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 NREL, U.S. Department of Energy (DOE), USA

Overview

Barriers

- **General**
  Cost.
  Weight and Volume.
  Efficiency.
  Refueling Time.
- **Reversible Solid-State Material**
  Hydrogen Capacity and Reversibility.
  Lack of Understanding.
  Test Protocols and Evaluation Facilities.
- **Crosscutting Relevance**
  Compressed Gas Systems Barrier:
  Sufficient Fuel Storage for Acceptable Vehicle Range.
  Off-Board Hydrogen Storage Barriers:
  Cost and Efficiency.

Partners

- **NREL Team**
- **Carbon-based Hydrogen Storage Center (CbHSC) Partners – NREL/DOE**
- **University of North Carolina**
- **NIST**

Carbon-Based Materials

- **High Surface Area Sorbents**
  - ✓Hybrid Carbon Nanotubes
  - ✓Aerogels (Metal-Doped Interconnected Carbon Particles)
  - ✓Graphite Nanofibers (GNF)
  - ✓Metal-Organic Frameworks
  - ✓**Conducting Polymers**

- **CbHSC Goals**
  - ✓Hydrogen Storage 6 wt.% and 45 g H_2/L
  - ✓Hydrogen Binding Energies Between ~20 and 40 kJ/mol (physiosorption ~4 kJ/mol; chemical bond ~160 kJ/mol)
  - ✓Relationship Between Nanoscale Structures & Hydrogen Binding Energies

