Best Practices for Characterizing Hydrogen Storage Properties of Materials

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Overview

Timeline

- Start - Feb 2007
- End - Sept 2007
- 30% complete

Budget

- Total project funding

  DOE $160K for FY07

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, Review

  and Contract Management
- University of California Berkeley
- IEA Task 22, Dr. Kuriyama AIST, Japan
- Review by other experts IEA Task 22

Objectives

What ?

- ***To prepare a reference document detailing best practices and limitations in measuring hydrogen storage properties of materials***
- Document to be reviewed by experts in the field (IEA/IPHE,etc.)
- 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

- 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.

Approach - Overview

- **Task 1: 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 2: 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 3: 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 4: 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 1: Kinetics Measurements

1) Definitions

- **Sorption:** Adsorption, Absorption, Desorption
- **Materials:** Metal Hydrides, Chemical Hydrides, Adsorption Materials

  Classes of materials overlap, but from a practical perspective can be divided between on-board and off-board reversible and from a mechanistic perspective can be further divided between: chemisorption, physisorption and something in-between
- **Capacity:** wt.%, mole H2, H/f.u., Standard liters H2

  Reversible, Usable, or Total Capacity

  What is standard? (wt.% vs. wt. ratio), ex. "excess hydrogen"

  How does this impact kinetics? Ex. Practical vs. mechanistic
- **Kinetics:** Practical vs. mechanistic rates (e.g. H2 % active vs. total capacity)

2) Purpose of measurements

- Practical measurements vs.
- mechanistic measurements

Task 1 cont.

3) Measurement methods

- Volumetric
- Gravimetric
- TPD, TPR, DTA, DSC, TEOM ….

4) Factors impacting measurements

- Activation
- Sample size
- Heat of formation $\rightarrow$ temperature excursions
- Heat transfer
- Delta P driving potential
- Performance link between kinetics and thermodynamics

5) Kinetic mechanisms

- Theory
- General limitations of applicability

6) Introduction to methods to improve kinetics

- Diffusion limited: Particle size reduction (nano)
- Dissociation: Catalysts
- Adsorption: Surface accessibility and transport

Key Accomplishments

- ***Task 1: Kinetics document 70% complete***

  – Compiled example measurements from the literature, to illustrate key issues associated with the four tasks outlined above.

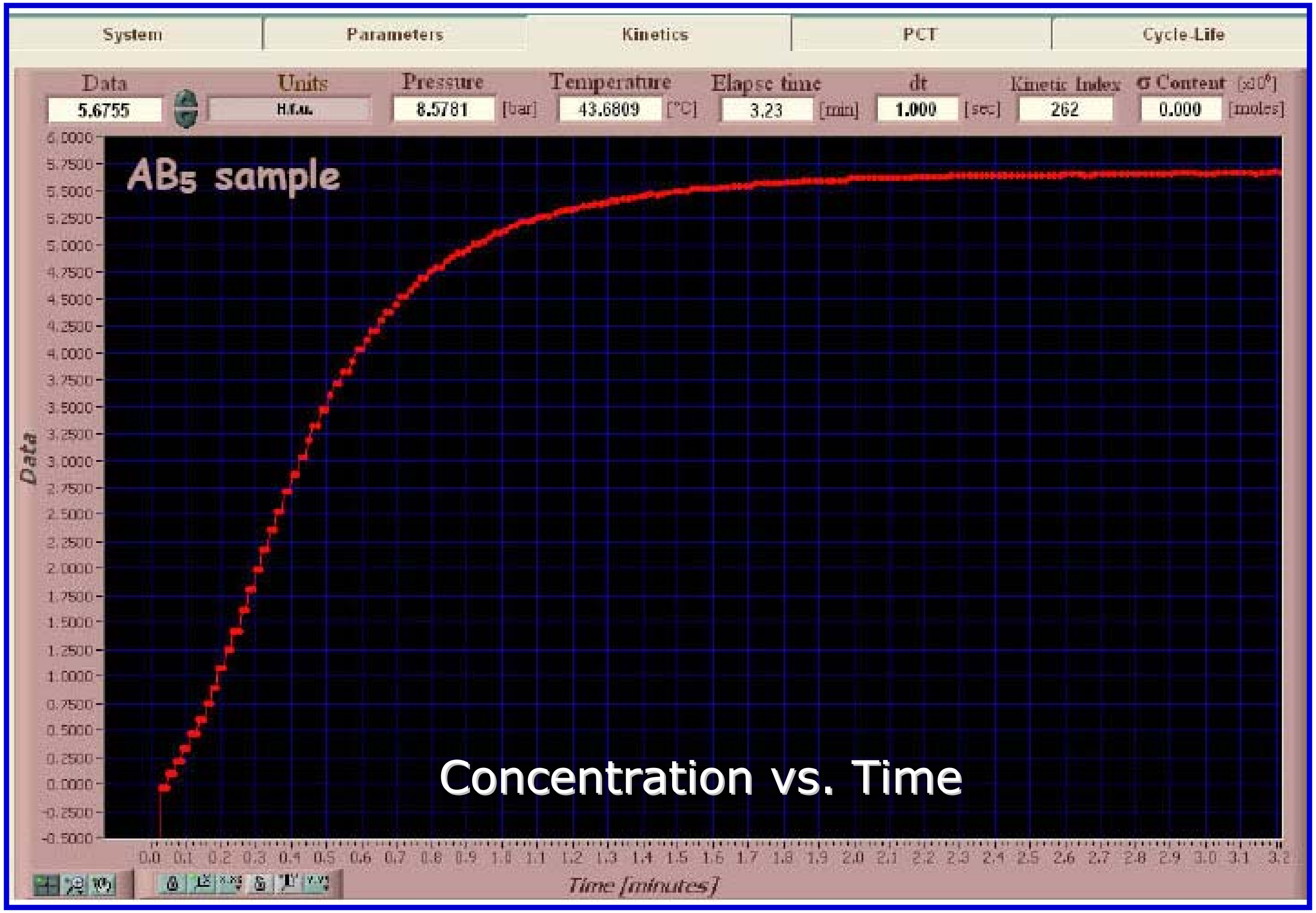
  – Performed example measurements on classic hydride materials to illustrate key issues associated kinetics and other measurements.

  – Materials included in presentation for project H-27 “International standardized testing practices for hydrogen storage materials” IEA HIA Task 22 Expert Workshop for fundamental and applied hydrogen storage materials development. 28 January – 1 February Monterey, California, USA.

  – Within IEA established collaboration with Dr. Nobuhiro Kuriyama and Dr. Tetsu Kiyobayashi of AIST (Advanced Industrial Science and Technology) Osaka, Japan.

  – Contributions to this project from world experts have been received including written materials, examples, presentation or editorial review of draft documents.

What are Kinetics Measurements ?

