

## IV.C.1i Conducting Polymers as New Materials for Hydrogen Storage

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### Objectives

- Confirm the brief report by Cho et al [1] that approximately 8 wt% (reversible) hydrogen gas storage in doped (metallic) forms of organic conducting polymers ("synthetic metals"), polyaniline and polypyrrole, can be attained.
- Determine optimum polymer preparative methods, chemical composition, polymer electrode potential, polymer crystallinity and morphology to give quantitative optimum conditions of hydrogen gas adsorption and desorption.
- Investigate hydrogen storage by the many known types of organic conducting polymers in their semiconducting and metallic forms, and in selected oxidation states.

### Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (B) System Cost
- (C) Efficiency
- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

(Q) Reproducibility of Performance

### Technical Targets

Values reported are material-based. Two types of materials polymerized from aniline (PANI- $\alpha$ -I and PANI- $\alpha$ -II) were used. The highest H<sub>2</sub> uptake values for PANI- $\alpha$ -I and PANI- $\alpha$ -II were 1% and 2.8%, respectively. The gravimetric capacity target for 2010 on a system basis is 6 wt%.

On-Board Hydrogen Storage System Targets (Data is Based on Material Only, Not System Value)

Storage Parameter	Units	2010 System Target	FY 2006 Result	FY 2007 Result
Specific Energy	kg H <sub>2</sub> /kg	(6 wt%)	N/A	2.8 wt%

### Accomplishments

- Confirmed by thermogravimetric analysis (TGA) that thermal pre-treatments on PANI (prior to hydrogen uptake measurements) could alter the properties of PANI for subsequent hydrogen uptake studies.
- Comparative studies using two types of PANI materials (PANI- $\alpha$ -I and PANI- $\alpha$ -II) showed that (i) PANI- $\alpha$  series samples exhibited a H<sub>2</sub>-dosing-pressure-dependent hydrogen uptake behavior and (ii) with other experimental conditions being equal, PANI- $\alpha$ -II outperformed PANI- $\alpha$ -I in hydrogen uptake.
- Preliminary results indicate gravimetric hydrogen uptake by PANI-based materials up to 2.8 wt%.
- Demonstrated by mass spectrometer (MS) that hydrogen could be released from PANI- $\alpha$ -II pre-dosed with 200 psi H<sub>2</sub> upon gentle heating.



### Introduction

Cho et al [1], reported that approximately 8 wt% (reversible) hydrogen gas storage in doped (metallic) forms of organic conducting polymers ("synthetic metals"), polyaniline and polypyrrole, can be attained at room temperature. The conclusions of our research group (at Penn) in collaboration with measurements at the National Renewable Energy Laboratory (NREL) agree with those of Roth et al [2] in that under the incompletely described experimental conditions given by

Cho et al no significant adsorption of  $H_2$  was observed. However, preliminary results (Penn and NREL) have shown an unusual desorption of  $H_2$  up to  $\sim -25^\circ\text{C}$  using temperature-programmed desorption (TPD) methods with one of the polyaniline materials synthesized at Penn. As conducting polymers (in doped, non-doped or partially doped forms) could possibly exist at any oxidation state lying within a continuum with no sharp chemical or spectroscopic boundary, it is necessary to systematically conduct hydrogen uptake studies using “unambiguous” conducting polymers for the screening, identification and optimization of the materials for hydrogen storage application.

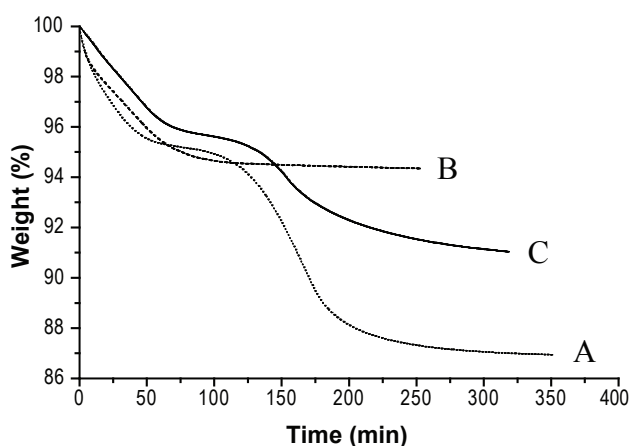
## Approach

The Penn group is primarily focused on the synthesis, processing, characterization and selection of PANI-based materials. The Penn group coordinates with project collaborators to carry out  $H_2$  desorption measurements (using NREL TPD facilities and TGA-MS facilities at the University of Houston).

