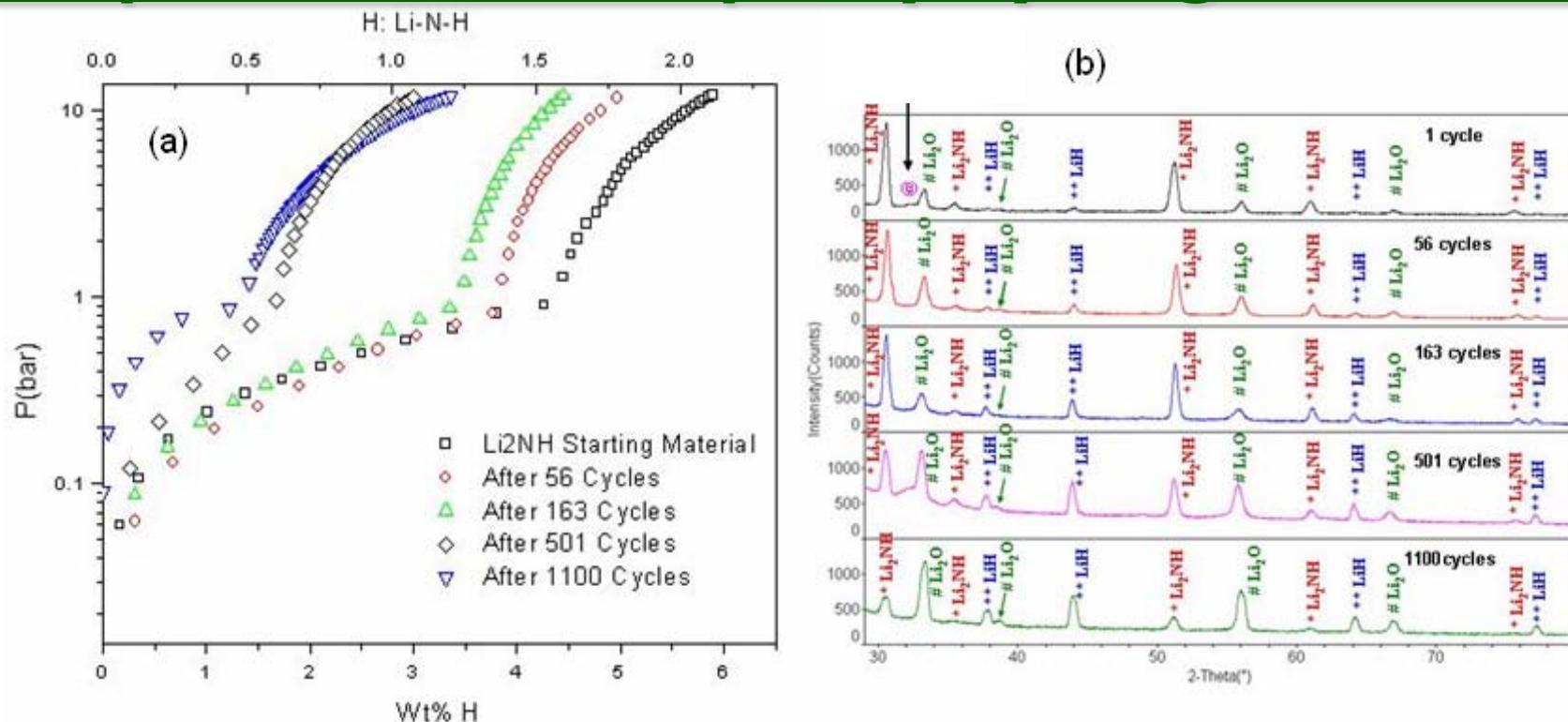


Average hydrogen desorption rate to 3.0 and 3.5 wt.% for the Li-Mg-N-H system (charging 100 bar, discharge to 0.5 bar , 200°C).

- **Fixed absorption/desorption cycle times leads to “apparent” loss in capacity, which is actually in part due to degradation in kinetics.**

Gross, K.J., Luo, W., Rönnebro, E. and Spangler, S., “Sorption Properties of Novel Hydrogen Storage Materials” Presentation, MH2004 Symposium on Metal-Hydrogen Systems, Fundamentals and Applications Krakow, Poland. 5–10 September 2004.

