Conducting Polymers as New Materials For Hydrogen Storage

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Overview

Timeline

- Start: 02/01/2005
- End: 01/31/2010
- Percent Complete: 50 %

Budget

- Total project funding
  - $ 663,652 (DOE)
  - $ 165,912 (Penn)
- Funding received in FY06:
  - $ 125,000 (DOE)
  - $ 32,187 (Penn)
- Funding for FY07:
  - $ 125,000 (DOE)
  - $ 32,187 (Penn)

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

- **HS CoE Partners**
- **NREL Team**
- **University of North Carolina**
- **University of Houston**

Project Objectives

Overall	**To identify and use the polyaniline species previously reported to give ~6 wt% H$_2$ storage by FY 2010** **Confirm the brief 2002 report by Cho et. al.* that ~6 wt% (reversible) H$_2$ storage in the doped (metallic) form of polyaniline, can be attained.** **Determine optimum polymer preparative methods, chemical composition, oxidation state and polymer crystallinity and morphology to give quantitative optimum conditions of H$_2$ adsorption and desorption.** **Investigate H$_2$ storage by other known types of organic conducting polymers in their semiconducting and metallic forms.**
2005	**Synthesis and Characterization of Polyaniline Nanofibers** – Large Quantity Synthesis of Different Forms of Polyaniline by Aqueous Oxidative Polymerization of Aniline. – Characterization by : UV-VIS, SEM; TPD (NREL); NMR (UNC) **Synthesis and H$_2$ Adsorption of Conducting Polymer Nanofibers Decorated with Traces of Metallic Nanoparticles of Pd, Ni, etc.** – Large Quantity Synthesis of Most Promising Forms of Polyaniline by Aqueous Oxidative Polymerization of Aniline and Decoration with Nanoparticles of Metals. – Characterization by : UV-VIS, SEM
2006	**H$_2$ Adsorption Studies Using Selected Polyaniline Species** – H$_2$ uptake studies by TGA and mass spectrometry – Materials Characterization by : TGA and SEM

*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).

Approach

To Identify the Polyaniline Species Responsible for the
Reported H_2 Storage of ~6 wt % and Achieve this Objective by FY 2010

TASKS:

- Use different pre-conditioning heating *(e.g. Thermogravimetric Analysis/Mass Spec)* treatments of polyaniline-based materials to determine the nature of the <u>actual</u> polymer undergoing H_2 absorption/desorption.

- Measure desorption of H_2 *(using NREL temperature programmed desorption facilities and TGA-MS facilities at University of Houston)* of the optimum oxidation state of polyaniline (after optimum pre-conditioning heating).

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

Results

Background:

Cho et al. (2002): ~6 wt.% adsorption of H_2 by the metallic form of the polyaniline species (presumably, Emeraldine.HCl) at "room temperature".

Roth et al. (2005): no H_2 adsorbed by the metallic form of polyaniline ("Emeraldine salt") at "room temperature" and at 77 K

Penn Group:

preparation, screening, identification and selection of samples based on conducting polymers for hydrogen storage application from polyaniline (PANI) materials, which can possibly exist

(1) at any oxidation state lying within a continuum containing three distinct oxidation states with no sharp chemical or spectroscopic boundary between them,

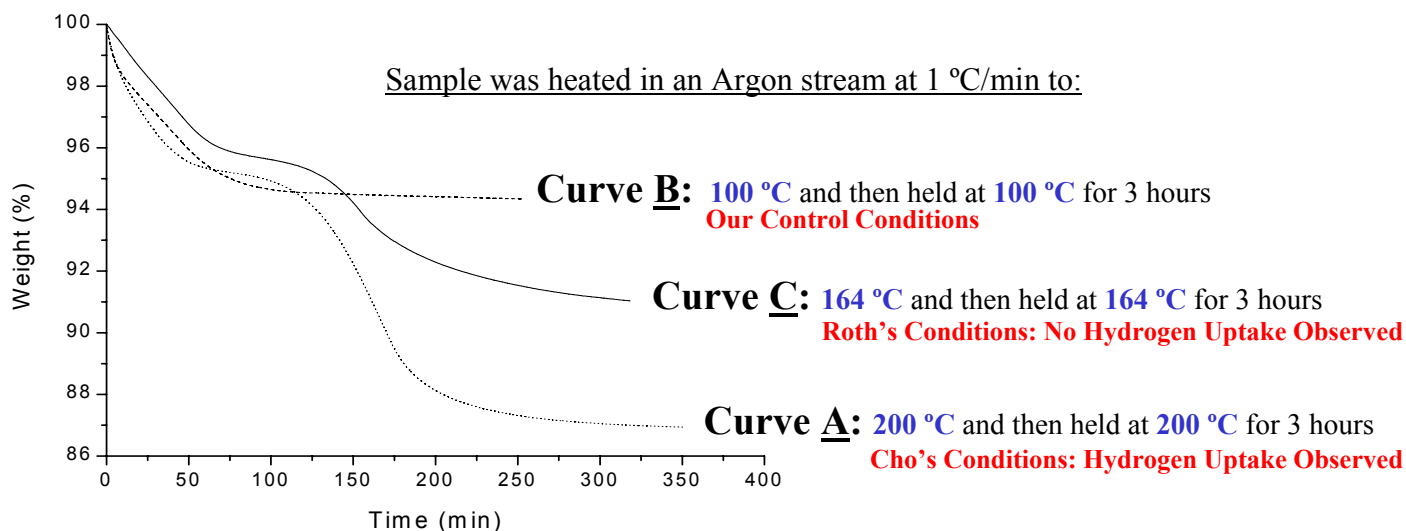(2) as doped, non-doped or partially doped form,

