

Conducting Polymers as New Materials For Hydrogen Storage

Alan G. MacDiarmid
University of Pennsylvania

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

May 16-19, 2006

STP15

Overview

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Timeline

- 02/01/2005
- 01/31/2010
- 30 %

Budget

- Total project funding
 - \$ 663,652 (DOE)
 - \$ 165,912 (Penn)
- Funding received in FY05:
 - \$ 75,000 (DOE)
 - \$ 31,250 (Penn)
- Funding for FY06:
 - \$ 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

- **CbHSC Partners**
- **NREL Team (M. Heben, A. Dillon)**
- **University of North Carolina (Y. Wu)**
- **NIST (C. Brown)**

Overall	<p>To identify and use the conducting polymer species previously reported to give ~8 wt% H₂ storage by FY 2010</p> <p>Confirm the brief 2002 report by Cho et. al.* that ~8 wt% (reversible) H₂ storage in doped (metallic) forms of organic conducting polymers (“synthetic metals”), polyaniline and polypyrrole, can be attained.</p> <p>Determine optimum polymer preparative methods, chemical composition, oxidation state and polymer crystallinity and morphology to give quantitative optimum conditions of H₂ adsorption and desorption.</p> <p>Investigate H₂ storage by other known types of organic conducting polymers in their semiconducting and metallic forms.</p>
2005	<p>Synthesis and Characterization of Conducting Polymer Nanofibers</p> <ul style="list-style-type: none"> – Large Quantity Synthesis of Different Forms of Polyaniline by Aqueous Oxidative Polymerization of Aniline. – Characterization by : UV-VIS, SEM; TPD (NREL); NMR (UNC)
2006	<p>Synthesis and H₂ Adsorption of Conducting Polymer Nanofibers Decorated with Traces of Metallic Nanoparticles of Pd, Ni, etc.</p> <ul style="list-style-type: none"> – 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

*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).

To Identify the Conducting Polymer Species Responsible for the Reported H₂ Storage of ~8 wt % and Achieve this Objective by FY 2010

TASKS:

- **Use nanofibers of polyaniline which we can easily prepare in large quantities.**
- **Use different pre-conditioning heating (e.g. *Thermogravimetric Analysis/Mass Spec*) treatments of commercial polyaniline and nanofibers of polyaniline to determine the nature of the actual polymer undergoing H₂ absorption/desorption.**
- **Measure desorption of H₂ (*using NREL temperature programmed desorption facilities*) of the optimum oxidation state of polyaniline (after optimum pre-conditioning heating).**
- **Measure H liability in polyaniline by exposure to D₂ atmosphere and evaluate the H-D formed.**
- **NOTE: POLYANILINE CAN ACT AS A SENSOR FOR H₂ (B.H. WEILLER, POSTER; MRS MEETING, SAN FRANCISCO, APRIL 17-21, 2006)**

Background:

[Cho et al. \(2002\)](#): ~8 wt.% adsorption of H₂ by metallic forms of the conducting polymers polyaniline (presumably, Emeraldine.HCl) and polypyrrole at “room temperature”.

[Roth et al. \(2005\)](#): no H₂ adsorbed by metallic forms of conducting polymer of polyaniline (“Emeraldine salt”) or polypyrrole at “room temperature” and at 77 K

[Penn Group \(2005\)](#): very little H₂ adsorbed by metallic polyaniline **BUT** unusual desorption of H₂ using metallic polyaniline (Emeraldine.HCSA) observed (in collaborative work with NREL) up to ~ -25 °C using TPD methods. (HCSA = Camphorsulfonic Acid; [non-volatile](#))

