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

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- Co-Authors -

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Differential Volumetric and Error Analysis : **Phil Parilla**
National Renewable Energy Laboratory

Measurements of Engineering Thermal Propertids : **Bruce Hardy**
Savannah River National Laboratory

- Overview -

Timeline

- Start – Feb 2007
- End – Continuing
- 97% complete

Budget

- Total project funding
  - DOE $1,208K
  - Contractor $323K
- Funding FY12 $126K
- Funding FY13 $94K

FY12 scaled back 25%

FY13 scaled back 20%

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

- 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.
- Progressive 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 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 2012/2013 -

Milestone	Results	%Comp
Complete H2 Storage Properties Sections	Final review and integration of sections 1-5 completed and delivered to DOE for upload to web.	100%
Integrate Error & dP Analysis Sections	In progress, waiting for final draft from NREL.	5%
Thermal Properties Section	Final review and integration of section 6 completed and delivered to DOE for upload to web.	100%
Mechanical Properties Section	Section 7 currently in progress. Final draft to be completed.	70%

- **Budget:** Scaled back from prior years, Deliverables unchanged, milestones spread out over longer time period.
- **Go/No-Go FY13:** If the deliverables have not been completed or are determined to provide no value to the program the project will be terminated.

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- 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.

Completed / In Progress

- 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. (All sections)
  - 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, Dr. Frederick Pinkerton, and Dr. Scott Jorgensen of General Motors GM. (Capacity, Engineering properties sections)
  - 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 Properties sections)
  - Dr. Renju Zacharia, Université du Québec à Trois-Rivières, Canada, IEA Task 22. (Thermodynamics section)
  - Dr. Tom Autrey, Dr. Scot Rassat, andDr. Ewa Rönnebro, Pacific Northwest National Laboratory, Richland WA, USA. (Thermodynamics section)
  - Dr. Maximilian Fichtner, Karlsruher Institute for Technology, Germany, IEA Task 22. (Engineering Thermal and Mechanical Properties sections)
  - Dr. Robert Bowman Jr., Consultant to U.S. Department of Energy. (Cycle Life, Engineering Thermal Properties sections)
  - Dr. Ewa Rönnebro, Pacific Northwest National Laboratories, USA. (Engineering Thermal Properties section)
  - Dr. Bart van Hassel, United Technologies Research Center, USA. (Engineering Thermal Properties section)
  - Dr. Lars Röntzsch, Fraunhofer Institute for Manufacturing Technology and Advanced Materials, Dresden, Germany. (Engineering Thermal Properties section)
  - Dr. Michel Latroche, Institut de Chimie et des Matériaux de Paris Est CNRS, France, IEA Task 22. (Engineering Thermal Properties section)
  - Dr. Patricia De Rango, Institut Néel CNRS, Grenoble, France, IEA Task 22. (Engineering Thermal Properties section)
  - Dr. Mike Veenstra, Dr. Jun Yang, and Dr. Andrea Sudik, Ford Motor Co., USA. (Engineering Thermal Properties section)
  - Dr. Bruce Hardy, Savannah River National Laboratory, USA. (Engineering Thermal Properties section)
  - Professor David Grant and Dr. Alastair Stuart, of the University of Nottingham, United Kingdom, IEA Task 22 (Engineering Thermal Properties section)

- Key Accomplishments -

2007 – 2012:

- ***Task 1: Final Introduction section 100% completed.***
- ***Task 2: Final Kinetics section 100% completed.***
- ***Task 3: Updated Capacity section, with review of Spillover by Tom Gennett and Phil Parilla (NREL) and Channing Ahn (CalTech) 100% completed.***
- ***Task 4: Final Thermodynamic section 100% completed.***
- ***Task 5: Final version Cycle Life 100% completed.***
- ***Task 6: Engineering Thermal Properties section 100% completed.***

2012 – 2013:

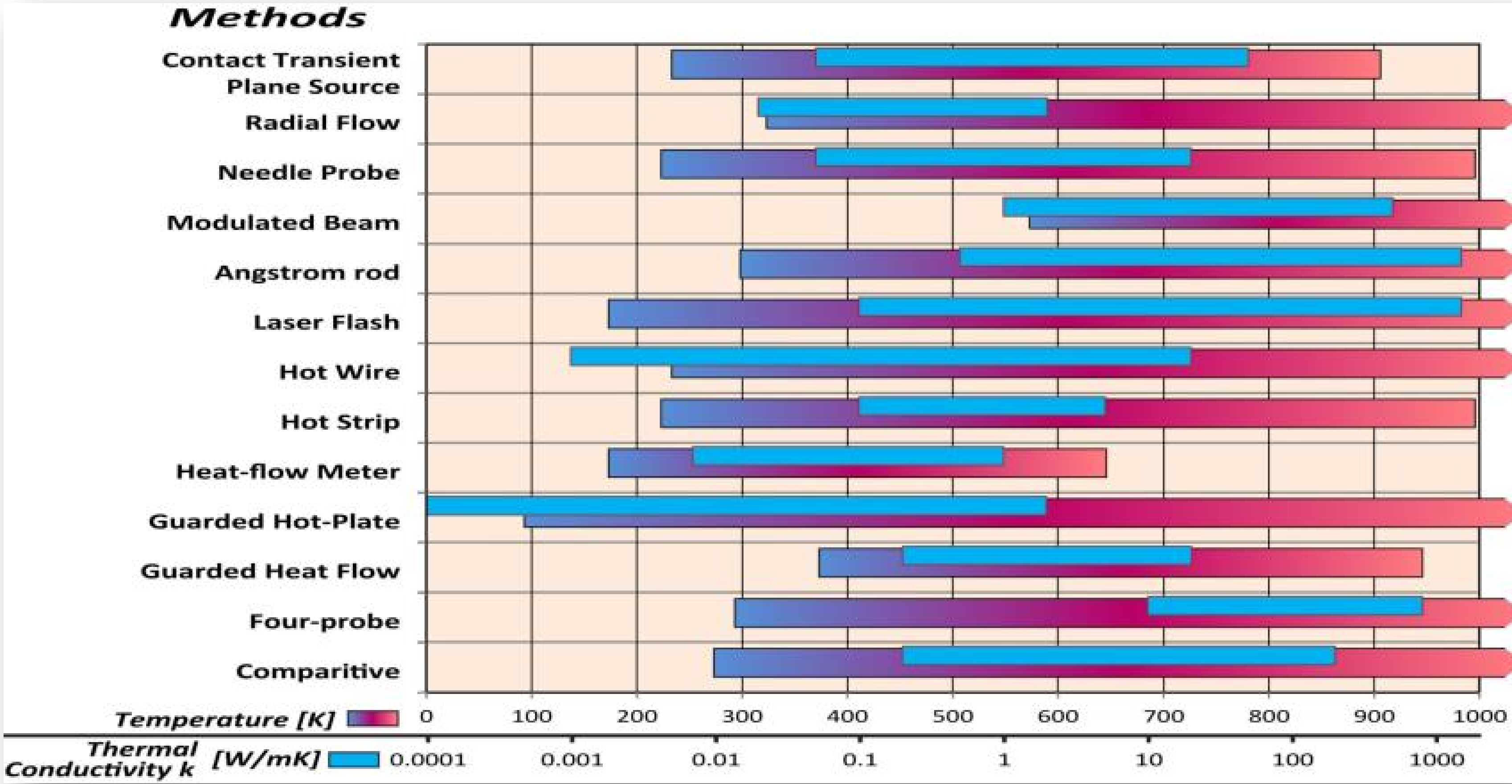
- ***Finalized integrated Tasks 1-5 Document posted to DOE website for world-wide access.***
- ***Final Task 6 Engineering Thermal Properties section Delivered to DOE February 2013.***
- ***Task 7: Engineering Mechanical Properties in progress.***

Please download the current Best Practices document from:

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

- Technical Accomplishments -

Section 6: Measurements of Engineering Thermal Properties of Hydrogen Storage Materials



Typical measurement methods for differing ranges of Thermal Conductivity and measurement temperatures.

(ranges may vary for specifically designed measurement systems)

Adapted from: Evitherm.org article, "Measurement Methods", http://www.evitherm.org/
Wikipedia article "Thermal Conductivity", http://en.wikipedia.org/wiki/Thermal_conductivity

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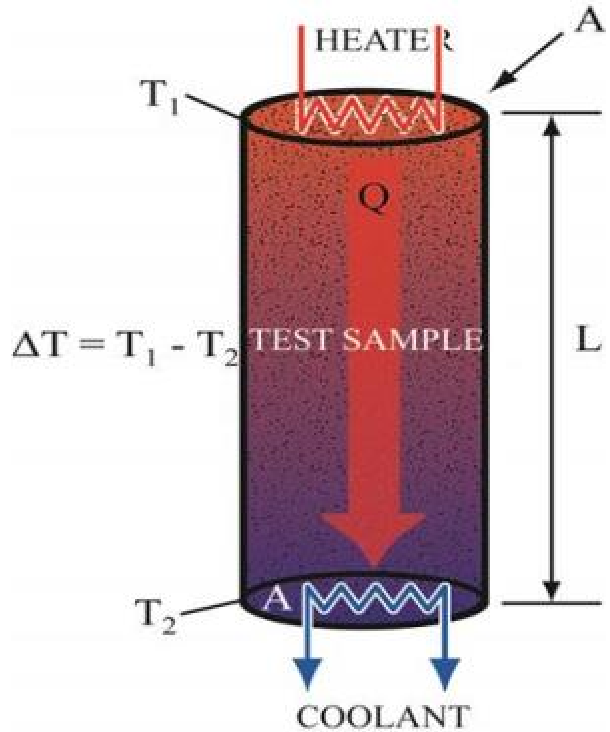
Example 1: Measurements Methods - Engineering Thermal Properties of Hydrogen Storage Materials