Electronic Polymers

Non-Doped: Semiconductors/Insulators

"dope" ↓ ↑ ***"de-dope"***

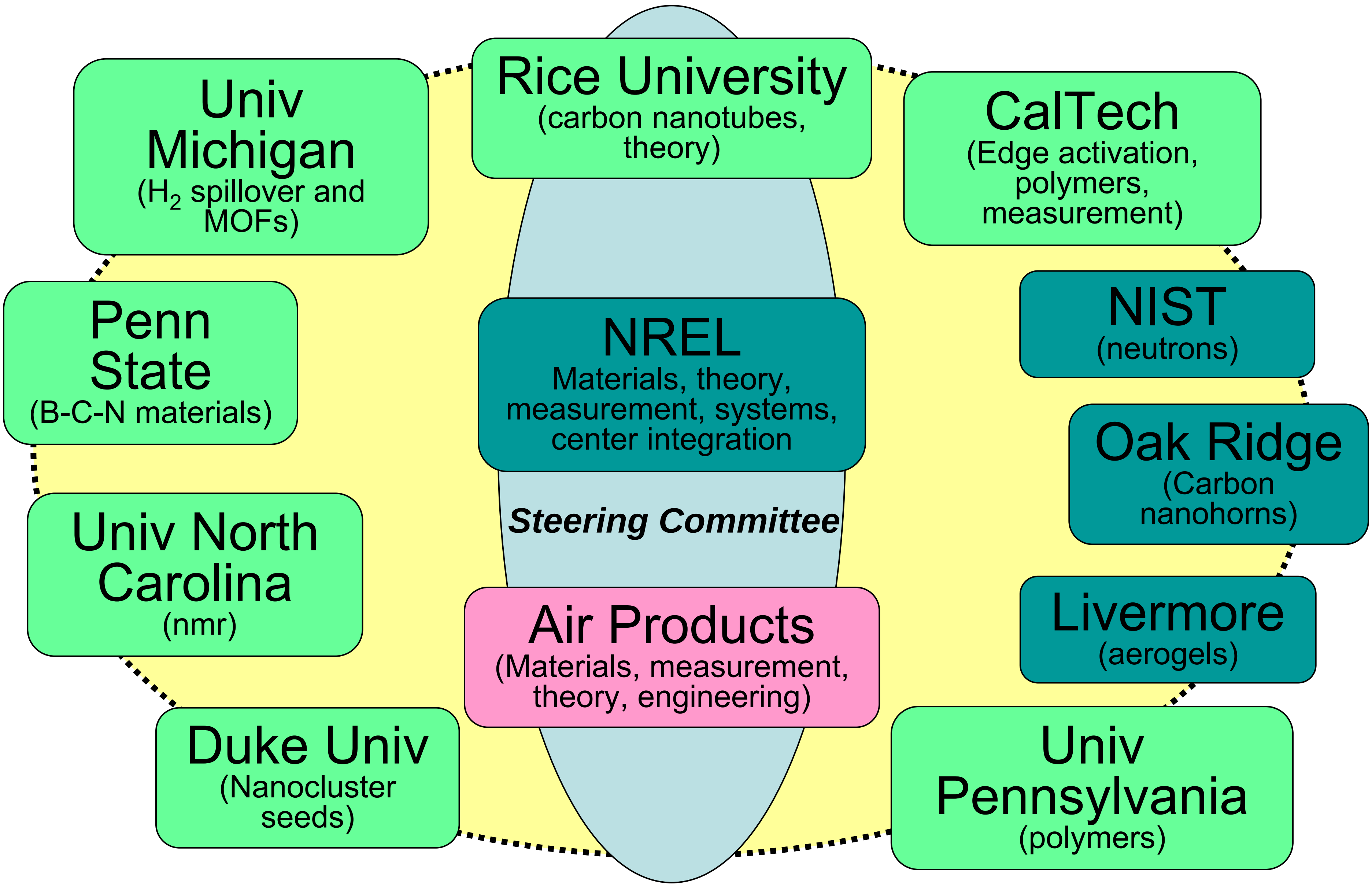
Doped: Conducting Polymers

("Synthetic Metals")

- **Doping: The unique, central, underlying and unifying theme in conducting polymers**
- **Controlled addition of known, small (<10%), non-stochiometric quantities of chemical species results in dramatic changes in electronic, optical, and *structural properties* of the polymer**
- **Doping is *reversible* (No degradation of the polymer "backbone")**
- **Doping and undoping by either chemical or electrochemical methods**

CbHS Center of Excellence Partners

9 USA university projects (at 7 universities), 4 USA government labs, 1 USA 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 the organic conducting polymers ("synthetic metals"), polyaniline and polypyrrole, can be attained.
- To determine optimum polymer synthetic 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.

† ***"There are as many different types of polyaniline as there are people who make it!"***

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

† **A.G. MacDiarmid et al., Synthetic Metals, 119 (2001) 27.**

Approach

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

- 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 following display)* 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.

MILESTONES

- Measure hydrogen adsorption/desorption capacity of at least 4 commercially available polyaniline samples and at least 4 University of Pennsylvania polyaniline samples (i.e. Tasks 1 and 4; see adjacent display)