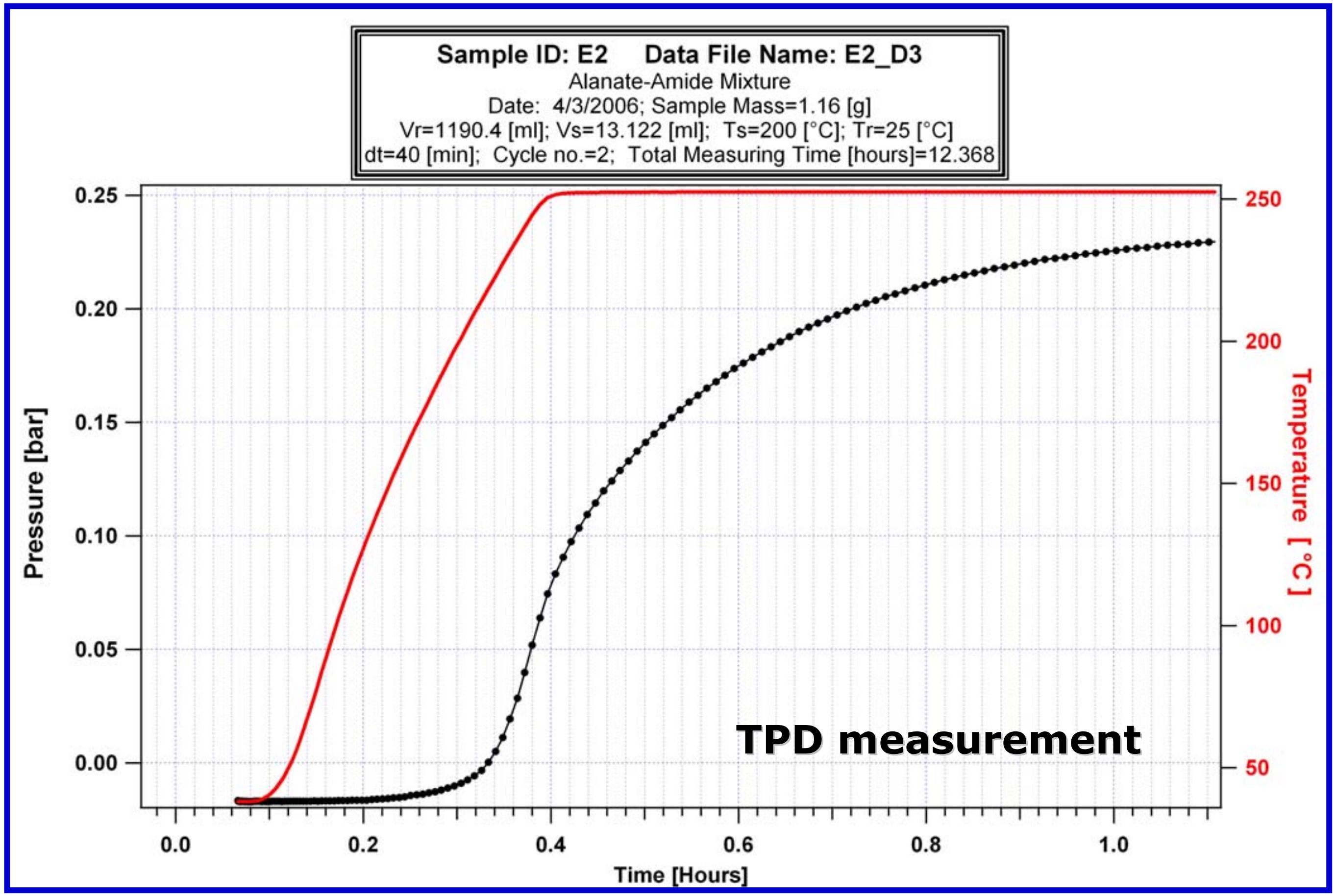


- **Classic Kinetics Measurement**
- **Intermetallic hydride ~ single phase transition**

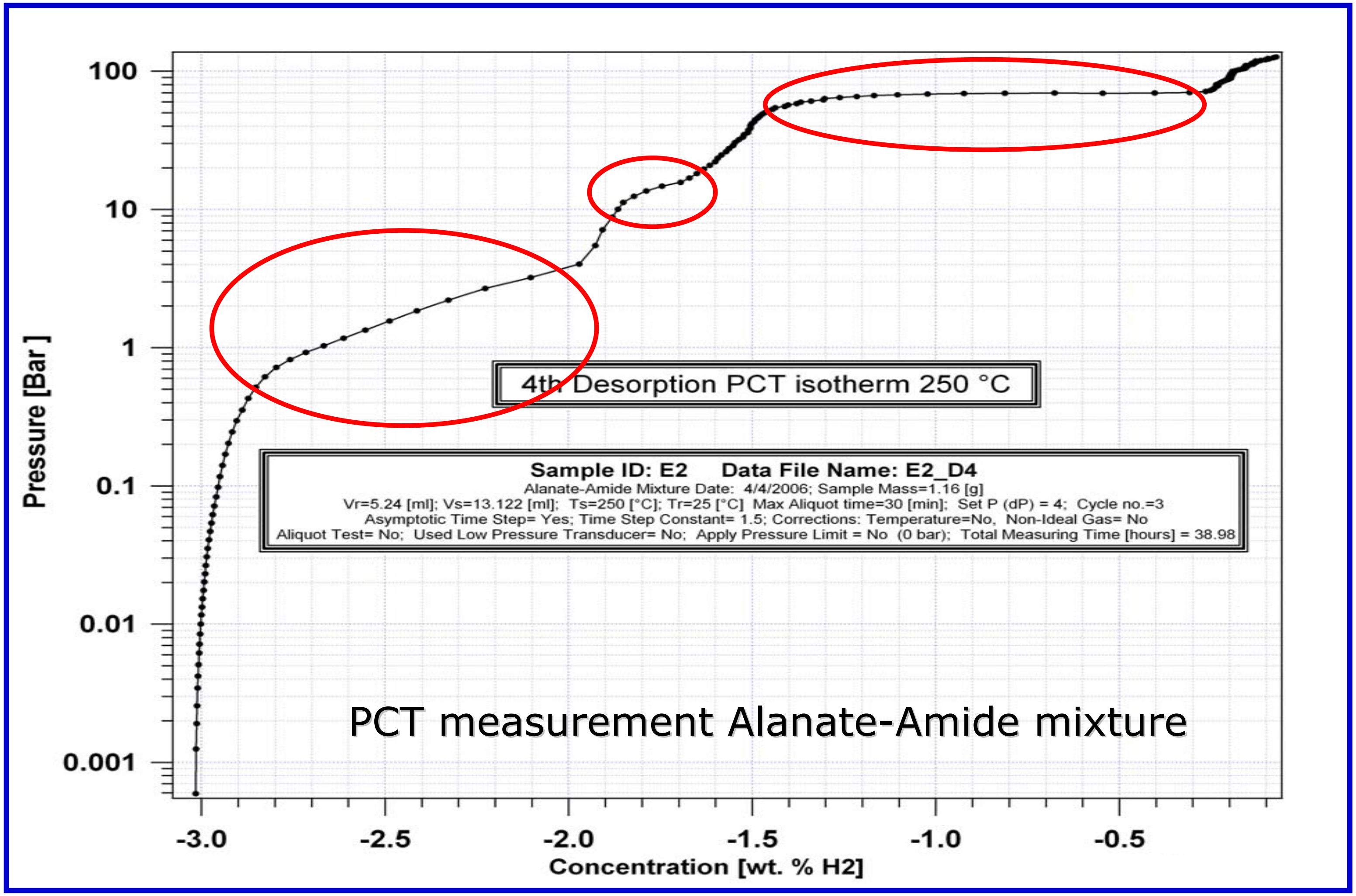
Hy-Energy Scientific

Example: Today's Materials - Complex systems!