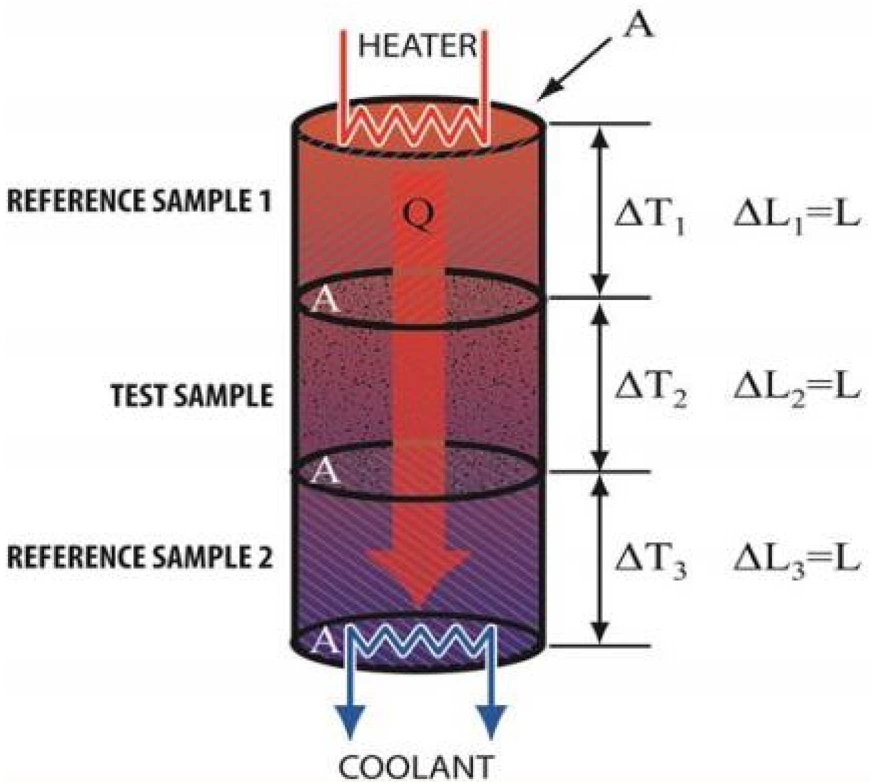


Simple Schematic of Axial Heat Flow Method.

$$Q = k\,A\,\Delta T\,/\,L$$

- **Thermal conductivity, k, can be determined by measuring Q, ΔT, A, and L** (Where k is the thermal conductivity, A is the surface area in the axial direction of the sample, ΔT is the temperature change from one end to the other in the sample, and L is the length of the sample. The heat flux Q can be measured either directly or indirectly).

Example 2: Measurements Methods - Engineering Thermal Properties of Hydrogen Storage Materials



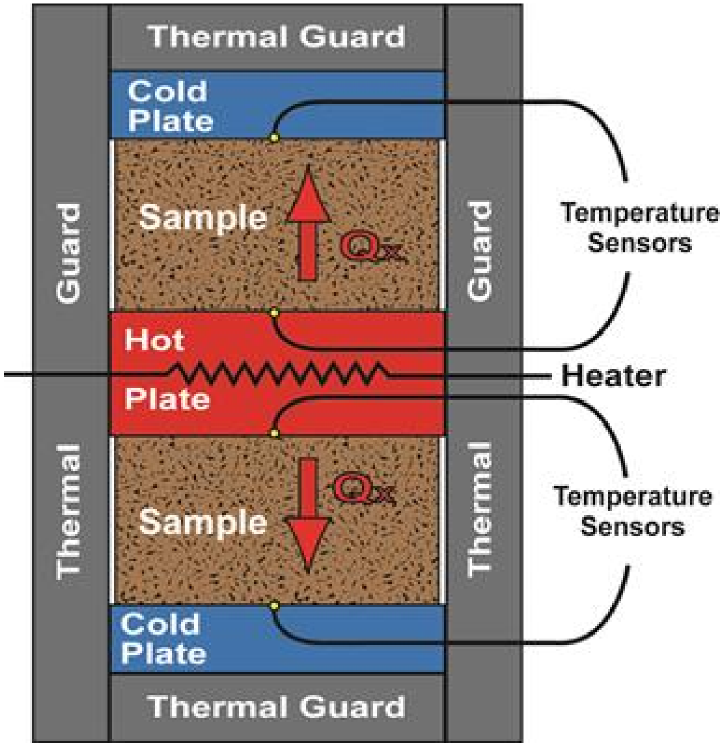
$$k_S = k_R\left(\frac{\Delta T_1 + \Delta T_3}{2\Delta T_2}\right)$$

Where k_R is the known thermal conductivity of the reference material in the flux gauge, ΔT_1 and ΔT_3 are the temperature differences across two identical reference materials in the flux, and ΔT_2 is the temperature difference in the axial direction between the two ends of the sample.

