

# Conducting Polymers as New Materials For Hydrogen Storage

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Part of the DOE Hydrogen Sorption Center of Excellence

May 15-18, 2007

STP2

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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

<p><b>Overall</b></p>	<p><b>To identify and use the polyaniline species previously reported to give ~6 wt% H<sub>2</sub> storage by FY 2010</b></p> <p><b>Confirm the brief 2002 report by Cho et. al.* that ~6 wt% (reversible) H<sub>2</sub> storage in the doped (metallic) form of polyaniline, can be attained.</b></p> <p><b>Determine optimum polymer preparative methods, chemical composition, oxidation state and polymer crystallinity and morphology to give quantitative optimum conditions of H<sub>2</sub> adsorption and desorption.</b></p> <p><b>Investigate H<sub>2</sub> storage by other known types of organic conducting polymers in their semiconducting and metallic forms.</b></p>
<p><b>2005</b></p>	<p><b>Synthesis and Characterization of Polyaniline Nanofibers</b></p> <ul style="list-style-type: none"> <li>– Large Quantity Synthesis of Different Forms of Polyaniline by Aqueous Oxidative Polymerization of Aniline.</li> <li>– Characterization by : UV-VIS, SEM; TPD (NREL); NMR (UNC)</li> </ul> <p><b>Synthesis and H<sub>2</sub> Adsorption of Conducting Polymer Nanofibers Decorated with Traces of Metallic Nanoparticles of Pd, Ni, etc.</b></p> <ul style="list-style-type: none"> <li>– Large Quantity Synthesis of Most Promising Forms of Polyaniline by Aqueous Oxidative Polymerization of Aniline and Decoration with Nanoparticles of Metals.</li> <li>– Characterization by : UV-VIS, SEM</li> </ul>
<p><b>2006</b></p>	<p><b>H<sub>2</sub> Adsorption Studies Using Selected Polyaniline Species</b></p> <ul style="list-style-type: none"> <li>– H<sub>2</sub> uptake studies by TGA and mass spectrometry</li> <li>– Materials Characterization by : TGA and SEM</li> </ul>

\*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

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**To Identify the Polyaniline Species Responsible for the Reported H<sub>2</sub> 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 actual polymer undergoing H<sub>2</sub> absorption/desorption.**
- **Measure desorption of H<sub>2</sub> (*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<sub>2</sub> atmosphere and evaluate the H-D formed.**

# Results

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## Background:

[Cho et al. \(2002\)](#): ~6 wt.% adsorption of H<sub>2</sub> by the metallic form of the polyaniline species (presumably, Emeraldine.HCl) at “room temperature”.

[Roth et al. \(2005\)](#): no H<sub>2</sub> 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,

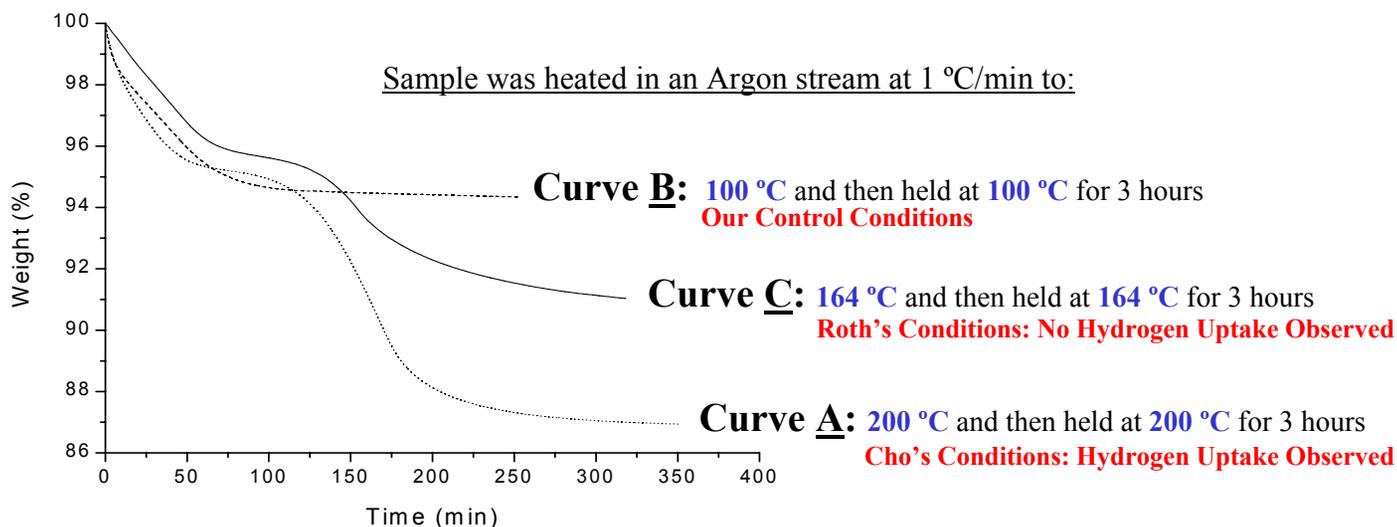
depending on the preparative method, sample history etc.

