

2007 DOE Hydrogen Program

Montana Palladium Research Initiative:

Use of Biological Materials and Biologically Inspired Materials for H₂ Catalysis

John W. Peters (PI), Trevor Douglas,
and Mark Young.

Department of Chemistry and Biochemistry
and
Center for Bioinspired Nanomaterials



DOE Project ID#: PDP3

This presentation does not contain any proprietary,
confidential, or otherwise restricted information



Overview

Timeline

- Start - Aug. 2006
- End - Dec. 2008

Budget

- Total project funding
\$1,303,041
 - DOE \$1,031,433

Barriers addressed

- Stability/Durability
- Oxygen Sensitivity
- Electron Donors
- Coupling

Partners

- Montana State University



DOE Project ID#: PDP3

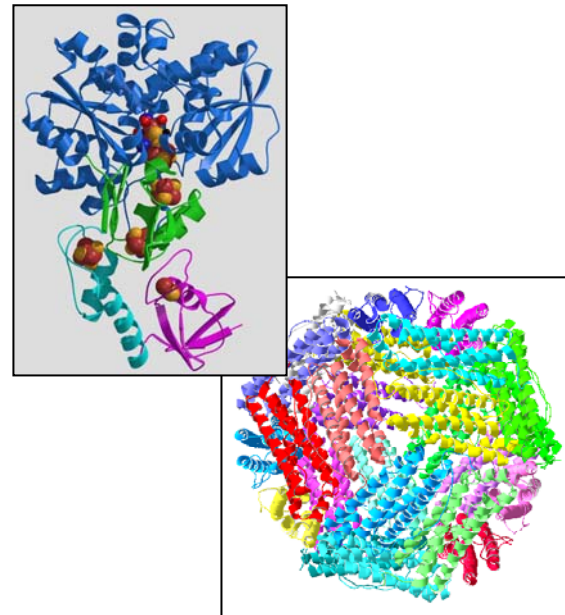


Approaches

Couple Different Catalyst Systems for
Light Driven Hydrogen Generation

Biological catalysts (Hydrogenases)

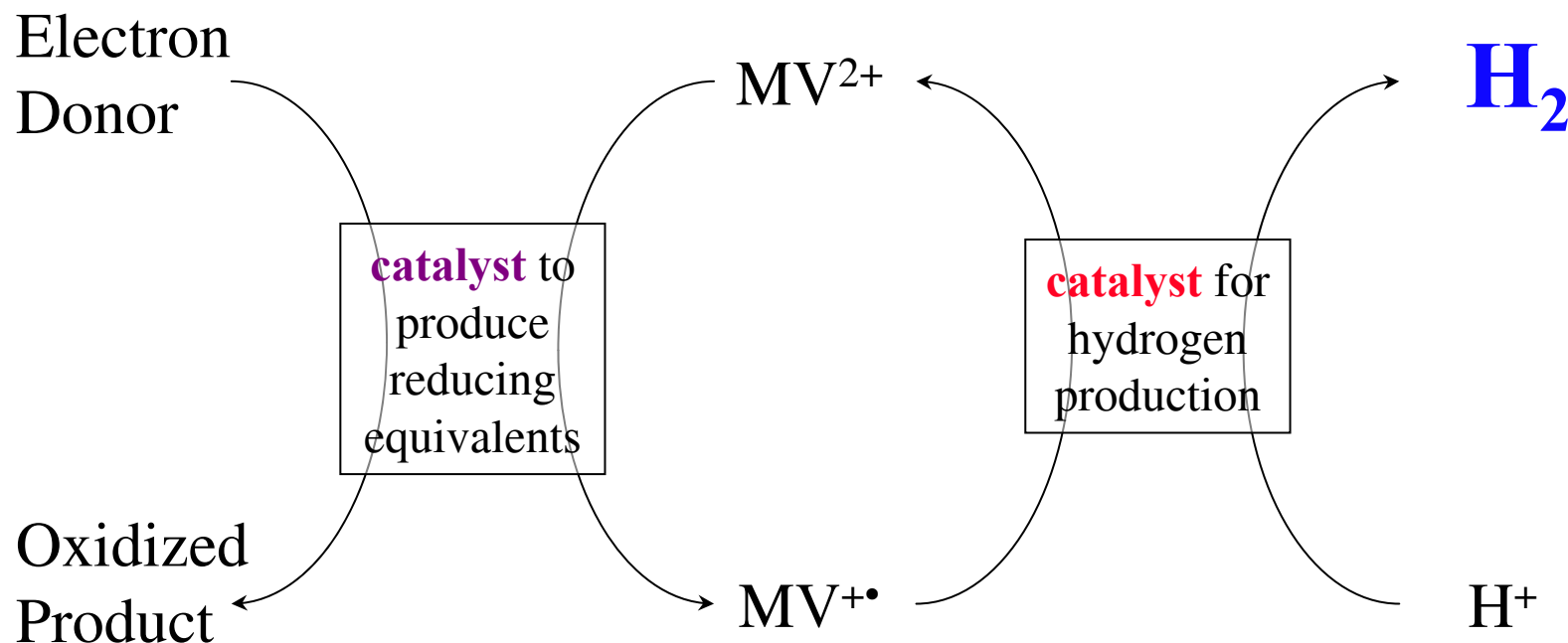
Nanoparticle Mimetic catalysts



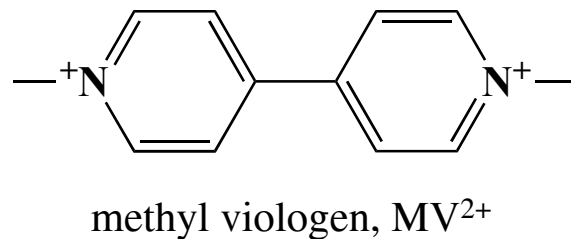
Objectives

1. Optimize the hydrogenase stability and electron transfer
2. Optimize the semiconductor nano-particle photocatalysis, oxygen scavenging, and electron transfer properties of protein nano-cages
3. Gel/Matrix immobilization and composite formulation of nano-materials and hydrogenase
4. Device fabrication for H₂ production