Alanate–Amide mixtures

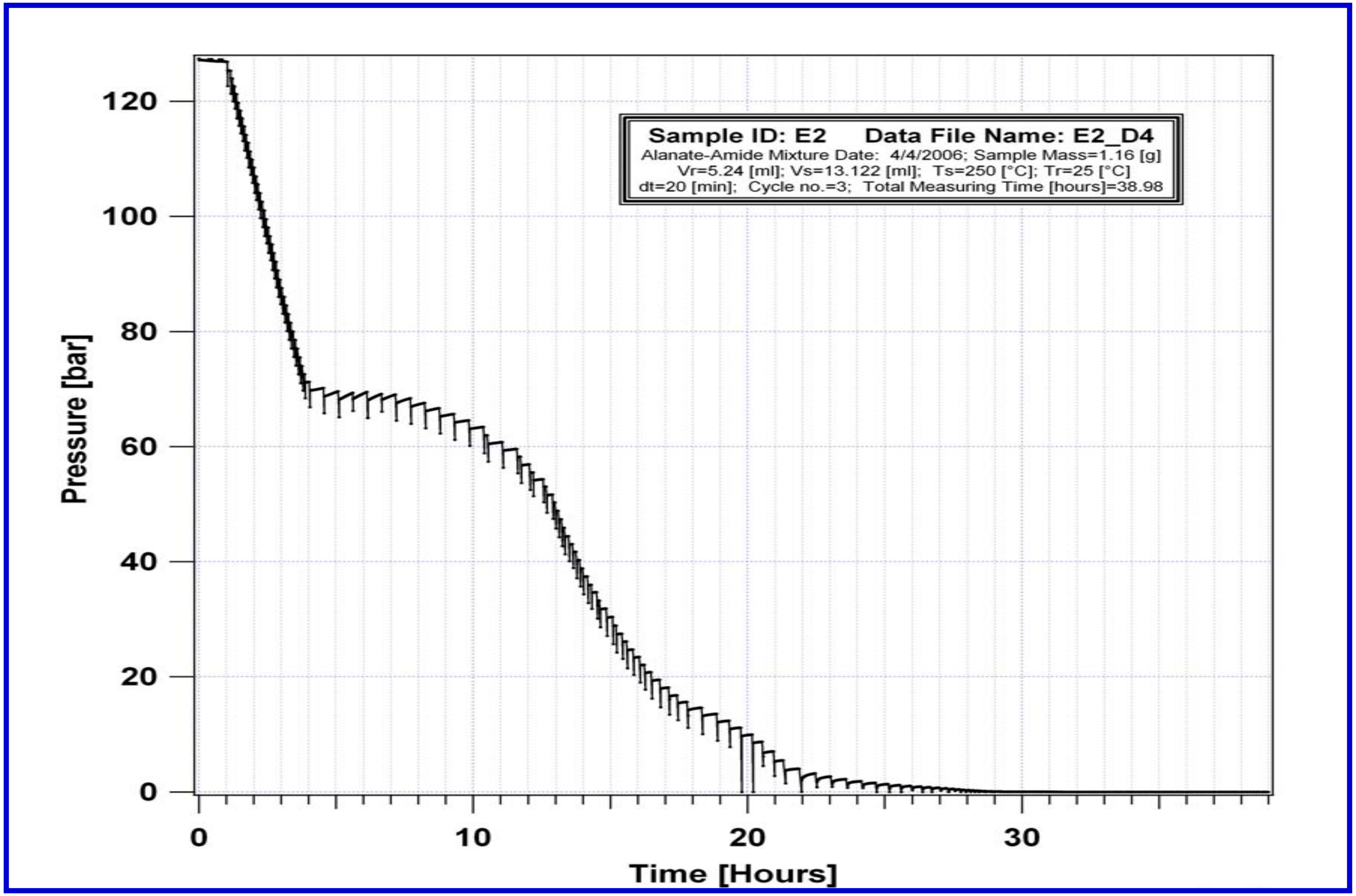


- **One or multiple reactions ?**
- **Only Hydrogen released ?**



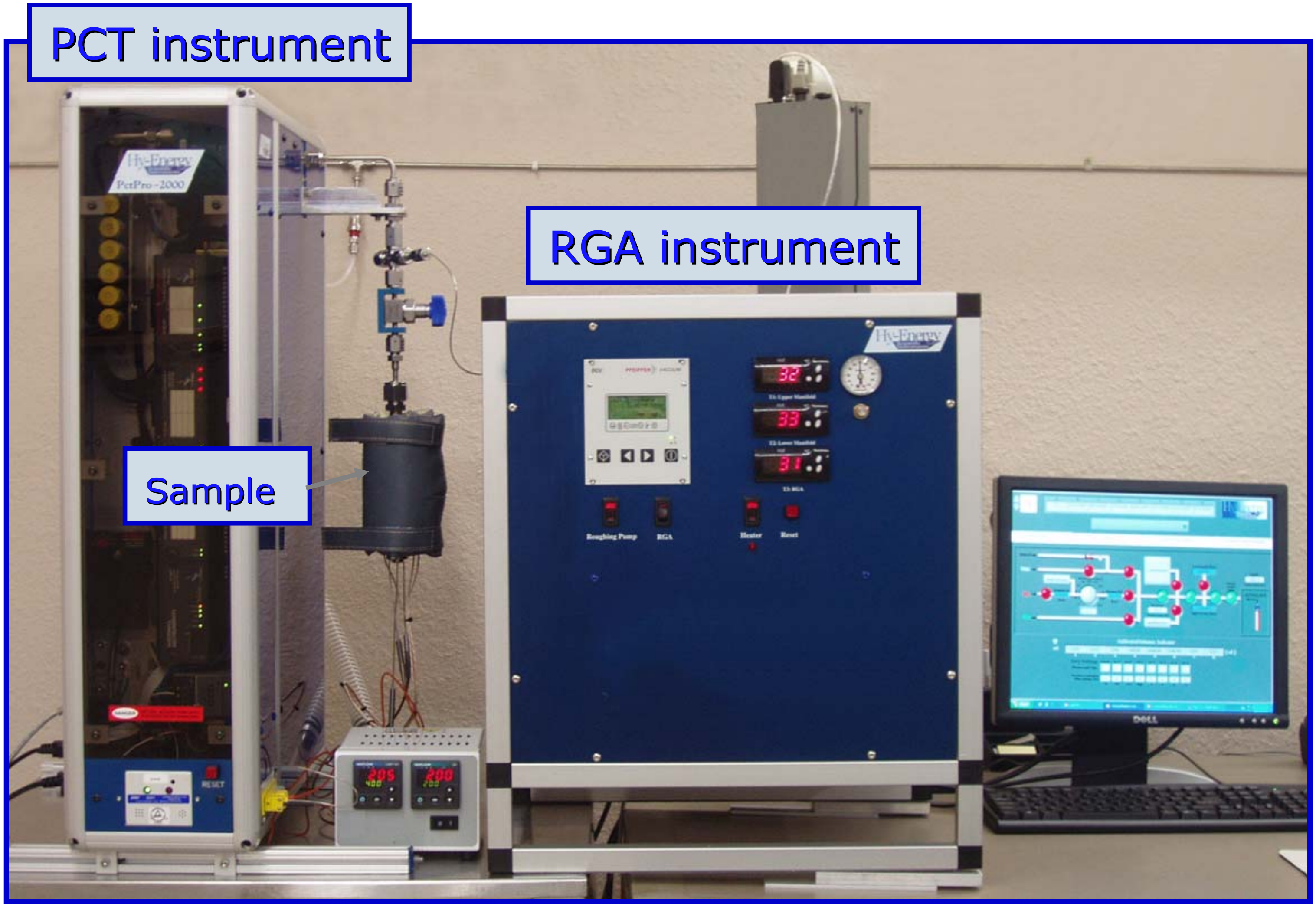
- **Multiple reactions apparent**
- **Wide range of Thermodynamic Stability**
- **Each contributes to total observed kinetics**