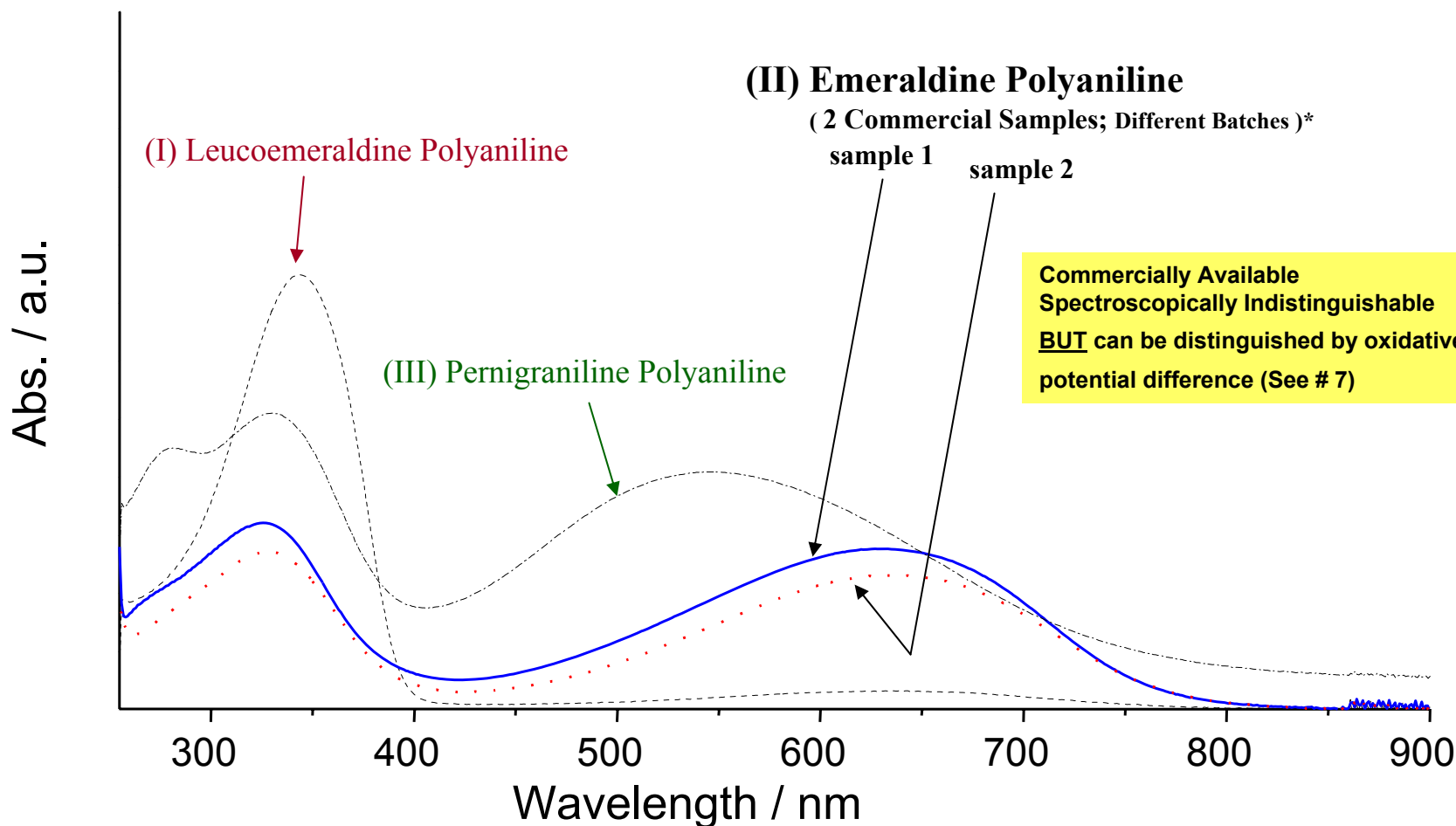
But polyaniline: a continuum of three different oxidation states with no sharp chemical or spectroscopic boundary between oxidation states [MacDiarmid, *Angew. Chem. Int. Ed.*, 40 (2001) 258].

Note: Chemical decomposition of Emeraldine.HCl possibly occurs during the previously reported “conditioning” pre-heating of samples (Discussed in #9).

Accomplishment

Definitive progress made in determining the form of polyaniline previously reported to adsorb/desorb H₂.

Spectroscopic (UV/VIS) Difference between Different Oxidation States of Polyaniline