- Determine volumetric and gravimetric limits of performance of commercially available polyaniline and University of Pennsylvania nanofibers, nanotubes and hollow nanospheres, and report on probability of meeting year 2010 system targets with anticipated system penalties (Go/No Go, i.e. Tasks 1 and 3; see adjacent display)
- Deliver sample exhibiting performance characteristics that will meet year 2010 system targets with determined system penalties to DOE-specified facility (Go/No Go, i.e. Tasks 2 and 3; see adjacent display)
- Deliver 1 kg active material that meets system goals for testing to DOE-specified facility (Task 3; see adjacent display)

"GO/ NO GO" DECISION POINTS (END OF 2006)

- 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 optimize 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.

TASKS / SUMMARY

TASK	2005	2006	2007	2008	2009
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 •SWNT-Conducting Polymers (CP) Composites - with or without added metals				**Go/No Go** (Polyaniline /SWNT-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 $\geq$ 6 % wt.**
Task 4 •Determine proton excahnge - D_2 / H to form HD					

KEY PARTS FROM CHO'S* PAPER

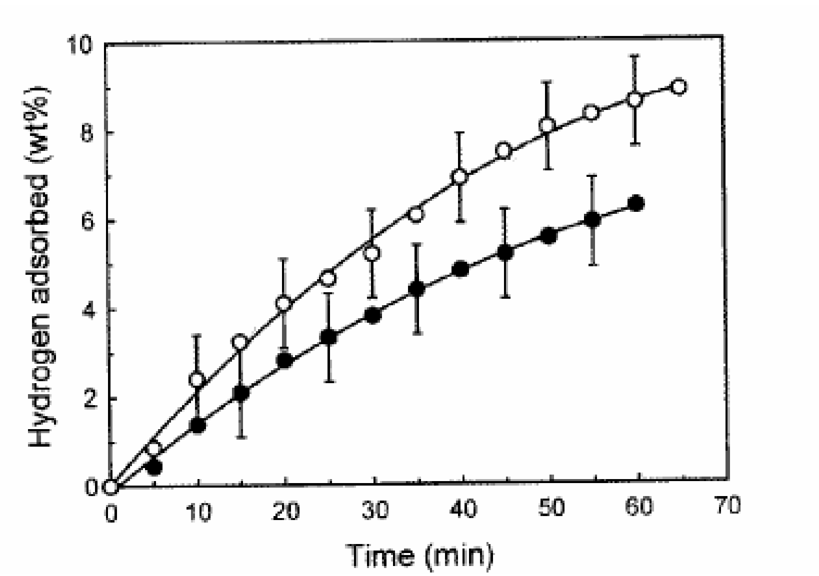


Figure 1. The amount of H_2 in wt. % for both (●) the polyaniline and (O) the polypyrrole treated with concentrated hydrochloric acid. The measurement was started after evacuation at 473 K and subsequently at room temperature at least 0.13 Pa.