PCT measurement Alanate-Amide mixture



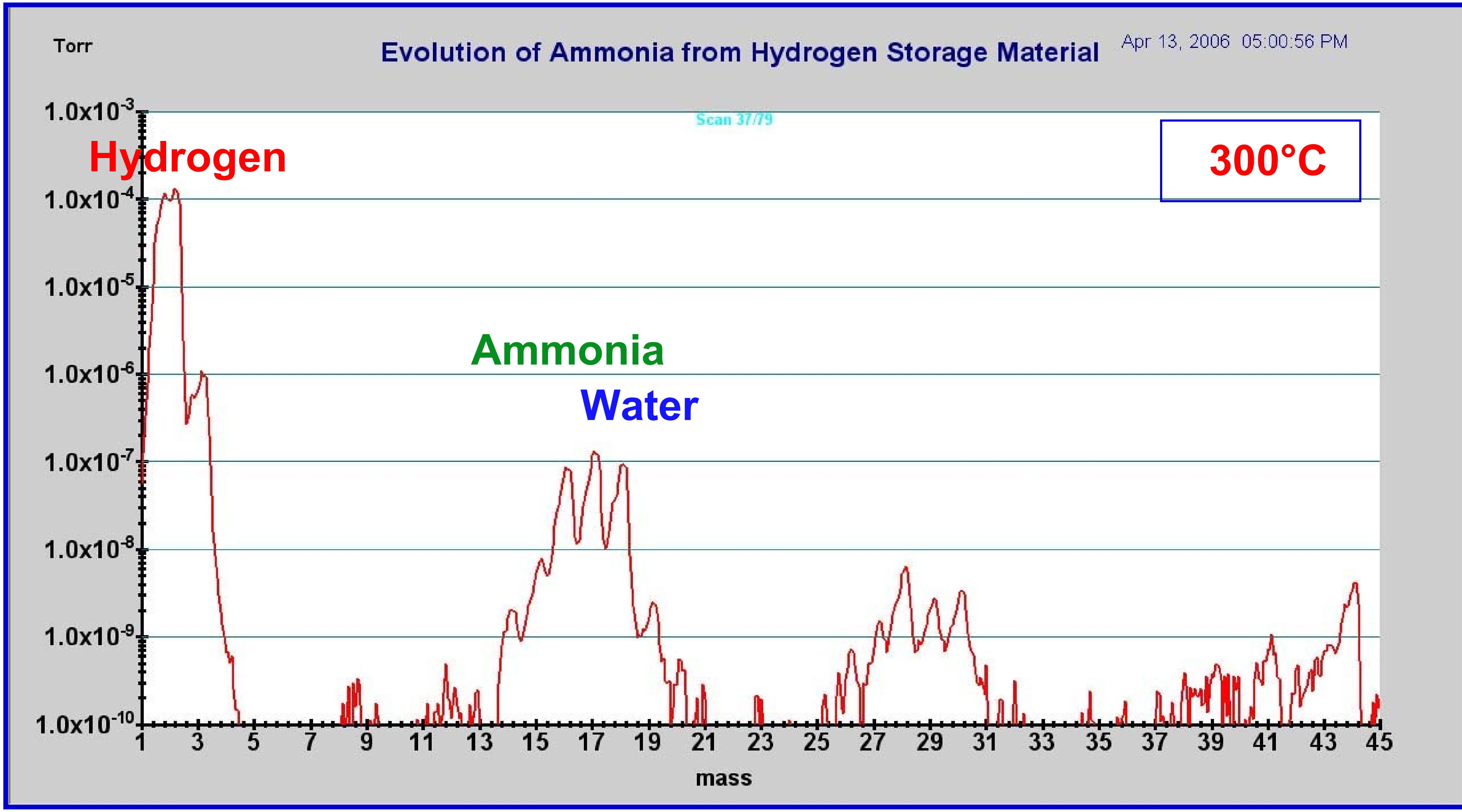
- **Kinetics of each reaction can be measured independently**

In Situ Residual Gas Analysis



- **Desorbed gas: Hydrogen only or side reactions?**
- **In situ RGA: real-time gas composition analysis**

In Situ Residual Gas Analysis

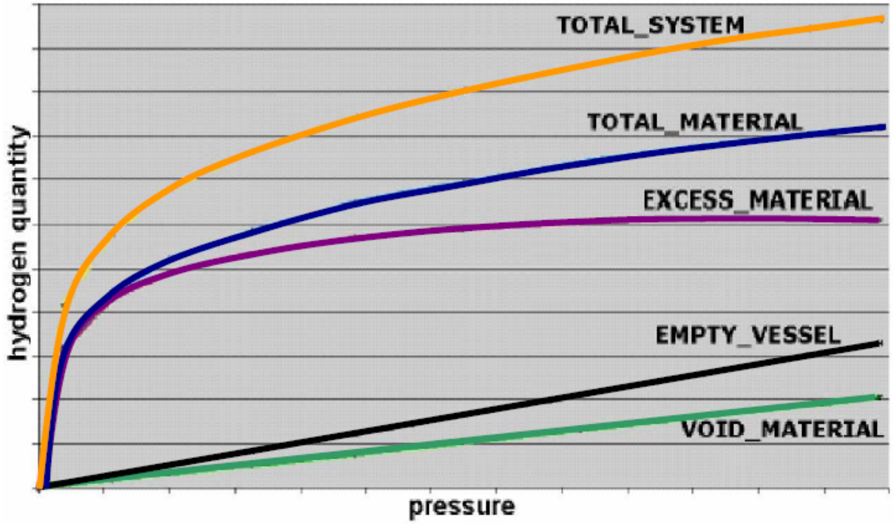


- **Alanate-Amide mixture:**

  Ammonia appears to be released during hydrogen desorption

Results Task 1.1: Universal Definitions Needed

- Stringent Definition of Storage Capacity Needed
  Confusion even caused on a materials level:
  Total, Absolute, Excess, Vessel values sometimes not properly defined
- In Materials Science, Excess Capacity Should be Used
- On an Engineering Level, Vessel Values Should be Used
  Total storage capacity of an Empty Vessel vs a Filled Vessel should be evaluated



Volumetric Methods:

Void H_2: Hydrogen being present in the macropores of the high-surface material (calculated using skeletal density)

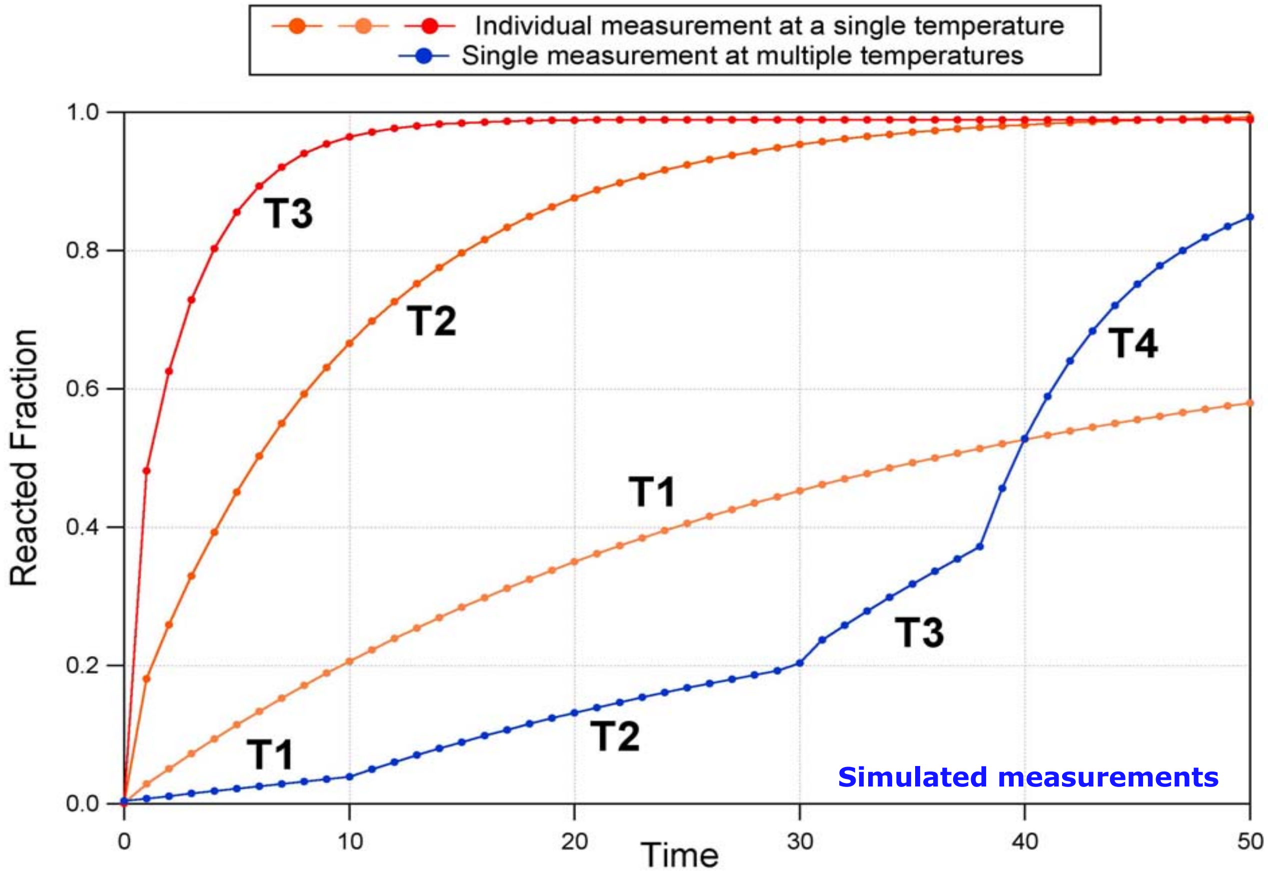
Excess adsorption H_2 : Quantity of hydrogen adsorbed on the adsorber (calculated using skeletal density)