## Accomplishment

Two samples, PANI- $\alpha$ -I and PANI- $\alpha$ -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)



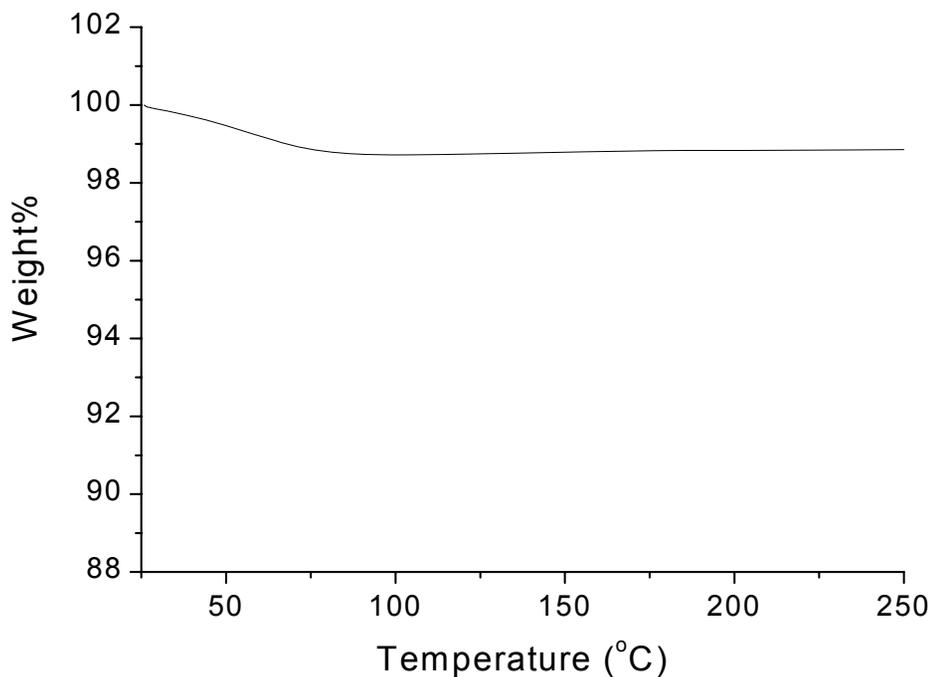
## **Accomplishment**

This study shows that previous H<sub>2</sub> sorption studies on polyaniline had not actually used any specific form of polyaniline! Cho\* (Curve A) preheated at 200 °C for an unspecified period of time. Roth\* (Curve C) preheated at 164 °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- $\alpha$ -I