Coupled Reactions to generate hydrogen

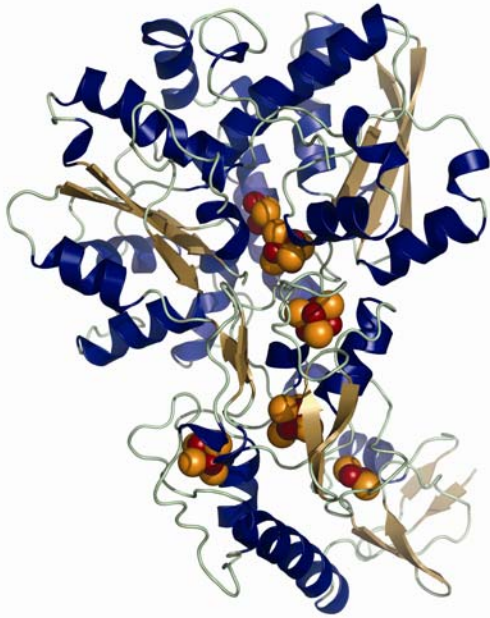


GOAL: use a **catalyst** to reduce an electron mediator (methyl viologen, MV^{2+}) with a variety of sacrificial electron donors. Hydrogenase and mimetic catalysts then use $MV^{+\bullet}$ to produce H_2 .

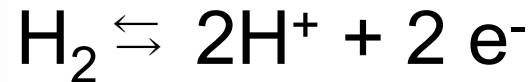
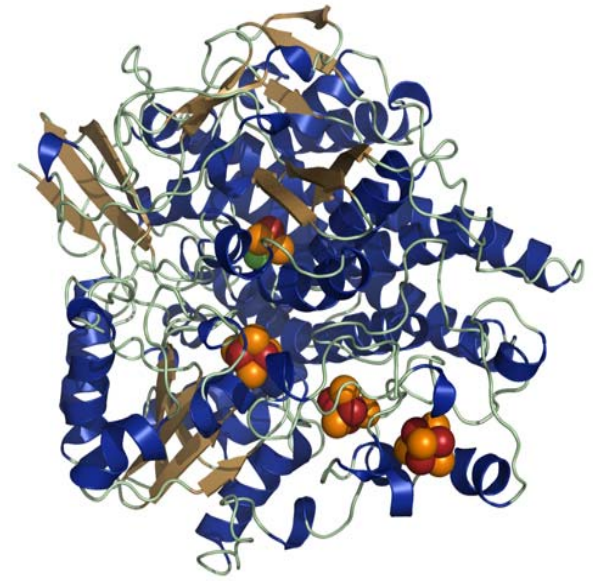


Hydrogenases: Highly evolved finely tuned catalysts for *hydrogen oxidation and proton reduction (hydrogen production)*

C. pasteurianum



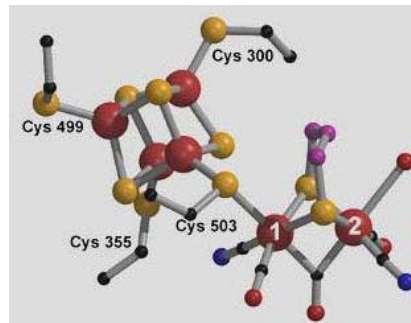
Desulfovibrio gigas



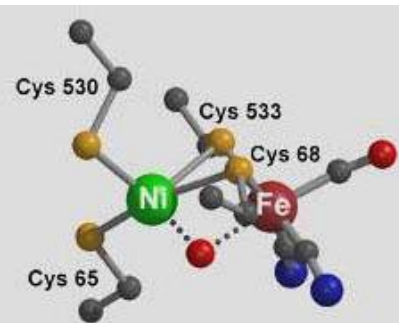
Cellular location

Membrane Associated
Soluble
Periplasmic
Cytoplasmic

“H Cluster”



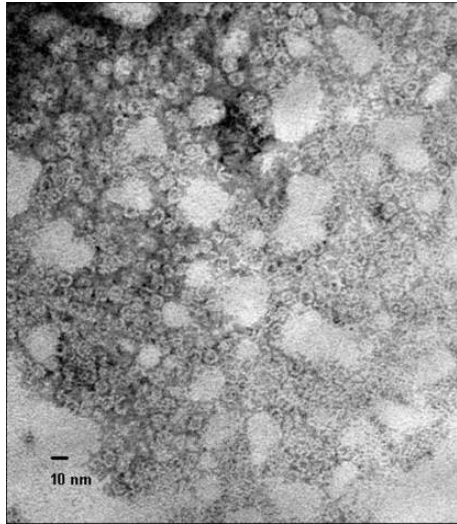
NiFe Cluster



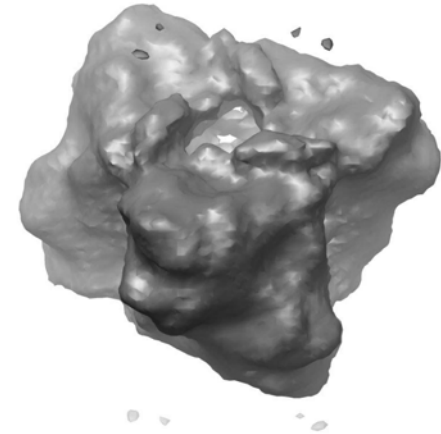
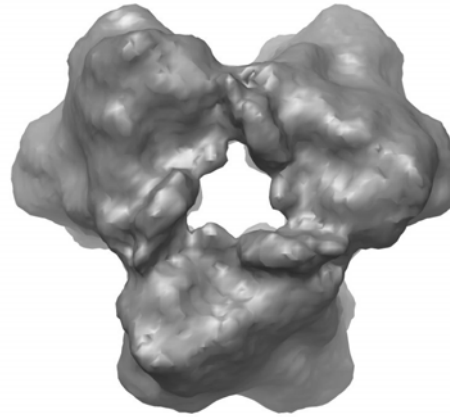
Microorganisms:

hydrogen, acetate-grown, methanogenic, green, purple, cyanobacteria; algae; fungus.