Example: Extrinsic Impurity Cycling of Li-Amide



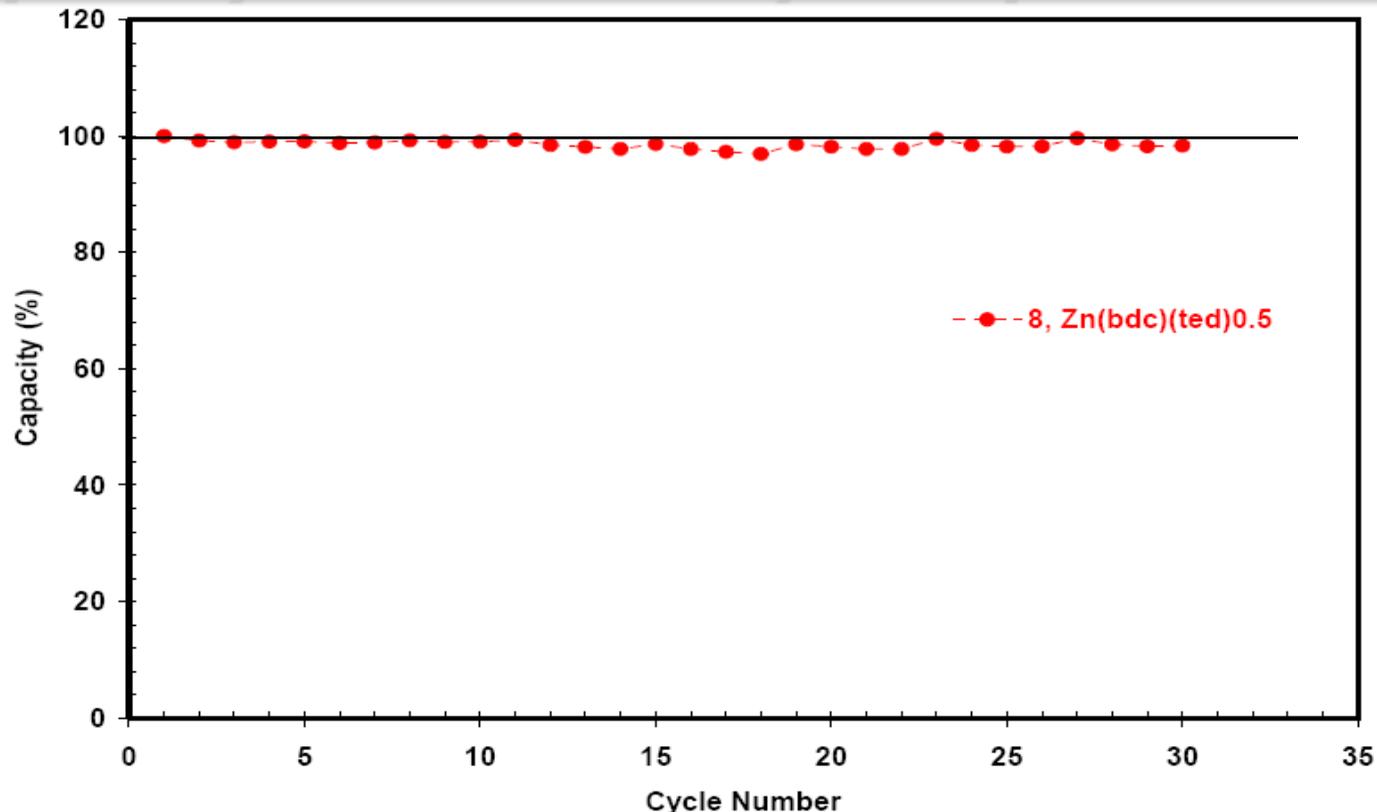
(a). Absorption isotherms of Li-amide obtained after non-equilibrium pressure cycling for 1, 56, 163, 501, 1100 cycles with impure hydrogen (ppm levels of O₂, H₂O and others). (b) Corresponding ex-situ X-ray diffraction pattern of the sample at the end of each desorption isotherm.

- Amide performance also degraded by impurities in commercial grade H₂.
- Full isotherms and phase analysis are critical for a true representation of hydrogen storage material performance after extended cycling.

