2006 DOE Hydrogen Program Review

Electron-Charged Graphite-Based Hydrogen Storage Material

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STP 13

Overview

Timeline

- Project start: July 1, 2005
- Project end: June 30, 2009
- Percent complete: 15%

Budget

- Total project funding
  - DOE share: $1,562K
  - Contractor share: $390K
- Funding received in FY05: $110K
- Funding for FY06: $150K

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

Partners

Superior Graphite Co.

Chicago, Illinois

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Objectives

Overall	Development of a hydrogen storage device for hydrogen quick charge and discharge, high wt% and vol% storage capacity, durability over many cycles, and safe handling and transport.
2006	• Select materials and conduct graphite-processing steps • Test and evaluation cycles for hydrogen storage • Construct an electron charge device and evaluate the concept with the modified graphite materials.
2007	• Prepare samples for independent evaluation • Investigate performance optimization and prototype container systems.

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Plan and Approach

60% Complete

Task 1. Proof of Feasibility

1. Select materials for intercalation
2. Test and evaluate hydrogen storage cycles
3. Theoretical calculation

Not started

Task 2. hydrogen Storage Optimization

1. Prepare samples for independent evaluation
2. Performance optimization
3. Investigate process steps

Not started

Task 3.Prototype Development and Process Scale Up

1. Pilot evaluation of production steps
2. Production cost and market potential

Not started

Task 4. production and Market Assessments

1. Build prototype systems
2. Analysis of market

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Technical Accomplishments/ Progress/Results

- Achieved 4.5Å space between graphite flakes. This 4.5Å can allow hydrogen molecules to enter.
- Intercalated different metals to change the graphite electronic configuration: Mg, Li, Al, and Ti etc.
- Achieved 1% hydrogen storage with graphite based materials in early-stage tests.
- Built an electron-charge device for hydrogen storage and observed the effect of external charges on the hydrogen storage.

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Accomplishments/Progress/ Results

Hydrogen Storage Material Development

- Graphite expansion and oxidation
- SEM and TEM analysis of the expansion
- Expanded graphite reduction and mechano-chemical intercalation
- Structure reorganization under heat treatment
- Hydrogen uptake and release using high temperature, high pressure TGA as well as Sievert devices

Graphite Samples for Hydrogen Storage Materials

Superior Batch	Sample Name	Notes
SO-4-40-05	GTI Compacted Worms	Worm structure
SO-4-40-08	GTI SLC 1520	High bulk density, spherical
SO-4-40-09	GTI SLA 1518	High bulk density, spherical
SO-4-40-07	GTI SCD310	Purified carbon black with graphite
SO-4-40-03	GTI 2935 GRAPH	Flat flakes
SO-4-40-04	GTI Fullerine	Fullerine graphite
SO-4-40-01	GTI 9039 RG	Boron graphite
SO-4-40-06	GTI SR11993	Unique SGCo
SO-4-40-02	GTI 2926 RGAPH	Flake graphite for plates
Batch 73703	GTI 4926	Flake graphite for plates

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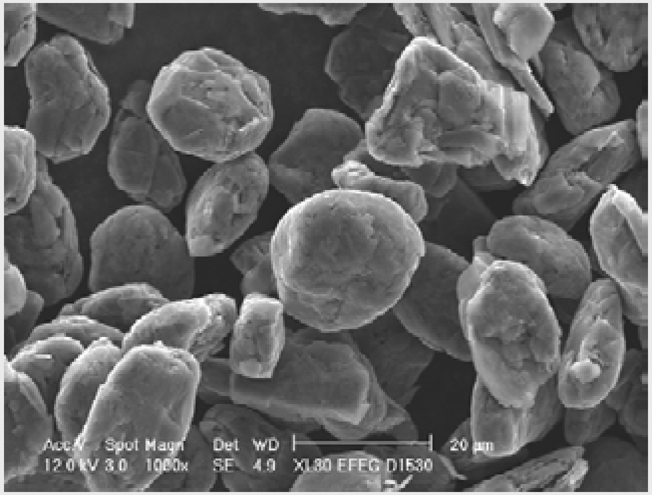
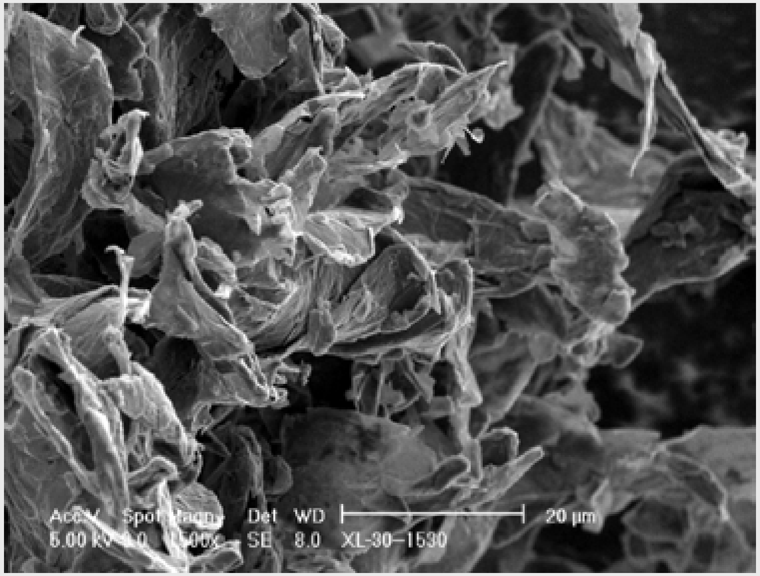
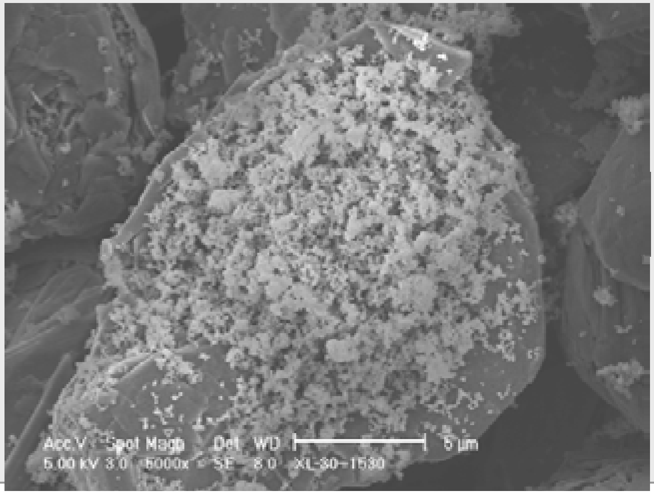
Accomplishments