Stable NiFe hydrogenase from purple sulfur bacteria form supermolecular structures

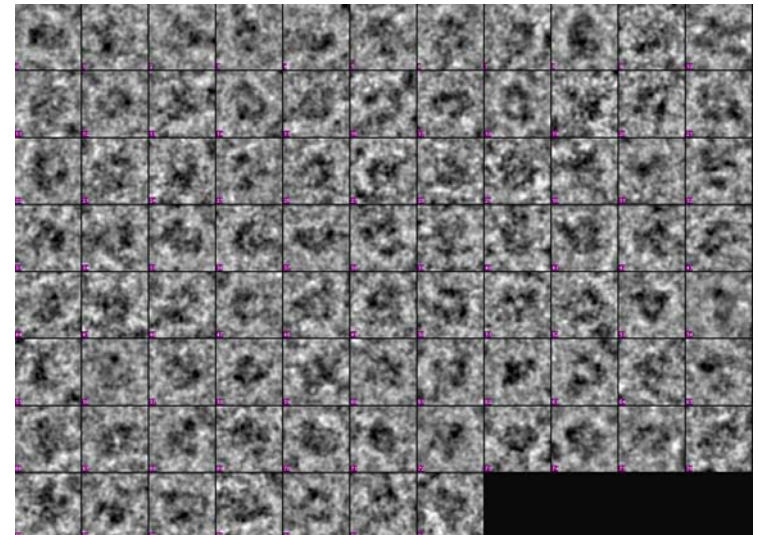


Electron microphotograph of hydrogenase complexes from *T. roseopersicina* negatively stained with 2% uranyl acetate

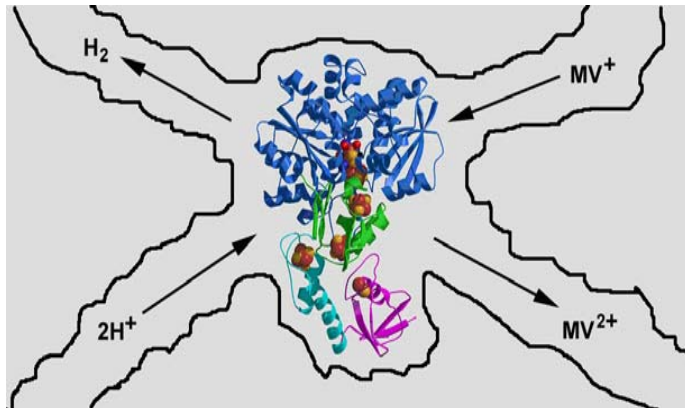


Cryo reconstruction of hydrogenase from *T. roseopersicina* at ~ 33 Å.

Properties	<i>Thiocapsa roseopersicina</i>
Large subunit	64kDa
Small subunit	34kDa
Temperature optimum , °C	80
Stability to Oxygen	stable



Encapsulation of purified active hydrogenases in tetramethyl ortho silicate gels.



- Nanoscopic encapsulation;
- Immobilization of unaltered enzyme
- “Heterogeneous material”

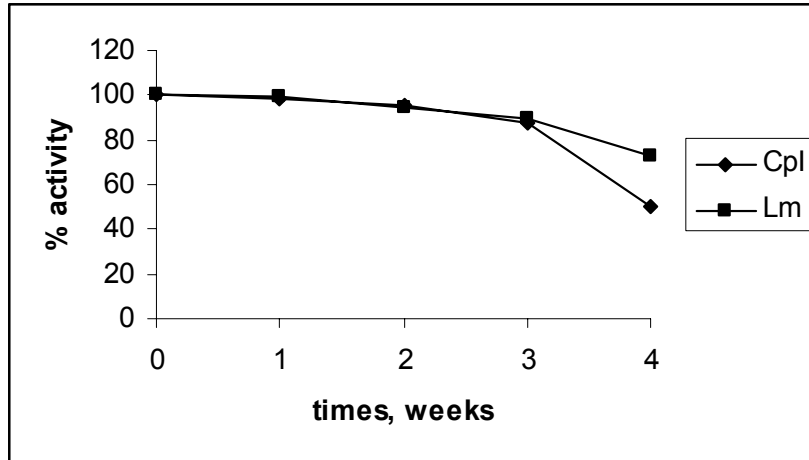
Recovery of hydrogenase activity* encapsulated in Sol-Gel

Hydrogenase	Solution	Gel	Solution/Gel (%)
<i>C. pasterianum</i> (extract)	12550	7581	60.4 ± 16
<i>L. modestogalophilus</i>	9150	6175	67.5 ± 9
<i>T. roseopersicina</i>	12600	8834	70.1 ± 3

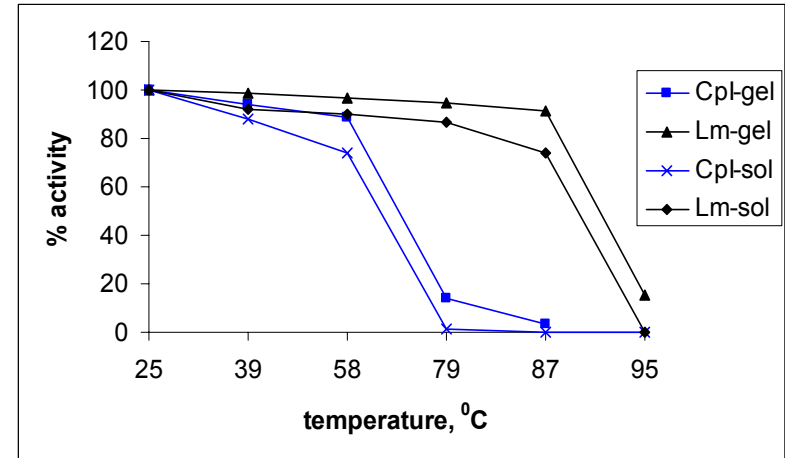
•Activity measure at 25° C indicated in nmol/min/mg protein. Values represent average rate over a four-hour period.

