Conducting Polymers as New Materials For Hydrogen Storage

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Part of the DOE Center of Excellence on Carbon-based Hydrogen Storage Materials

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STP42

This presentation does not contain any proprietary or confidential information

Overview

Timeline

- 01/01/2005
- 09/30/2009
- New Start

Budget

- Total project funding
  - $ 829,564 (DOE)
  - $ 165,912 (Penn)
- $75,000 (FY05)

Barriers

- **General**
  - A. Cost.
  - B. Weight and Volume.
  - C. Efficiency.
  - E. Refueling Time.
- **Reversible Solid-State Material**
  - M. Hydrogen Capacity and Reversibility.
  - N. Lack of Understanding.
  - O. Test Protocols and Evaluation Facilities.
- **Crosscutting Relevance**

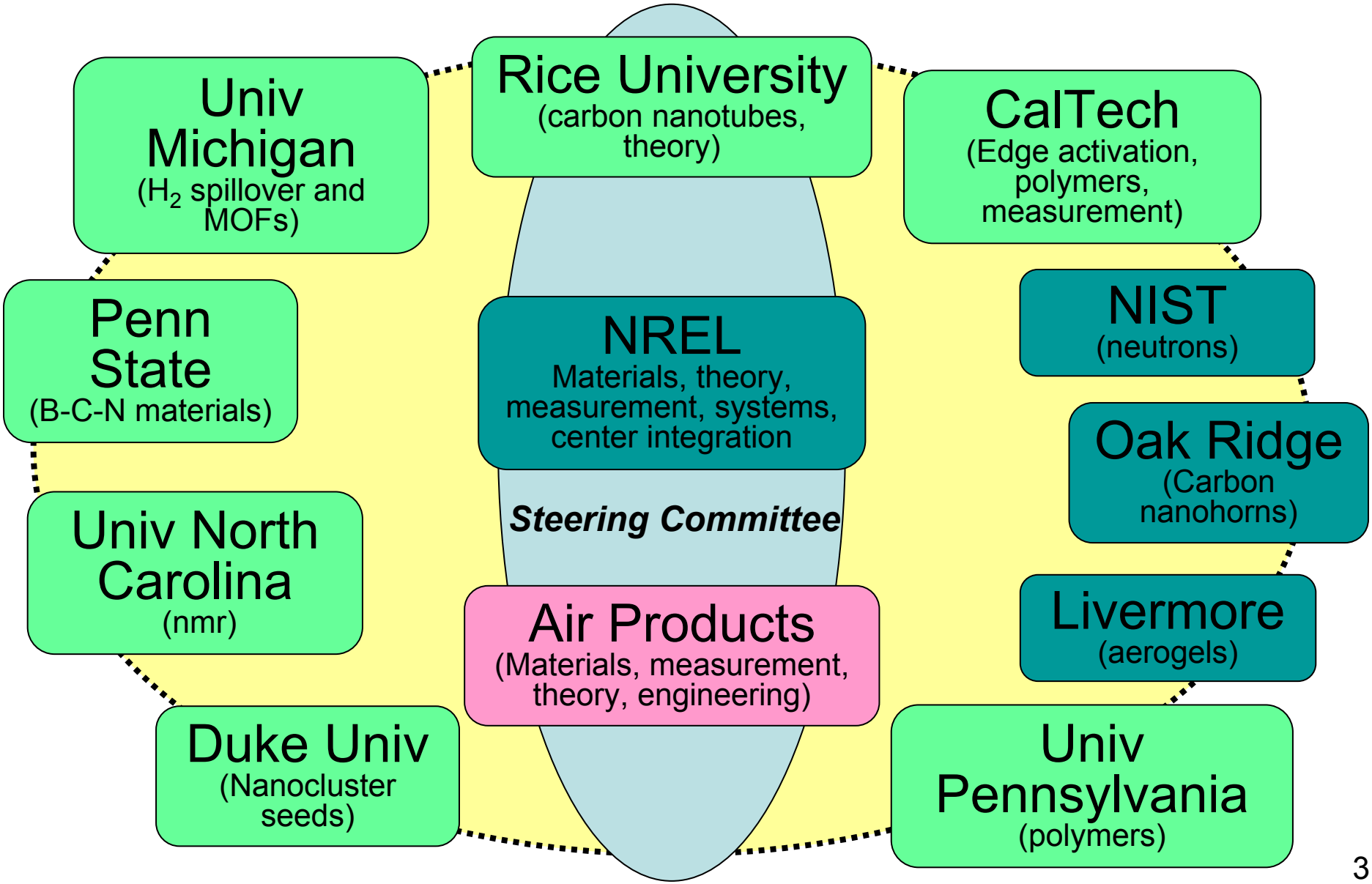
  Compressed Gas Systems Barrier H:
  Sufficient Fuel Storage for Acceptable Vehicle Range.
  Off-Board Hydrogen Storage Barriers S & T:
  Cost and Efficiency.

