

the Energy to Lead

2009 DOE Hydrogen Program Review

Electron-Charged Hydrogen Storage Materials

Chinbay Q. Fan
Gas Technology Institute

May 20, 2009

Project ID #
STP_02_fan

Overview

Timeline

- Project start: July 1, 2005
- Project end: Sept 30, 2010
- Percent complete: 55%

Budget

- Total project funding
 - DOE share: \$1,562K
 - Contractor share: \$390K
- Funding received in FY08: \$275,785
- Funding for FY09: \$303,010

Barriers

- Cost: use inexpensive graphite
- Weight and volume: use high density graphite, maximizing capacity
- Efficiency: add electron charge to increase storage rate
- Durability: use electron charge to control cycles
- Refueling Time: use electron charge to increase fueling rate
- Codes and Standards
- System Life-Cycle Assessments

Objectives

Overall	Development of a hydrogen storage material and device for hydrogen quick charge and discharge, high wt% and vol% storage capacities, good durability over many cycles, and safe handling and transport.
2008	<ul style="list-style-type: none">• Combine internal electron-charge (doping) and external charge to increase hydrogen storage capacities• Investigate performance optimization and prototype container systems
2009	<ul style="list-style-type: none">• Reselect the best hydrogen storage materials for charge modifications• Carbon-based materials, such as AX-21 and other high surface carbon using polymer as precursor; metal-modified carbon; and borane-ammonia

Milestone or Go/No-Go Decision

Month/Year	Milestone or Go/No-Go Decision
Sept., 2008	<p>Task 1. Test and evaluate cycles for hydrogen storage Modify the electron charge distribution structure (Framework structure) to obtain a 50% hydrogen storage rate increase. Fueling kinetics study: does the electron charge make desorption fast? Theoretical calculation: how much charge is needed to get 6 wt%?</p> <p>Task 2. Observe and detect charge distribution under electrostatic charge.</p> <p>Task 3. Optimize charge control agent (CCA) and charge transfer agent (CTA) to help polarizing storage materials.</p>

Milestone or Go/No-Go Decision

Month/Year	Milestone or Go/No-Go Decision
July 30, 2009	<p>Task 4. Characterize the electron device and the material properties of the carbon based material with CCA/CTA (pore size, density, surface area, etc)</p> <p>Task 5. Prepare samples for independent evaluation. Install framework structure to improve charge distribution</p> <p>Task 6. Scale-up to an 11 liter tank for fueling demonstration to show 50% hydrogen storage increase.</p> <p>Multi-kilogram samples/prototype system containers: 11 liter tank for fueling demonstration to show a 50% hydrogen storage increase.</p>

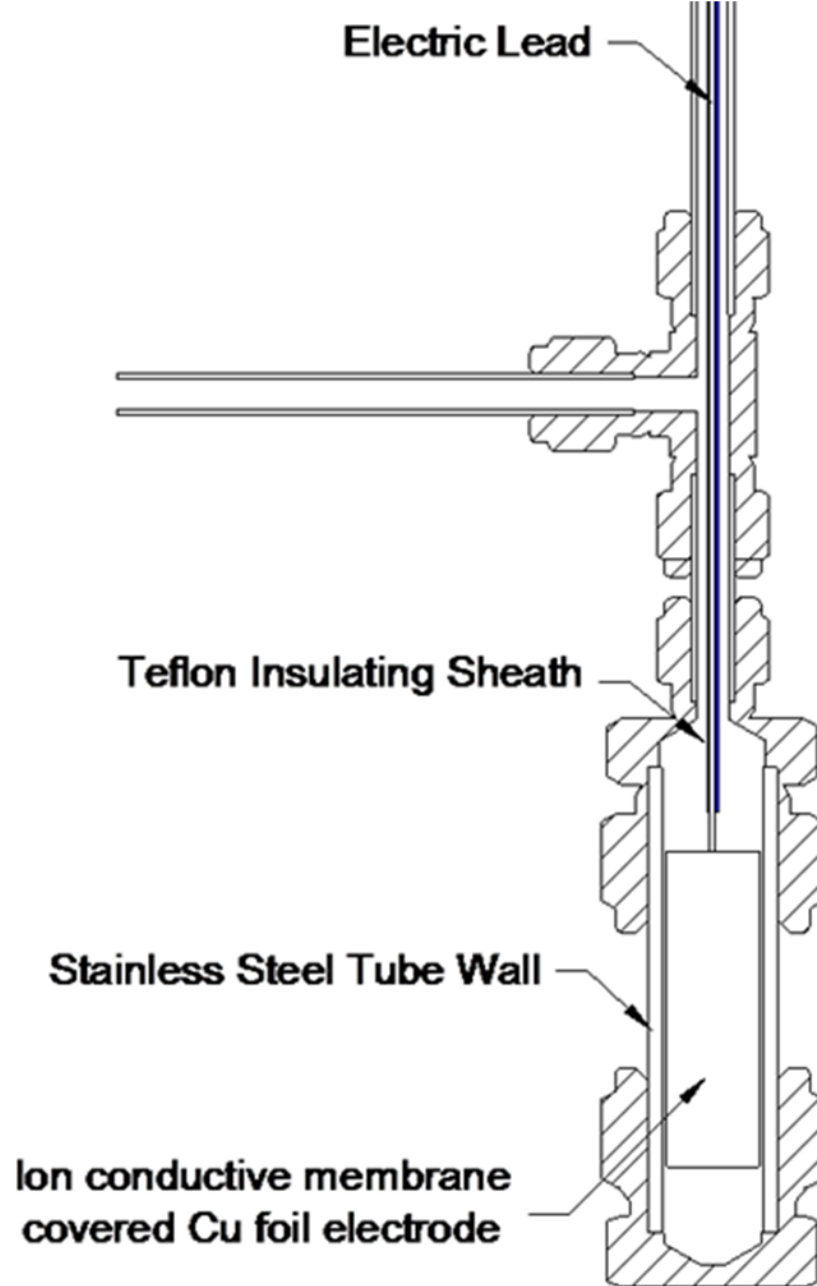
Approach

- Hydrogen storage is based on hydrogen adsorption, which is involved in electron shift (physi-sorption) and electron transfer (chemi-sorption).
- Use external electron charge to increase hydrogen adsorption and alter hydrogen desorption kinetics.
- Use internal electron-rich or -poor material to change carbon-based material surface electron density, which affects hydrogen storage.