room temperature to 250°C

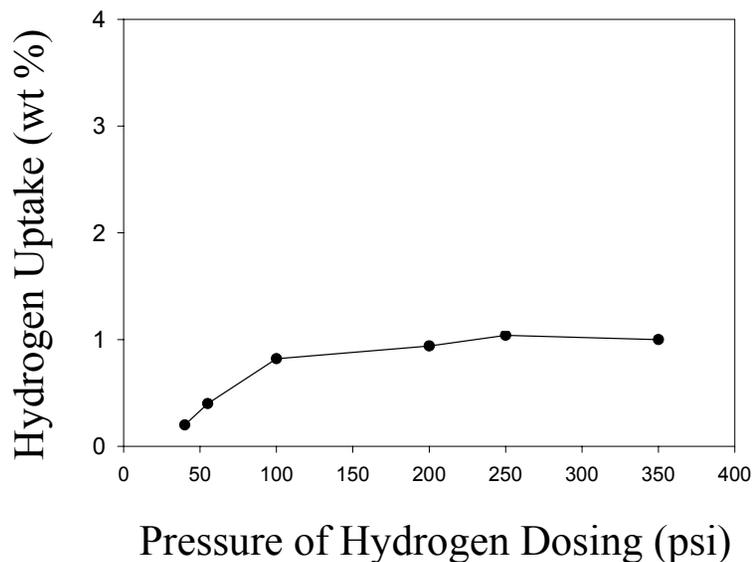


### Accomplishment

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 250°C
- (2) PANI- $\alpha$ -I can tolerate thermal treatment up to 250°C

# Hydrogen Uptake Study using PANI- $\alpha$ -I by TGA



Experimental Procedure:

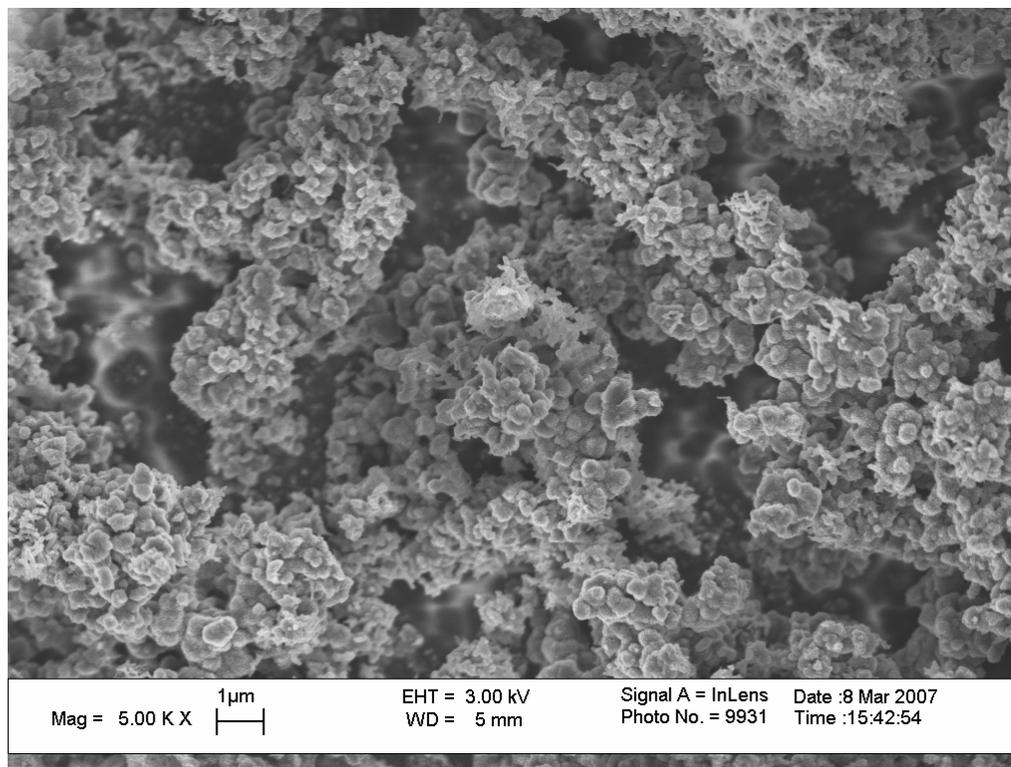
- (1) each PANI- $\alpha$ -I sample dosed with H<sub>2</sub> under a given pressure for 2 hours
- (2) control: PANI- $\alpha$ -I without exposure to H<sub>2</sub>
- (3) TGA: room temperature to 225°C