Different Graphite Shapes Fabricated and Tested



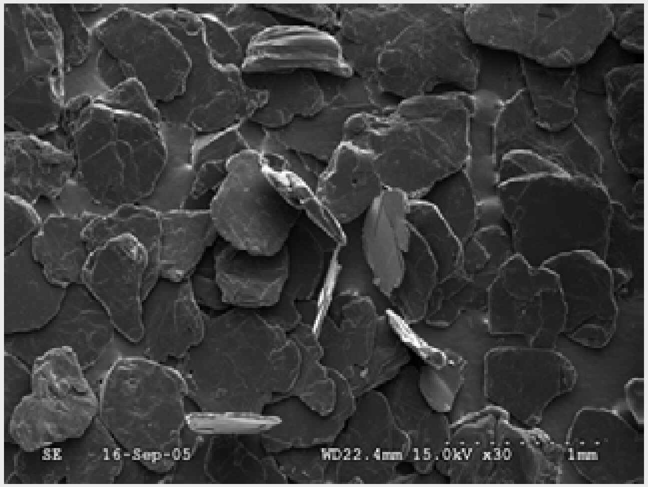




Graphite shape modification, metal intercalation, and coating for hydrogen storage

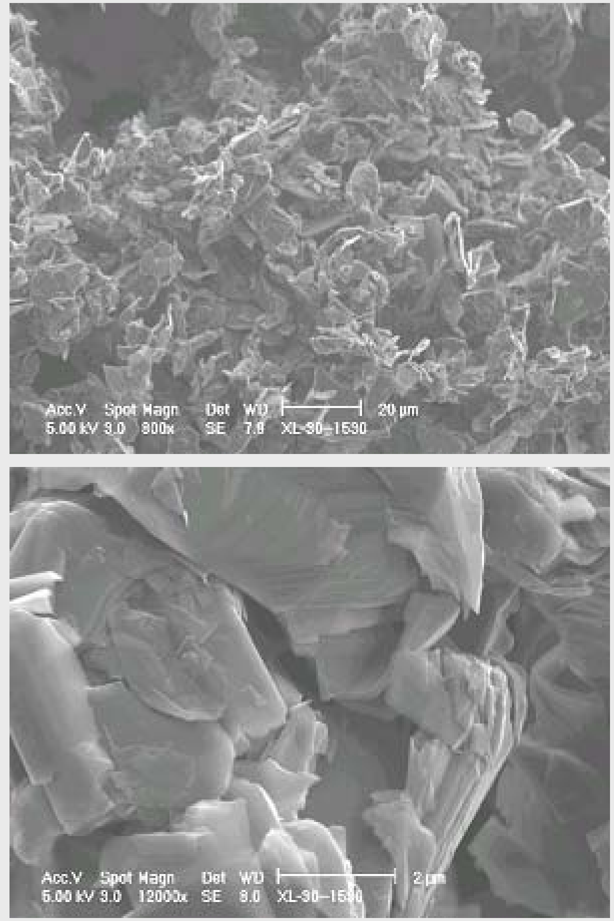
Accomplishments

Graphite Expansion



Thermally Purified
natural crystalline flake graphite G2900G8

air-milling



2939APH
(D50~10um; BET surface area: 9 m2/g)