Simple Schematic of Comparative Method.

- **In comparative thermal conductivity measurements, a standard material with a known thermal conductivity and precise thickness is placed in series with the sample to be measured. The heat flux through the standard material can be calculated fairly accurately by measuring the temperatures on each side of the standard.**

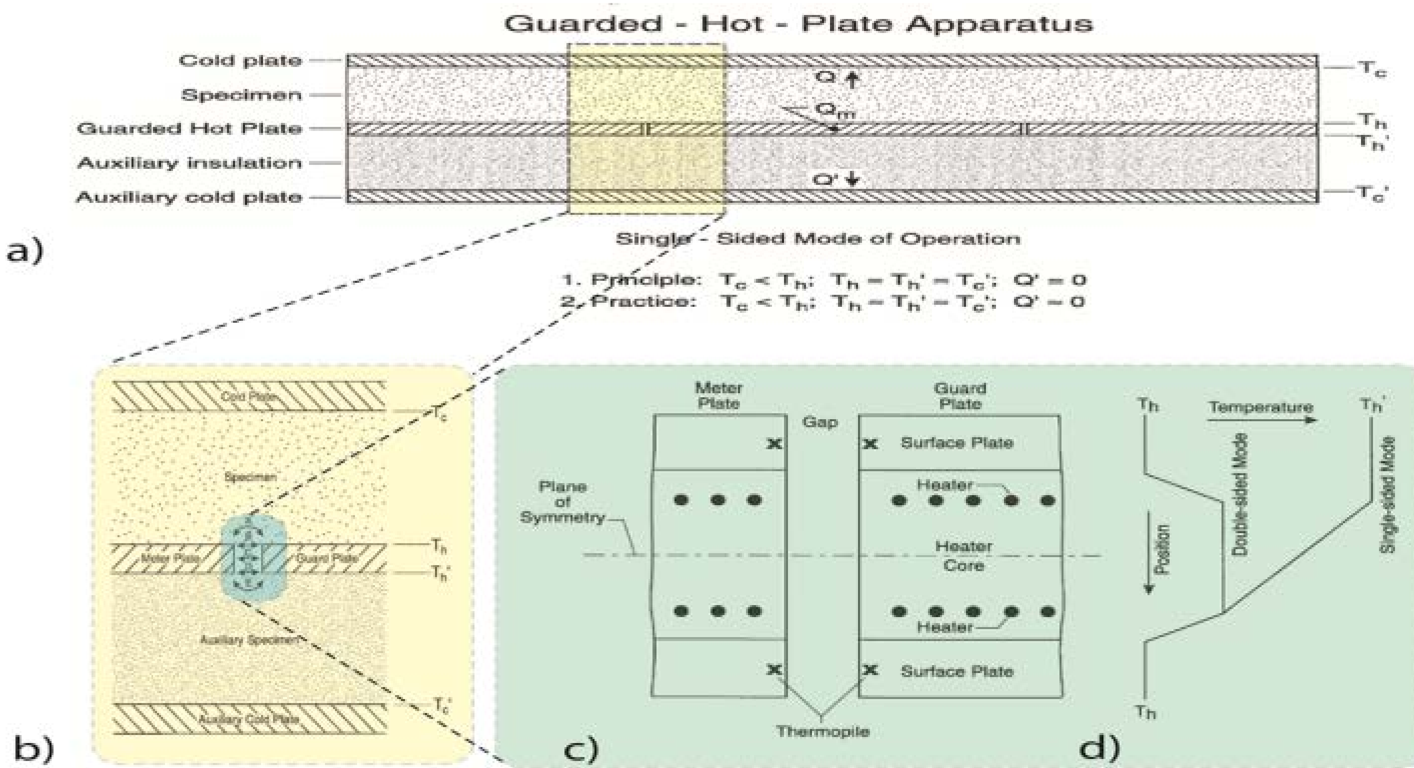
Example 3: Measurements Methods - Engineering Thermal Properties of Hydrogen Storage Materials



Schematic of Basic Guarded Hot Plate Design.

- **The Guarded Hot Plate method uses unidirectional heat transfer through a pair of identical samples. A temperature gradient within each sample is formed by producing a known heat flux to a hot plate between the samples while providing a heat sink at a cold plate on the opposite side of each sample. The temperatures at each side of the samples are measured when the system reaches steady state. Using the heat flux, sample thickness and surface areas, and temperature measurements, Fourier's unidirectional heat conduction equation can then be applied to easily calculate an effective thermal conductivity for the samples.**