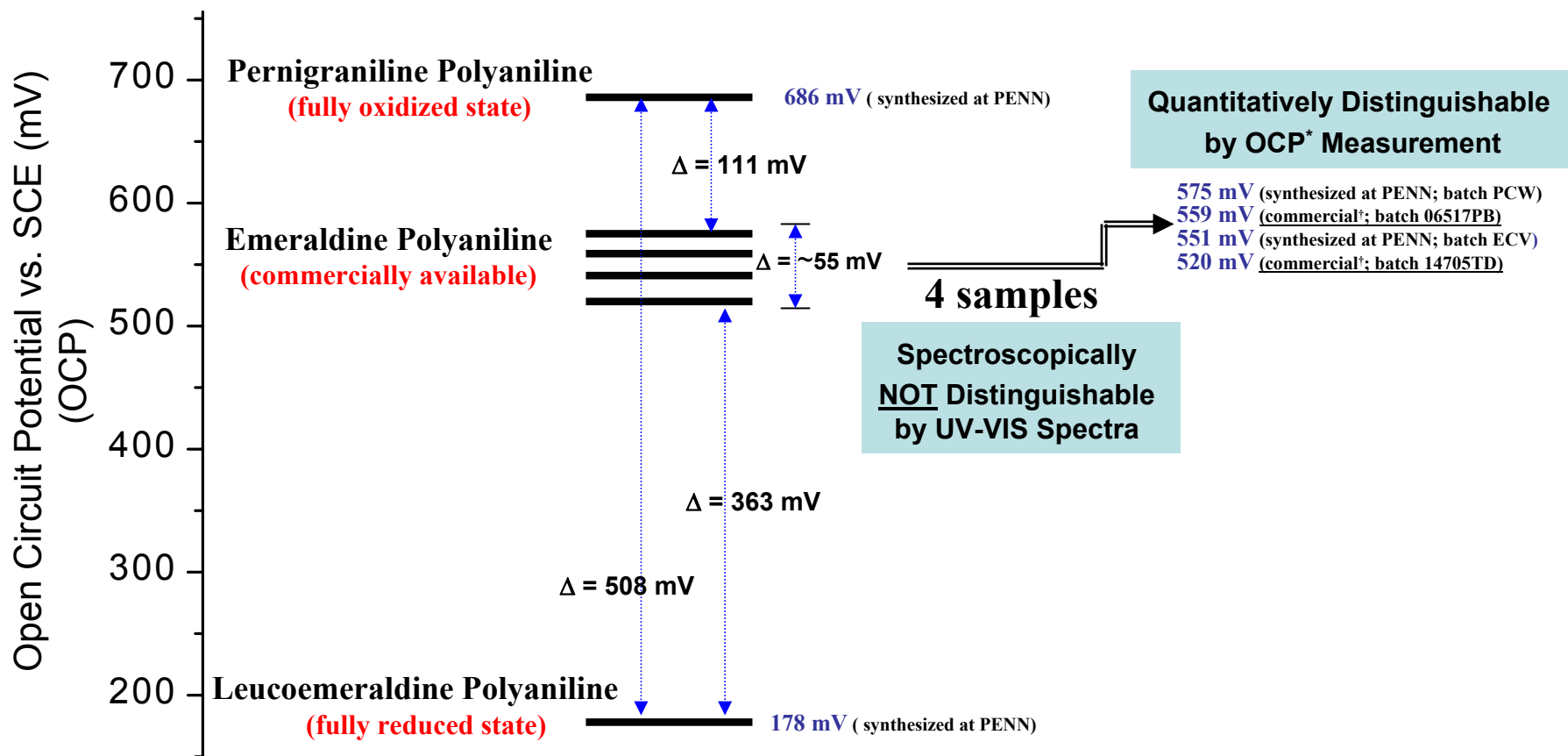


Accomplishment:

UV/VIS spectra cannot be used to identify the polyaniline used in previously reported H₂ adsorption studies
BUT oxidation potentials can be used (as shown in #7).

* Aldrich, Catalogue No. 530689; Batches 06517PB and 14705TD.

Development of a Method for Determining Oxidation Potentials of the Form of Polyaniline Used in Previously Reported H₂ Adsorption Studies by Polyaniline