Plan and Approach

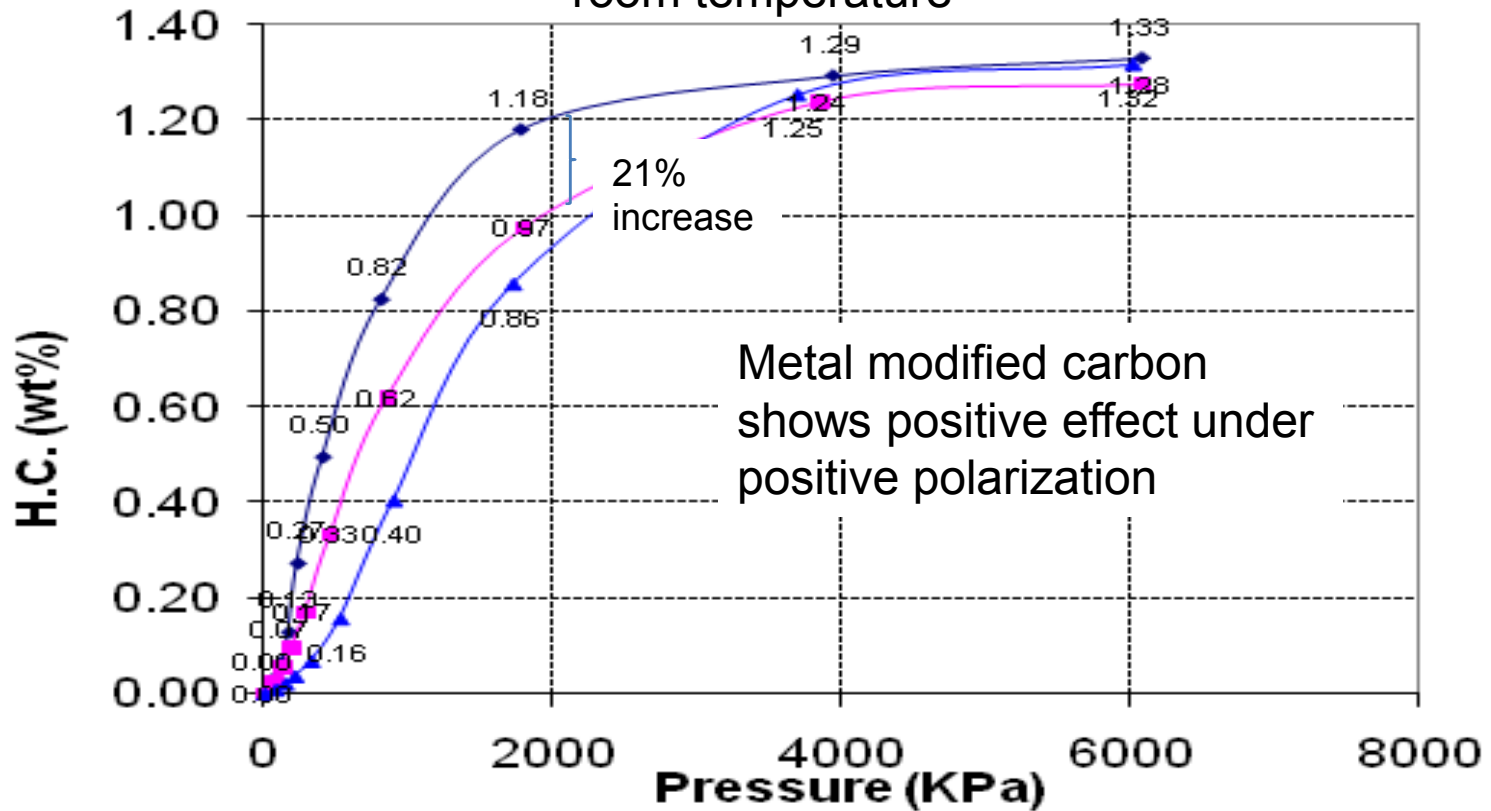
- Select and synthesize carbon-based materials
- Test and evaluate cycles for hydrogen storage
- Test external electron charge effect on hydrogen storage
- Dynamic TGA and Sievert Tests