Step 1

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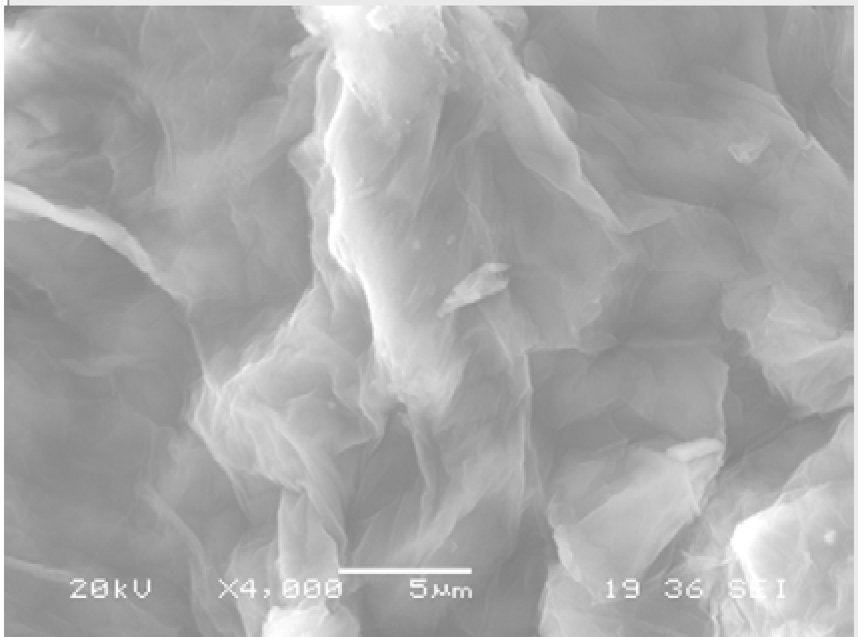
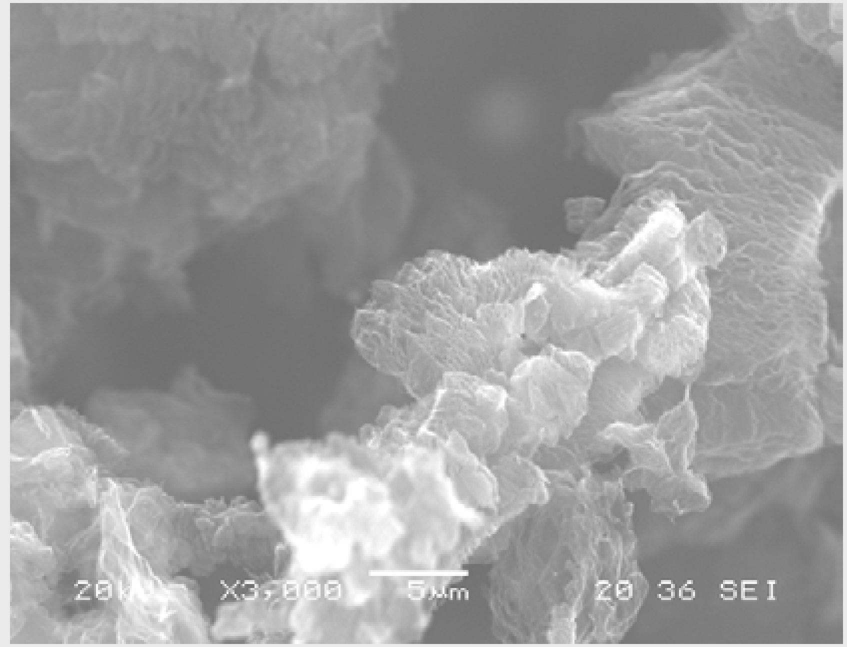
Accomplishments