Hydrogenase stability can be enhanced by encapsulation

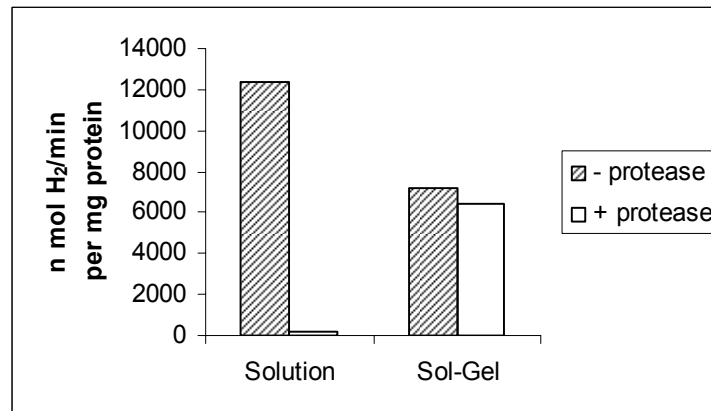
Increased half-life and increased temperature stability



Sol-gel encapsulated hydrogenases from *C. pasterianum* (Cpl) and *L. modestogalophilus* (Lm) retain activity for a month.

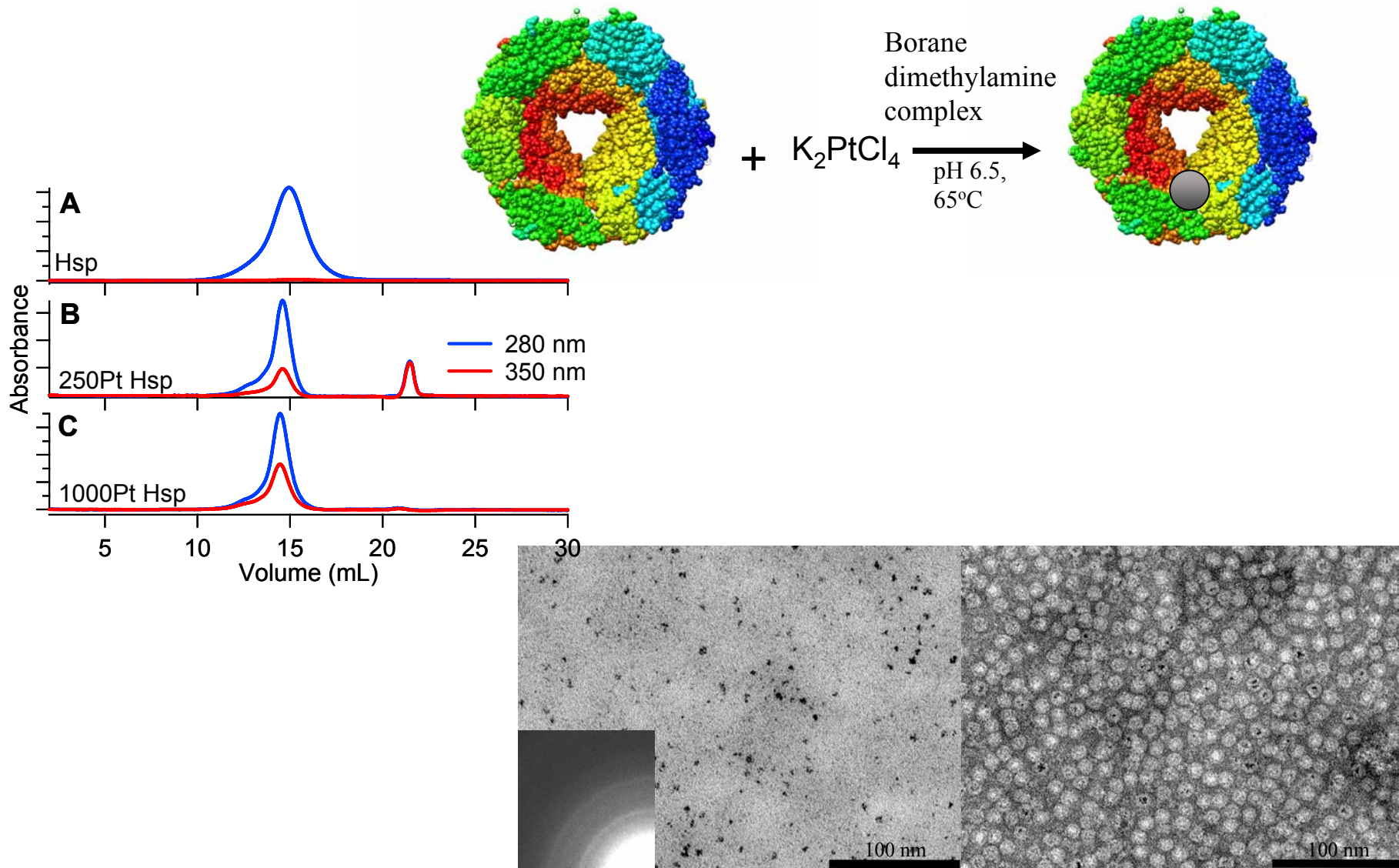


Stability of hydrogen production activity of Cpl and Lm hydrogenases enhanced when encapsulated