Approach



Technical Accomplishment and Progress

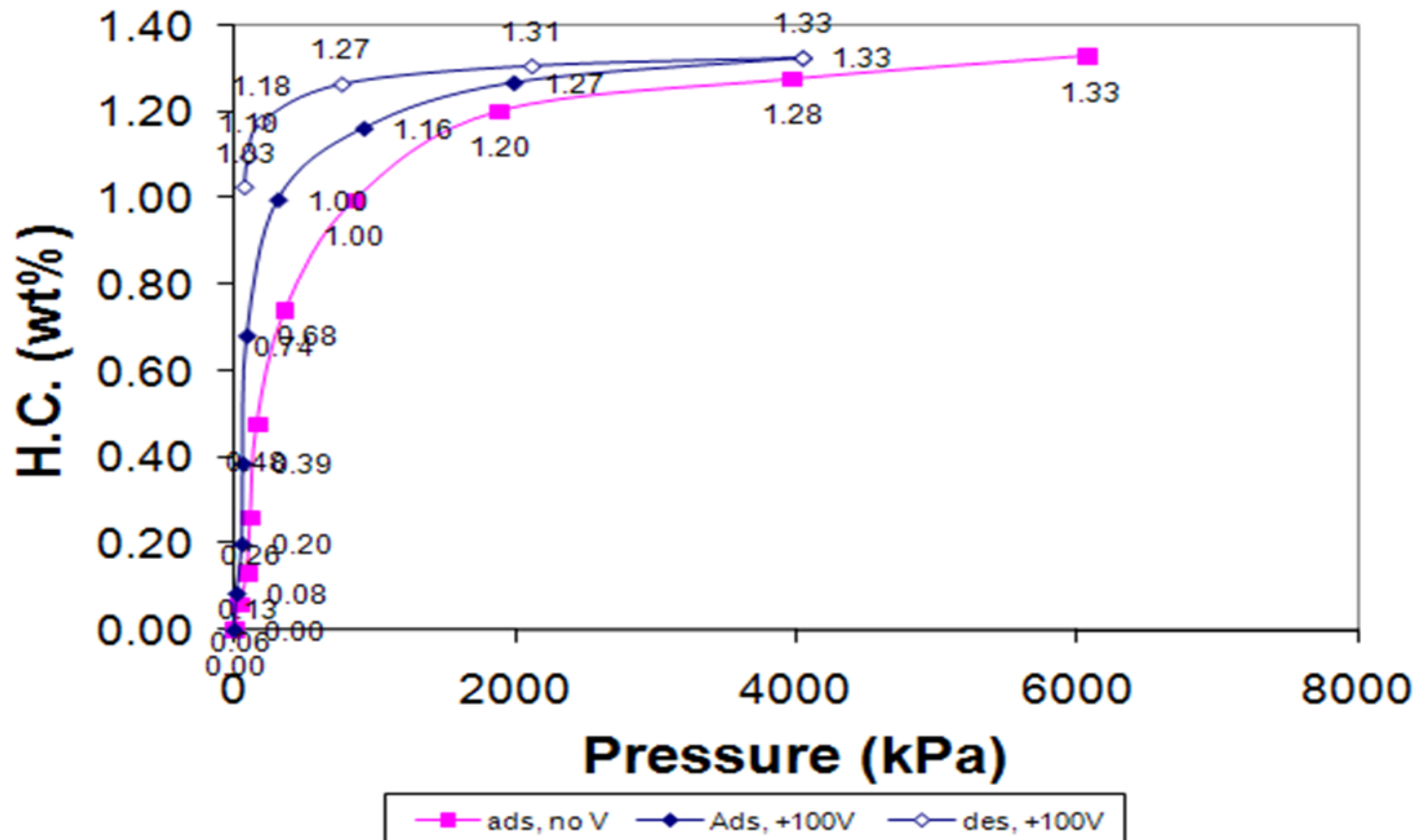
Metal modified AX-21 shows electrostatic effect at low pressure at room temperature



◆ +100V 10/22/2008 ■ 0V 10/18/2008 ▲ -100V 10/21/2008

Technical Accomplishment and Progress

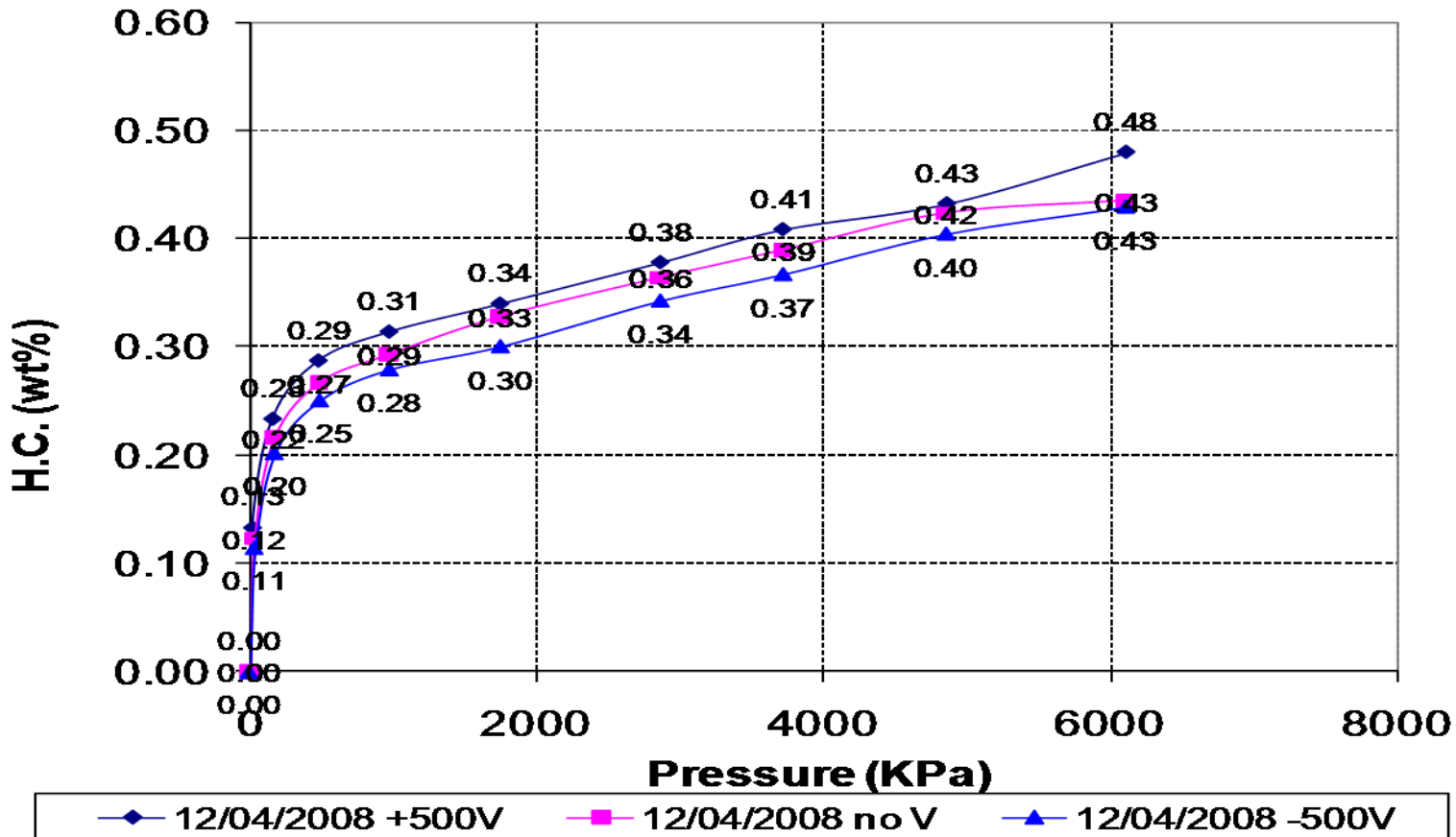
Electro-static polarization also affects desorption: positive charge makes desorption slower (ca. 10% at 1MPa), negative charge faster