Partners

- **NREL Team**
- **CbHSC Partners**
- **University of North Carolina**
- **NIST**

CbHS Center of Excellence Partners

9 university projects (at 7 universities), 4 government labs, 1 industrial partner



Project Objectives

- To confirm the recent brief report by Cho et. al.* that approximately 6 wt% (reversible) hydrogen gas storage in doped (metallic) forms of organic conducting polymers ("synthetic metals"), polyaniline and polypyrrole, can be attained.

- To determine optimum polymer preparative methods, chemical composition and polymer crystallinity and morphology to give quantitative optimum conditions of hydrogen gas adsorption and desorption.

- To investigate hydrogen storage by the many known types of organic conducting polymers in their semiconducting and metallic forms.

*S.J. Cho, K.S. Song, J.W. Kim, T.H. Kim and K. Choo, "Hydrogen Sorption in HCl-Treated Polyaniline and Polyoyrrole: New Potential Hydrogen Storage Media". *Fuel Chemistry Division, 224th National Meeting of the American Chemical Society* 47, 790-791 (2002).

KEY PARTS FROM CHO'S* PAPER

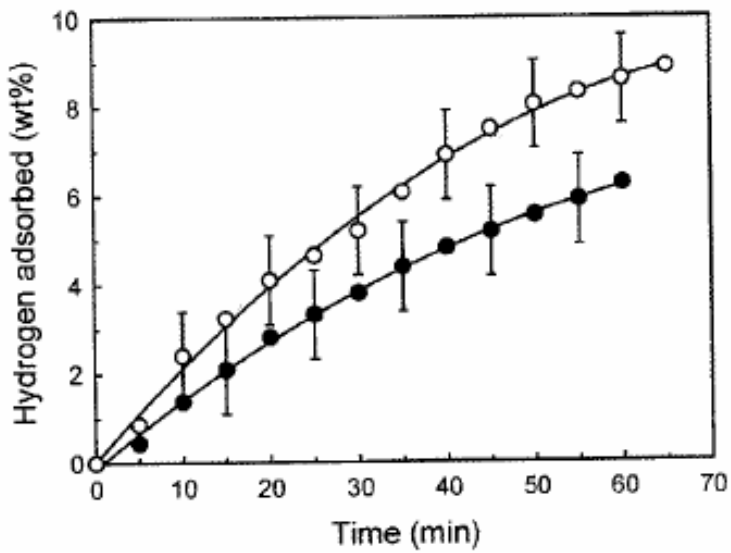


Figure 1. The amount of H_2 in wt. % for both (●) the PANI and (O) the Ppy treated with concentrated hydrochloric acid. The measurement was started after evacuation at 473 K and subsequently at room temperature at least 0.13 Pa.

Table 1. Summary of the hydrogen storage in metal hydrides, multiwalled carbon nanotubes and the acid treated conducting polymer measured using the same adsorption apparatus.

Sample	Press. (atm)/ Temp. (K)	Wt. %
† $MmNi_{4.7}Al_{0.3}$	10 ~ 20 / 298	1.2
† $MmNi_{4.8}Al_{0.2}$	10 ~ 20 / 298	1.3
$Ti_{0.7}Zr_{0.3}$ $Mn_{1.0}Cr_{0.9}Ni_{0.02}Fe_{0.03}$	10 ~ 20 / 298	2.0
MWNT	90 / 298	0.8
HCl-Treated PANI	90 / 298	6.0
HCl-Treated Ppy	90 / 298	8.0

† = "Mischmetals", i.e., a mixture of the early lanthanide metals, including Ce.

- Commercial (Aldrich) polyaniline (PANI) and polypyrrole used.
- The hydrogen storage can also be varied widely depending on the method of the modification process of the polymer using the concentrated hydrochloric acid, specifically, the exchange or removal level of the dopants, the drying temperature and the rigidity of the polymer backbone.

* Cho et al., *Fuel Chem. Div., 224th Nat. Mtg. Am. Chem. Soc.* 47, 790-791 (2002).

Approach

- Use nanofibers of polyaniline which we can easily prepare in large quantities (see following slides).

- Use different treatments *(e.g. conc. of HCl, etc.)* of commercial polyaniline and nanofibers of polyaniline.