Considerations: Cycle Life Testing of Physisorption Materials

- **Very few cycle life properties studies of physisorption materials exist.**
- **Even though storage is through weak surface interactions of molecular hydrogen, it can not be assumed that performance degradation does not occur with hydrogen cycling for all physisorption materials.**
- **Measurements are difficult because typical 77K temperatures will have to be consistently maintained throughout hundreds of cycles.**
- **However, kinetics are generally fast, therefore, pressure cycling can be done within a reasonable time. Thermal cycling may not be needed.**
- **Because physisorption capacity measurements are susceptible to large errors (as described in Capacity Section), it is critical that evaluation of long-term cycling performance be done using isotherms done under identical conditions at regular cycling intervals. It is unlikely to be sufficient to simply compare maximum uptake (or release) per cycle.**
- **Impurities in the hydrogen supply are likely to impact cycle-life performance (e.g. MOF's that decompose with water contact). Yet some impurities (Air...) may condense out before storage.**
- **Studies involving natural gas storage have shown that impurities in the gas accumulate in high surface area carbon adsorbents. However, this principally impacts low pressures capacities (<2 bar) which might not be utilized in hydrogen storage applications.**

Example: Cycle Life of Physisorption Materials



Hydrogen physisorption capacity on MOF $\text{Zn}(\text{bdc})(\text{ted})_{0.5}$ at 77 K as a function of adsorption/desorption cycles. Each point represent maximum uptake (% of full capacity) of the adsorption isotherm.

- **Knowledge of Cycle Life properties of reversible physisorption materials is essential.**
- **Capacity in example fluctuates with cycles, but has a general downward trend.**

Jeongyong Lee, "Synthesis and gas sorption study of microporous metal organic frameworks for hydrogen and methane storage", Ph.D. Thesis (2007), Rutgers, the State University of New Jersey, New Brunswick

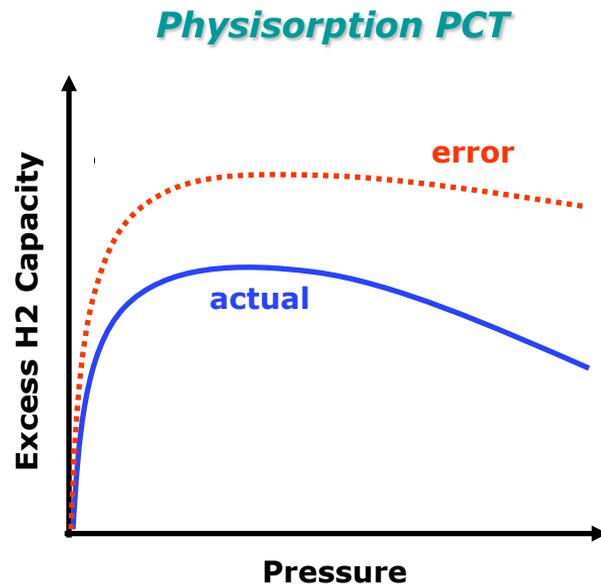
DOE Special Request

PI: Dr. Phil Parilla, NREL

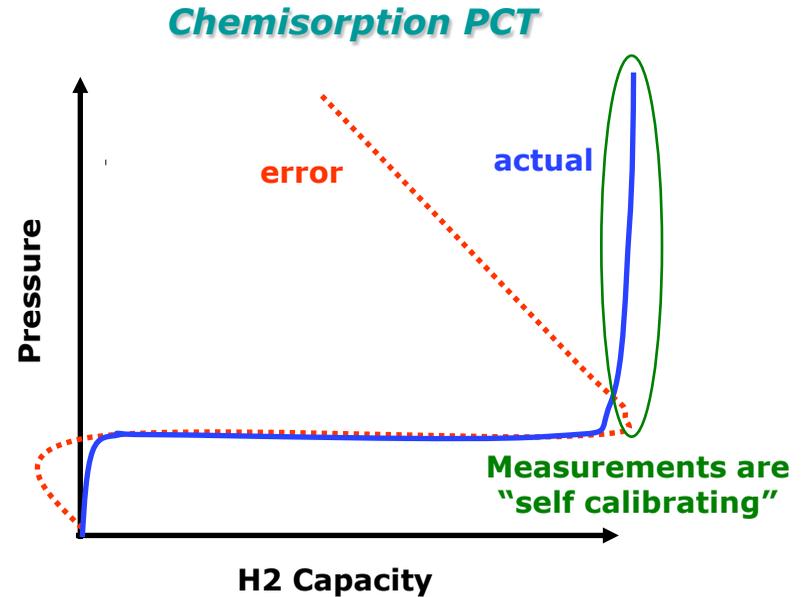
- **Add a more in-depth analysis of source and propagation of errors specifically in making Physisorption PCT measurements.**
- **Provide an in-depth evaluation of differential pressure method of making PCT or Capacity measurement specifically with respect to high-surface area materials.**
- **The results of this work will be written up and incorporated into the “Best Practices” document.**
- **Improve communication of standardized terminology and reporting practices of materials and system storage capacity**
- **Both the analysis of source and propagation of errors and the evaluation of the differential pressure method are currently underway with progress being communicated with the Best Practices project.**