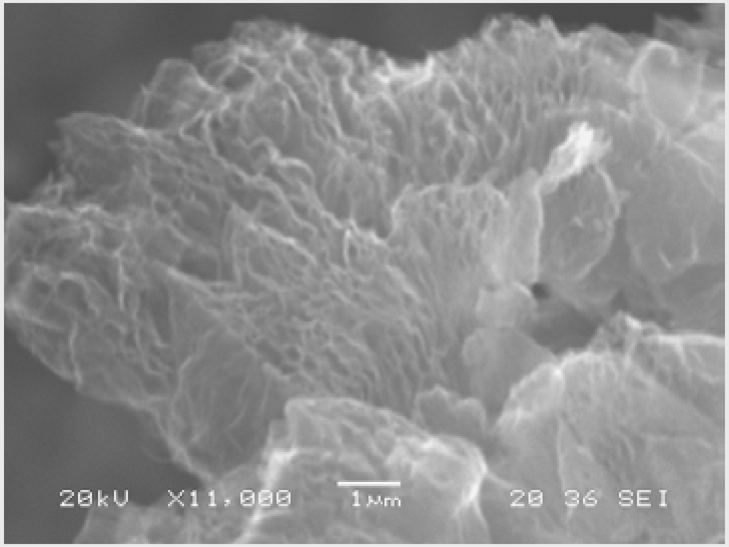


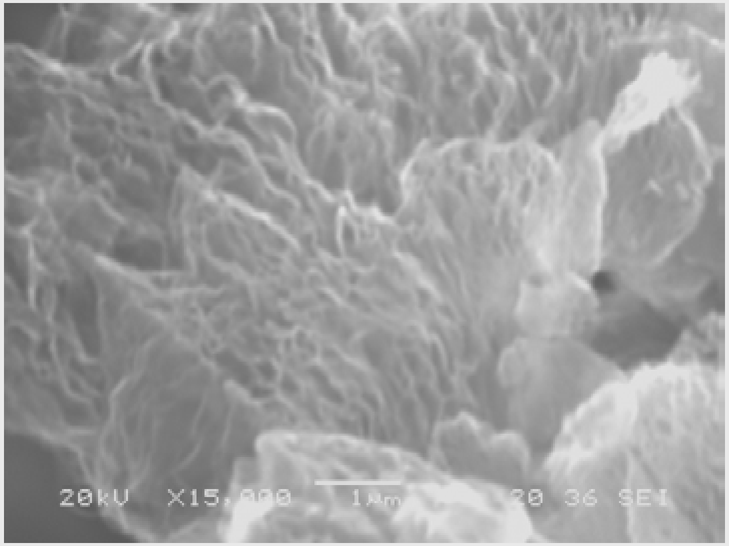
Aggressive intercalation + oxidation →

Step 2

Accomplishments

Enlarged SEM showing high surface area

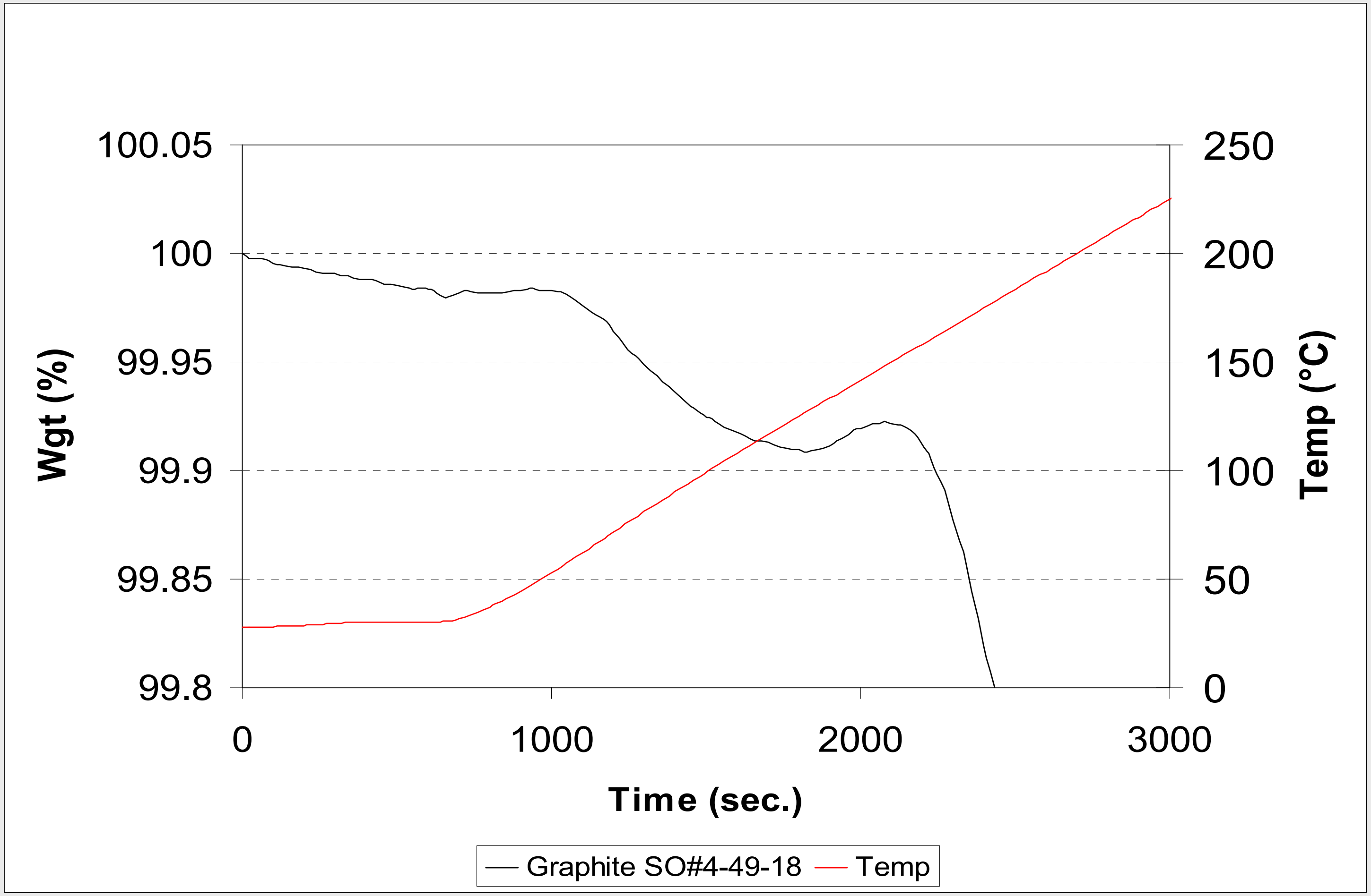




BET surface area: 700 m2/g

The space between graphite layers is more than 4.5Å

TGA of the Expanded Graphite for Hydrogen Storage



TGA Used for Fast Screening for Hydrogen Storage and Cycle Lifetime

- High temperature, high pressure thermo gravimetric analysis (TGA) is used to test the hydrogen storage and cycle lifetime.
- Look for the storage capacity decay under different pressures.
- Screen material modification to increase the hydrogen storage capacity and decrease hydrogen charge/discharge decay rate.