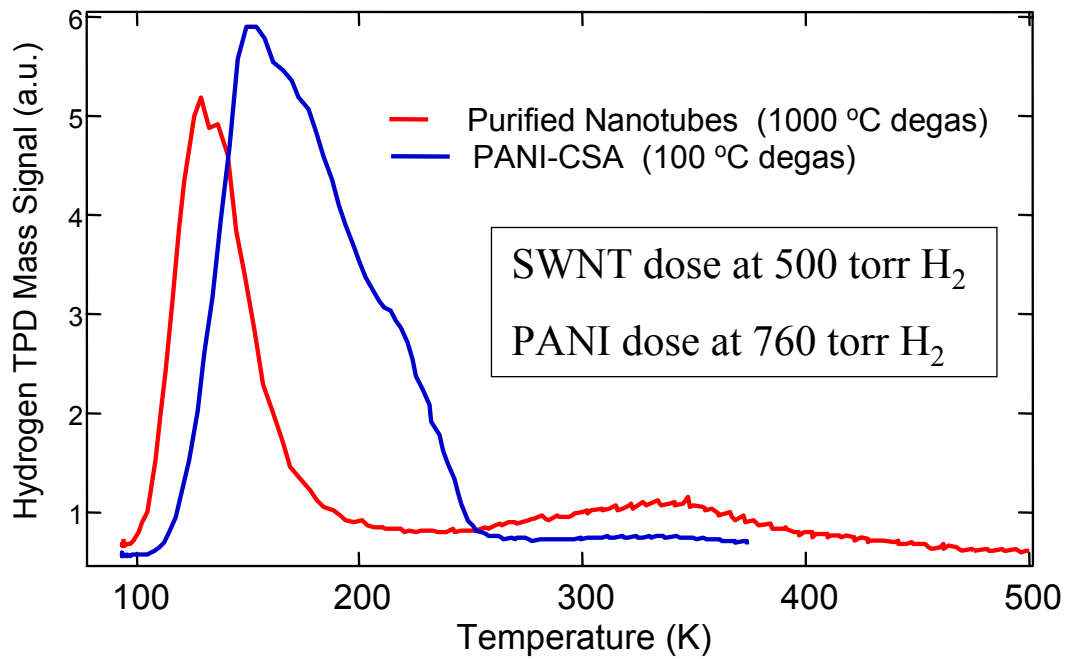
- For quick screening use desorption of H_2 *(using portable H_2 mass spectrometer recently purchased; see slide #14)* after treatment of a selected form of polyaniline at a given pressure and temperature of gaseous H_2.

- Measure H liability in polyaniline by exposure to D_2 atmosphere and evaluate H-D formed.

Results

Comparison of Conducting Polymers to SWNTs

- Very preliminary Temperature Programmed Desorption (TPD) studies by M. Heben Group at DOE labs, Golden, CO
- Polyaniline nanofibers doped with CSA (Camphorsulfonic Acid), PANI-CSA (one phase w/Triton X100 and stirring doped)
- Investigating the report By Cho et al.* of 6 wt% storage in PANI