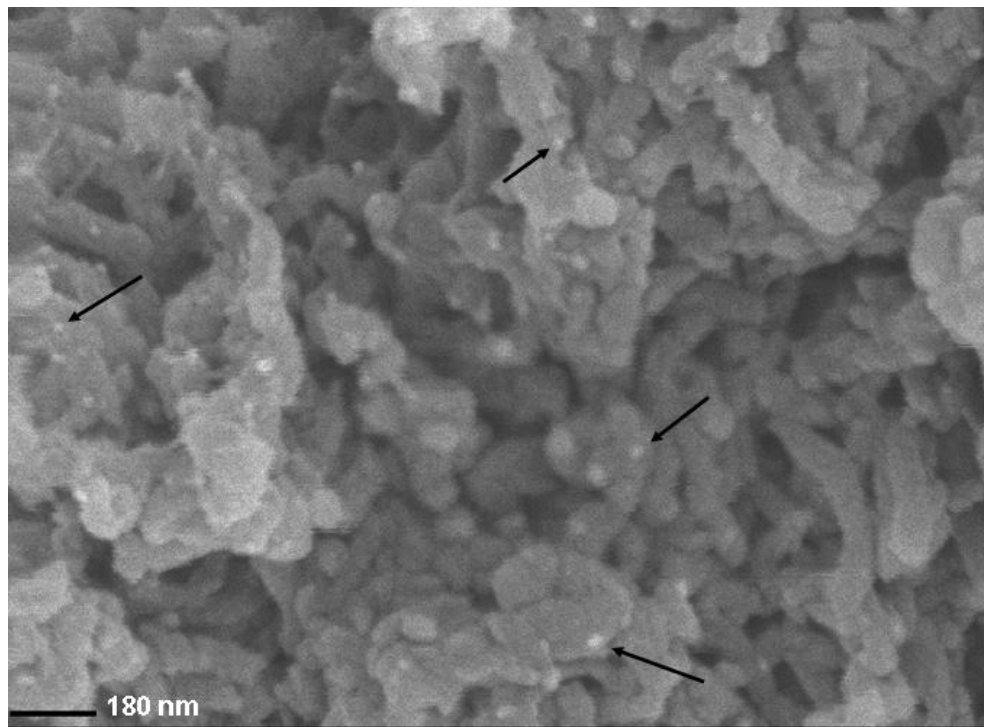


Accomplishment:

Determination of actual oxidation states of the spectroscopically indistinguishable emeraldine polyaniline reported to adsorb ~8 wt% of H₂

* Open circuit potential; † Aldrich, Catalogue No. 530689

Synthesis of Emeraldine Polyaniline Samples Decorated with Pd Metal Nanoparticles:
(To Check Spillover Effect on Nano-structured Polyaniline)



SEM of Polyaniline Decorated with Palladium Nanoparticles
(indicated by arrows; ~40 nm in diameter)

Preparation:

Use leucoemeraldine polyaniline (the most highly reduced form of polyaniline) to reduce palladium salt to metallic Pd on the surface of nanostructured polyaniline

Accomplishment:

Nanostructured polyaniline can be decorated with Pd metal nanoparticles
(to be used to investigate spill-over effect of H₂ adsorption on nanostructured polyaniline)

Future Work

Remainder of FY 2006:

- (1) Continue Temperature Programmed Desorption and NMR studies of H₂ on Polyaniline.**
- (2) Obtain Direct Atomic and Nanoscale Information Related to H₂ Adsorption Sites on Polyaniline and Diffusion Mechanisms by Neutron Scattering Measurements at NIST.**
- (3) Prepare Samples for Further H₂ Storage Studies by Optimizing the Chemical Composition of Emeraldine.HCl by Heating.**
 - NREL: significant quantities of HCl liberated (mass spec.) at 100 °C during “degassing” pre-heating of sample.
 - Penn [Epstein and MacDiarmid, *Synthetic Metals*, 41 (1991) 765] TGA, 10 °C/min.: some wt. loss by 100 °C.
 - Therefore, Penn will do TGA under same conditions used for the “degassing” pre-heating treatment used by Cho and by Roth (164 °C).



FY 2007:

(1) Prepare Isomeric Forms of Emeraldine Base Formed on Heating Emeraldine Base

at or below 300 °C. [Sun and MacDiarmid, *Synthetic Metals*, 41-43 (1991) 135].

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

- H₂ Temperature Programmed Desorption Studies on pernigraniline polyaniline base (with NREL).
- H₂ NMR in the presence of pernigraniline polyaniline base (with Prof. Wu at Univ. North Carolina).

(3) H₂ Temperature Programmed Desorption Studies on Polyaniline Decorated with Traces of Metallic Pd, Ni, etc.

- A “go” decision will be made if we are successful in obtaining $> \sim 1\text{wt. \% H}_2$ storage by polyaniline. We can then determine what changes in the chemical composition, oxidation state, morphology, dopant, surfactant, etc., increases the H_2 storage and proceed to higher H_2 adsorption.
- If $< 1\text{ wt. \%}$ of reversible H_2 is obtained under a variety of experimental conditions, then the effect of incorporation of metals and coordinated metal ions in the polymer will be studied in greater detail.