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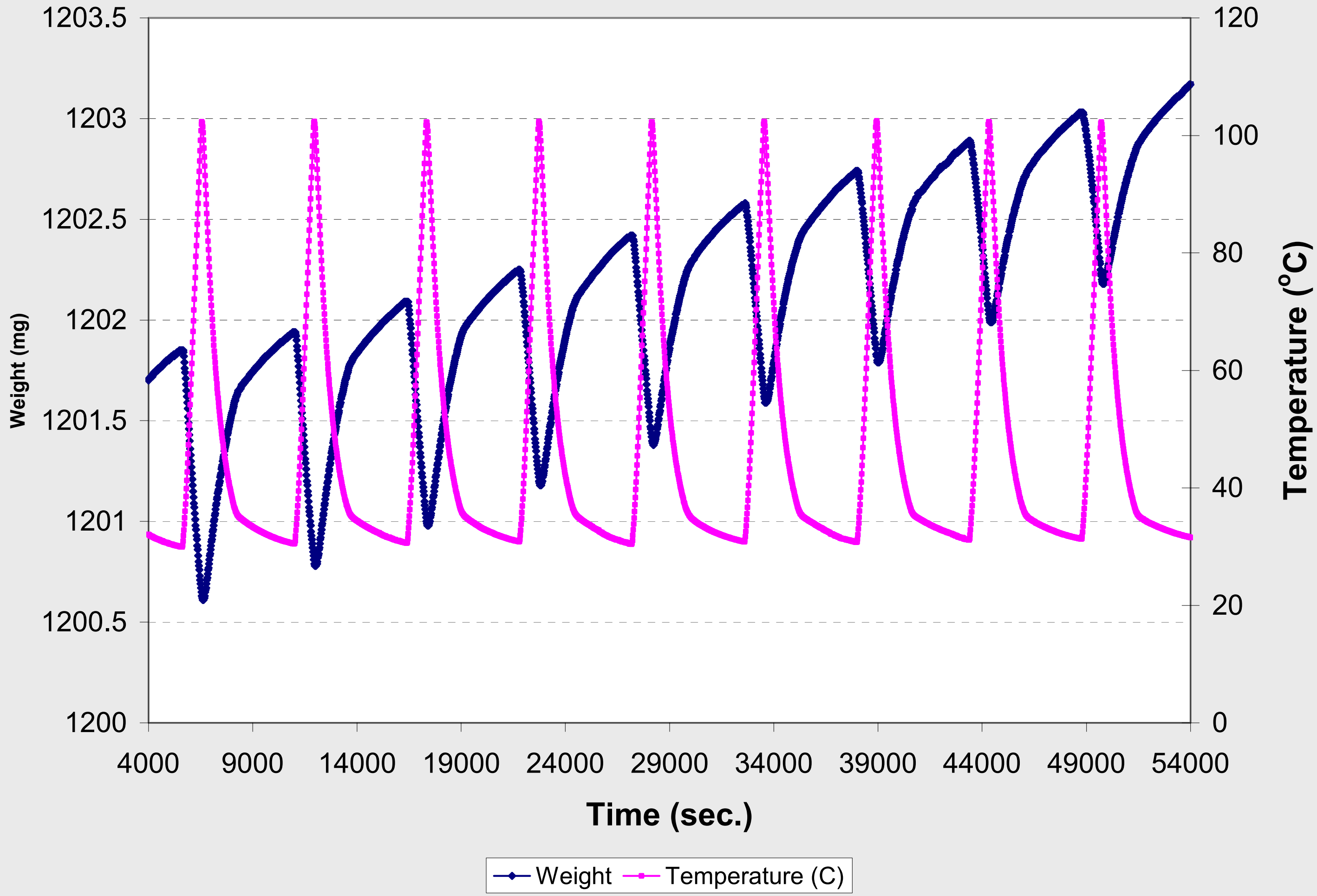
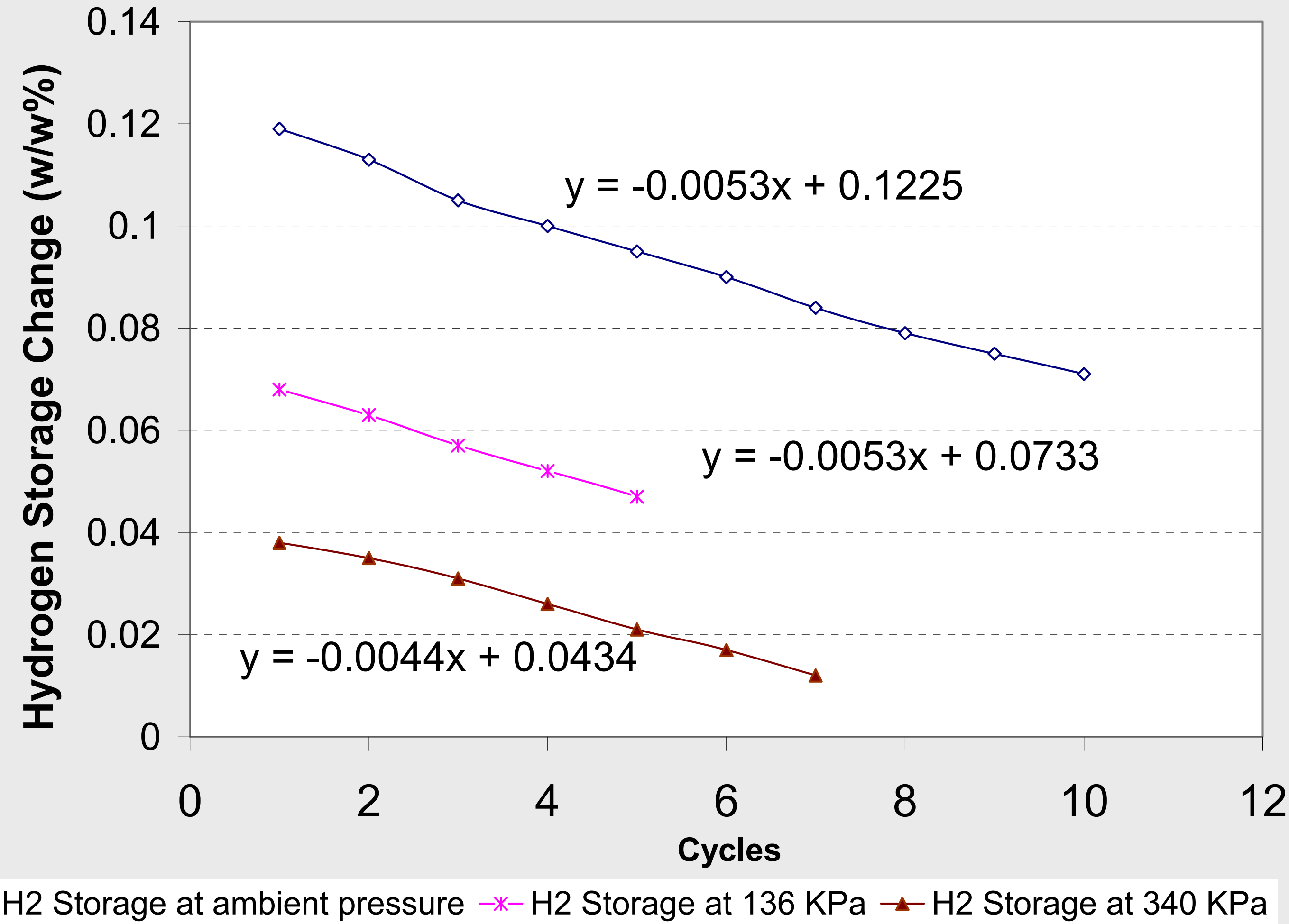
Hydrogen Uptake/Release Cycle on Graphite-based Material