Current Issues: Physisorption Storage Materials

- **Physisorption vs. Chemisorption capacity measurement errors**



H₂ adsorbed over entire pressure range



Limited Pressure range for hydrogen absorption

- **Accuracy requires proper "Null" calibration (Analysis by Phil Parilla)**
- **Clarification of terminology and reporting of materials and system storage capacity**
- **Very high surface area: subject to contamination**
- **Very low packing density: subject to estimated skeletal density errors**

Collaboration: Phil Parilla, NREL

Null Calibration Analysis

- Volume

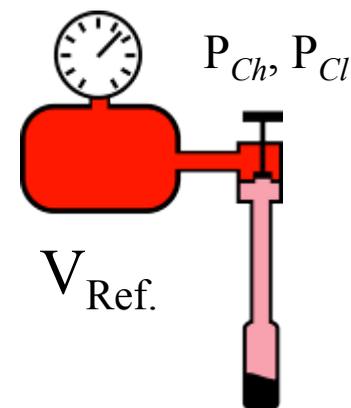
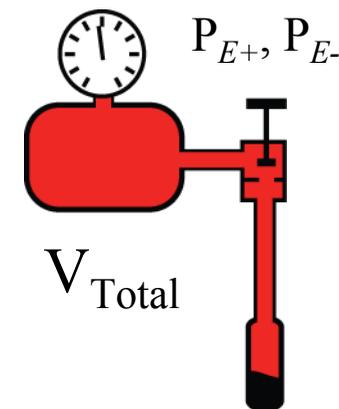
- **Absolute calibration** (V_{Ref})

- Affects absolute scale of sorption
 - Measured with an external standard
 - Can be verified with a known material

- **Null calibration** ($\gamma = V_{Tot}/V_{Ref}$)

- **This is the most critical calibration**
 - This effectively calibrates V_{Tot}
 - For Gibbsian excess, must be done for each sample
 - Measured in a no adsorption situation will determine γ
 - Verified by measuring 'zero' adsorption
 - This is equivalent to measuring $V_{skeletal}$ or $\rho_{skeletal}$