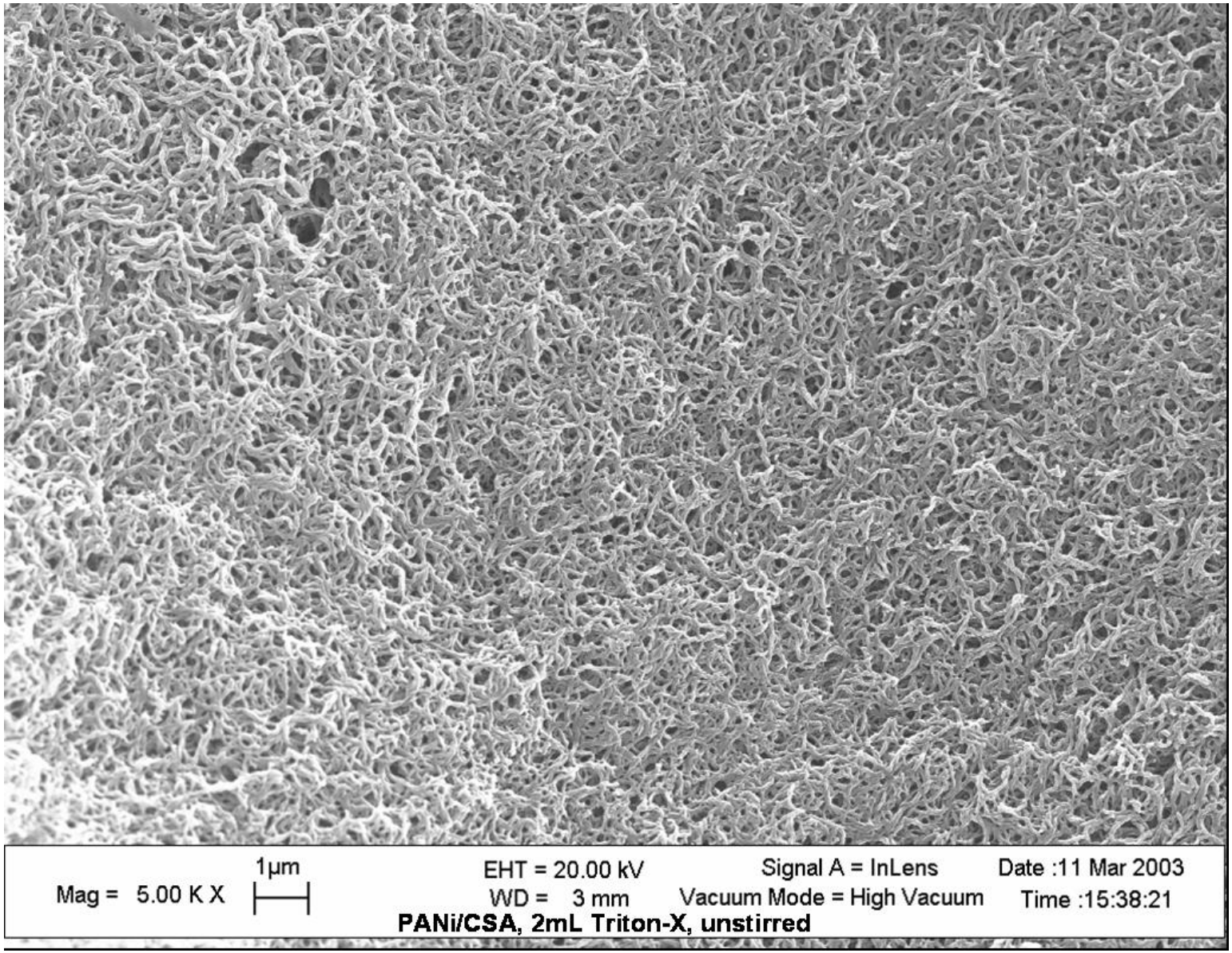


- PANI-CSA: extremely broad desorption peak (~ -165 °C to -25 °C) with a shoulder at ~ -60 °C. This could indicate the presence of a variety of different binding sites and though it is not room temperature, it is quite accessible through standard cooling methods.
- Potential roles of the surfactant and dopant are considered to be of very great importance for further study.

* Cho et al., *Fuel Chem. Div., 224th Nati. Mtg. Am. Chem. Soc.* 47, 790-791 (2002).