## Results

The TGA data presented in Figure 1 shows that the change in the composition of doped PANI (PANI.HCl) could occur in different ways during “pre-heating” treatments. (Note: this experiment is not a hydrogen uptake study. The purpose of this study is to show the effect of thermal “pre-treatments” on PANI.HCl.)

Curve A: The method used by us involved commercial polyaniline (emeraldine base) from Aldrich Co. After doping with concentrated HCl, the PANI.HCl



**FIGURE 1.** TGA curves of PANI.HCl subject to three different thermal treatment conditions. Each PANI.HCl sample was first heated in an argon stream at  $1^\circ\text{C}/\text{min}$  from room temperature to (A)  $200^\circ\text{C}$ , (B)  $100^\circ\text{C}$  and (C)  $164^\circ\text{C}$ . After the specified temperature was reached, the temperature was held constant for 3 hours. (The PANI.HCl was pre-dried at  $87^\circ\text{C}$  under dynamic vacuum for 24 hours.)

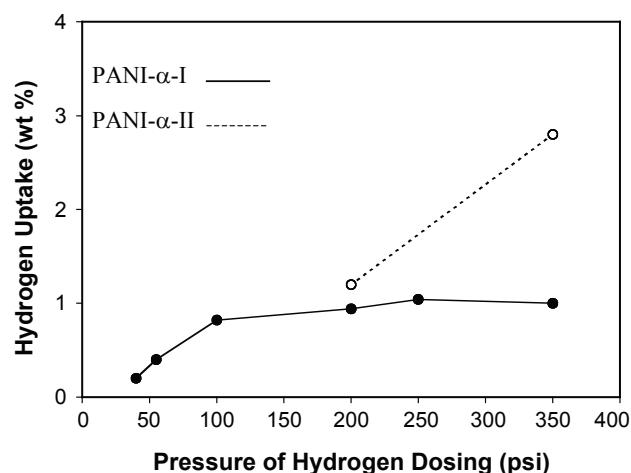
was dried at  $87^\circ\text{C}$  (dynamic vacuum) for 24 hours and was used to obtain curve A by the following procedure. The sample was heated in an argon stream at  $1^\circ\text{C}/\text{min}$  to  $200^\circ\text{C}$  and then held at  $200^\circ\text{C}$  for 3 hours in the TGA study. Up to the first point of inflection, there was a total weight loss of 4.9%. The gas evolved was proven by MS (NREL) to be water. The second weight loss (from the first point of inflection) to the termination of the study was 8.2%. The gas evolved was proven by MS (NREL) to be HCl. It can be seen from curve A that even after the initial drying process, the polyaniline still contained strongly adsorbed water.

Curve B: The experiment was performed on part of the original sample as prepared for curve A except that after reaching  $100^\circ\text{C}$ , the temperature was held at  $100^\circ\text{C}$  for 3 hours. Approximately 5.8% weight loss (of  $H_2O$ ) was observed. No weight loss of HCl was observed.

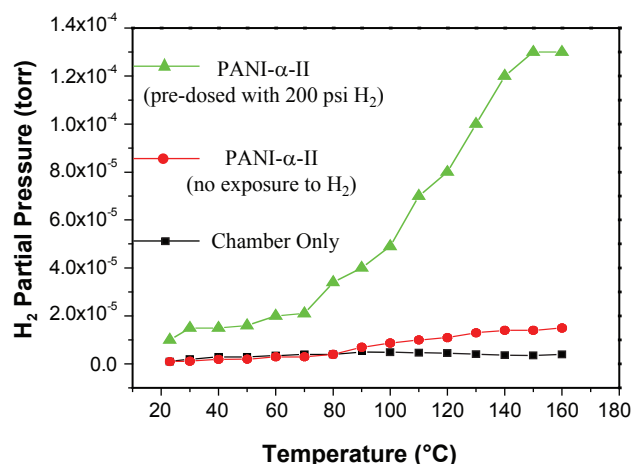
Curve C: The experiment was performed on part of the original sample as prepared for curve A except that after reaching  $164^\circ\text{C}$ , the temperature was held at  $164^\circ\text{C}$  for 3 hours. We found that the weight losses were similar to curve A, but smaller, as might be expected from the heating conditions.