Project Summary

- **Relevance:**

Develop low-cost, carbon-based conducting (organic) polymer materials for H₂ storage.

- **Approach:**

Identify and characterize the chemical sub-species of conducting polymers responsible for the previously reported ~8 wt% H₂ adsorption by polyaniline and polypyrrole.

- **Technical Accomplishments and Progress:**

- Observed unusual H₂ desorption using polyaniline nanofibers doped with camphorsulfonic acid and synthesized in the presence of the surfactant Triton X-100.
- Discovered two factors of probably critical importance in H₂ adsorption by polyaniline.

- **Technology Transfer/Collaboration:**

Active partnership with UNC (Professor Y. Wu) and NREL (Dr. M. Heben).

- **Proposed Future Research:**

Systematic preparation and characterization of conducting polymer samples by selected chemical and/or physical treatments for H₂ adsorption/desorption studies.

“MOONLIGHTING” ! A

(VARIOUS SOURCES OF FINANCIAL SUPPORT)

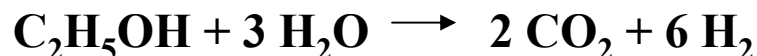
JOIN

“HYDROGEN ECONOMY”

WITH

“BIOETHANOL ECONOMY”

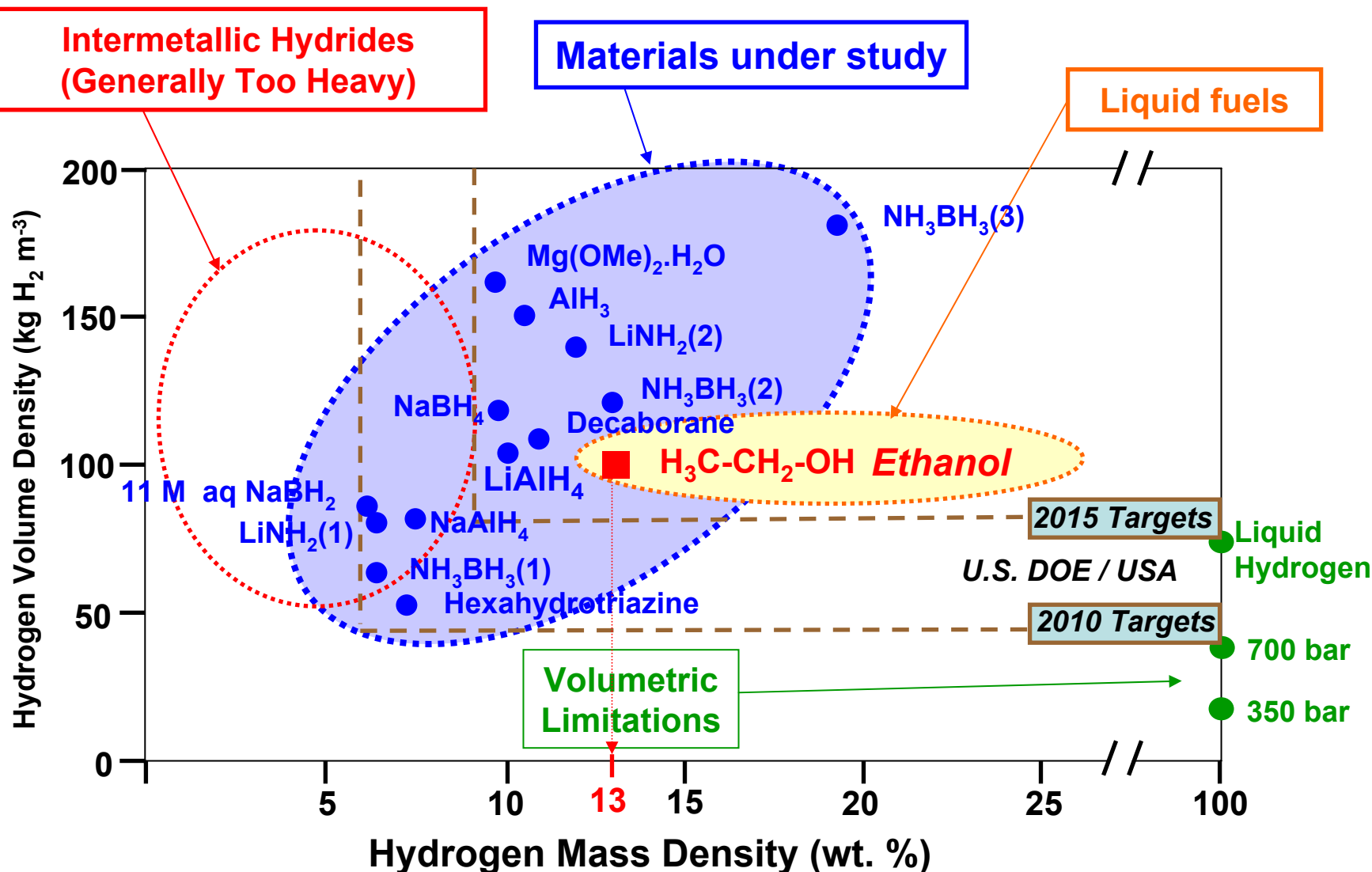
**PRODUCE H₂ FROM BIOETHANOL BY A NOVEL
NON-CATALYTIC, ENVIRONMENTALLY FRIENDLY METHOD**