$$n = \frac{P V}{R T z(P, T)}$$

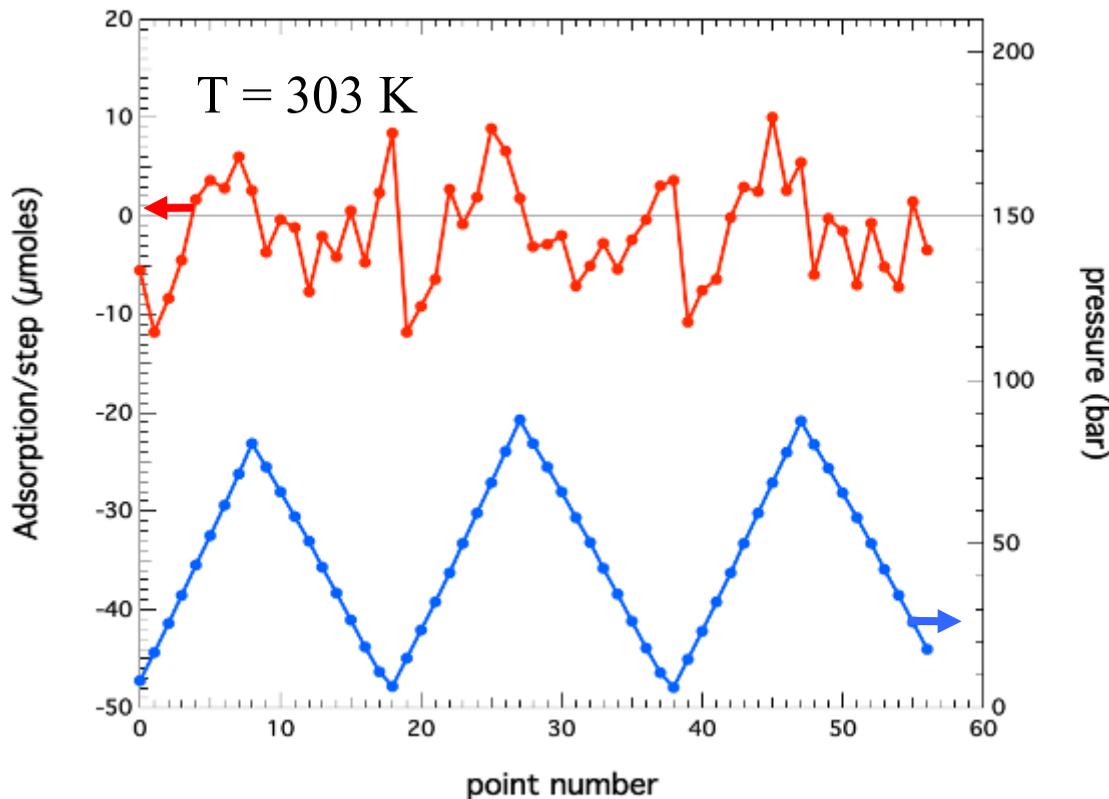


$$n_{ads} = \frac{V_{Ref}}{RT} \left[\left(\frac{P_{Ch}}{z_{Ch}} - \frac{P_{Cl}}{z_{Cl}} \right) - \gamma \left(\frac{P_{E+}}{z_{E+}} - \frac{P_{E-}}{z_{E-}} \right) \right]$$

Collaboration: Phil Parilla, NREL

Reducing Error in Physisorption Measurements

The true performance of the system is determined by measuring zero adsorption on blank or empty sample holder



- **With empty container, get calibration constants with standard procedures using He gas**
- **Then measure empty container with H₂ for ‘adsorption’**
- **This tests both the hardware and the data analysis**
- **Accumulated error here was about 70 micromoles in 56 steps**

P.A. Parilla, HSCoE Technical Exchange Meeting, 2/17/10

Collaboration: Phil Parilla, NREL Non-Isothermal Measurements

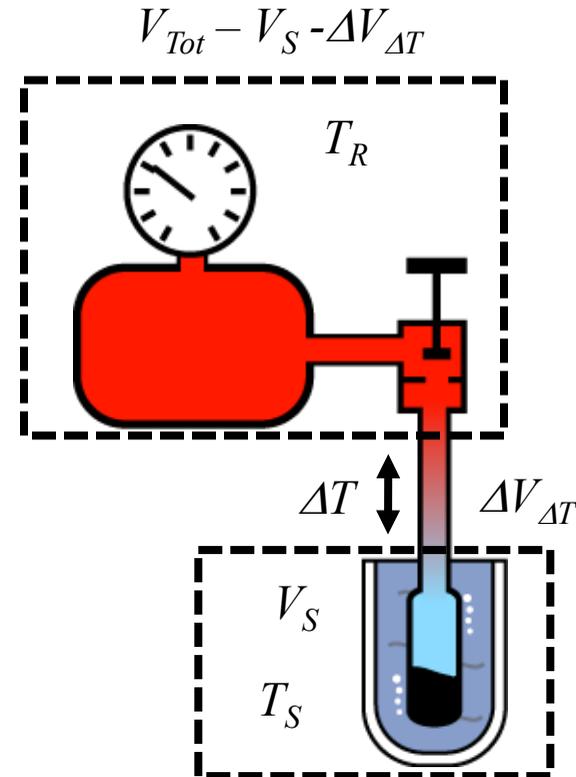
- **Still a 2-state system**

- V_{Ref} & V_{Tot}
- V_{Tot} now has 3 T zones
 - $V_{sample} = V_S$ at $T = T_S$
 - $\Delta V_{\Delta T}$ with a temperature gradient
 - Remainder is at $T = T_R$;
($V_{Tot} - V_S - \Delta V_{\Delta T}$)