Total material H_2: Total amount of hydrogen being stored by the high-surface material

- Importance of the Volumetric Storage Density of the Adsorber
  Apparent density of the storage material should always be measured
  Volume change with state of charge should be accounted for

Taken from presentation by: Dr. Ulrich Eberle, Adam Opel AG "GM Fuel Cell Activities"
WE-Heraeus-Seminar – October 2005, Bad Honnef, Germany

Results Task 1.2: Purpose of Measurements



- Measurements of delivery rates vs. temperature
- Data usually collected as a complete sorption at a set temperature
- However, poor kinetics allow a suite of temperatures in one sorption

Arrhenius Behavior of Sorption Rates

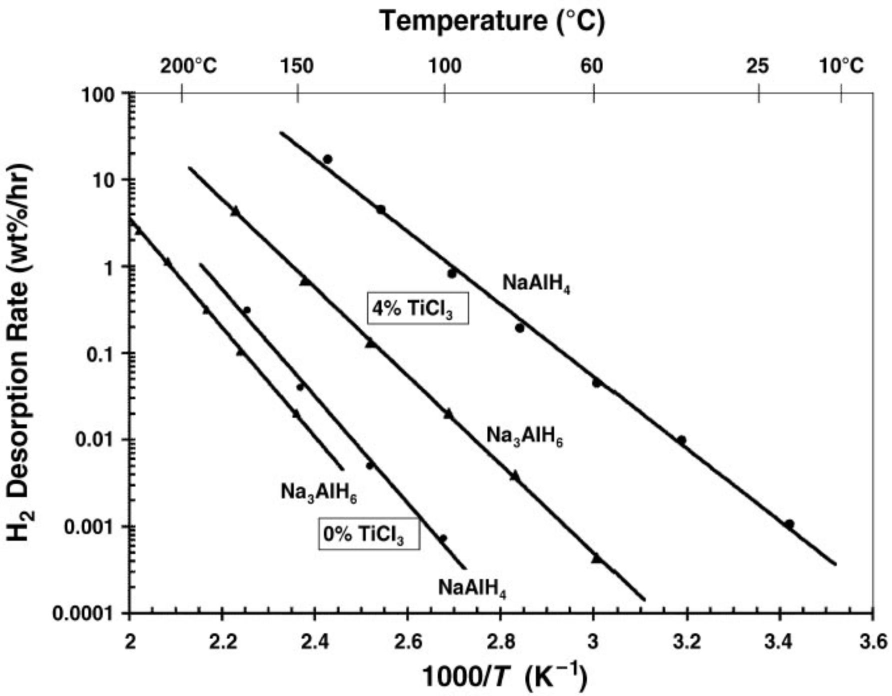


Figure 5. Arrhenius lines for $NaAlH_4$ and Na_3AlH_6 decompositions for 0 mol% and 4 mol% added catalyst precursor $TiCl_3$.[12]

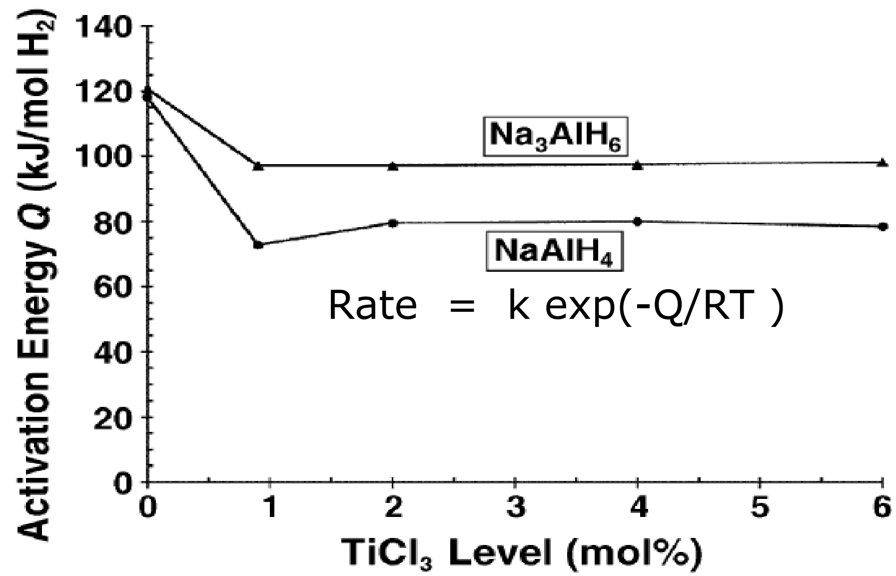
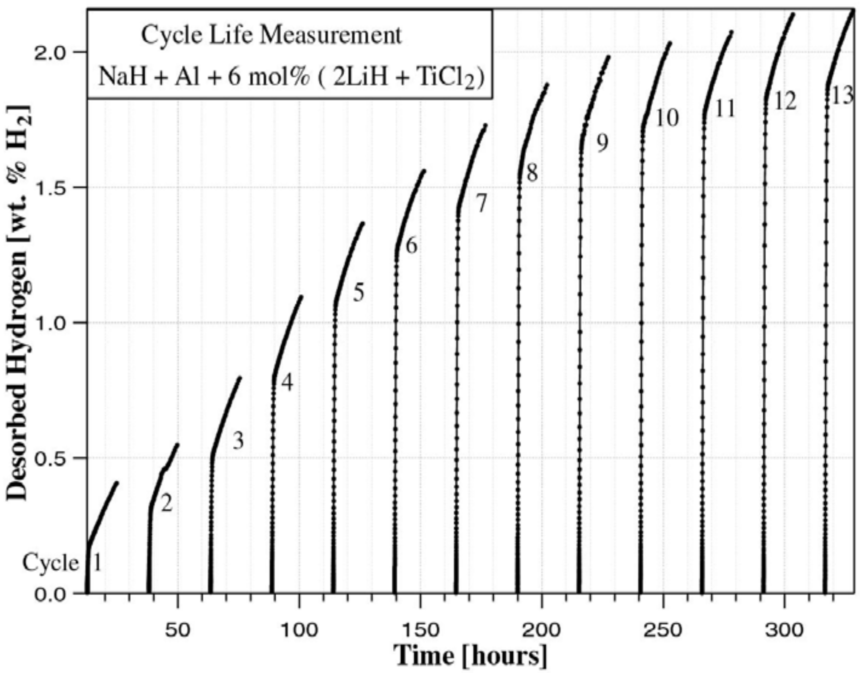