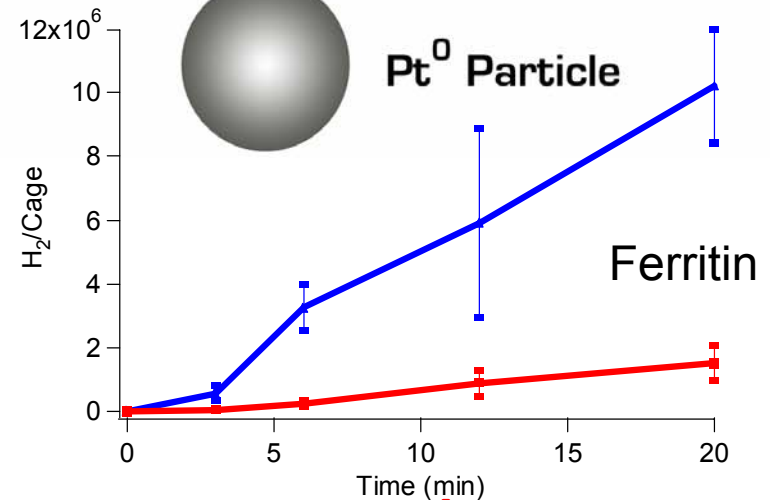
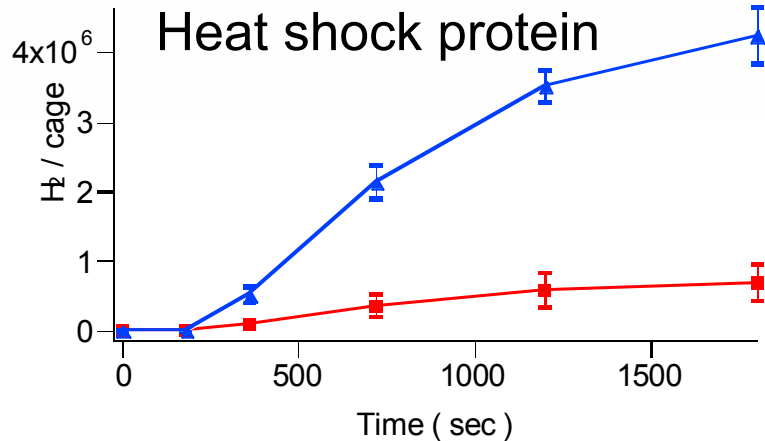
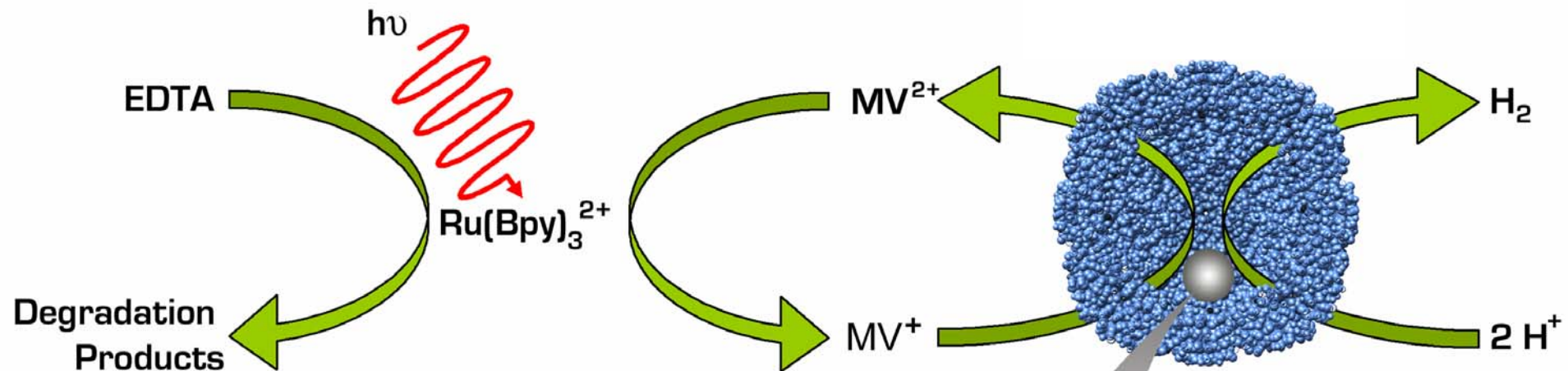


Encapsulated hydrogenases are insensitive to proteases.

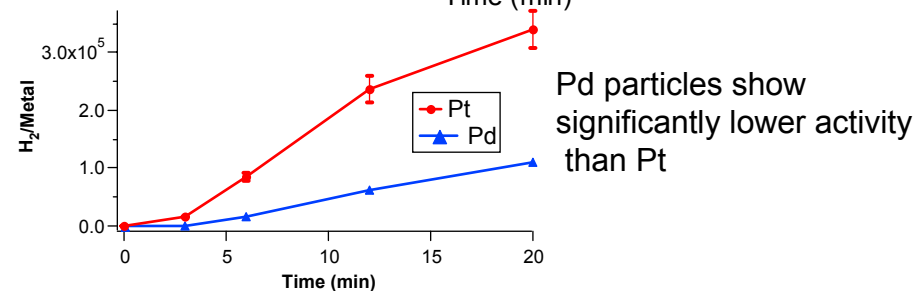
Synthesis of Pt^0 inside of Protein Cage Architecture