Details of Error Reduction in Design of Advanced Guarded-Hot Plate Instruments

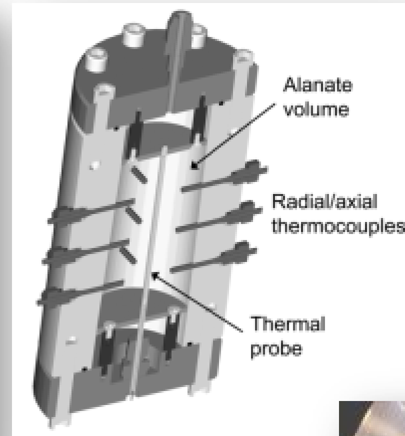


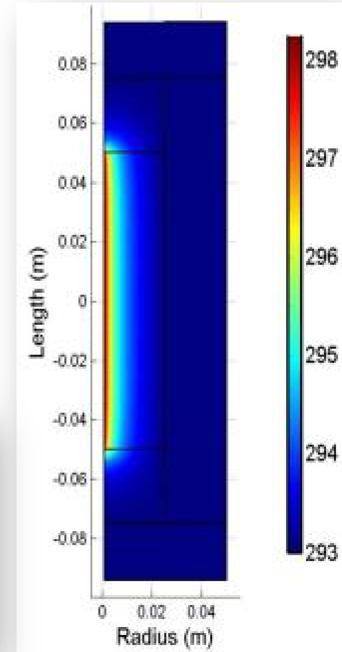
a) Schematic diagram of an advanced single-sided mode of operation Guarded-Hot-Plate apparatus, b) heat flows at gap region, c) hypothetical Guarded-Hot-Plate with distributed heat source, and d) Corresponding temperature profile for double- and single-sided mode of operation.

- **Heat leaks lead to error in the determination of Thermal Conductivity.**
- **Today's equipment is expected to employ advanced methods for reducing such sources of error.**

Adapted from"Standard Practice for Using a Guarded-Hot-Plate Apparatus or Thin-Heater Apparatus in the Single-Sided Mode", ASTM International, Designation: C 1044 – 98, Reapproved (2003), standard downloaded from www.bzfxw.com

Example: In-Situ Measurement System





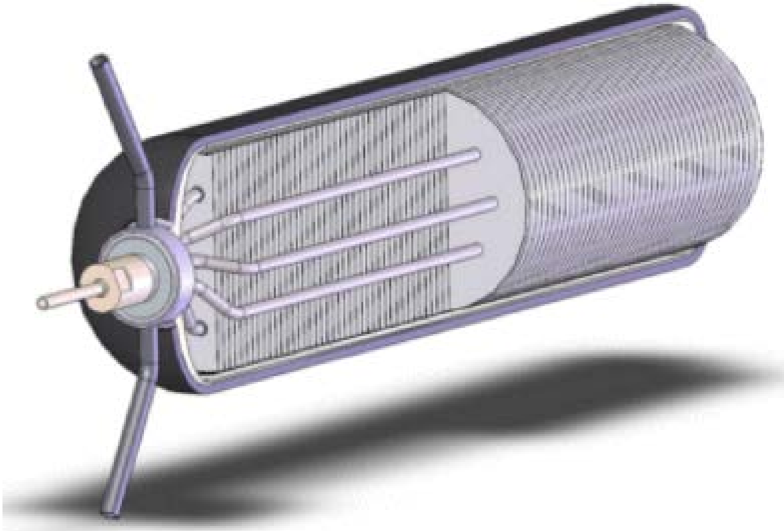
Instrumented chamber to measure: Thermal conductivity and wall resistance as a function of phase, temperature, cycle, morphology, and pressure.

- **Ideally one would like to measure the thermal conductivity of hydrogen storage materials "In-situ", preferably, under different hydrogen pressures, temperatures, hydrogen contents, and after progressive cycling.**
- **This significantly narrows the field of methods that are applicable to such measurements.**

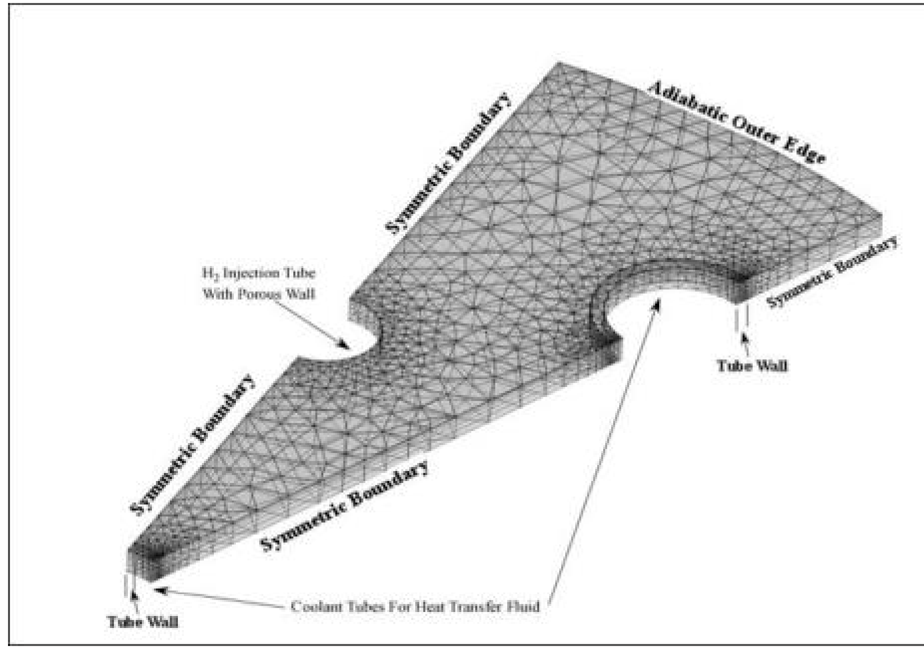
K. Gross et al. "Hydride Development for Hydrogen Storage", DOE Hydrogen and Fuel Cells Annual Merit Review, Berkeley, CA May 19-22, 2003. Dedrick, D.E., Kanouff, M.P., Replogle, B.C. and Gross, K.J., "Thermal properties characterization of sodium alanates", J. Alloys and Compounds, Vol. 389, (2005) p. 299–305.