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 Polyaniline	**90 / 298**	**6.0**
HCl-Treated Polypyrrole	90 / 298	8.0

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

- **Commercial (Aldrich Co.) polyaniline (PANI) and polypyrrole (Ppy) used.**
- **Hydrogen storage reportedly varying greatly depending on the synthetic method and processing.**

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

UNDERSTANDING CHO'S WORK

"There are as many different types of polyaniline as there are people who make it!" *

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 presented! (… and also potential catalysts for fuel cells).

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

*** A.G. MacDiarmid et al., Synthetic Metals, 119 (2001) 27.**

MORPHOLOGY OF POLYANILINES

Aniline

Oxidant

Solvent (**water**)

(1) Acidic Medium (**e.g. pH < 1**)

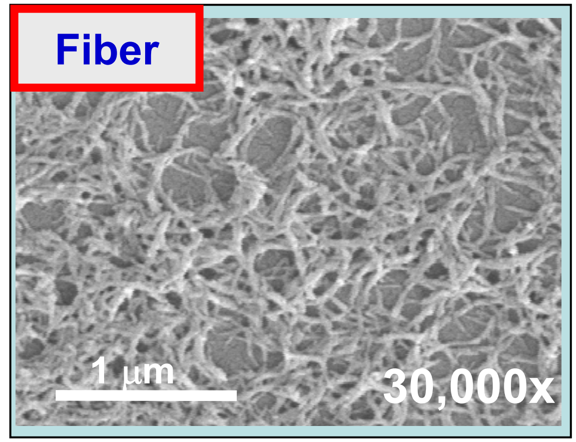
(2) Basic Medium (**e.g. pH > 10**)

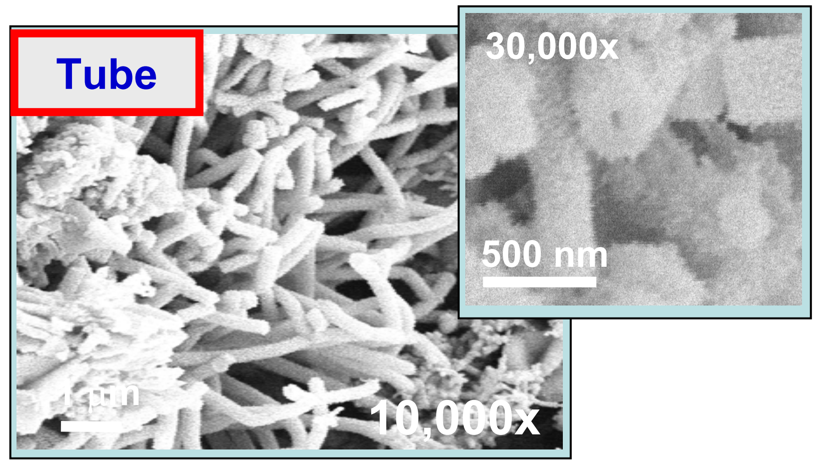
(3) Buffer System

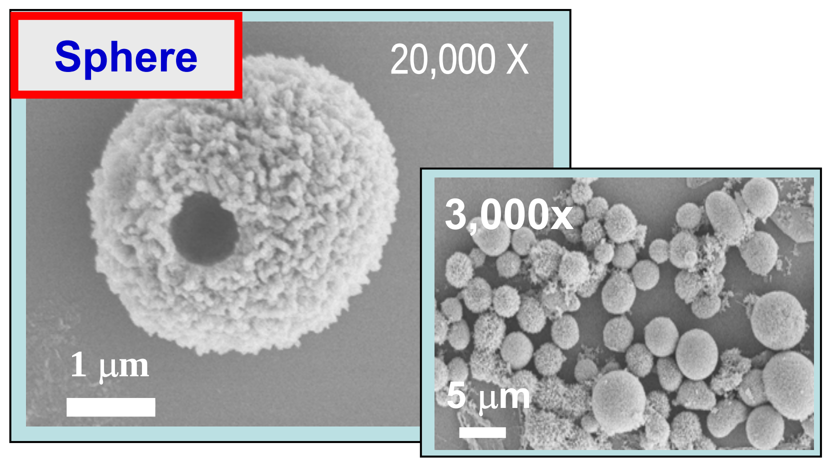
(4) No Acid / No Base / No Buffer Added

(5) Temperature Control

(6) Template (**e.g. surfactant**)