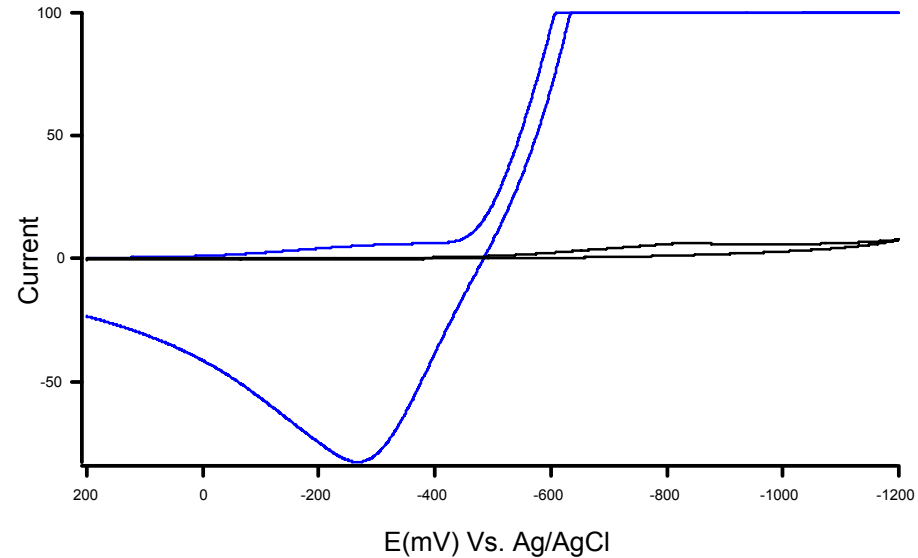
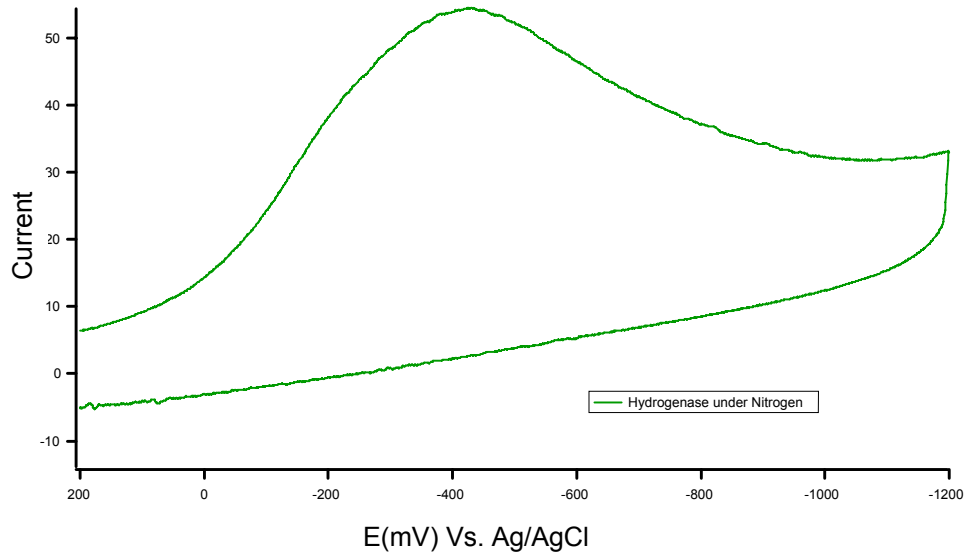
Coupled Photocatalysis for H₂ Production



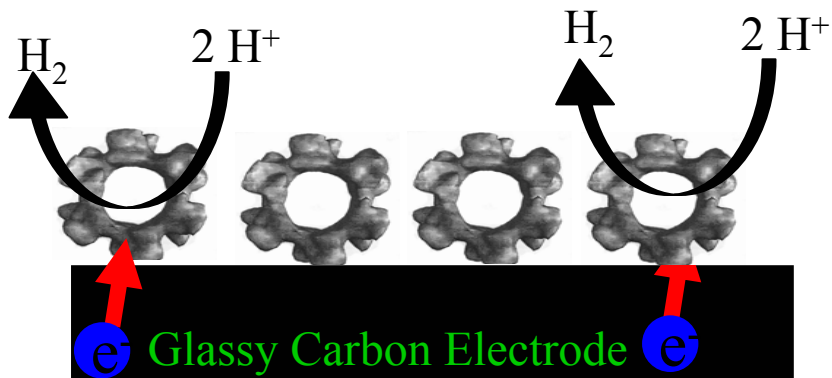
Initial rates (Pt): $4.47 \times 10^3 \text{ H}_2/\text{sec}/\text{Hsp}$
 $1.5 \times 10^4 \text{ H}_2/\text{sec}/\text{ferritin}$
 (Hydrogenase $\Rightarrow 6 \times 10^3 \text{ H}_2/\text{sec}/\text{hydrogenase}$)