depending on the preparative method, sample history etc.

Accomplishment

Two samples, PANI-α-I and PANI-α-II, were selected for our hydrogen storage study.

Change in composition of doped polyaniline (polyaniline.HCl) during pre-heating ("pre-conditioning")

TGA studies (With Dr. A. McGhie, Materials Science Department, Univ. of Pennsylvania)

Sample was heated in an Argon stream at 1 ºC/min to:

Curve B: 100 ºC and then held at 100 ºC for 3 hours
Our Control Conditions

Curve C: 164 ºC and then held at 164 ºC for 3 hours
Roth's Conditions: No Hydrogen Uptake Observed

Curve A: 200 ºC and then held at 200 ºC for 3 hours
Cho's Conditions: Hydrogen Uptake Observed

(Graph: Weight (%) vs. Time (min), Weight axis 86 to 100, Time axis 0 to 400)
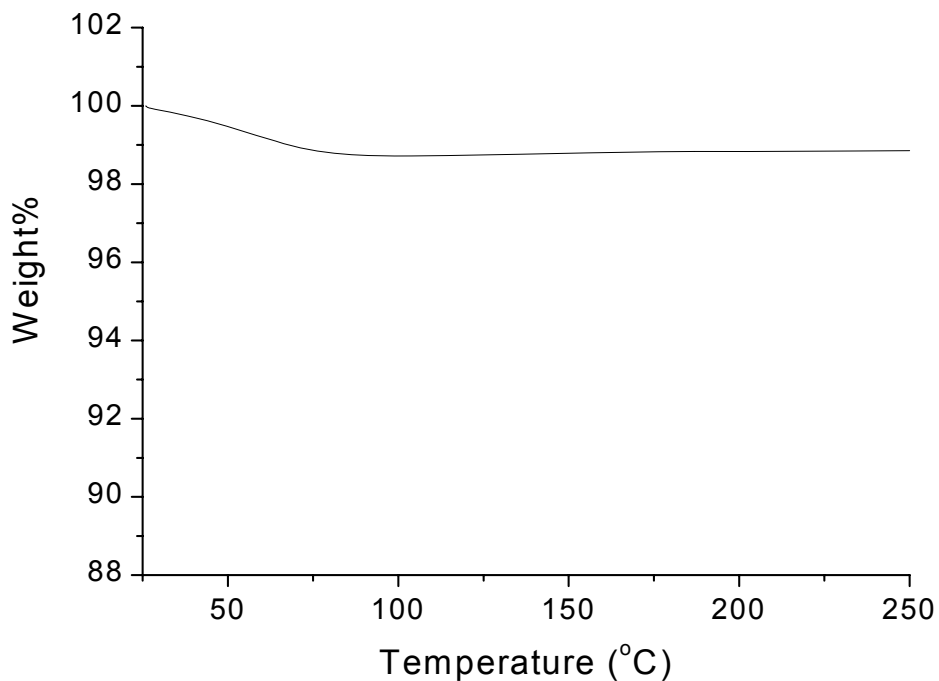
Accomplishment

This study shows that previous H_2 sorbtion studies on polyaniline had <u>not</u> actually used any specific form of polyaniline! Cho* (Curve A) preheated at 200 ^{o}C for an unspecified period of time. Roth* (Curve C) preheated at 164 ^{o}C for 3 hours.