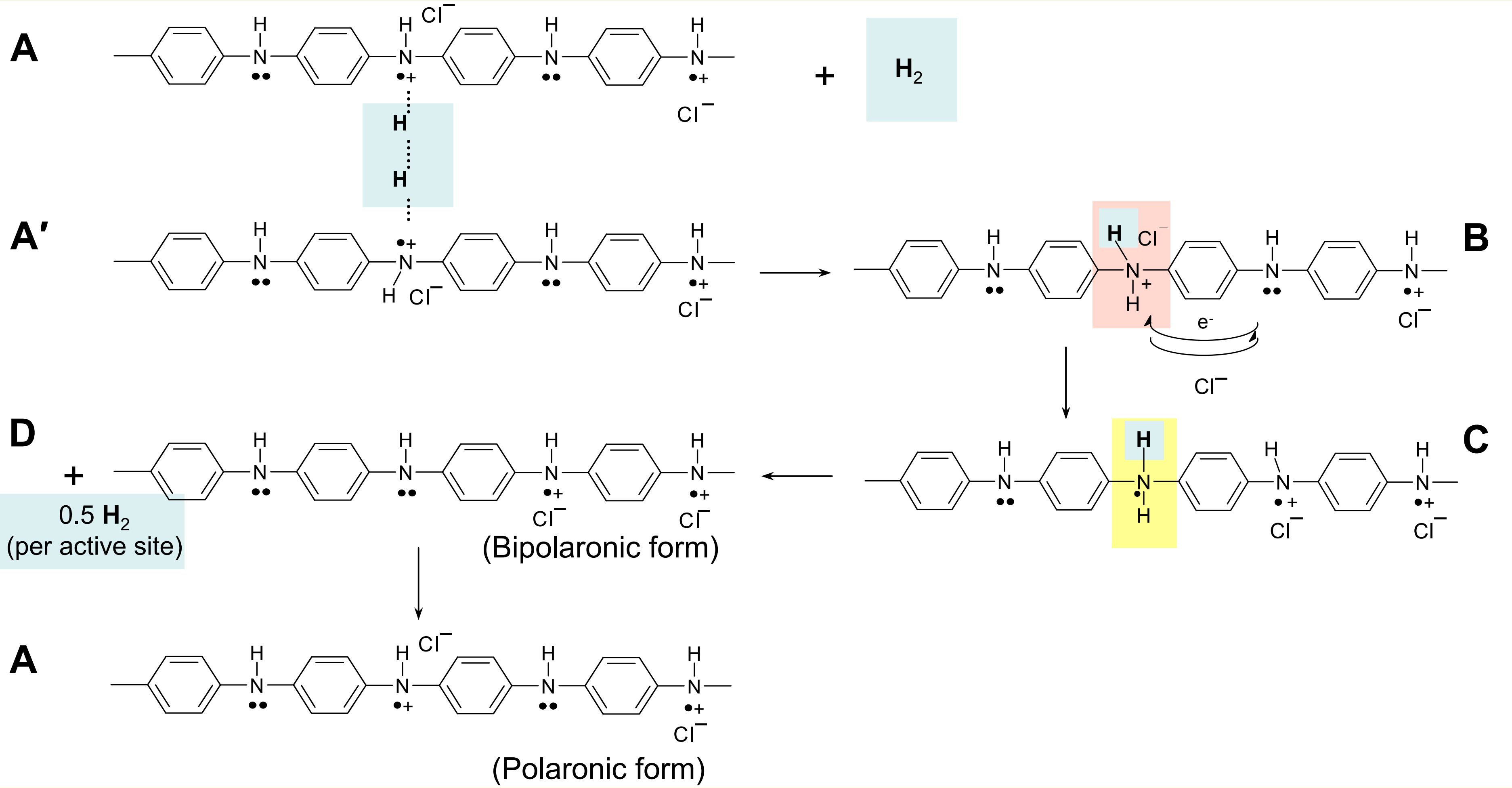






Proposed of H_2 Adsorption/Desorption By Synthetic Metals

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

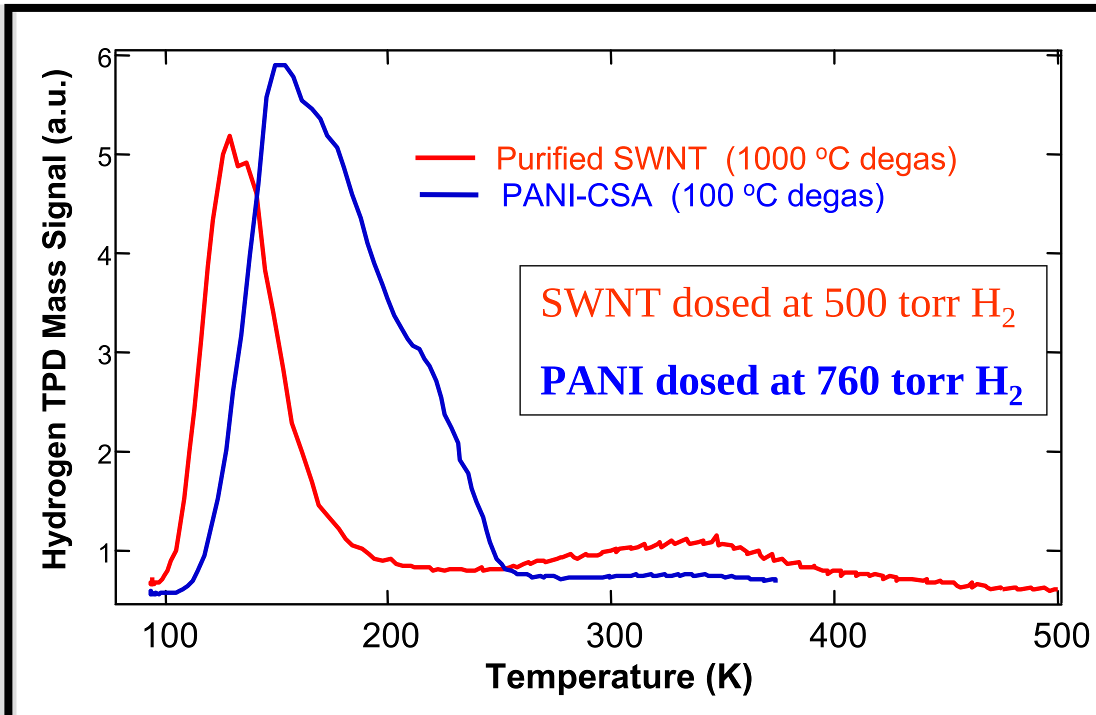


(**A**) Segment of HCl-doped paramagnetic polyaniline chain; (**A'**) Adjacent polyaniline chain, identical to **A**; (**B**) Metastable polyaniline species containing a conventional ammonium ion; (**C**) polyaniline containing a neutral (unstable) **"ammonium metal",** which spontaneously decomposes 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'**.

Results

Comparison of Conducting Polymers to Single Wall (carbon) Nanotubes (SWNT)

- Very preliminary Temperature Programmed Desorption (TPD) studies by M. Heben Group at DOE labs, Golden, CO.
- Polyaniline (PANI) nanofibers doped with CSA (camphorsulfonic acid) in presence of surfactant (Triton X100).