Figure 6. Activation energies Q for $NaAlH_4$ and Na_3AlH_6 decompositions as a function of added $TiCl_3$.[12]

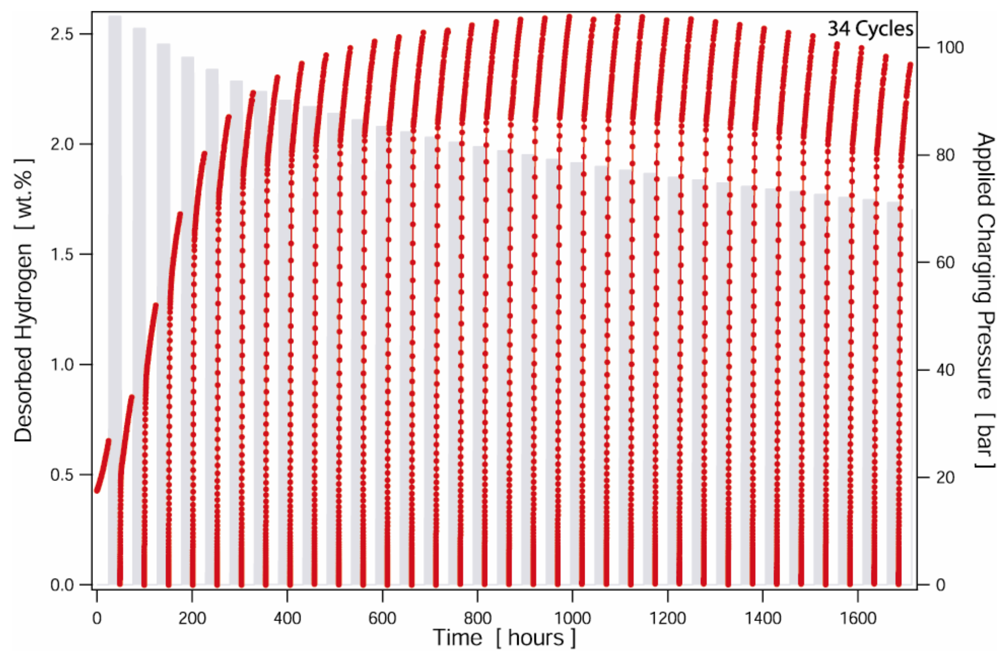
- **Used to understand and optimize additives for enhanced kinetics.**
- **Measured by increasing temperature in steps during desorption.**
- **Rate determined by linear fit to data at each temperature.**

B. Bogdanovic´ and G. Sandrock, MRS Bulletin, Sept. 2002

Activation Effects and Kinetics



Alanate: Pre-reacted additive

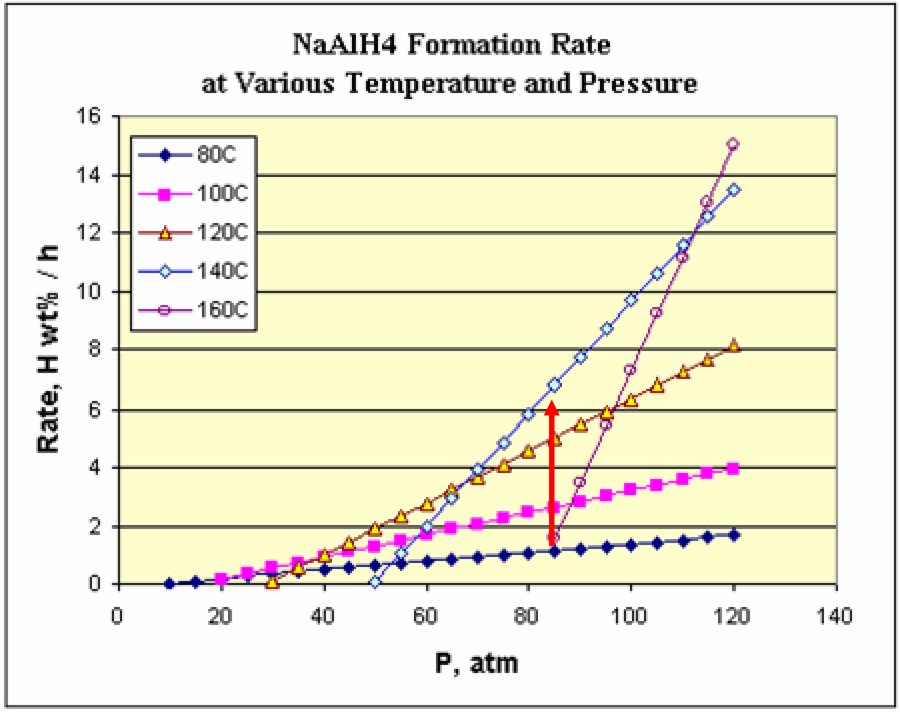


Alanate: Nano-TiO_2 additive

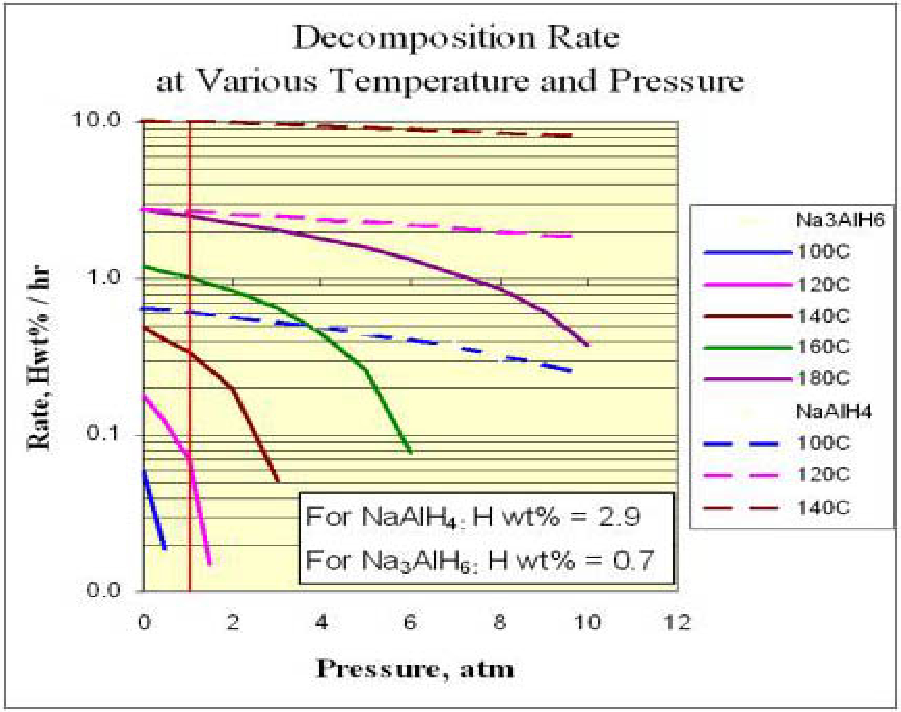
- **Several cycles may be required to achieve representative capacity and kinetics**
- **Kinetics will change with cycling: May be misinterpreted as capacity loss**

1) K.J. Gross, W. Luo, E.H. Majzoub, G. Roberts, S.Spangler, D. Dedrick, T. Johnson, J. Chan, 2003 annual report, US DOE Hydrogen and Fuel Cells program. 2) K.J., Gross, E.H., Majzoub, S.W. Spangler, J. Alloys and Compounds, 356-357 (2003) 423. 3)K.J. Gross, Presentation US DOE Hydrogen and Fuel Cells Annual Merit Review, Berkeley, CA May 19-22, 2003.