*S.J. Cho, K.S. Song, J.W. Kim, T.H. Kim and K. Choo, *Fuel Chemistry Division, 224th National Meeting of the American Chemical Society* 47, 790-791 (2002) and B. Panella, L. Kossykh, U. Dettlaff-Weglikwska, M. Hirscher, G. Zerbi, S. Roth, *Synthetic Metals*, 151 (2005) 208.

TGA Profile of PANI-α-I
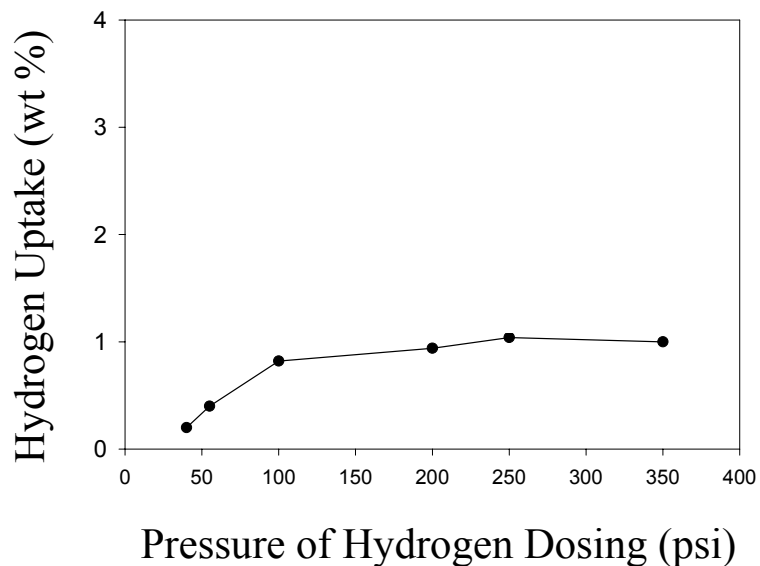## room temperature to 250ºC

Accomplishment

This result shows that

(1) unlike PANI.HCl used by Cho and Roth (see slide 6), after the initial weight loss due to the liberation of adsorbed water, no more weight loss was observed up to 250ºC

(2) PANI-α-I can tolerate thermal treatment up to 250ºC

Hydrogen Uptake Study using PANI-α-I by TGA

Hydrogen Uptake (wt %) vs Pressure of Hydrogen Dosing (psi)
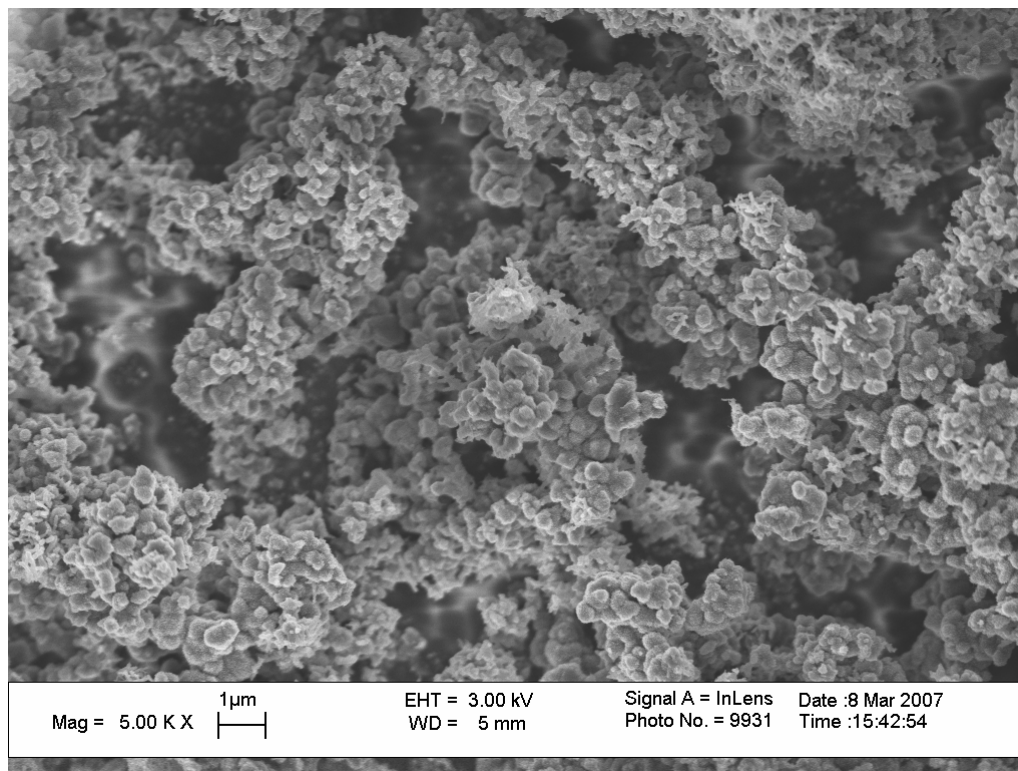
Experimental Procedure:

(1) each PANI-α-I sample dosed with H_2 under a given pressure for 2 hours

(2) control: PANI-α-I without exposure to H_2

(3) TGA: room temperature to 225ºC

Ignatiev Group, University of Houston

Accomplishment

PANI-α-I shows a H_2-dosing-pressure-dependent hydrogen uptake behavior by up to 1.00 wt%
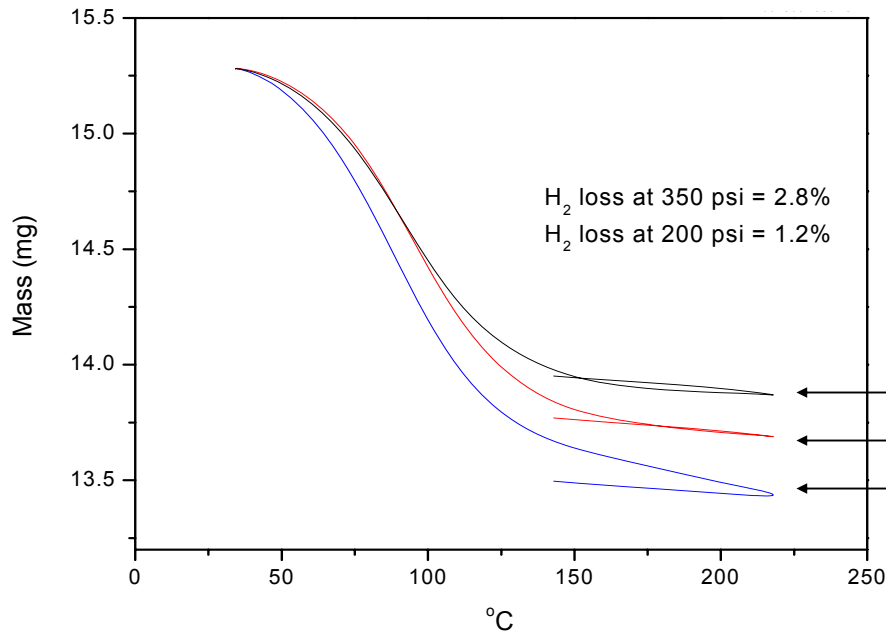
SEM Image of PANI-α-II

(SEM: Aimei Wu, University of Texas-Dallas)

Accomplishment

PANI-α-II, with distinctive nanostructured features, was prepared for our hydrogen storage study

Hydrogen Uptake Study using PANI-α-II by TGA

H$_2$ loss at 350 psi = 2.8%
H$_2$ loss at 200 psi = 1.2%

PANI–α-II; No H$_2$

PANI-α–II; H$_2$ 200 psi

PANI-α–II; H$_2$ 350 psi

Experimental Procedure:

(1) each PANI-α-II sample dosed with H$_2$ under a given pressure for 2 hours

(2) control: PANI-α-II without exposure to H$_2$
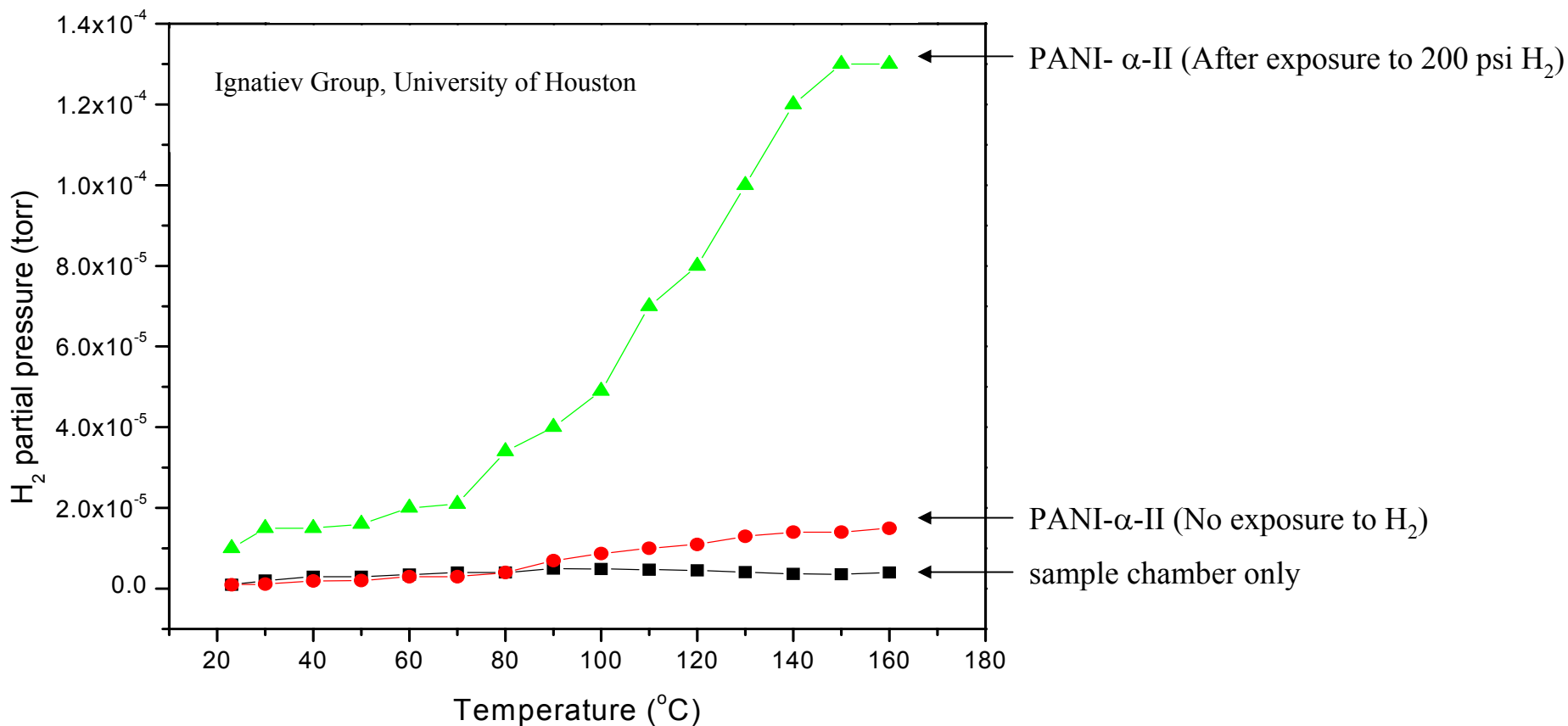
(3) TGA: room temperature to 225ºC

Ignatiev Group, University of Houston

__Accomplishment__

PANI-α-II shows a H$_2$-dosing-pressure-dependent hydrogen uptake behavior by up to 2.80 wt%

Mass Spectrometric Measurement of PANI-α-II Dosed with H_2

Ignatiev Group, University of Houston

PANI- α-II (After exposure to 200 psi H_2)

PANI-α-II (No exposure to H_2)

sample chamber only

Y-axis: H_2 partial pressure (torr)

X-axis: Temperature (^{o}C)

Accomplishment

This comparative study shows the liberation of H_2 by PANI-α-II dosed with 200 psi H_2 upon gentle heating up to 160ºC