Hydrogen storage capacity increases while the hydrogen release decreases.

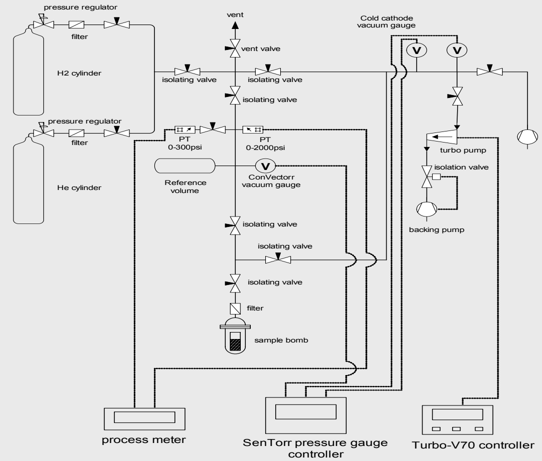


Hydrogen Storage Capacity Decays with Cycles under Different Pressures



Sievert Method to Test Hydrogen Storage Capacities

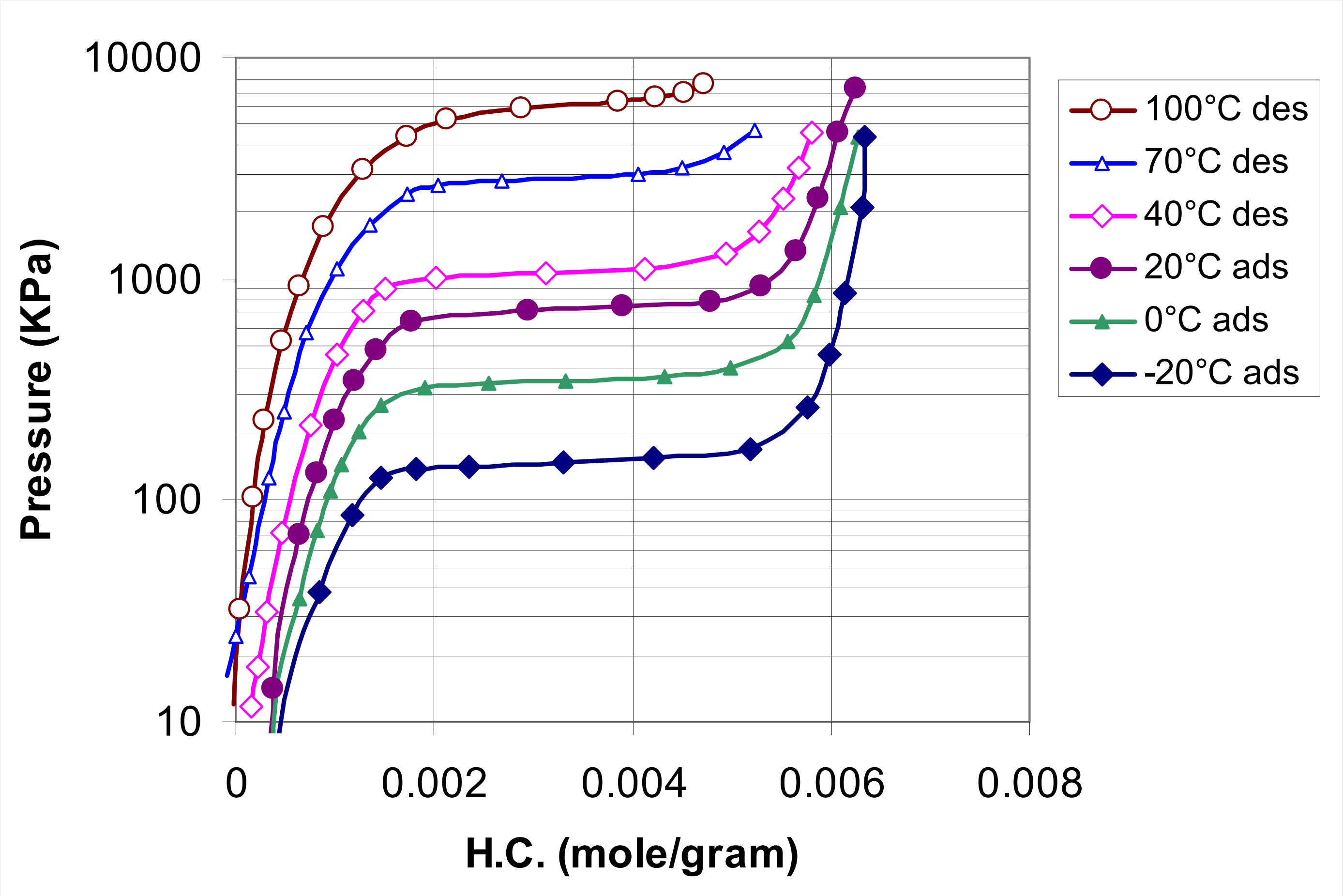
- Measure the hydrogen storage and release capacity at steady state under different temperatures.
- Calculate the enthalpy (ΔH) of the hydrogen adsorption