Results

Polyaniline Nanofibers Doped with Camphorsulfonic Acid (CSA) - PANI-CSA



Results

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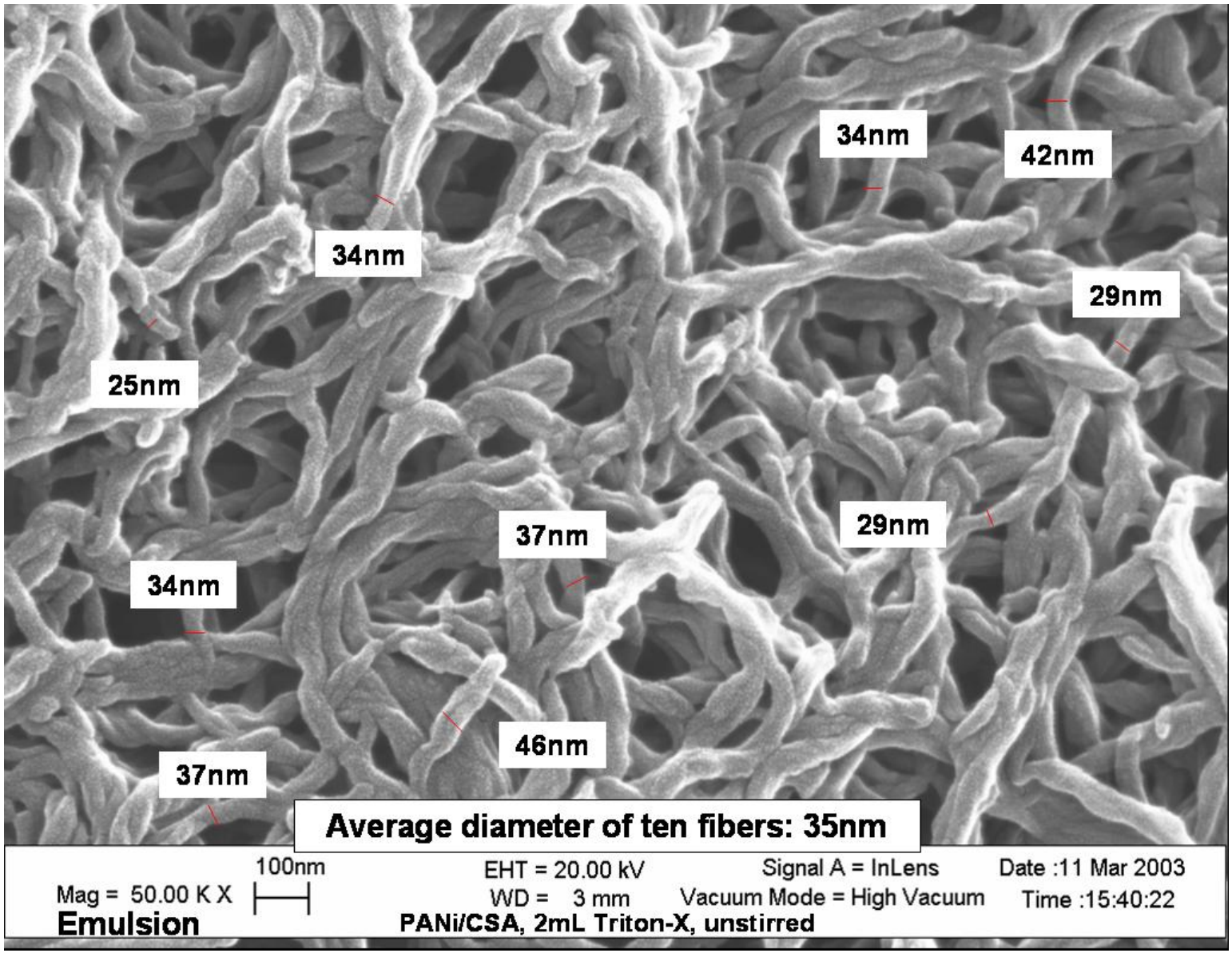
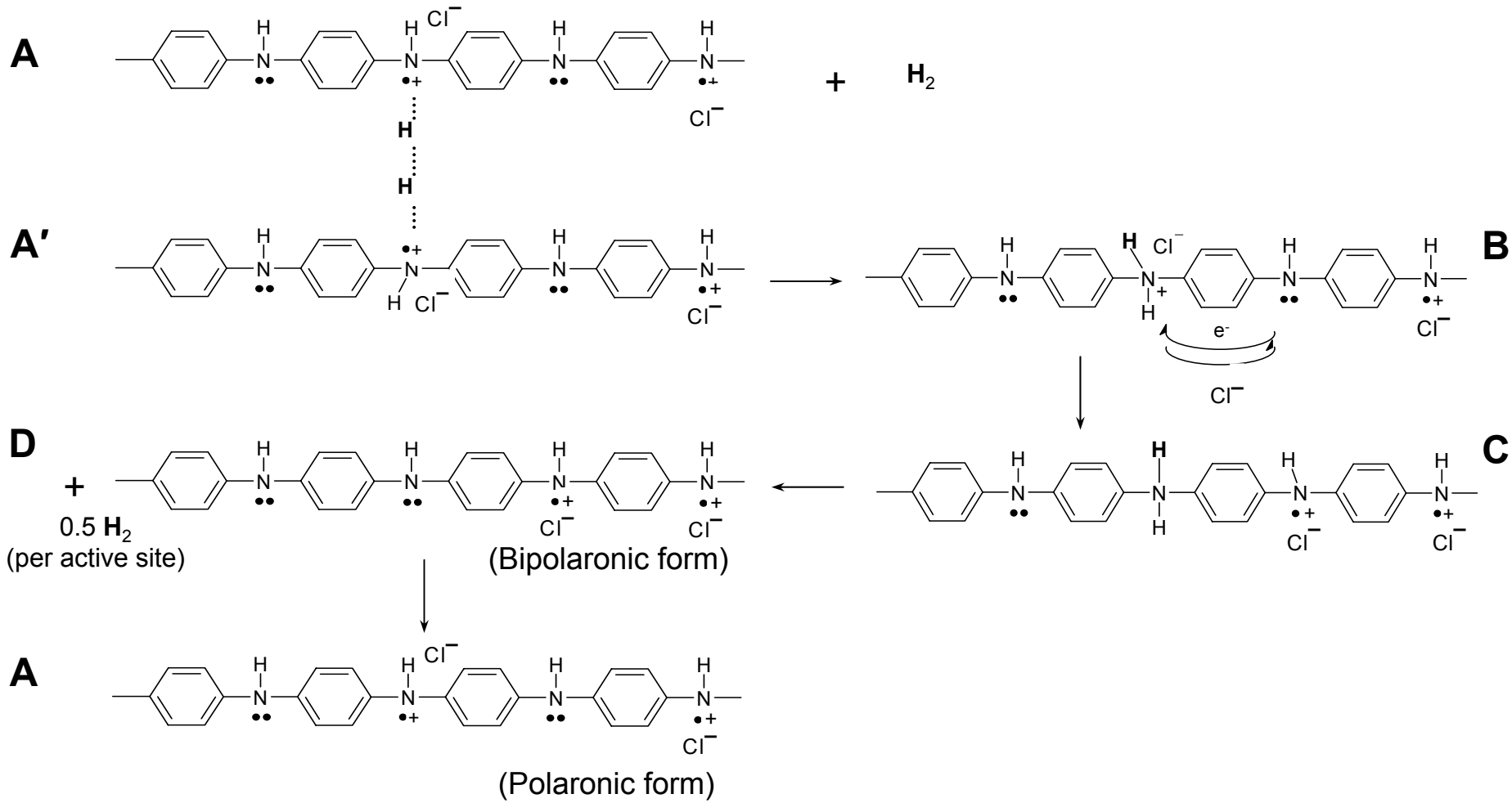