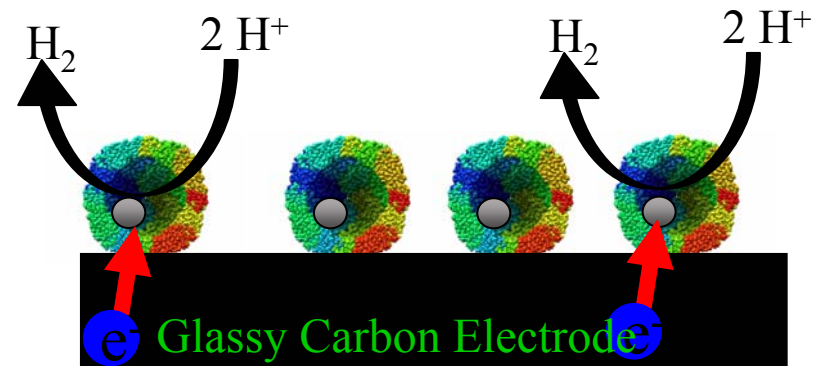
Cyclic Voltammetry



Hydrogenase



Synthetic Mimic



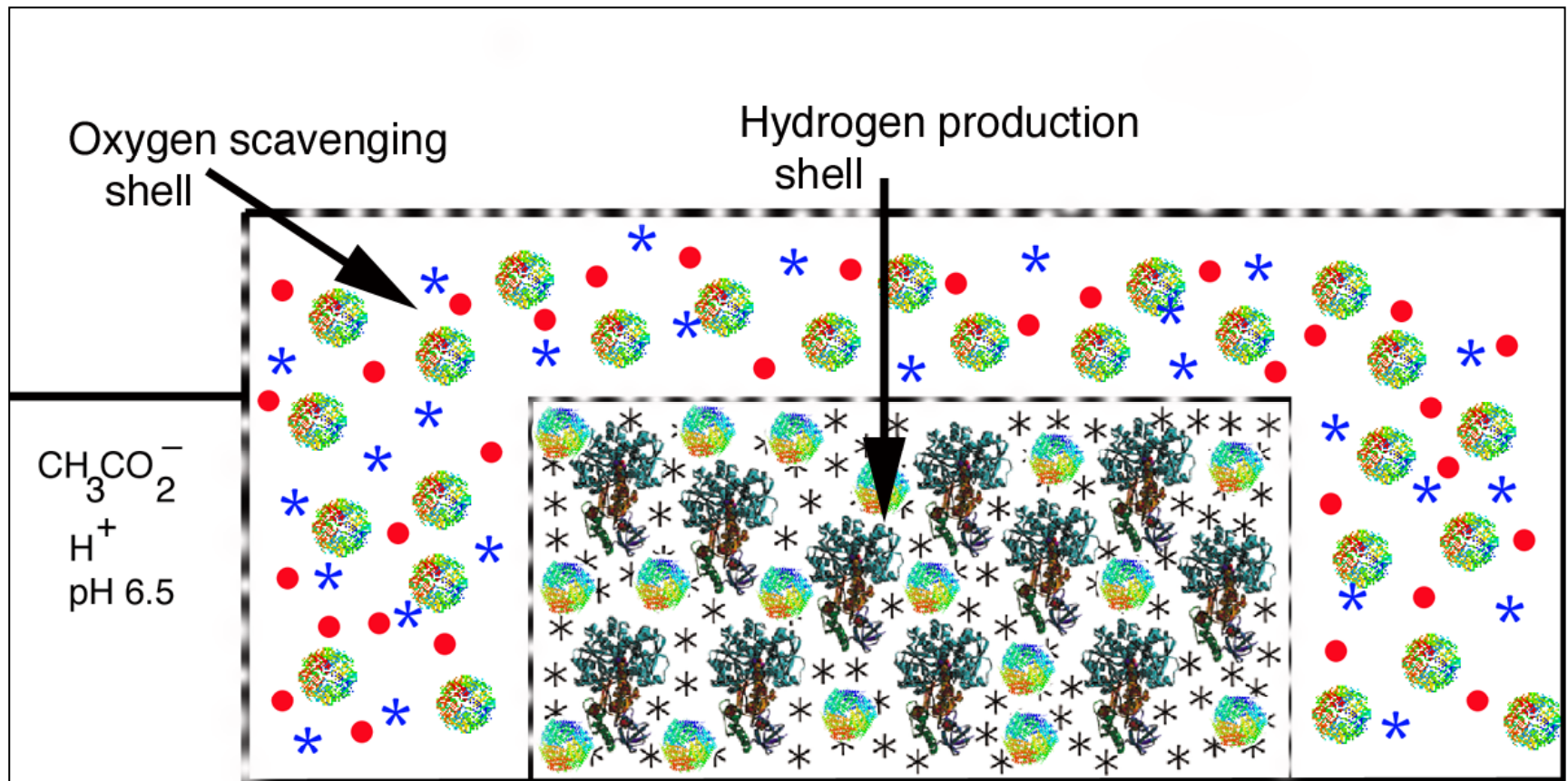
Current properties in the context of technical targets

	Biomimetics	Hydrogenases
Continuous hydrogen production	> 60 min	> 60 min
O ₂ tolerance	Insensitive to O ₂	Insensitive Reversibly oxidized in the presence of O ₂ and retains activity
Efficiency of photon-to-H ₂	Currently assessing*	Currently assessing*

- Reported quantum efficiency of Ru(bpy)₃²⁺ photoreduction of MV²⁺ to MV⁺ using EDTA as sacrificial reductant is 25%. (Johansen, O. *et al Chem. Phys. Letters*, **1983**, 94, 113-117)

- We are currently assessing the efficiency of the MV⁺ to H₂ with both the hydrogenases and synthetic systems.

Long-Term Goal – Device for photocatalytic hydrogen production – composite materials (nanoparticles and hydrogenase enzymes)



Hydrogen Safety

The most significant hydrogen hazard associated with this project is:

Accidental ignition of hydrogen gas; leading to injury of personnel and damage to equipment from both fire and explosive debris such as: glassware and/or chemicals

Hydrogen Safety

Our approach to deal with this hazard is:

Follow lab protocol of wearing safety glasses,
gloves

Keep glove box H₂ level below 3%

Vent gases in fume hood

Keep away from open flame and flammable
chemicals

Keep quantity of H₂ production to a minimum

In event of accidental explosion contact

Jeff Shada, Safety and Risk Management,
Advanced Tech Park, 406-994-2711

2007 DOE Hydrogen Program

Montana Palladium Research Initiative: Palladium-Based Membrane on a Porous Steel Substrate

Dr. Corby Anderson

John Krstulich

Montana Tech / CAMP

May 15, 2007

This presentation does not contain any proprietary,
confidential, or otherwise restricted information

Project ID #: PDP 3



Overview

Timeline

- Start Date: 1/1/2007
- End Date: 12/31/2007
- 10% Complete

Budget

- Total Project Funding
 - DOE: \$469,164.00
 - Contractor: \$117,291.00
- Funding Received in FY06: \$0
- FY07 Funding: \$586,455.00

Barriers

- Membrane Durability
- Membrane Defects
- Flux Rate for Membrane

Targets:

		2006	2010
Flux Rate	scfh/ft2	200	250
Durability	hr	8,760	26,280

Partners

- Montana State University



Objectives

- Design membrane substrate with emphasis on strength, surface finish, and consistent pore size.
- Develop full density palladium membrane layer that is thin, with high flux rate, high impurity tolerance, durable in operating conditions, and a strong adherence to the substrate.
- Safely perform module testing.