Seivert's Apparatus

Pressure/Composition Isotherm Curves of the Graphite-based Hydrogen Storage Material

Storage capacity: 0.8 ~ 1.0 wt%



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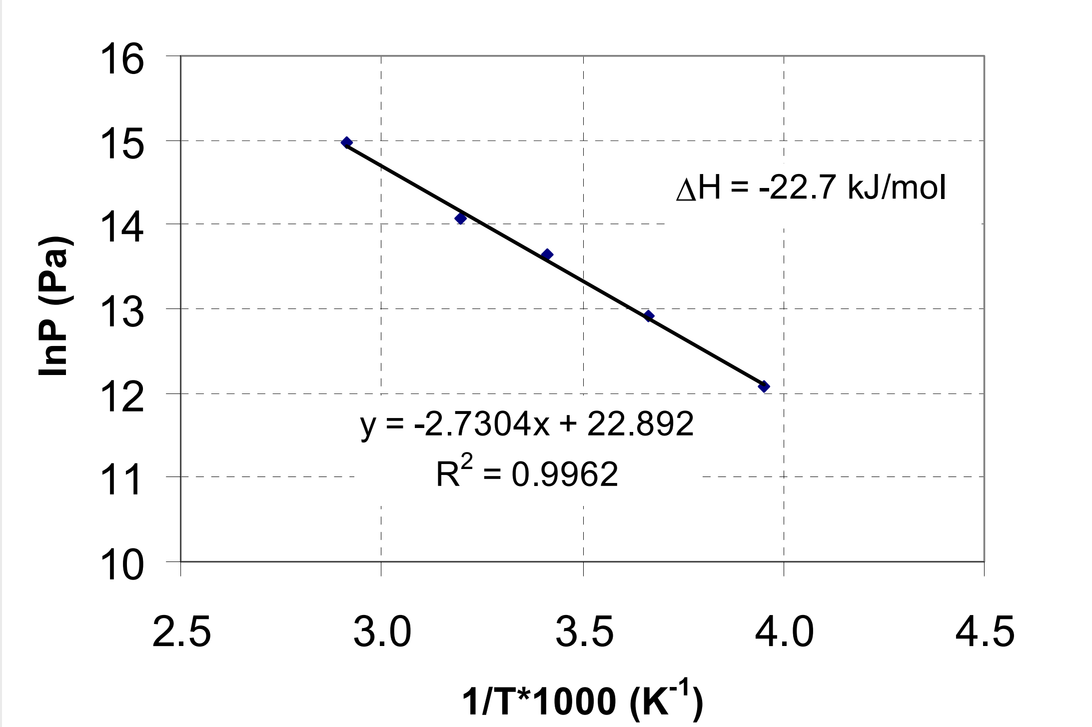
Heat (ΔH) of the Metal Modified Graphite Material Derived from PCT Curves



The heat release (ΔH) of the metal modified graphite material for hydrogen adsorption is –22.7 kJ/mol. The theoretical calculation of pure metal alloy for hydrogen adsorption is approximately –33 kJ/mol. The metal modified graphite has low heat produced in the hydrogen adsorption.