Metal modified carbon has positive effect under positive polarization at room temperature. Des no V is overlap to ads no V. 5 min per data

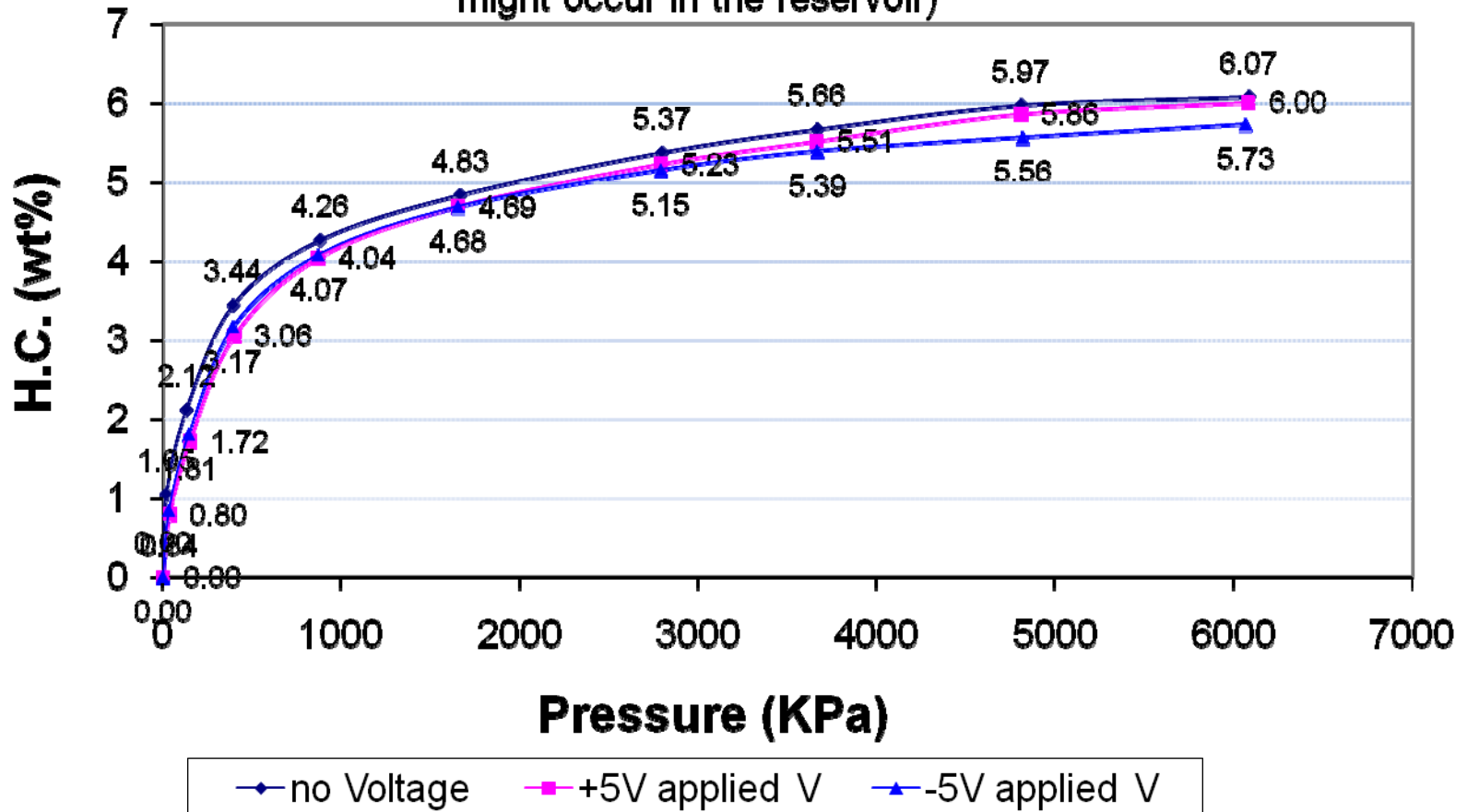
Technical Accomplishment and Progress

Electro-static polarization has less effect on the metal modified AX-21 at Storage at 77K
Metal modification decreases low temperature physical adsorption because the kinetics is slow