This study shows that previous  $H_2$  sorption study on PANI had not actually used any specific form of PANI. (Note: Cho et al [1] (curve A) preheated at  $200^\circ\text{C}$  for an unspecified period of time. Roth [2] (curve C) preheated at  $164^\circ\text{C}$  for 3 hours.)

Figure 2 shows the curves of hydrogen uptake (wt%) vs. the pressure of hydrogen dosing for PANI- $\alpha$ -I and PANI- $\alpha$ -II. The data in Figure 2 indicates that PANI- $\alpha$ -I and PANI- $\alpha$ -II exhibit a  $H_2$ -dosing-pressure-dependent  $H_2$  uptake behavior. The data also show that  $H_2$  uptake by PANI- $\alpha$ -I becomes saturated ( $\sim 1$  wt%) as the  $H_2$  dosing pressure exceeds 100 psi. Higher  $H_2$  uptake (up to  $\sim 2.8$  wt%) can be obtained by PANI- $\alpha$ -II. In general,



**FIGURE 2.** Curves of Hydrogen Uptake (wt%) by PANI- $\alpha$ -I and PANI- $\alpha$ -II vs. Pressure of Hydrogen Dosing



**FIGURE 3.** MS Measurements of Hydrogen Liberation from PANI- $\alpha$ -II Pre-Dosed under 200 psi H<sub>2</sub> vs. PANI- $\alpha$ -II without Exposure to H<sub>2</sub>

with other experimental conditions being equal, PANI- $\alpha$ -II outperforms PANI- $\alpha$ -I in H<sub>2</sub> uptake.

In Figure 3, a comparative MS study shows that H<sub>2</sub> can be released from PANI- $\alpha$ -II (pre-dosed under 200 psi H<sub>2</sub>) upon gentle heating.

## Conclusions and Future Directions

Our research indicates that the properties of PANI-based materials could be affected by thermal pre-treatments. Therefore, ambiguous thermal pre-treatments on PANI-based materials should be avoided in the future H<sub>2</sub> uptake studies. Moreover, we also demonstrated that H<sub>2</sub> uptake by PANI-based materials varied among different sub-species of PANI-based materials. For example, compared to PANI- $\alpha$ -I (~1 wt% H<sub>2</sub> uptake), promotion of H<sub>2</sub> uptake by PANI- $\alpha$ -II (~2.8 wt%) was observed in our study.

Future studies will include:

- Continue TPD and nuclear magnetic resonance studies of H<sub>2</sub> on PANI materials.

- Obtain direct atomic and nanoscale information related to H<sub>2</sub> adsorption sites on polyaniline and diffusion mechanisms by neutron scattering measurements at the National Institute of Standards and Technology.
- H<sub>2</sub> TPD studies on polyaniline decorated with traces of metallic Pd, Ni, etc.
- Use the different forms of “Penn PANI” and Professor Ignatiev’s different H<sub>2</sub> adsorption/desorption measurement techniques.
- Integrate the work with Dr. Liu at Argonne National Laboratory.

## FY 2007 Publications/Presentations

1. E.C. Venancio, P-C. Wang, A.R. McGhie and A.G. MacDiarmid, Study of the Change in Chemical Composition of Doped Polyanilines Using Thermal Analysis, 2006 Thermal Analysis Forum of Delaware Valley, Delaware, December, 2006.
2. P-C. Wang, E.C. Venancio, A.R. McGhie and A.G. MacDiarmid, Thermal Isomerization of Polyaniline Emeraldine Base: Preparation of Potential New Polymeric Materials for Hydrogen Storage, 2006 Thermal Analysis Forum of Delaware Valley, Delaware, December, 2006.
3. P-C. Wang, E.C. Venancio, A.R. McGhie and A.G. MacDiarmid, Rational Screening and Identification of the Active Polyaniline-Based Materials for Hydrogen Storage Application, 2007 Energy Mini-Symposium at PENN, Pennsylvania, March, 2007.

## References

1. S.J. Cho, K.S. Song, J.W. Kim, T.H. Kim, K. Choo, Abstract Paper, Fuel Chemistry Division, 224th National Meeting of the American Chemical Society, 47(2) (2002) 790.
2. B. Panella, L. Kossykh, U. Dettlaff-Weglikwska, M. Hirscher, G. Zerbi, S. Roth. *Synthetic Metals*, 151 (2005) 208.