Mechanism of H_2 Adsorption/Desorption

Proposed mechanism for H_2 dissociation via interaction with free-spins on adjacent polyaniline chains to form N-H bonds in metastable species:



(**A**) Segment of HCl-doped paramagnetic polyaniline chain; (**A'**) Adjacent polyaniline chain, identical to **A**; (**B**) Metastable polyaniline species containing a conventional ammonium ion; (**C**) polyaniline containing a neutral (unstable) ammonium species, which spontaneously decomposes to (**D**) with liberation of ½H_2. The whole process repeats with **D**, which is identical to **A** and **A'** . Identical processes occur with **A** and **A'**.

Future Work

- **Remainder of FY2005:**

  - ✓ Continue the studies on the unusual features related to the interaction of H_2 with certain forms of polyaniline as observed in preliminary studies at NREL in Dr. M. Heben's group will be continued.

  - ✓ NMR studies by members of the Carbon-Based Hydrogen Storage Center (CbHSC) such as those at the University of N. Carolina, may assist in understanding H storage capacity and mechanism of adsorption.

Future Work

- **FY 2006:**

  - ✓ Continue TPD and NMR studies.

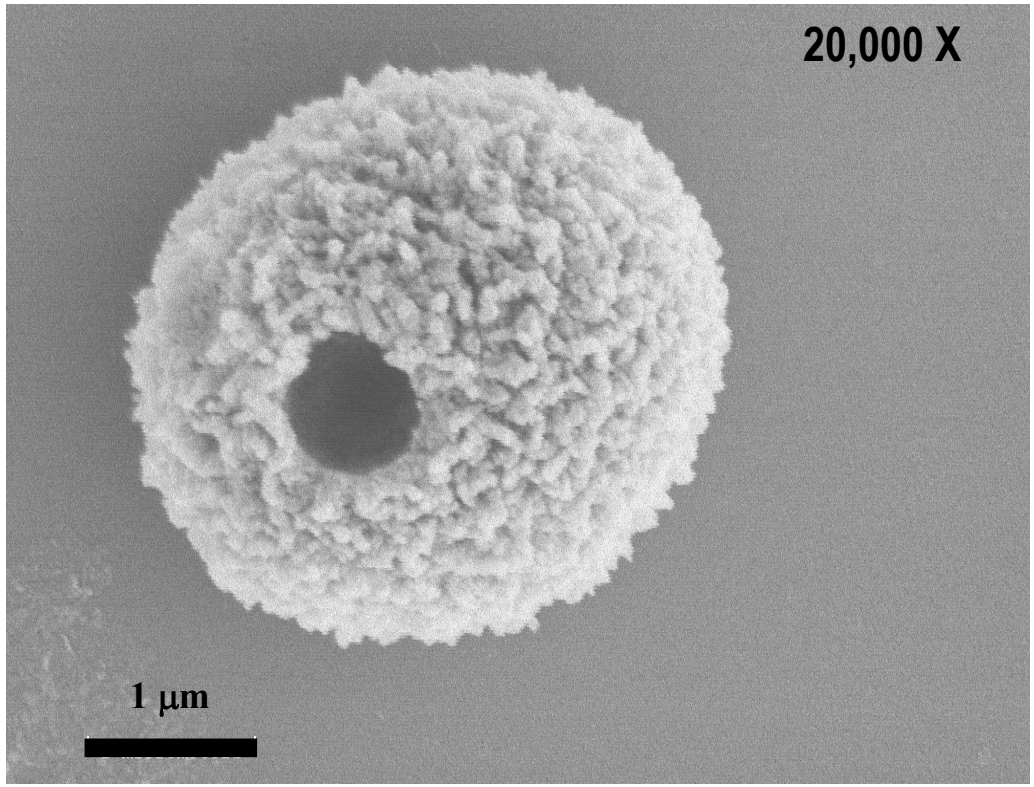
  - ✓ Neutron scattering measurements at NIST may yield direct atomic and nanoscale information related to hydrogen adsorption sites and diffusion mechanisms.