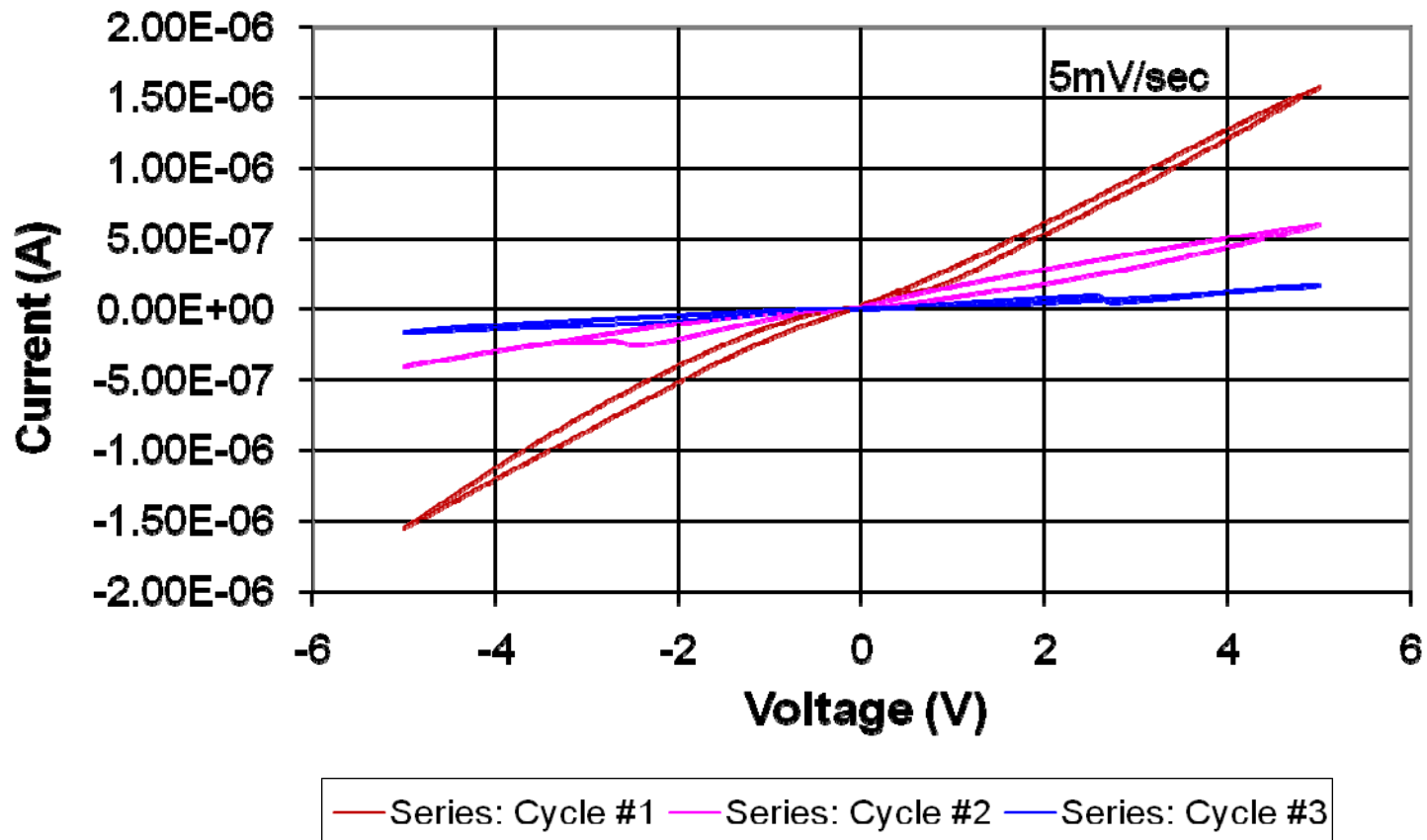
Technical Accomplishment and Progress

AX21 without metal modification under 5 V polarization at 77K (short might occur in the reservoir)