Ignatiev Group, University of Houston

## Accomplishment

PANI- $\alpha$ -I shows a H<sub>2</sub>-dosing-pressure-dependent hydrogen uptake behavior by up to 1.00 wt%

# SEM Image of PANI- $\alpha$ -II

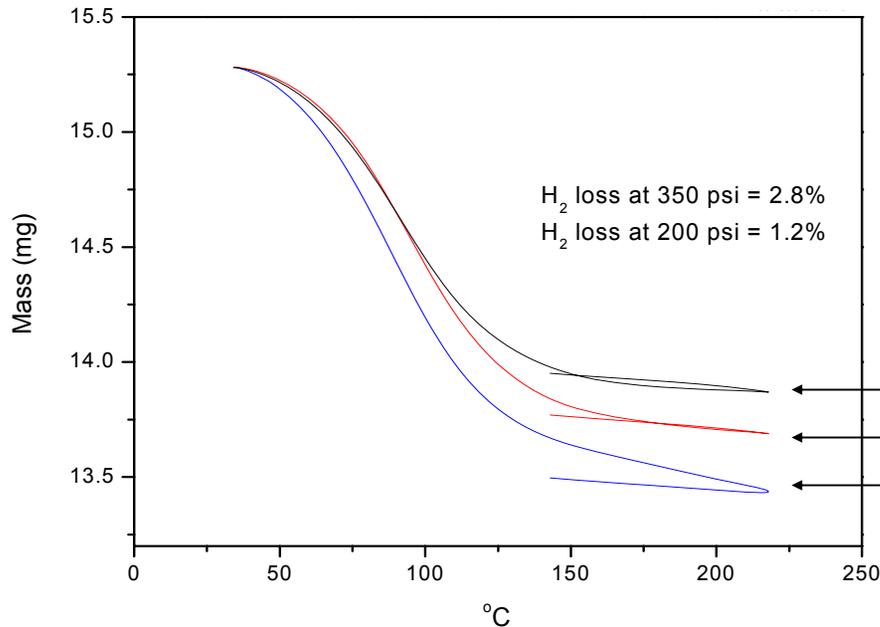


(SEM: Aimei Wu, University of Texas-Dallas)

## Accomplishment

PANI- $\alpha$ -II, with distinctive nanostructured features, was prepared for our hydrogen storage study

# Hydrogen Uptake Study using PANI- $\alpha$ -II by TGA



Experimental Procedure:

- (1) each PANI- $\alpha$ -II sample dosed with H<sub>2</sub> under a given pressure for 2 hours
- (2) control: PANI- $\alpha$ -II without exposure to H<sub>2</sub>
- (3) TGA: room temperature to 225°C