Impact of pressure on Kinetics



Calculated hydrogen absorption rates for $NaAlH_4$ as a function of pressure at different temperatures.

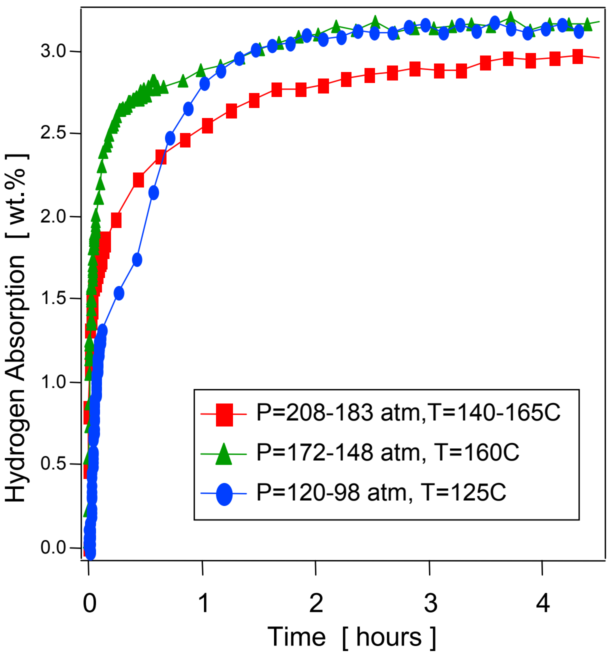


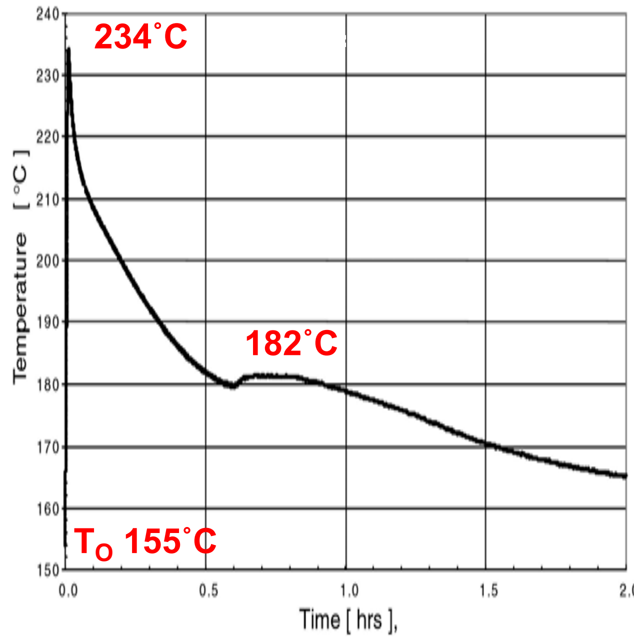
Calculated hydrogen desorption rates for $NaAlH_4$ and Na_3AlH_6 as a function of pressure at different temperatures.

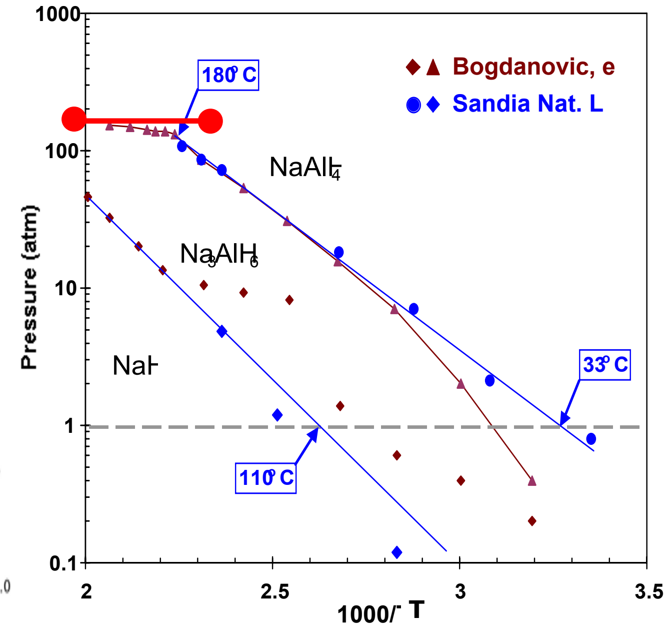
- **ΔP drives kinetics, Not the applied Pressure**
- **Desorption measurements typically made against vacuum**
- **Desorption against 1+atm more appropriate for performance evaluation**

K.J. Gross, W. Luo, E.H. Majzoub, G. Roberts, S.Spangler, D. Dedrick, T. Johnson, J. Chan, "Hydride Development for Hydrogen storage", 2003 annual report, US DOE Hydrogen and Fuel Cells program.