Modeling: the Need for Acurate Experimental Data

Example Study - Configuration



Example of a Shell, Tube and Fin Hydride Bed Configuration.[1]



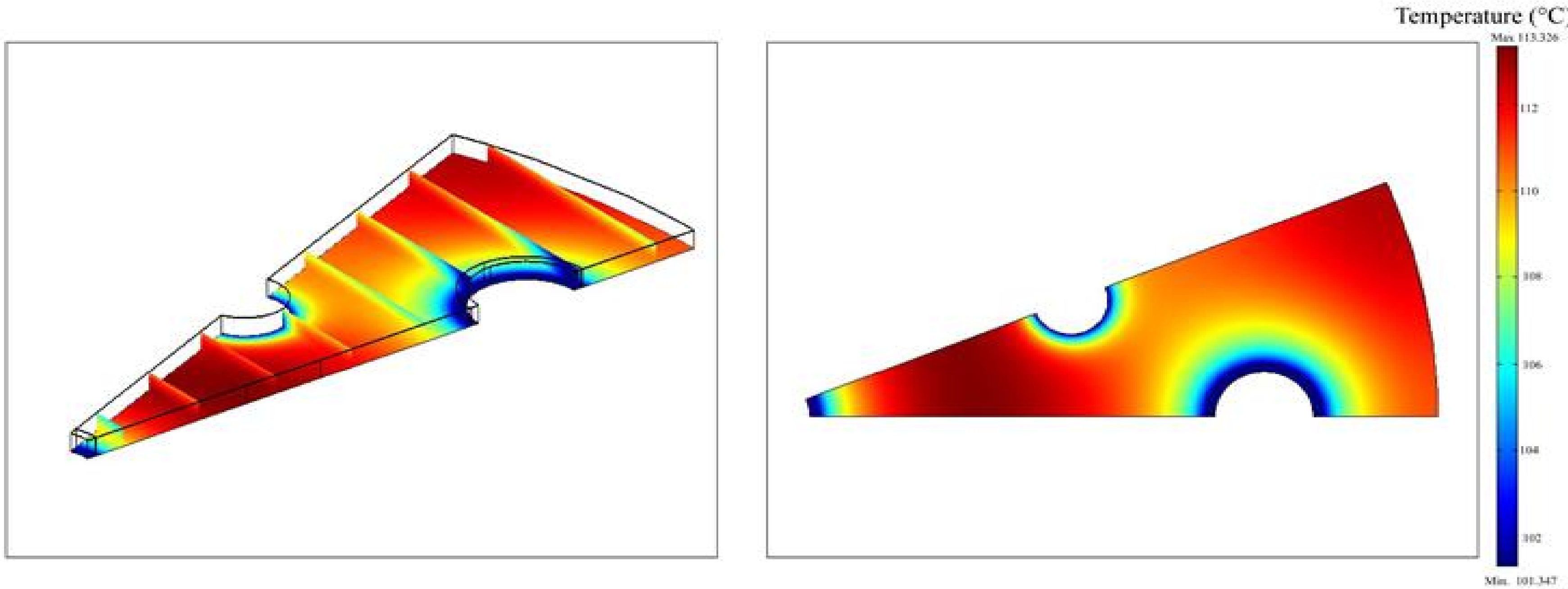
Geometry for a 3-dimensional Shell, Tube and Fin Computations Model.[2]

- **As an example, detailed 2 and 3-dimensional finite element models were applied to a storage system utilizing $TiCl_3$ catalyzed sodium alanate ($NaAlH_4$).[2] The storage system had the configuration of a cylindrical shell, tube and fin heat exchanger. The low thermal conductivity of the alanate necessitated design features that maintained a relatively short length scale for heat transfer within the bed.**

1: Mosher, D., Tang, X., Arsenault, S., Laube, B., Cao, M., Brown, R. and Saitta, S. "High Density Hydrogen Storage System Demonstration Using NaAlH4 Complex Compound Hydrides". DOE Hydrogen Program Annual Peer Review, Arlington, VA, 2007. 2: Hardy, B.J., Anton, D.L. "Hierarchical methodology for modeling hydrogen storage systems. Part II: Detailed models". Int. J. of Hydrogen Energy, 34 (2009), p. 2992-3004.