Energy Density And Specific Energy Are Key To Meeting Performance Target

COMBINE “HYDROGEN ECONOMY” WITH “BIOETHANOL ECONOMY”

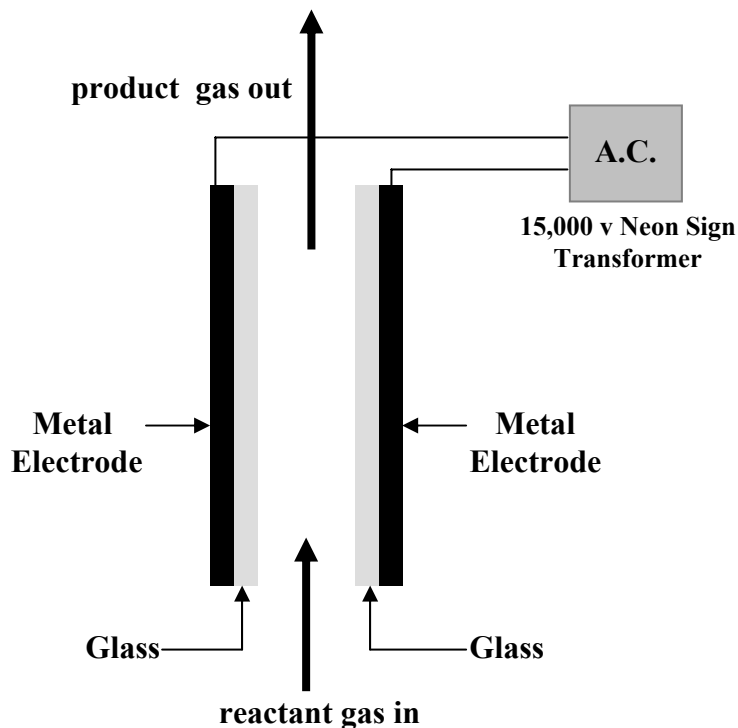
B



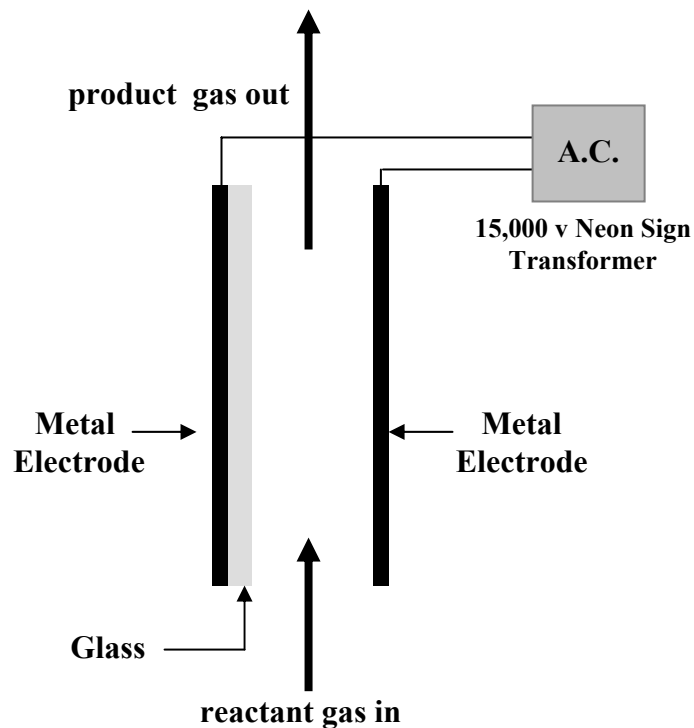
SILENT ELECTRIC DISCHARGE OR CORONA DISCHARGE

C

Same Principle as FET (Field Effect Transistor)