Kinetics Measurements and Heat Transfer



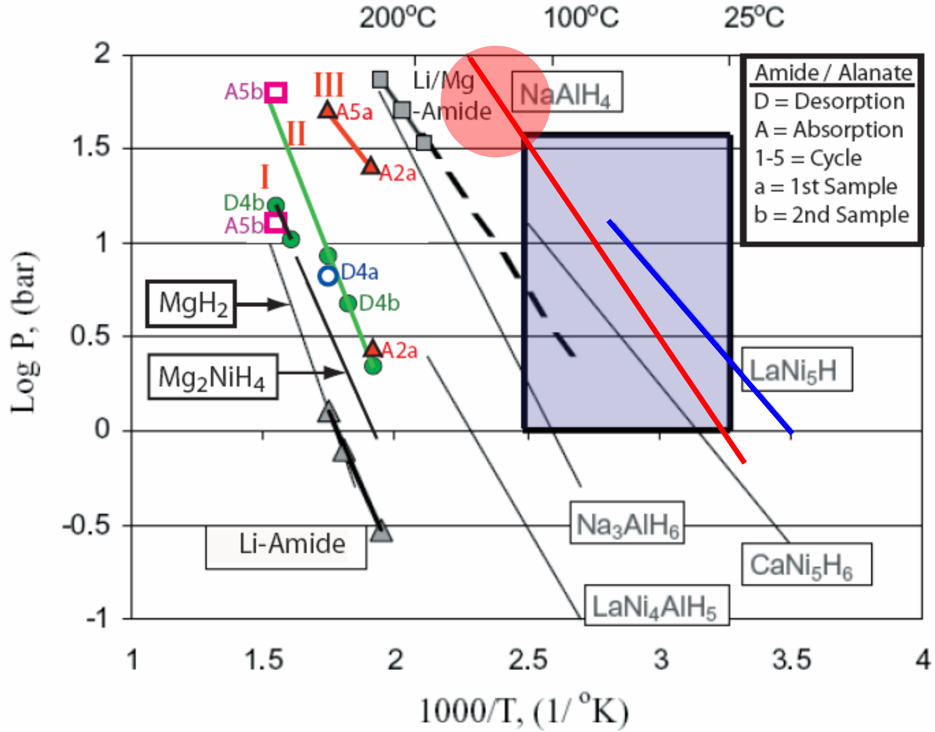


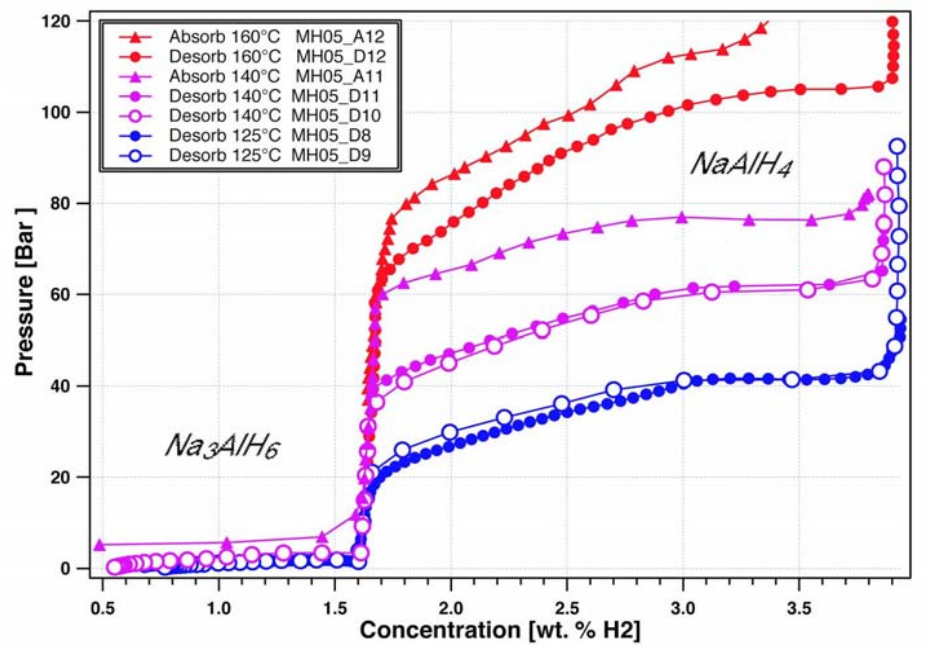


100g Scaleup Bed Ti/Zr-Alkoxide Doped $NaAlH_4$

- **Rapid charging produces large ΔH heating effects**
- **Reaction enthalpy can melt $NaAlH_4$ (182˚C)**
- **Temperature measurements shows self-melting and resolidification**
- **Sorption kinetics affected by heat transfer**

Kinetic vs. Thermodynamics





Example: PCT measurements of $NaAlH_4$ and Na_3AlH_6

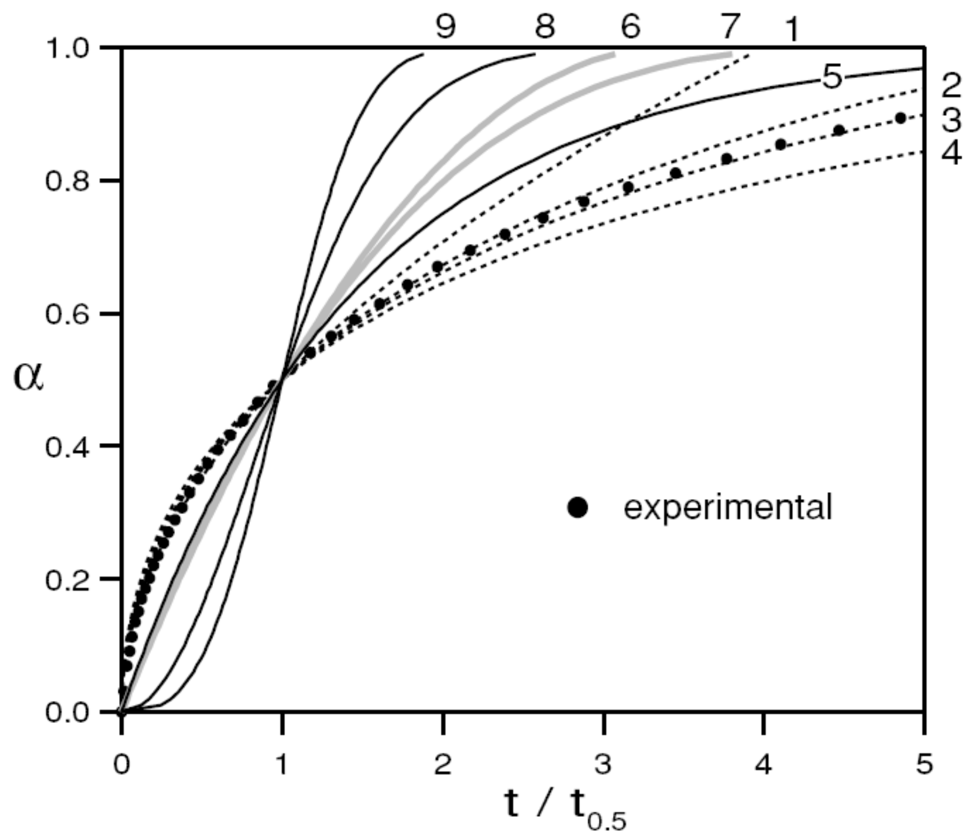
- **Operating temperatures and pressures are determined as much by kinetics as thermodynamics.**
- **Important to understand to what extent kinetics influences performance**
- **Because kinetic properties may be altered through materials engineering**

K.J. Gross et al., Presentation US DOE Hydrogen and Fuel Cells Annual Merit Review, Berkeley, CA May 19-22, 2003

Results Task 1.5: Kinetic Mechanisms

Kinetics curves based on different solid state kinetics models

1) One dimensional diffusion
2) Diffusion in a cylinder
3) Diffusion in a sphere
4) Diffusion in a sphere
5) 1st order phase transformation
6) Constant velocity phase-boundary propagation in a cylinder
7) Constant velocity phase-boundary propagation in a sphere
8) Nucleation and growth
9) Circles are measured kinetic data for absorption of hydrogen at 100°C by a mechanically milled composite sample of Mg, Mg2Ni and La.



- **Caveat for interpreting experimental measurements: In the absence of cells designed specifically for these measurements, the behavior is dominated by heat transfer making the determination of rate limiting mechanisms difficult to impossible.**

Sharp, J. H., Brindley, G. W., Narahari-Achar, B. N., J. Am. Ceram. Soc., 49 (1966) 379.

Collaborations

- Contributions to this project from world experts have been received including written materials, examples, presentation or editorial review of draft documents from:
  - Dr. Nobuhiro Kuriyama and Dr. Tetsu Kiyobayashi , AIST, Japan, IEA Task 22.
  - Dr. Philip Parilla, National Renewable Energy Laboratory, Golden CO, USA.
  - Dr. Gary Sandrock, Consultant to DOE / Sandia National Laboratory
  - Professor Sam Mao and Russell Carrington, University of California Berkeley
  - Professor Channing Ahn, California Institute of Technology, USA , IEA Task 22.
  - Professor Evan Gray, Director Nanoscale Science and Technology Centre, Griffith University, Brisbane, Australia , IEA Task 22.

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.
  - Effect of activation, kinetics and poisoning on capacity to be considered.
- ***Thermodynamics***
  - The objective of this task is to establish methodologies for determining equilibrium thermodynamics of hydrogen storage materials.
  - We will define measurement protocols to separate true equilibrium conditions from kinetic effects.
  - We will examine details of new measurement techniques for the 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: Kinetics, Capacity, Thermodynamic and Cycle Life.

- ***Accomplishments:*** Task 1 approaching completion. Achieving a high-level of participation from experts in the field.

- ***Collaborations:*** Official collaboration with NREL and International collaboration through IEA task 22 with AIST Japan.

- ***Future Work:*** Complete Task 1: Kinetics including review process. Continue work on Tasks 2-4 Capacity, Thermodynamic and Cycle Life measurements.

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