Modeling: the Need for Acurate Experimental Data

Example Study - Results

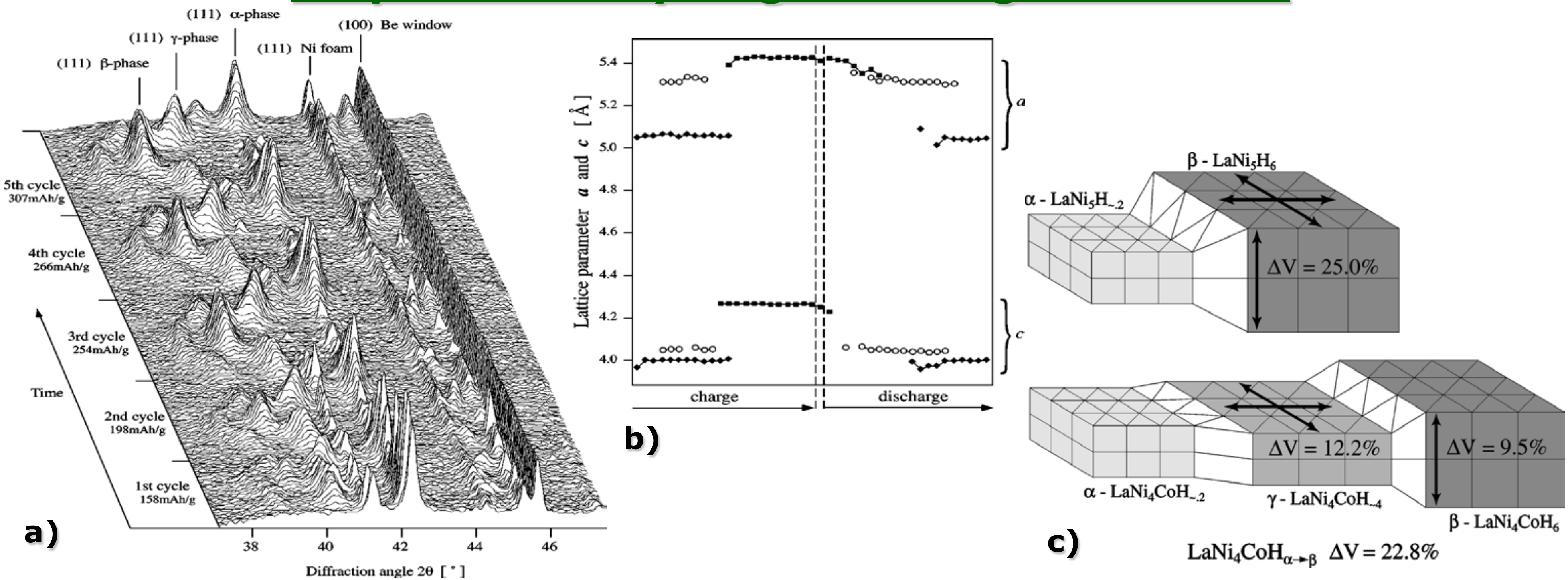


Isometric and plan views of temperature profile for 3D model at 40 seconds. Base of isometric figure is at bed mid-plane (center of the hydride bed layer between fins).

- **The image (left) shows the reduction in temperature from the mid-plane of the hydride layer to the mid-plane of the fin. The plan view (right) shows the temperature profile over the mid-plane of the hydride layer. Such modeling aids in understanding and designing for large temperature gradients in hydride-based storage beds. An important requirement is the input of accurately measured parametric data.**

Hardy, B.J., Anton, D.L. "Hierarchical methodology for modeling hydrogen storage systems. Part II: Detailed models". Int. J. of Hydrogen Energy, 34 (2009), p. 2992-3004.

Section 7: Measurements of Engineering Mechanical Properties of Hydrogen Storage Materials