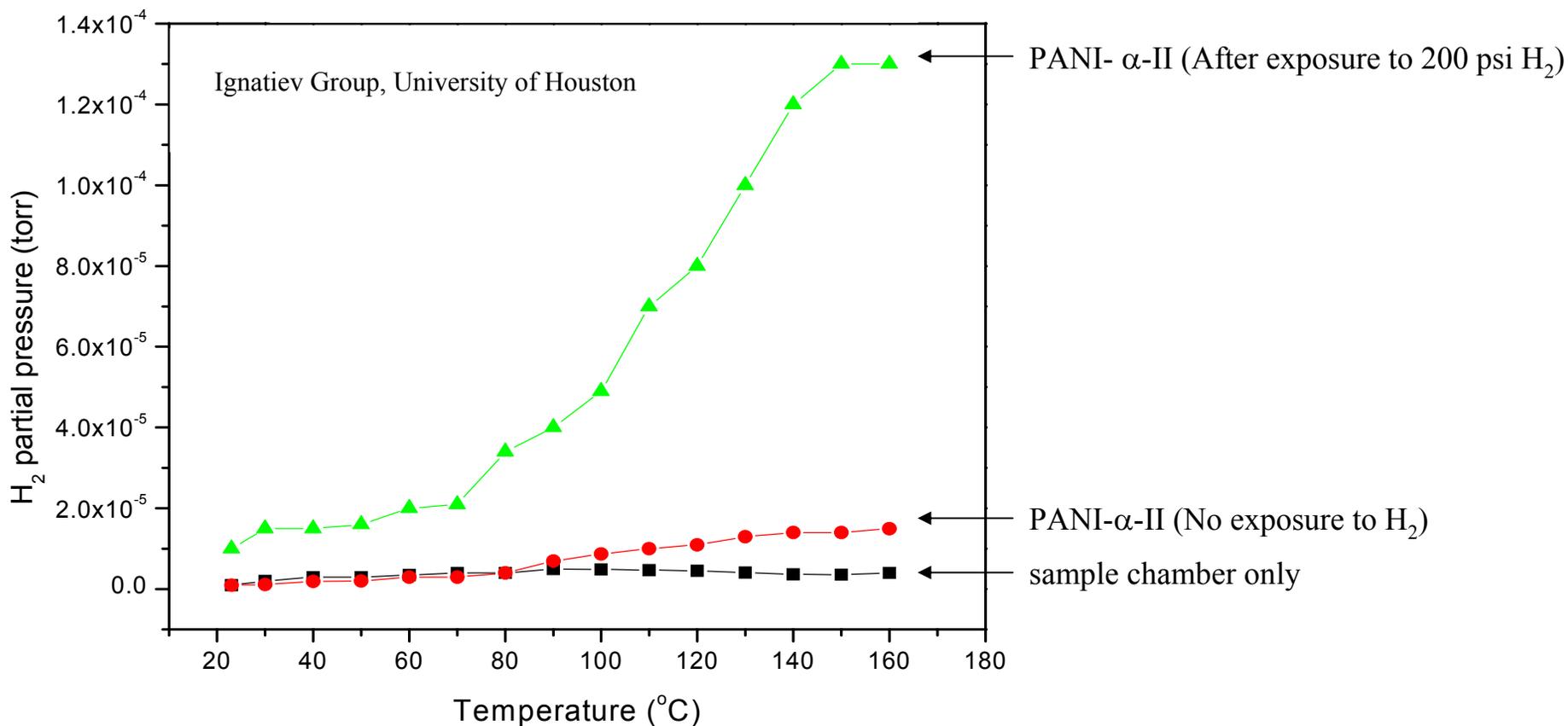
Ignatiev Group, University of Houston

- ← PANI- $\alpha$ -II; No H<sub>2</sub>
- ← PANI- $\alpha$ -II; H<sub>2</sub> 200 psi
- ← PANI- $\alpha$ -II; H<sub>2</sub> 350 psi

## Accomplishment

PANI- $\alpha$ -II shows a H<sub>2</sub>-dosing-pressure-dependent hydrogen uptake behavior by up to 2.80 wt%

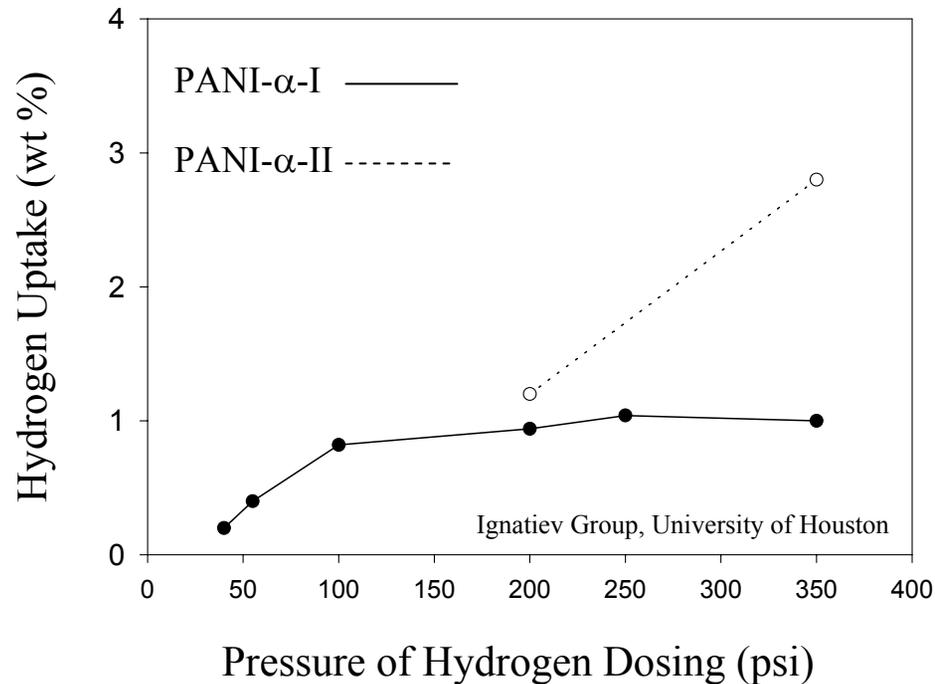
# Mass Spectrometric Measurement of PANI- $\alpha$ -II Dosed with H<sub>2</sub>