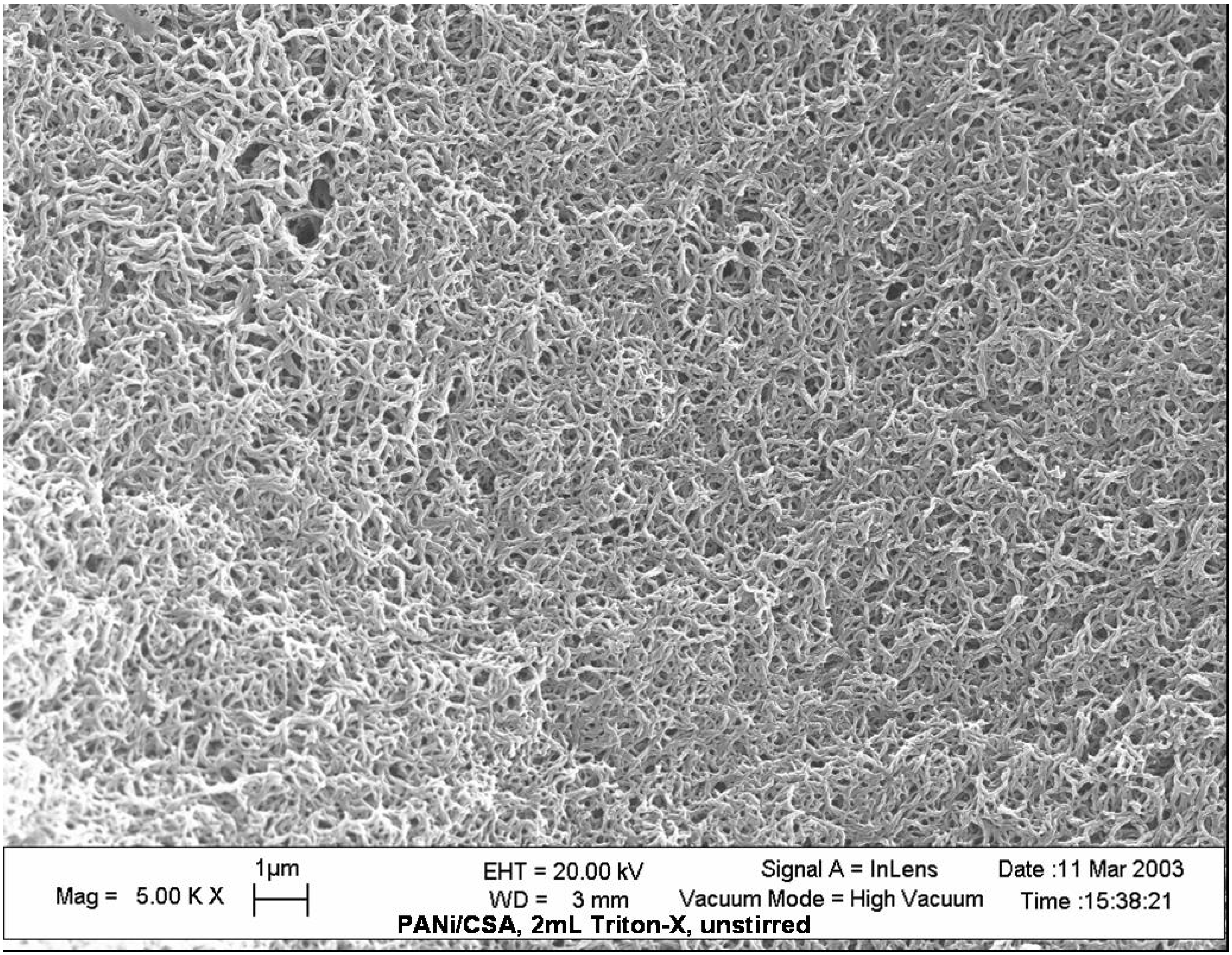


- PANI-CSA: extremely broad desorption peak (~ -165 °C to -25 °C) with a shoulder at ~ -60 °C. This could indicate the presence of a variety of different binding sites and though it is not room temperature, it is quite accessible through standard cooling methods.
- Potential roles of the surfactant and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