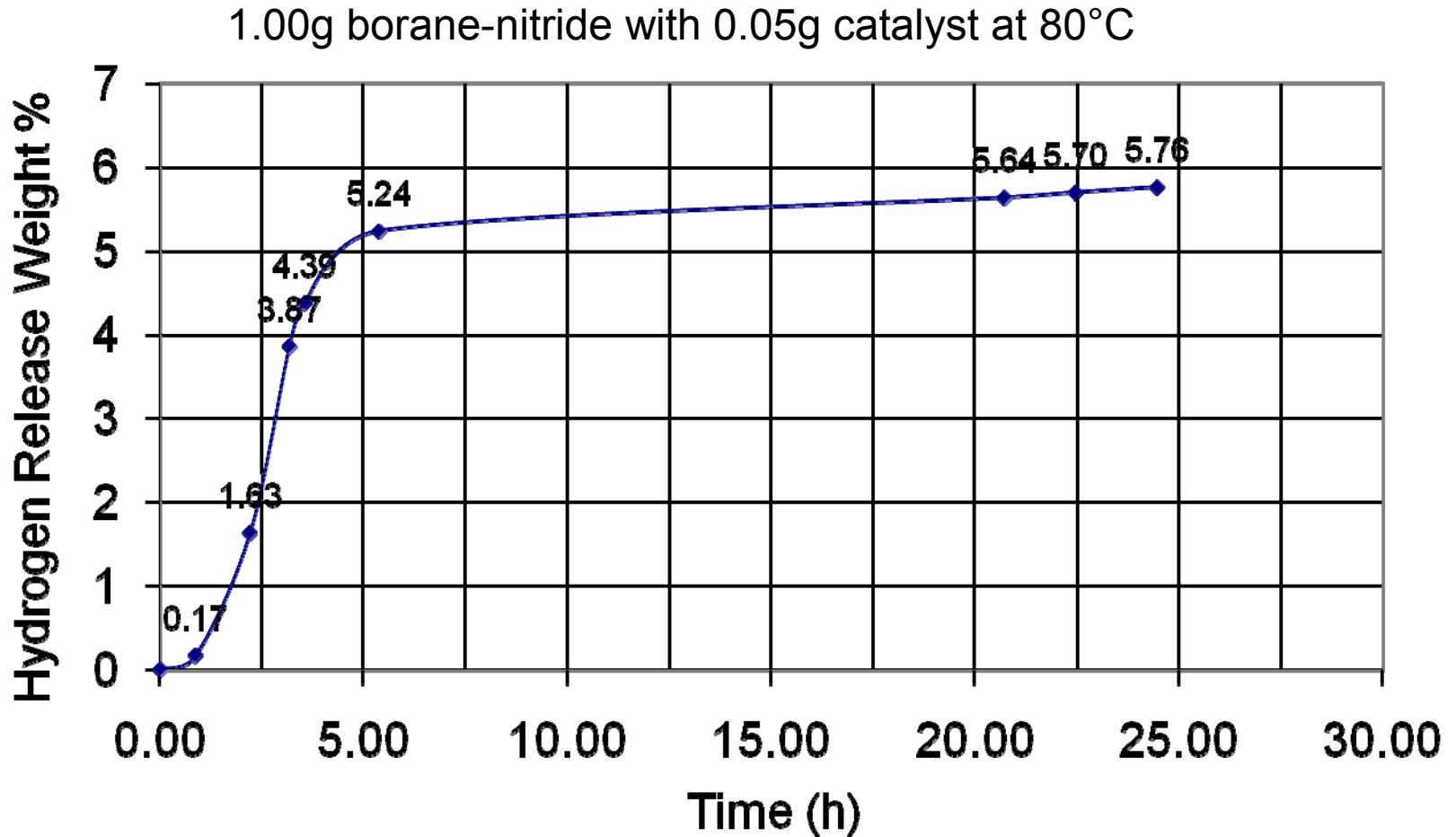


Technical Accomplishment and Progress

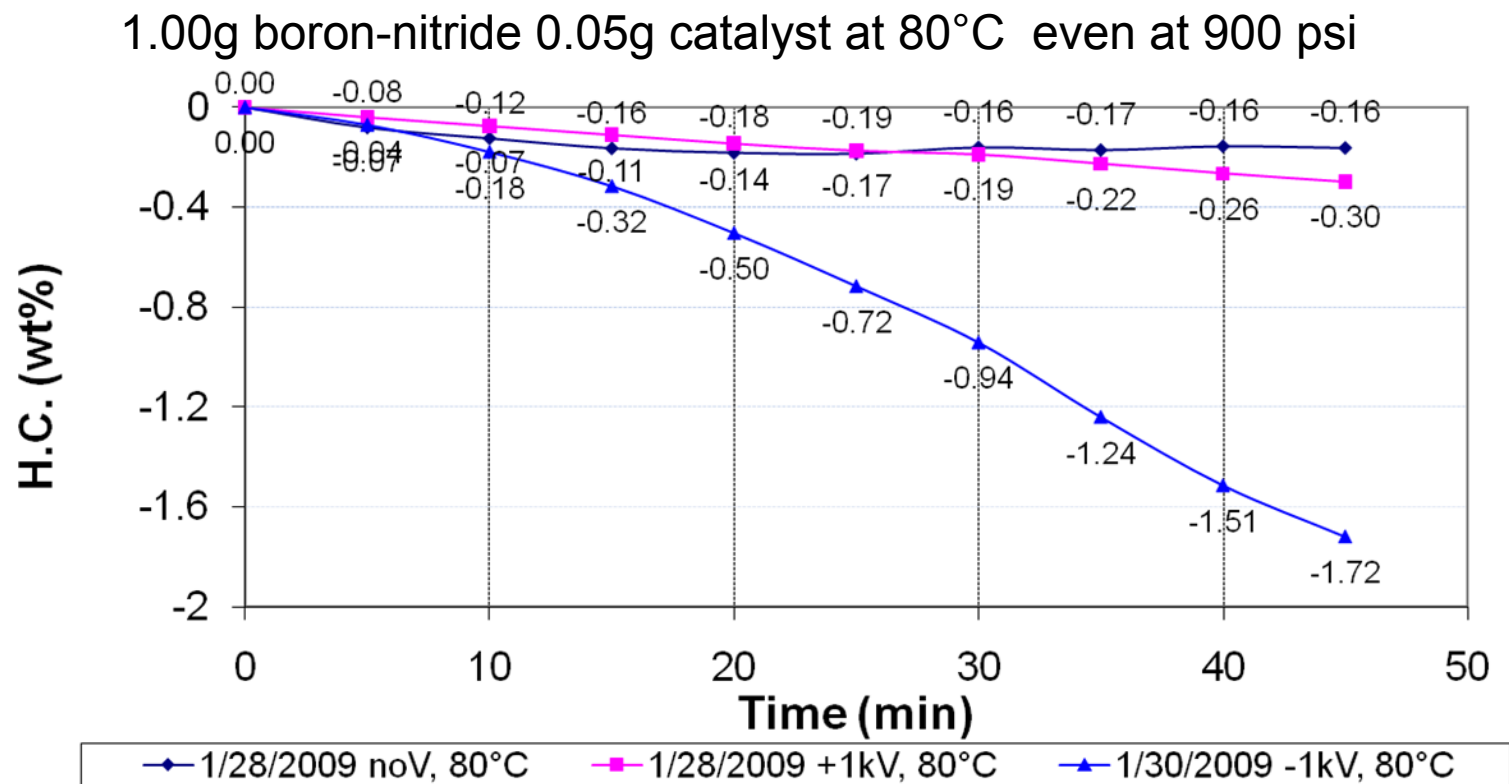
Cyclic voltammograms show NO internal short was observed in the system and verify that the adsorption increase/decrease was NON-Faradaic.