  - ✓ Examination of the surface area and microporosity by standard gas adsorption studies of the nanofibers of an electronic polymer in collaboration with our CbHSC partners will be most important.

Future Work

Hollow Nano/Micro Spheres of New Forms of Aniline-Based Materials

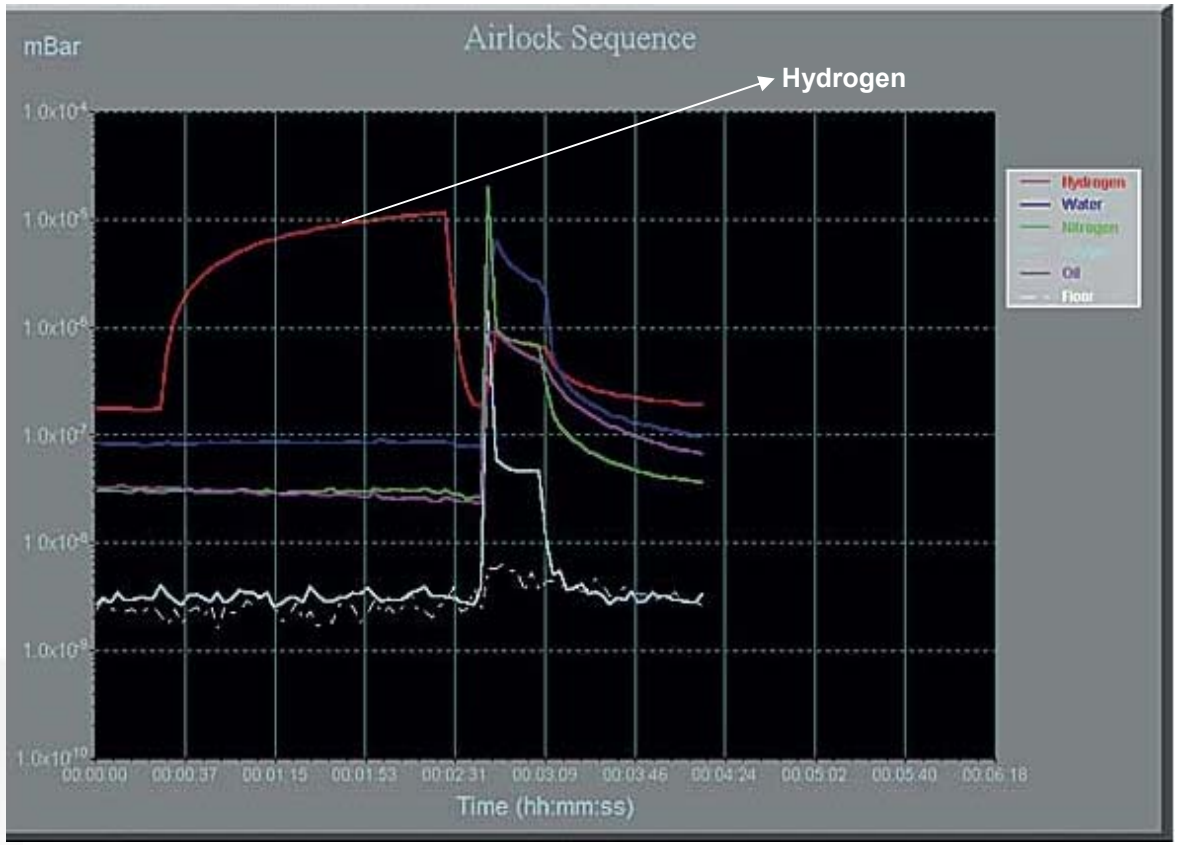
- Use of new types aniline-based Materials.
- Control of sphere and hole sizes opens up new opportunities for hydrogen storage.