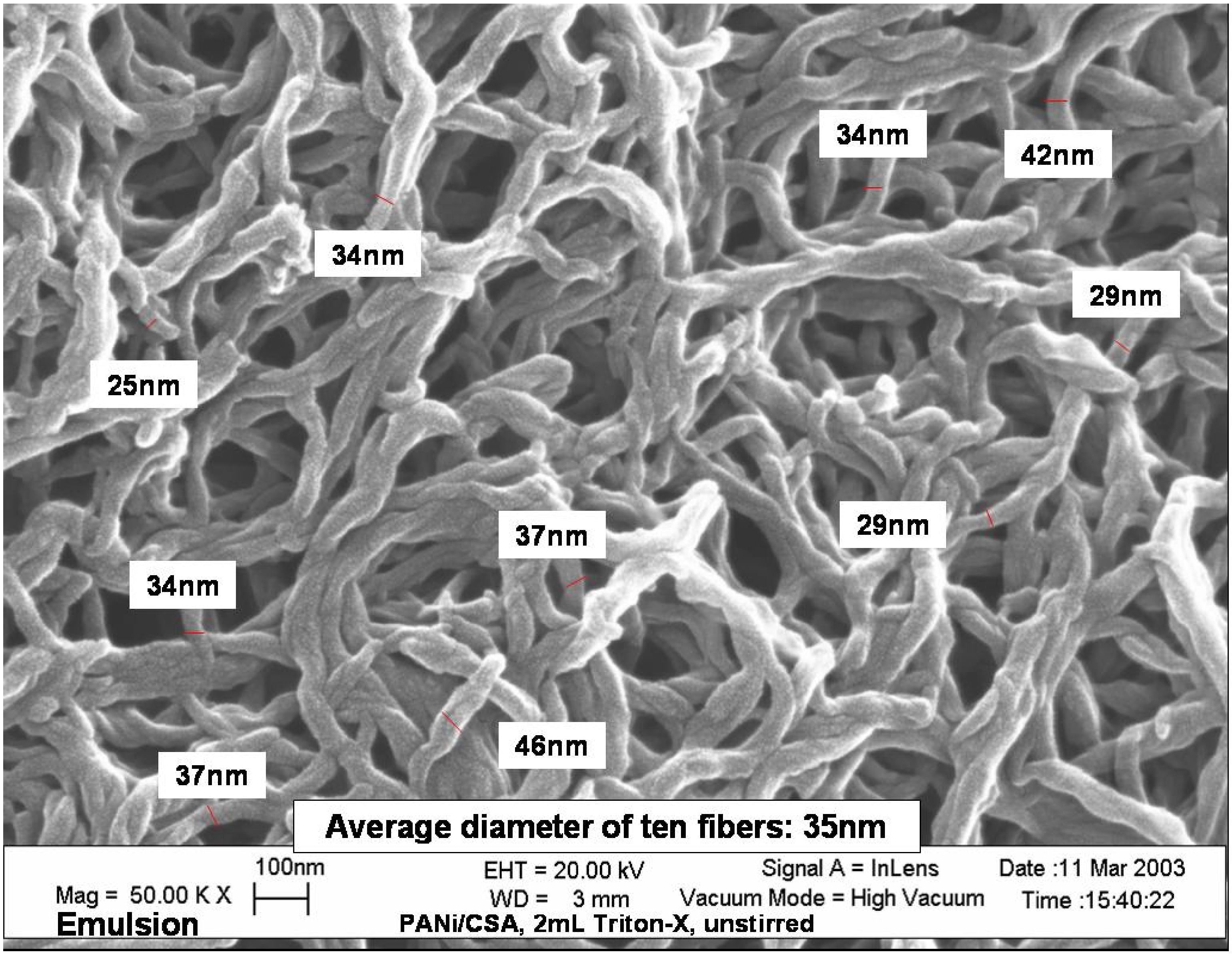
Results

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



Results

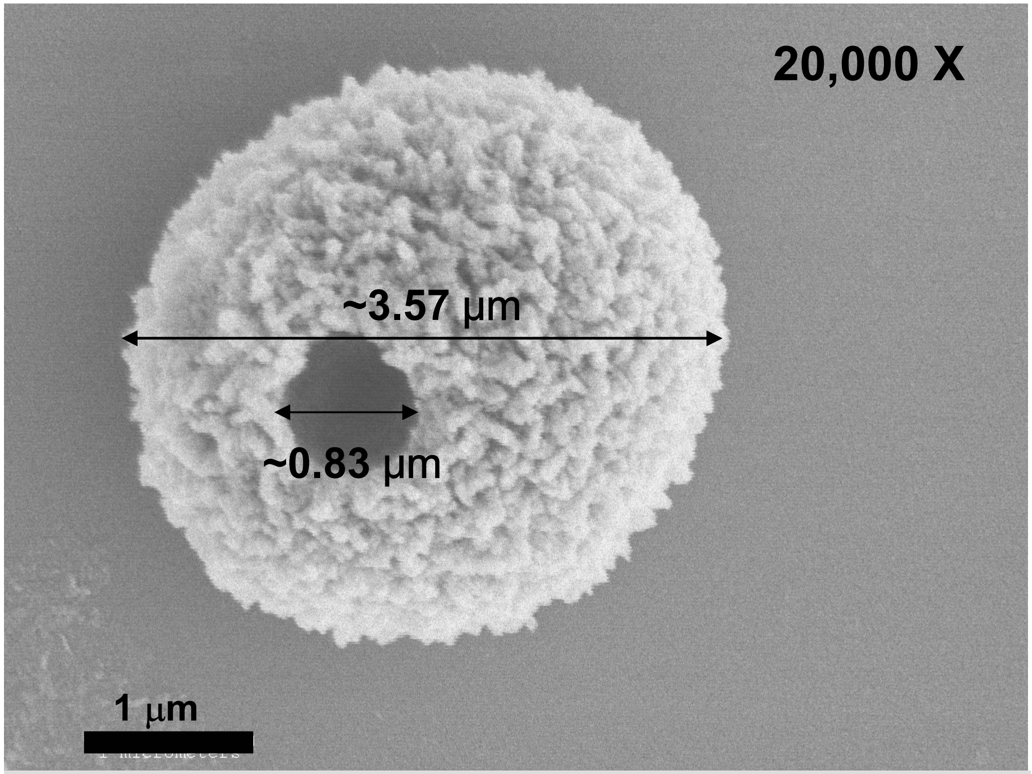
Polyaniline Nanofibers Doped with Camphorsulfonic Acid (CSA) - PANI-CSA



Future Work

- Continue the studies of the interaction of H_2 with certain forms of polyaniline as observed in preliminary studies at NREL in Dr. M. Heben's group.
- NRM studies by members of the CbHSC (Univ. of North Carolina): understanding H storage capacity and mechanism of adsortion.
- Neutron scattering measurements at NIST – direct atomic & nanoscale information related to hydrogen adsorption sites and diffusion mechanisms.
- Examination of the surface area and microporosity by standard gas adsorption studies (in collaboration with our CbHSC partners).
- Use of new forms of aniline-based Materials: control of sphere and hole sizes opens up new opportunities for hydrogen storage.