Technical Accomplishment and Progress



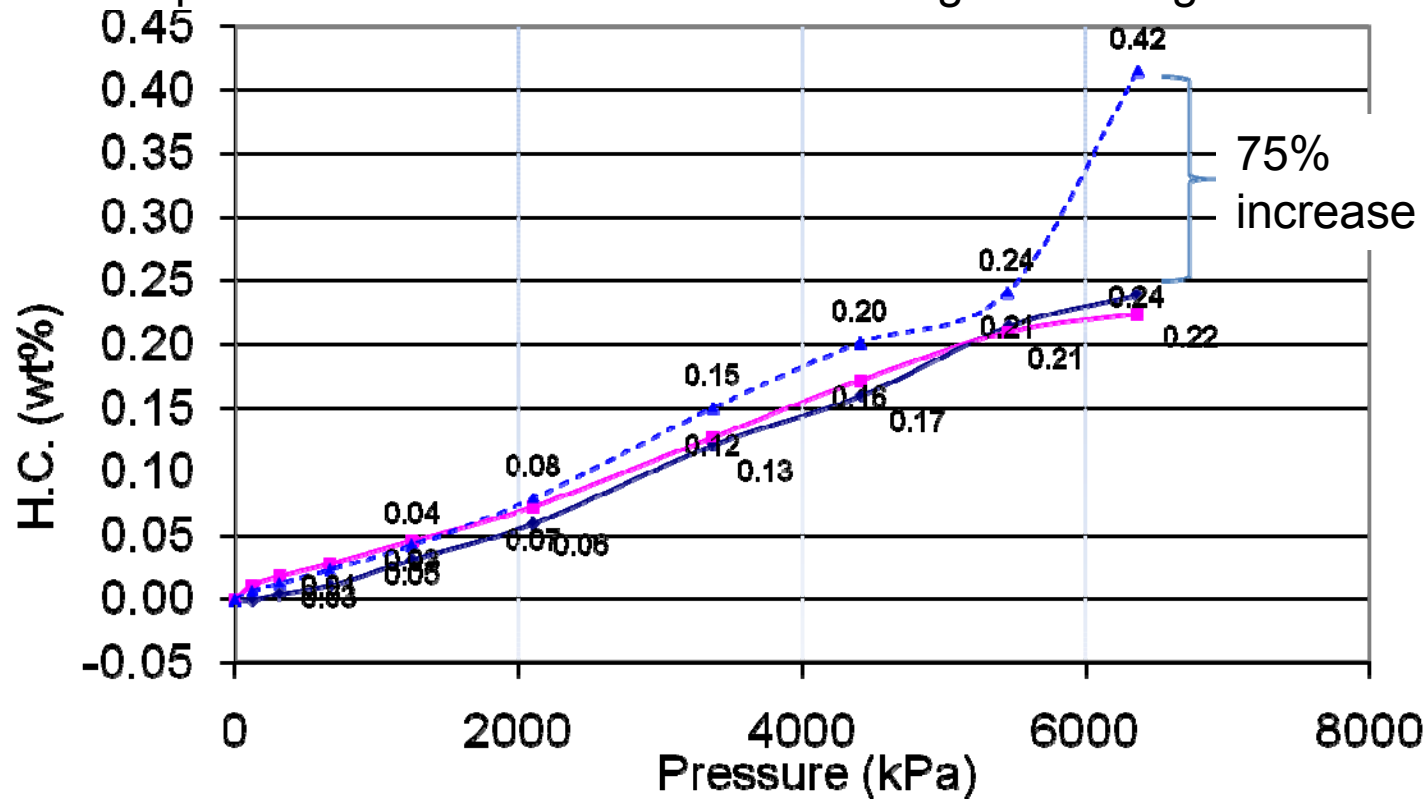
Non-faradaic Electrochemical Modification of Catalysis (NEMCA) Increases the Hydrogen Release Rate



Ref. slide 14, at 900 psi, the decomposition of borane nitride for 1.5 wt% takes 2.5 hours without electrical charge, only 40 minutes with negative charge. The decomposition rate under electrical charge at different pressures will be generated.

Electron Charges Increase Hydrogen Storage

1.00g boron-nitride 0.05g catalyst at 80°C. The threshold point occurs when pressure increases to 6MPa with negative charge

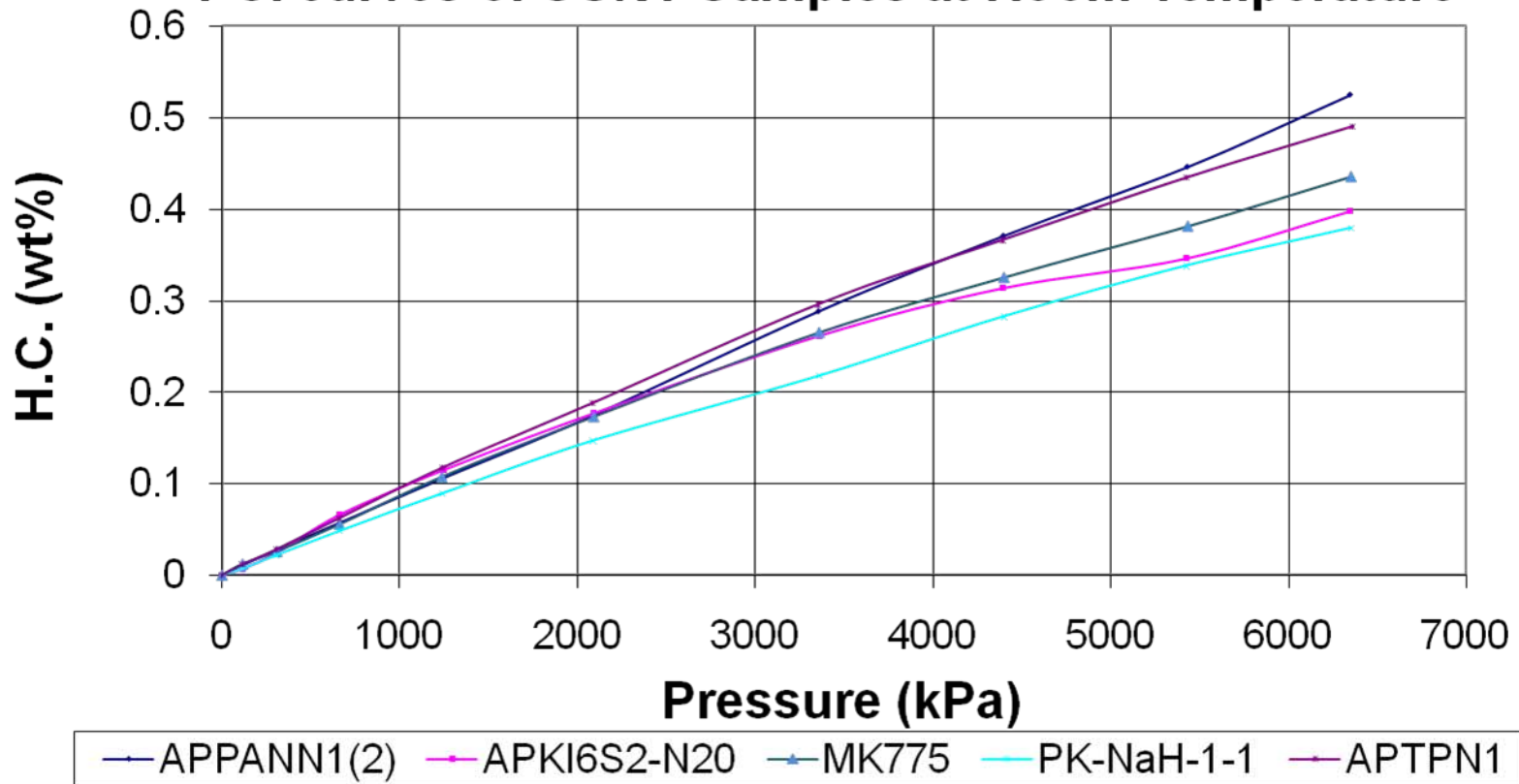


—●— 2/20/2009 noV, 80°C, T#1 —■— 2/23/2009 +1kV, 80°C, T#1 -▲- 2/23/2009 -1kV, 80°C, T#1