Plan and Approach

<p>15% Complete</p>	<p>Task 1: Porous Metal Substrate Development</p> <ul style="list-style-type: none"> •Evaluate metal powder for free form fabrication •Develop various substrate models •Create sintering schedule •Fabricate substrates •Determine substrate porosity 	<p>0% Complete</p>	<p>Task 3: Plate Membrane onto Substrate</p> <ul style="list-style-type: none"> •Develop plating procedure •Complete membrane plating on substrate •Evaluate plating effectiveness
<p>10% Complete</p>	<p>Task 2: Palladium Based Membrane Development</p> <ul style="list-style-type: none"> •Evaluate palladium and palladium alloys •Determine application method (electroless plating, chemical vapor deposition, etc.) •Assess substrate surface treatment 	<p>10% Complete</p>	<p>Task 4: Separation Module Testing</p> <ul style="list-style-type: none"> •Design and fabricate testing apparatus with safety emphasis •Test membrane integrity (density) •Test hydrogen separation effectiveness •Test operating condition durability



Technical Accomplishments

This is a new and recently funded program for Montana Tech / CAMP.

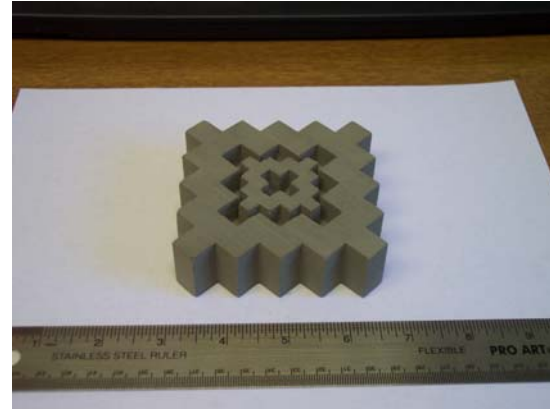
- It has been determined that a Prometal R2 3D Printer can be used to perform the free form fabrication of the metallic substrate. This machine is manufactured by Ex-One of Irwin, Pennsylvania.
- Test piece using 30 mm stainless steel powders has been successfully fabricated.
- Montana Tech / CAMP has in-house expertise for welding porous stainless steel onto machined stainless steel necessary for attachment.
- Electroless plating has been determined to be appropriate for fabricating the palladium membrane.
- A preliminary design for the module testing apparatus has been developed.
- It has been determined the Montana Tech's Scanning Electron Microscope, equipped with a back-scatter detector and MLA software can be used for composition identification.



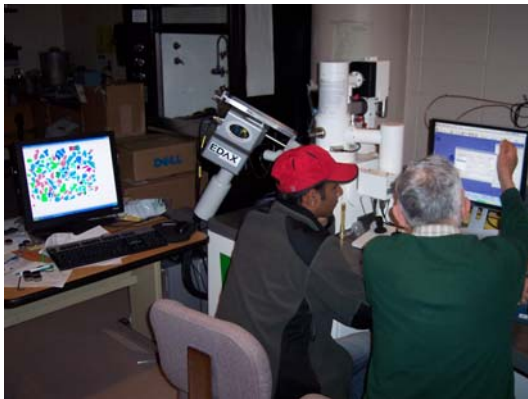
Technical Accomplishments



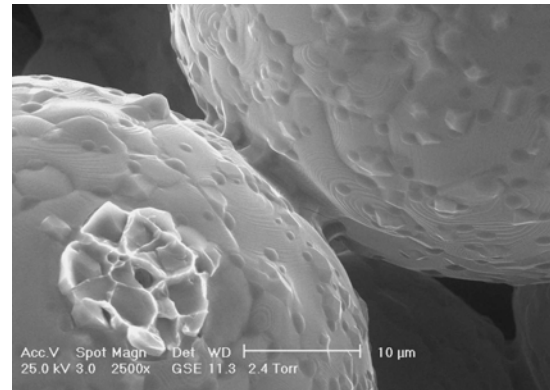
Prometal R2 3D Printing Machine
at Montana Tech / CAMP



Un-sintered test piece fabricated with
Prometal R2 and 30mm stainless
steel powder



SEM with back-scatter detector
and MLA software at Montana
Tech / CAMP



Sintered metal particles displaying
“particle necking”. Courtesy of Ex
One Irwin, Pennsylvania.



Future Work

- Fabricate metallic substrate with favorable composition, shape, pore size, and surface morphology.
- Calculate sintering schedule for metallic substrate to optimize porosity and strength.
- Develop plating procedure for uniform thin dense membrane, with tolerance to impurities, operational durability, and adequate adherence to substrate.
- Design and manufacture module testing apparatus with emphasis on safety.



Summary Table

Technical Targets: Dense Metallic Membranes for Hydrogen Separation and Purification				
Performance Criteria	Units	2006 Status	2010 Target	2015 Target
Flux Rate	scfh/ft ²	>200	250	300
Module Cost (including membrane material)	\$/ft ² of membrane	1,500	1,000	<500
Durability	hr	<8,760	26,280	>43,800
Operating Capability	psi	200	400	400-600
Hydrogen Recovery	%	60	>80	>90
Hydrogen Quality	% of total (dry) gas	99.98	99.99	>99.99



Project Safety

Concern:

Potential Hydrogen Gas Build-up

Precautions:

- The integrity of the membrane module will be tested using helium gas.
- The testing apparatus will be designed to include appropriate pressure indicators and pressure relief valves. This will be used for testing the membrane module with hydrogen or gases containing hydrogen.
- All module testing will be conducted in a well ventilated area, most likely under a chemical hood with gas monitoring meters.



Project Safety

Concern:

Free form fabrication with metal powders.

Precautions:

- The upper chamber of the Prometal R2 has been retro-fitted with the capability to provide four complete air exchanges per minute. The lid has an air bladder that creates a seal and the upper chamber is under a slight vacuum.
- The Prometal R2 electrical components contain redundant grounding for equipment and potted electrical contacts.
- The Prometal R2 has been retro-fitted with non-metallic bearings on moving parts.