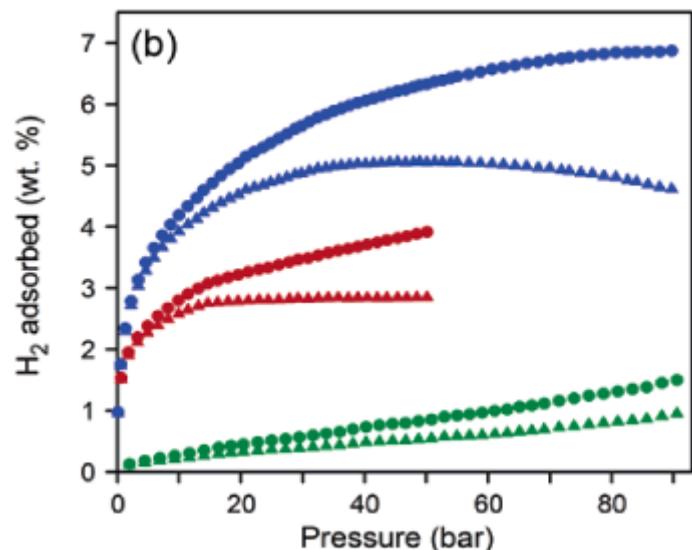
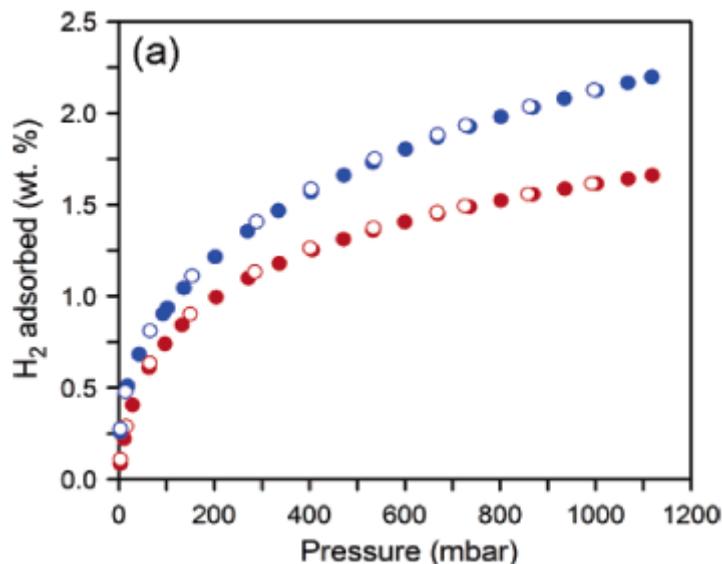
- **Temperature profile**

- Critical to keep constant over time
- Need an additional calibration step to determine V_S

- **Must determine $V_{skeletal}$ at room temperature or higher as He adsorption is too great at low T**