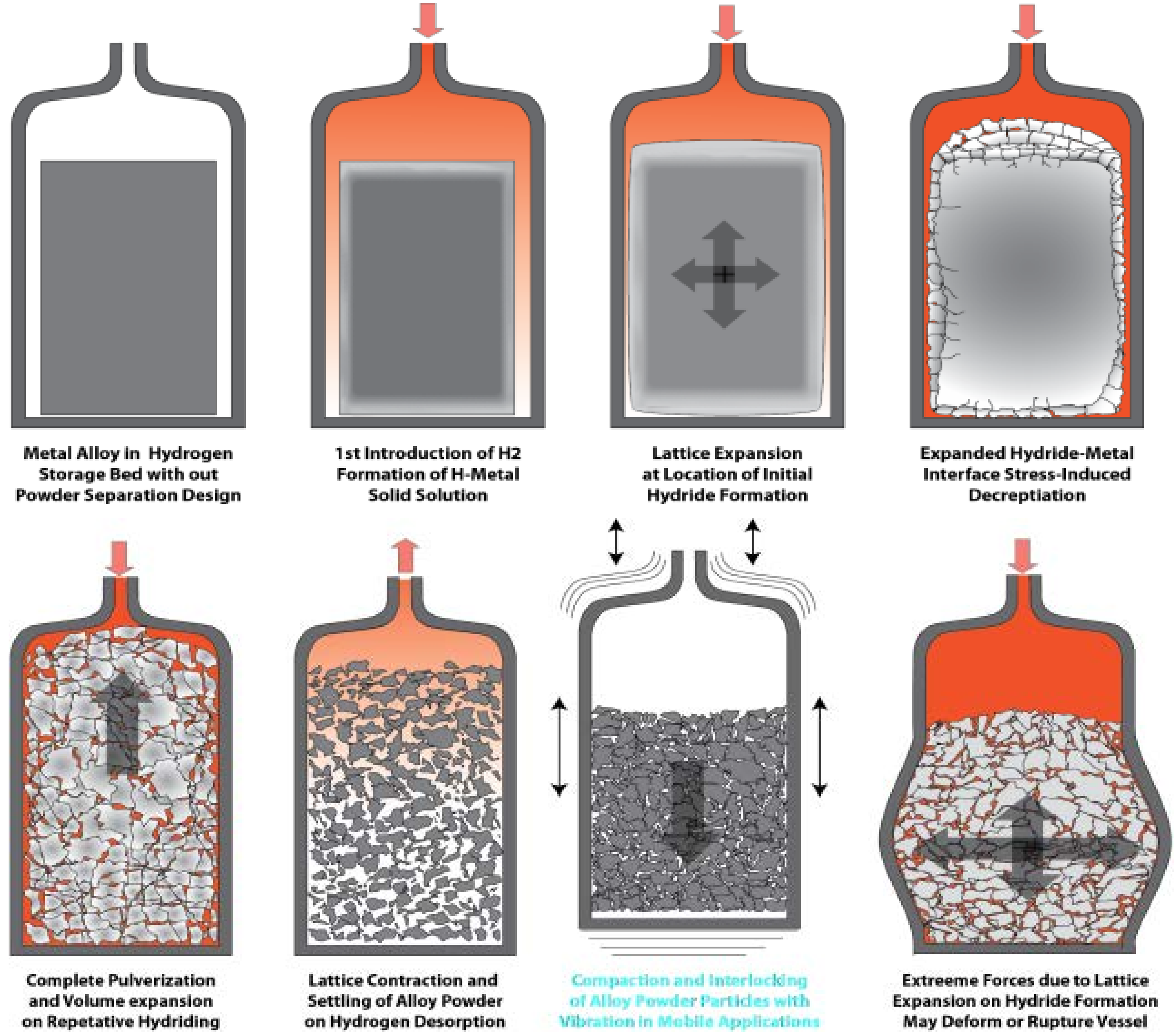


a) A compiled series of *in situ* XRD measurements during electrochemical hydriding of the alloy $LaNi_4Co$ showing phase changes and the structural behavior of the active material, b) Calculated lattice parameters a and c during charge and discharge of (♦) α and (▪) β-phases, and c) Schematic representation of the two-step lattice expansion associated with the α-to-γ and the γ-to-β phase transitions.

- **Lattice volume expansion on hydriding has a significant impact on the mechanical properties of hydride storage materials. *In situ* X-ray and Neutron diffraction provide details of volume changes during hydriding.**

Daniel Chartouni adn Karl Gross "Phase Transitions in LaNi4Co during Electrochemical Cycling An In Situ X-Ray Diffraction Study", J. Electrochem. Soc. 2001 volume 148, issue 3, p. 241-248

Potential Impact of Mechanical Properties of Hydrides



Schematic Illustration of Hydride Expansion in Confined Storage Vessel.

- **Measurements of lattice expansion on hydriding is important for designing storage beds to accommodate volume expansion.**

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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.**

- Future Work -

- ***Engineering Mechanical Properties***
  - Final draft of the Mechanical 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.
- ***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).
- ***Gas Permeability Measurements of Hydrogen Storage Materials***
- ***Compatibility Measurements of Containment Materials***

Current Project / ***Potential Future Work***

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- 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, Cycle Life, Engineering Thermal Properties, and Engineering Mechanical Properties Measurements.
- ***Accomplishments:*** Task 1, 2, 3, 4, 5, and 6 completed. Task 7 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 (32) as well as industry.
- ***Future Work:*** FY2012 - Finalize Task 7 (Engineering Mechanical Properties), and Integration of applicable NREL work.
- ***Document:***

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

Thank You!

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