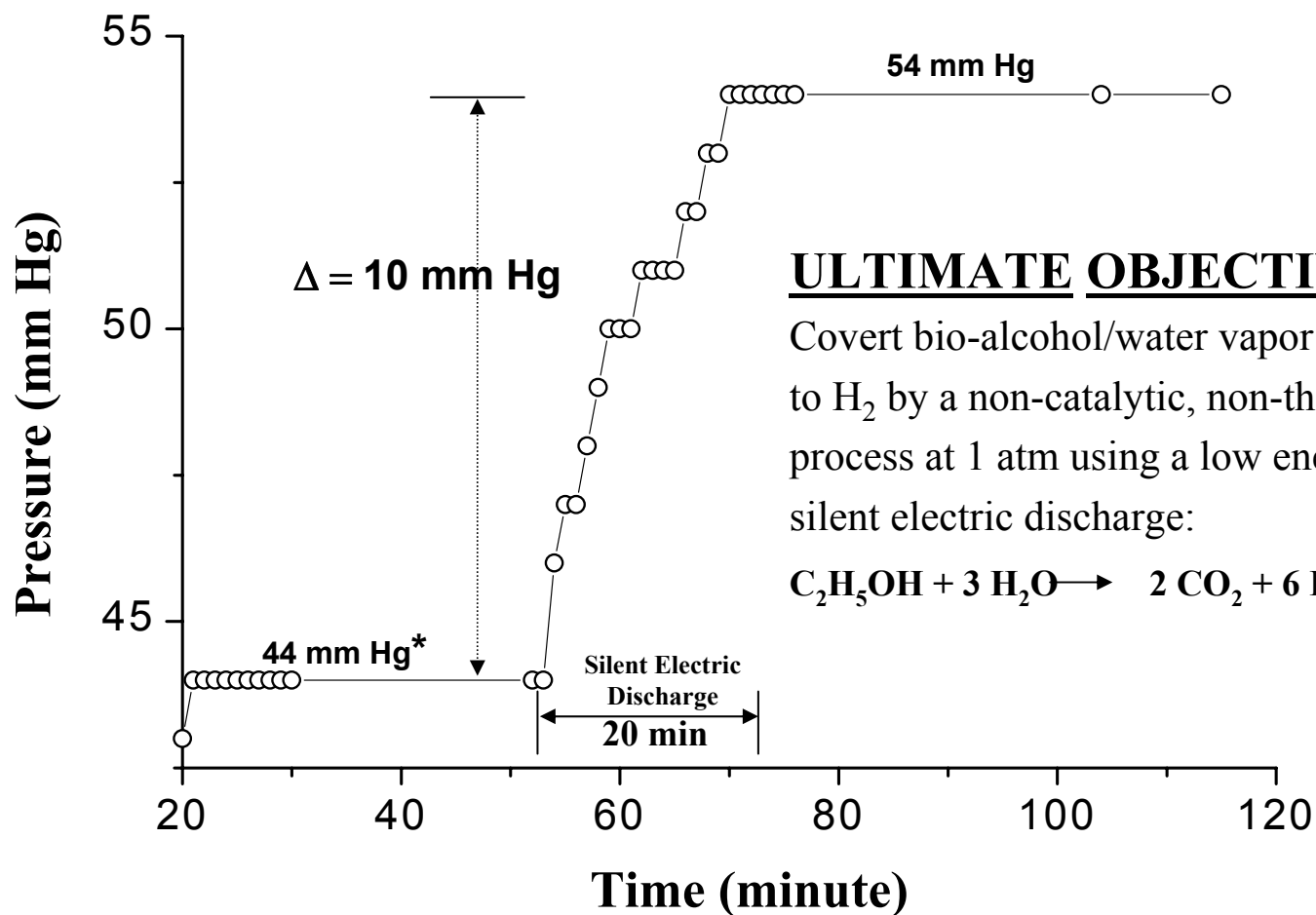
SILENT ELECTRIC
DISCHARGE



CORONA
DISCHARGE

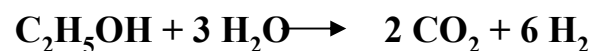
Pressure as a Function of Time in a Silent Electric Discharge Reactor Starting with Ethanol Vapor D