Technical Accomplishment and Progress

Hydrogen Storage Material Screening without Electrical Charge

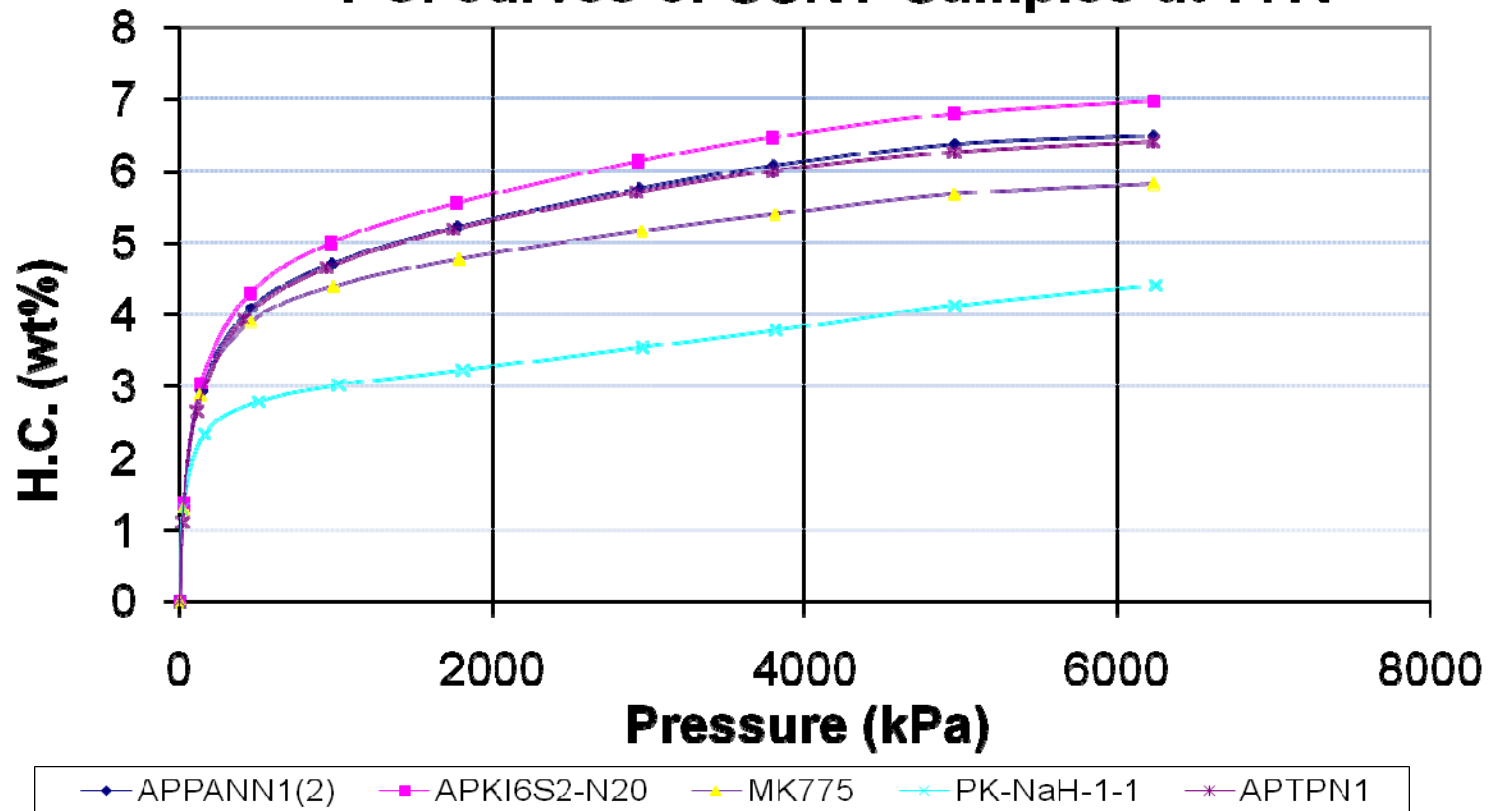
PCI curves of SUNY Samples at Room Temperature



Technical Accomplishment and Progress

Hydrogen Storage Material Screening without Electrical Charge

PCI curves of SUNY Samples at 77K



Technical Accomplishment and Progress

Hydrogen Storage Material Screening without Electrical Charge

Summary of SUNY samples at 6300kPa

Sample name	R.T. (wt%)	77k (wt%)
APPANNI(2)	0.52	6.49
APKI6S2	0.40	6.98
MK775	0.44	5.82
PK-NaH-1-1	0.38	4.41
APTPN1	0.49	6.42

Proposed Future Work

- Continue boron nitride (hydrogen storage more than 6 wt%) research and external charge bias to increase the hydrogen storage rate. Characterize the external charge effect on material physical and chemical properties (pore size, density, surface area, etc).
- Prepare samples for independent evaluation.
- Install framework structure to improve charge distribution.
- Scale-up to an 11 liter tank for fueling demonstration to show 50% hydrogen storage increase.

Conclusions

- External electron charge does affect the hydrogen storage, however different substrates shows different effects
- For metal modified AX-21, at 2MPa, the hydrogen storage rate increased approximately 20% using positive charge
- Negative charge helps boron nitride dehydrogenation kinetics (4 times faster at 900psi) and increases the reversible hydrogenation
- External charge effect on pure carbon material is limited.

Cooperation

- State University of New York at Syracuse: Prof. Cabasso group
- Japanese CCA Manufacturer
- ATMI
- University of Houston

Acknowledgements

- Financial Support by DOE: DE-FG36-05GO15010.
- DOE Supervisors: Jesse J. Adams, Monterey Gardiner, Carole J. Read, Sunita Satyapal
- State University of New York at Syracuse: Prof. Cabasso group
- Japanese CCA Manufacturer
- ATMI