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



FOR THIS MICROSPHERE:

Thickness of wall ~0.23 µm

Empty Volume inside: ~15.6 $(\mu m)^3$

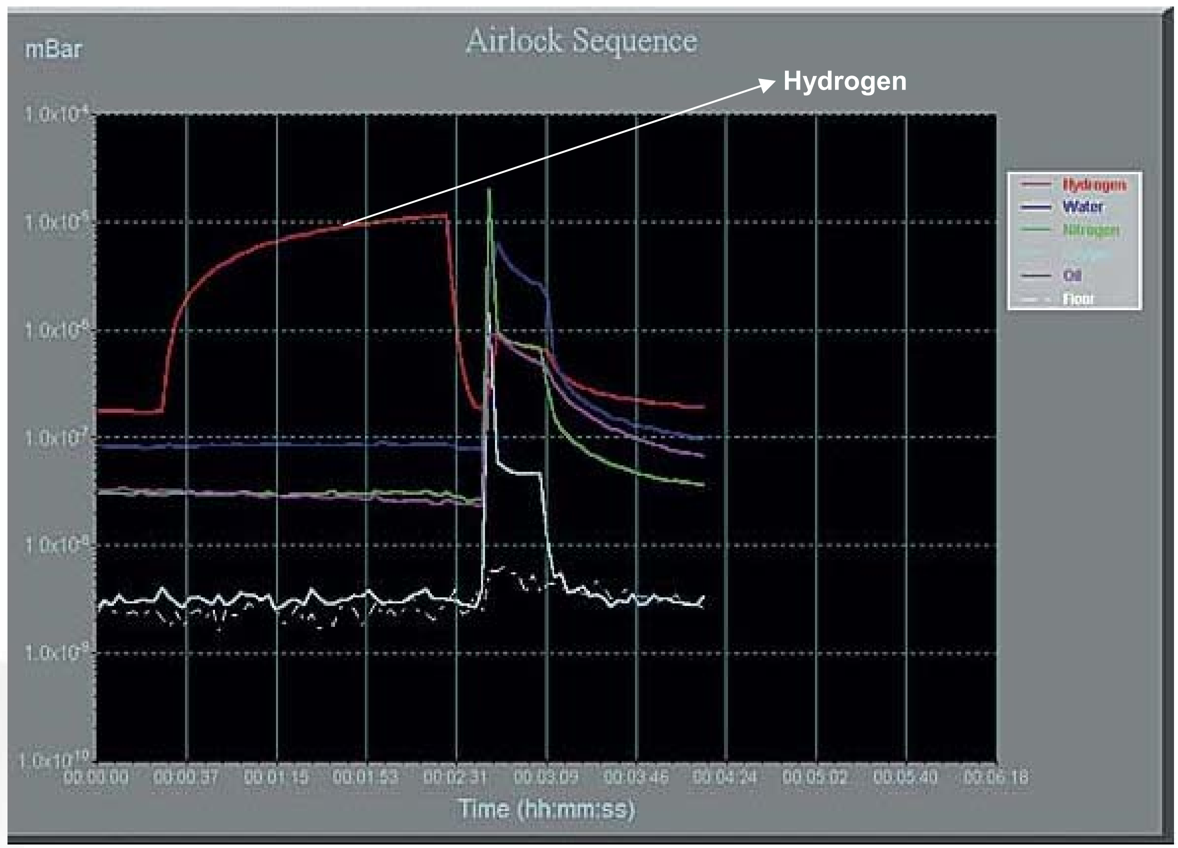
[Note: radius of C atom: 7.7 x 10^{-5} µm (0.77 Å)]

* E.C. Venancio, P.C. Wang and A.G. MacDiarmid, "*The Azanes: A Class Of Material Incorporating Nano/Micro Self-Assembled Spheres Obtained By Aqueous Oxidative Polymerization Of Aniline*", Synthetic Metals, Accepted for Publication (April 2005).

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

Acknowledgments

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