Promotion of Hydrogen Uptake by PANI-α-II
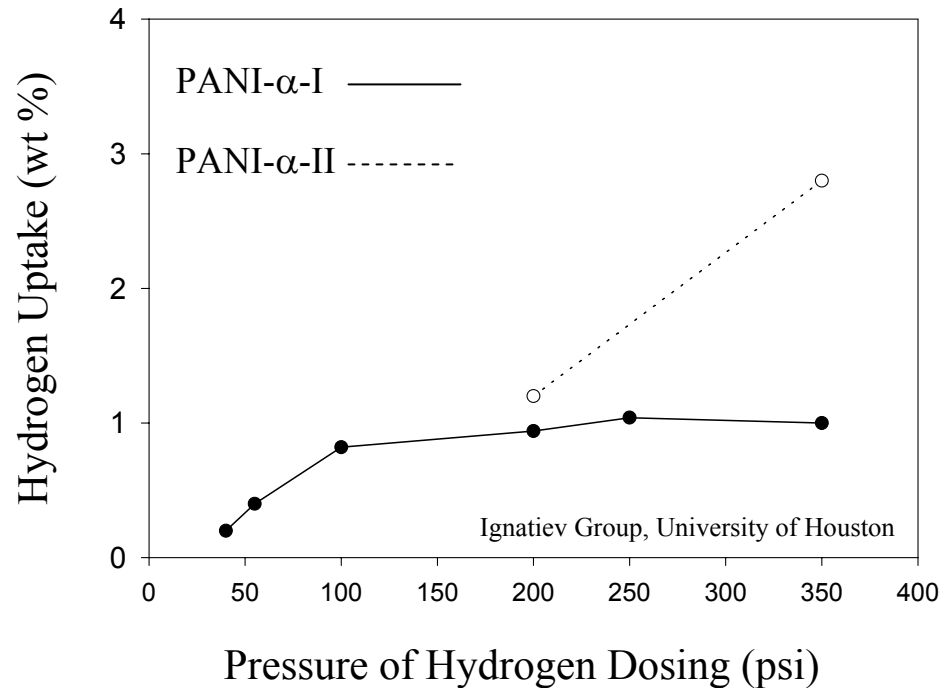
Accomplishment

(1) Two PANI-α series samples used in the present study exhibit a H_2-dosing-pressure-dependent hydrogen uptake behavior.

(2) With other experimental conditions being equal, PANI-α-II outperforms PANI-α-I .

Future Work

Remainder of FY 2007 and FY 2008

(1) Continue Temperature Programmed Desorption and NMR studies of H_2 on Polyaniline.

(2) Obtain Direct Atomic and Nanoscale Information Related to H_2 Adsorption Sites on Polyaniline and Diffusion Mechanisms by Neutron Scattering Measurements at NIST.

(3) Use Pernigraniline Base (Most Highly Oxidized Form of Polyaniline).

H_2 Temperature Programmed Desorption Studies on pernigraniline polyaniline base (with NREL).

H_2 NMR in the presence of pernigraniline polyaniline base (with Prof. Wu at Univ. North Carolina).

(4) H_2 Temperature Programmed Desorption Studies on Polyaniline Decorated with Traces of Metallic Pd, Ni, etc.

(5) Use the different forms of "Univ. Penn PANI" and Prof. Ignatiev's different H_2 adsorption/desorption measurement techniques.

Project Summary

- **Relevance:**

  Develop low-cost, carbon-based conducting (organic) polymer materials for H_2 storage.

- **Approach:**

  Identify and characterize the chemical sub-species of conducting polymers responsible for the previously reported ~6 wt% H_2 adsorption by polyaniline.

- **Technical Accomplishments and Progress:**

  Observation of H_2 uptake using the "University of Penn. PANI" by up to 2.8 wt%.

- **Technology Transfer/Collaboration**:

  Active partnership with UNC (Professor Y. Wu), NREL (Dr. M. Heben) and UH (Professor A. Ignatiev).

- **Proposed Future Research:**

  Systematic preparation and characterization of conducting polymer samples by selected chemical and/or physical treatments for H_2 adsorption/desorption studies.

Project Summary

- **Major Findings:**

    1. A PANI sample, PANI-α-II (synthesized at PENN), gave ~2.8 wt% H_2 uptake (measured at UH), ~1/2 of that reported by Cho and DOE's FY2010 goal. The results reported by Cho in 2002 have not completely been replicated in MacDiarmid group.

    2. The H_2 uptake study using PANI-α series samples showed H_2 uptake could be increased by up to ~180% (see Slide 12) as the experimental conditions for the synthesis of PANI were modified.

    3. Major variables that can critically affect H_2 uptake studies using PANI materials experimentally identified in the past year: thermal pre-treatment and conditions during material synthesis (in particular, pH)

- **Lessons Learned:**

    As the form of polyaniline can vary with its preparation method and/or post-synthesis treatments, systematic screening of PANI samples is required for the successful identification/discovery of the desired PANI materials for H_2 storage application.

    PANI decorated with trace amount of Pd nanoparticles prepared via the reaction of leucoemeraldine (most reduced form of PANI) and $PdCl_2$ should be considered as an alternative PANI-based candidate for this study.

Summary Table

On-Board Hydrogen Storage System Targets (**Data is based on material only, not system value)				
Storage Parameter	**Units**	**2010 System Target**	**FY06 Result**	**FY07 Result**
Specific Energy	kg H_2/kg	(6 wt.%)	N/A	2.8 wt%