Future Work

Construct a TPD System (Penn/UTD)
Screening of Conducting Polymer-Based Samples

Mass Spectrometer – Model QMS 100



Hydrogen Plot (Vs. Time)

Company: Stanford Research Systems

Total Cost: $ 23,131.00

CRITICAL MILESTONES FOR FY2005 EFFORT

Can the previous report on reversible H_2 adsorption by *(any type of)* polyaniline be confirmed by this present study?

- If the answer is "yes", then a vast new potential class of organic H_2-adsorbing materials is confirmed! (… and also potential catalysts for fuel cells).

- If the answer is "no" then:
  - Incorporate metal species in electronic polymers *(by coordination with N <u>or</u> S in the electronic polymer backbone)*.
  - Investigate reversible H_2 adsorption by mixed metal oxides (*c.f.* Chu et al.)

"GO/ NO GO" DECISION POINTS (END FY2006)

- A *"go"* decision will be made if we are successful in obtaining > 1wt. % H_2 storage by polyaniline. We will then determine what changes in the morphology, dopant, surfactant, etc., increases the H_2 storage and hence understand what causes the H_2 adsorption.

- If < 1 wt. % of reversible H_2 is obtained under a variety of experimental conditions, then the effect of incorporation of coordinated metal ions in the polymer will be studied.

MILESTONES (5 YEARS PROJECT)

- Measure hydrogen adsorption/desorption capacity of at least 4 commercially available polyaniline samples and at least 4 U. Penn polyaniline samples (3Q Year 1)

- Determine volumetric and gravimetric limits of performance of commercially available polyaniline and U. Penn nanofibers, nanotubes and hollow nanospheres, and report on probability of meeting FY10 system targets with anticipated system penalties (Go/No Go: 3Q Year 2)

- Deliver sample exhibiting performance characteristics that will meet FY10 system targets with determined system penalties to DOE-specified facility (Go/No Go: 3Q Year 3)

- Deliver 1 kg active material that meets system goals for testing to DOE-specified facility (4Q Year 5).

DELIVERABLES (5 YEARS PROJECT)

- Brief quarterly reports indicating status and progress (each quarter)
- Annual CbHSC workshop held in conjunction with program review (May, each year)
- Annual written reports including technical data and other results indicating status toward the 2010 targets (4Q, each year)
- Material samples at Go/No Go decision points and end of project for testing at NREL and one other facility specified by DOE (3Q Year 2, 3Q Year 3, and 4Q year 5)
- Final report (4Q Year 5)

TASKS / SUMMARY (5 YEARS PROJECT)

TASK	FY2005	FY2006	FY2007	FY2008	FY2009
Task 1 •H_2 Adsorption/Desorption •Polyaniline commercial/Penn			**Go/No Go** (Polyaniline: Commercial/ Penn) **Down-select best sample**		
Task 2 •H_2 Adsorption/Desorption •Polyaniline – chemical treatment •SWNTs-Conducting Polymers (CP) Composites - with or without added metals				**Go/No Go** (Polyaniline /SWNTs-CP)	**Down-select best sample**
Task 3 •Delivery materials to Center Partners - Characterization / Test - H_2 storage properties and mechanism					**Down-select best sample: H_2 storage ≥ 6 % wt.**
Task 4 •Determine proton excahnge - D_2 / H to form HD					

Hydrogen Safety

The most significant hydrogen hazard associated with this project is:

Hydrogen Gas Leakage

The most significant hazard associated with this project would in principle be hydrogen leakage. In our studies this hazard appears to be insignificant since we will use hydrogen at a pressure of 1 atm or less. Moreover, the total volume of hydrogen contained in our laboratory will be only 0.056 m^3. However, any accidental release of this volume into the laboratory is negligible.

Hydrogen Safety

Our approach to deal with this hazard is:

Any opening of hydrogen gas bottle and connection to a portable mass spectrometer will be performed in a standard laboratory hood in good working condition. A series of guidelines will be implemented in order to handle hydrogen safely. These guidelines are:

(1) Use of appropriate designs, procedures, and materials; keep constant watch to detect immediately any possible hydrogen leaks; access control to the hydrogen-working area;

(2) Effort will be done to eliminate potential ignition sources as well as establish and adhere to hazardous classified locations;

(3) In case of fire, it will be handled safely and the immediate authority at the department of chemistry as well as at the University of Pennsylvania will immediately be notified;

(4) All personal will be trained and formal procedures will be used;

(5) The University of Pennsylvania has an Office of Environmental Health and Radiation Safety (EHRS: http://www.ehrs.upenn.edu) that will be solicited to supervise and advise our activities and safety procedures.