(from 100% ethanol; ~21°C)



ULTIMATE OBJECTIVE :

Covert bio-alcohol/water vapor mixture to H_2 by a non-catalytic, non-thermal process at 1 atm using a low energy, silent electric discharge:



* Vapor pressure of ethanol at 20°C : 43.6 mm Hg (ref: International Critical Tables, p. 290)
See also W. Löb, Biochem. Z., **20** (1909) 126.

Modified
Back-up Slides

Alan G. MacDiarmid
University of Pennsylvania
Philadelphia, PA

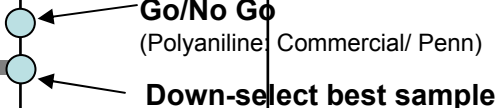


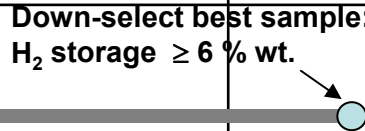
MILESTONES (5 YEARS PROJECT)

- 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					
Task 2 •H ₂ Adsorption/Desorption •Polyaniline – chemical treatment •SWNTs-Conducting Polymers (CP) Composites - with or without added metals					
Task 3 •Delivery materials to Center Partners - Characterization / Test - H ₂ storage properties and mechanism				Down-select best sample: H₂ storage ≥ 6 % wt. 	
Task 4 •Determine proton exchange - D ₂ / H to form HD					

Back-Up Slides will be added after this poster (I am working on resizing the format of the text; DOE has no comments on the contents of the backup slides)

Publications

1. E.C. Venancio, P.C. Wang, A.G. MacDiarmid. The Azanes: A Class of Material Incorporating Nano/Micro Self-Assembled Hollow Spheres Obtained by Aqueous Oxidative Polymerization of Aniline. *Synthetic Metals*, **156**, 357-369 (2006).
2. A.G. MacDiarmid, M.J. Heben, E.C. Venancio, S.K. Manohar, A.C. Dillon, K.E.H. Gilbert. Conducting Polymers as Potential New Materials for Hydrogen Storage. In: IPHE International Hydrogen Storage Technology Conference, June 2005, Lucca, Italy.

Critical Assumptions and Issues

- Enhancement of the hydrogen binding sites:
 - We know from our previous results that different types of polyaniline gives different results for hydrogen storage (TPD and NMR results)*.
 - We are preparing different samples with different chemical composition and oxidation states. (1) Polyaniline has a continuum of oxidation states within which three major oxidation states are included, i.e. leucoemeraldine (reduced state), emeraldine (intermediate oxidation state) and pernigraniline (most oxidized state); (2) metal-decorated (Palladium and Nickel) polyaniline samples are being prepared[†] and they will be studied for hydrogen storage; (3) we know from previous results from the CbHS Center that materials modified with metals such as platinum and palladium present the so called *spillover effect*, which could also be observed in polyaniline samples (and in other types of conducting polymers, such as polypyrrole) decorated with metallic nanoparticles, i.e. palladium.

* A.G. MacDiarmid, DOE Quarterly Reports: (1) October 31, 2005; (3) January 30, 2006.

[†] E.C. Venancio et al., *Electrochimica Acta*, **12**, 1495-1501 (2002)

Critical Assumptions and Issues (*cont.*)

- New approach for hydrogen storage using carbon-based materials
 - We know from our previous work that electric silent discharge can be used to promote *unusual* chemical reactions, such as the conversion of a mixture of silane and dimethyl ether into methylidisilane which liberates considerable amount of hydrogen*.
 - We are developing a silent discharge setup to produce hydrogen from ethanol. Ethanol contains ~13 wt.% of hydrogen. Ethanol is a liquid and it can be easily stored on board.
 - The silent discharge system can be designed to operates on board of a vehicle at atmospheric pressure and room temperature. In addition, very low current are used in silent discharge.

* A.G. MacDiarmid et al., Inorganic Chemistry, **5**, 2040-2042 (1966).