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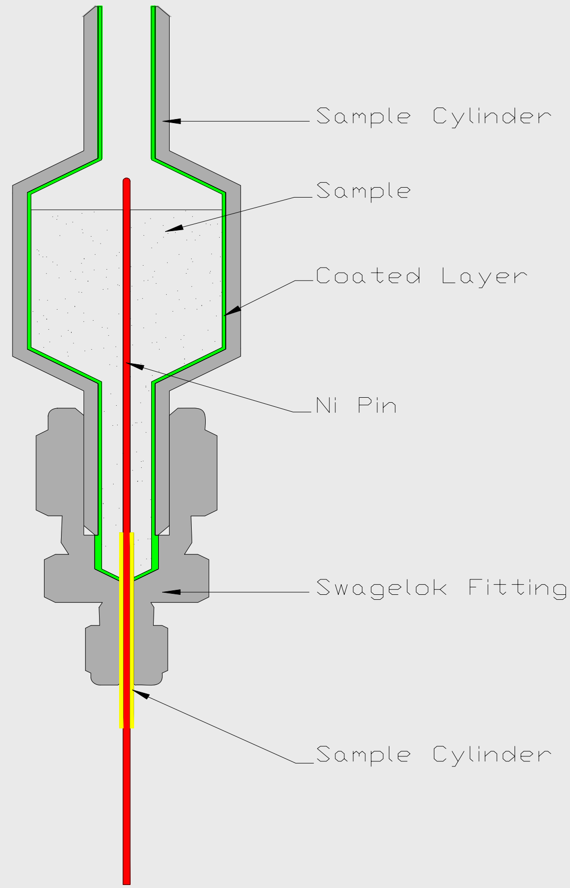
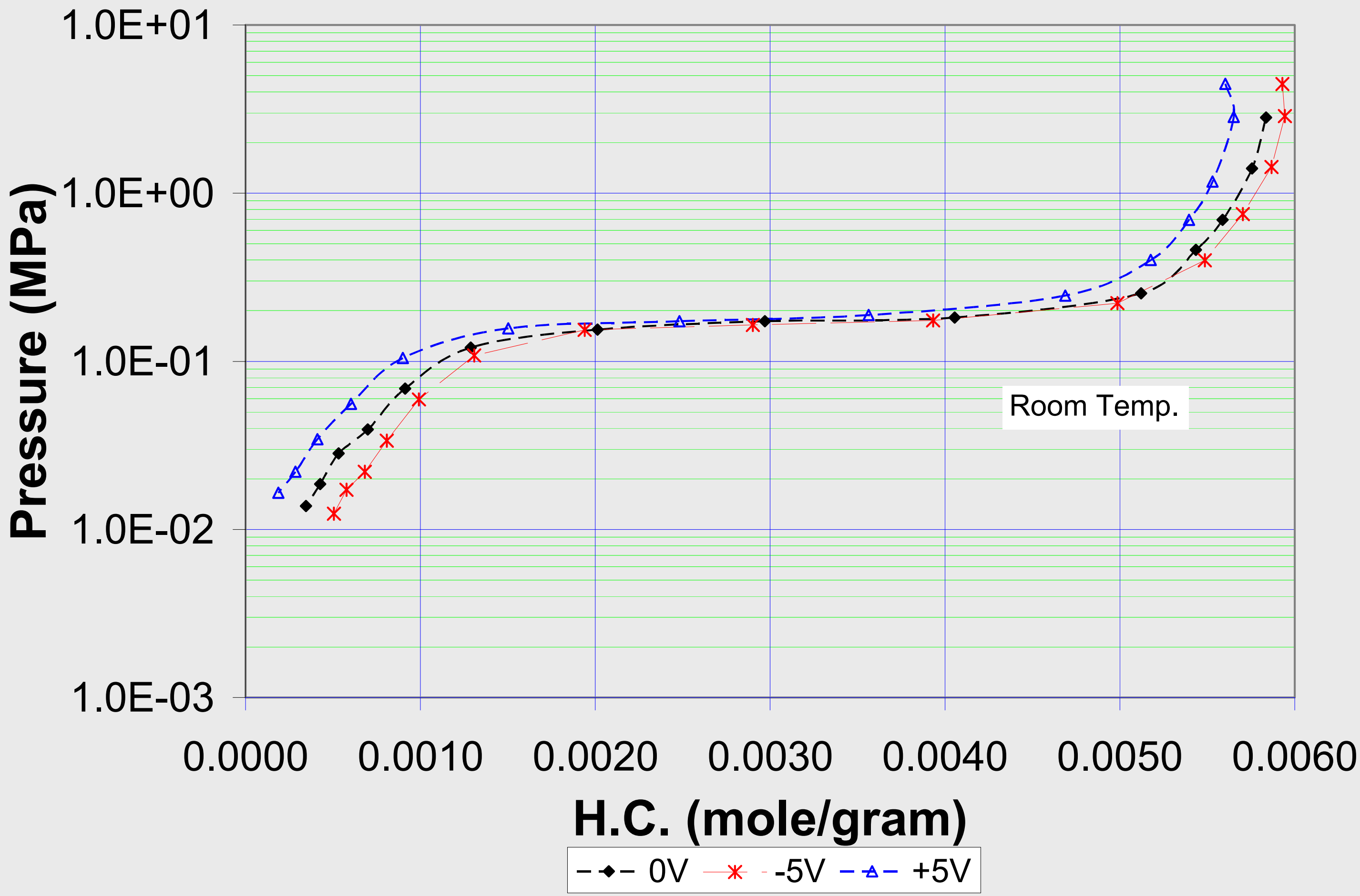
Electron-charged Device for Hydrogen Storage



Electron-charge Effect on Hydrogen Storage



Electron-Charge Effect on Hydrogen Storage

- The PCT shift is related to the electronic structure of the substrate. Electron-rich material needs positive charges and electron-poor material needs negative charges.
- External charge shifts the chemi-sorption to physi-sorption and shifts physi-sorption to chemi-sorption with different charges.
- Exploring benefits in conventional metal hydride and newer materials

Future Work

- Test and evaluation cycle for hydrogen storage
  1. Modify testing apparatus
  2. Test the expanded and intercalated graphite materials
  3. Investigate the electron charge effect on different hydrogen storage substrates.
- Calculate and compare the theoretical charge sufficient for the hydrogen storage target

Future Work

- Prepare samples for independent evaluation
- Investigate performance optimization and prototype container system
- Investigate process steps for production
- Preliminary analysis of production costs
- Pilot-evaluation of key production steps
- Prepare samples and prototype containers for independent evaluation

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Summary

- Demonstrated the hydrogen storage capacity 0.8~1.0 Wt% of graphite-based materials.
- Achieved 4.5Å space between graphite flakes
- Demonstrated the external electron charges affect the hydrogen storage. The PCT curves of the graphite-based materials show that the positive charges reduce the hydrogen storage and negative charges increase the hydrogen storage

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