## Accomplishment

This comparative study shows the liberation of H<sub>2</sub> by PANI- $\alpha$ -II dosed with 200 psi H<sub>2</sub> upon gentle heating up to 160°C

# Promotion of Hydrogen Uptake by PANI- $\alpha$ -II



## Accomplishment

- (1) Two PANI- $\alpha$  series samples used in the present study exhibit a H<sub>2</sub>-dosing-pressure-dependent hydrogen uptake behavior.
- (2) With other experimental conditions being equal, PANI- $\alpha$ -II outperforms PANI- $\alpha$ -I .

# Future Work

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## Remainder of FY 2007 and FY 2008

- (1) Continue Temperature Programmed Desorption and NMR studies of H<sub>2</sub> on Polyaniline.**
- (2) Obtain Direct Atomic and Nanoscale Information Related to H<sub>2</sub> Adsorption Sites on Polyaniline and Diffusion Mechanisms by Neutron Scattering Measurements at NIST.**
- (3) Use Pernigraniline Base** (Most Highly Oxidized Form of Polyaniline).
  - H<sub>2</sub> Temperature Programmed Desorption Studies on pernigraniline polyaniline base (with NREL).
  - H<sub>2</sub> NMR in the presence of pernigraniline polyaniline base (with Prof. Wu at Univ. North Carolina).
- (4) H<sub>2</sub> 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<sub>2</sub> adsorption/desorption measurement techniques.**

# Project Summary

- **Relevance:**

Develop low-cost, carbon-based conducting (organic) polymer materials for H<sub>2</sub> storage.

- **Approach:**

Identify and characterize the chemical sub-species of conducting polymers responsible for the previously reported ~6 wt% H<sub>2</sub> adsorption by polyaniline.

- **Technical Accomplishments and Progress:**

Observation of H<sub>2</sub> 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<sub>2</sub> adsorption/desorption studies.

# Project Summary

- **Major Findings:**

1. A PANI sample, PANI- $\alpha$ -II (synthesized at PENN), gave  $\sim 2.8$  wt% H<sub>2</sub> uptake (measured at UH),  $\sim 1/2$  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<sub>2</sub> uptake study using PANI- $\alpha$  series samples showed H<sub>2</sub> uptake could be increased by up to  $\sim 180\%$  (see Slide 12) as the experimental conditions for the synthesis of PANI were modified.
3. Major variables that can critically affect H<sub>2</sub> 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<sub>2</sub> storage application.

PANI decorated with trace amount of Pd nanoparticles prepared via the reaction of leucoemeraldine (most reduced form of PANI) and PdCl<sub>2</sub> should be considered as an alternative PANI-based candidate for this study.

# Summary Table

<u>On-Board Hydrogen Storage System Targets</u> (*Data is based on material only, not system value)				
<b>Storage Parameter</b>	<b>Units</b>	<b>2010 System Target</b>	<b>FY06 Result</b>	<b>FY07 Result</b>
Specific Energy	kg H <sub>2</sub> /kg	(6 wt.%)	N/A	2.8 wt%