Elucidation of Capacity Definitions: Physisorption Materials



"Material" Hydrogen Capacity Definitions



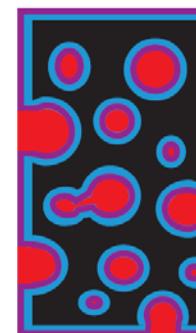
Porous Material



Excess H₂ Capacity



Absolute H₂ Capacity



Total H₂ Capacity

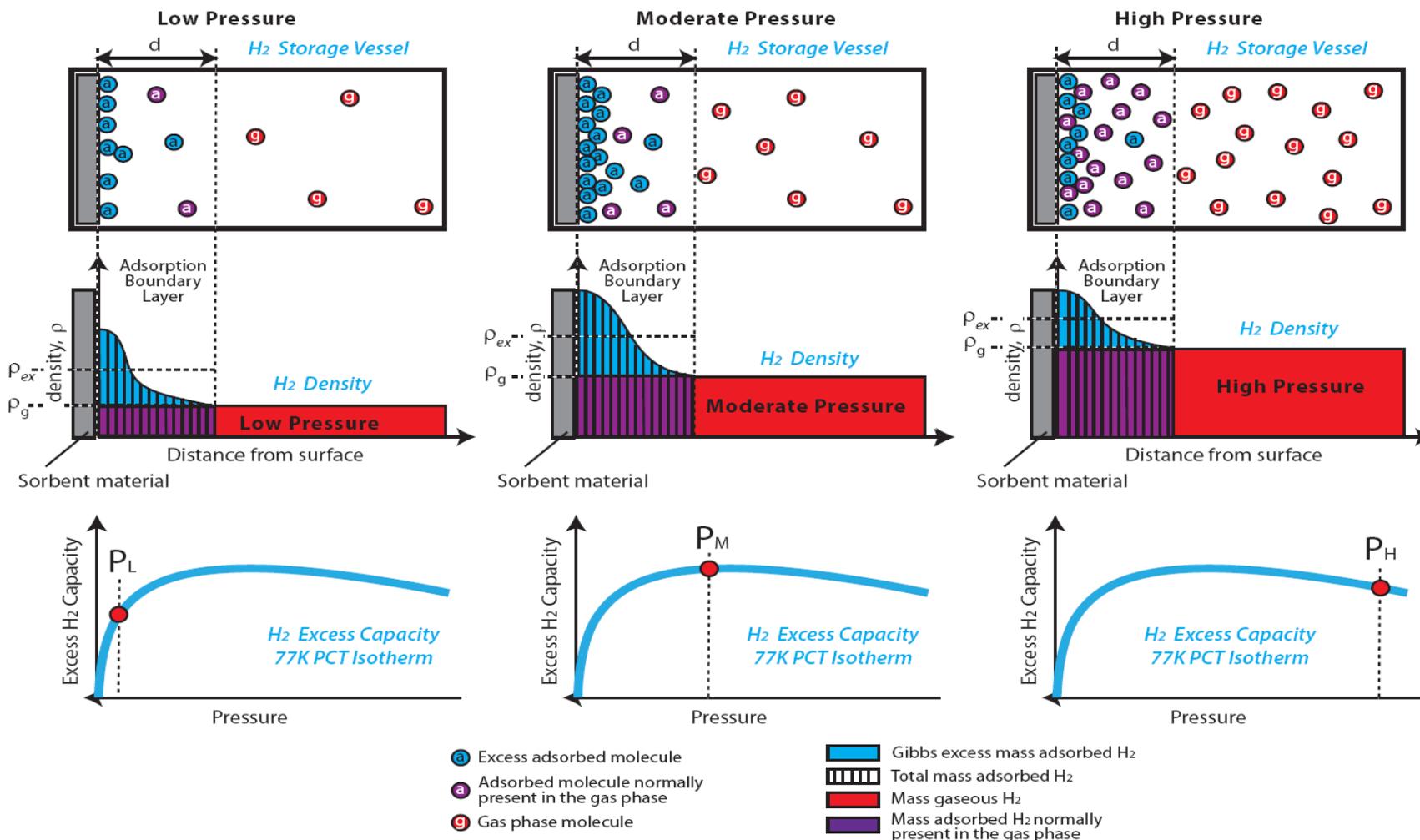
- Excess adsorbed molecule
- Adsorbed molecule normally present in the gas phase
- Gas phase molecule

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: Physisorption 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.**

- *Future Work* -

- ***Thermodynamics***

- Final version of the thermodynamics section will be incorporated into the full document and uploaded to the DOE website for public review and comment.
- Public comments will be addressed in the final versions of the full document.

- ***Cycle-life Properties***

- Final version of the thermodynamics section will be incorporated into the full document and uploaded to the DOE website for public review and comment.
- Public comments will be addressed in the final versions of the full document.

- ***Engineering Thermal Properties***

- First draft of the Engineering Thermal Properties section will be completed.
- Final draft will be reviewed by experts in the field.
- Reviewer's edits and comments of the will incorporated into the final document.

- ***Engineering Mechanical Properties***

- Outline of the first draft of the Mechanical Properties section will be completed

- ***NREL Collaboration***

- Integrate results from NREL's work on the analysis of source and propagation of errors and the evaluation of the differential pressure method into the Best Practices document (Phil Parilla).
- Integrate procedures and methodologies learned from NREL's project on Spillover investigations and characterization/validation into Best Practices (Tom Gennett and Phil Parilla).

- 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, 2, and 3 completed. Task 4, 5 and 6 in progress.
Achieving a high-level of participation from experts in the field.
- **Collaborations:** Official collaboration with NREL, multiple co-authors and International collaboration through IEA task 22 as well as industry.
- **Future Work:** Finalize Task 4 and 5 (Thermodynamic, Cycle Life measurements), complete Task 6 (Engineering Thermal Properties), begin Task 7 (Engineering Mechanical Properties), Integration of applicable NREL work.
- **Document:**

http://www1.eere.energy.gov/hydrogenandfuelcells/storage/test_analysis.html

Thank You!



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