2007 DOE Hydrogen Program

Montana Palladium Research Initiative:

Use of Biological Materials and Biologically Inspired Materials for H_2 Catalysis

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and Mark Young.

Department of Chemistry and Biochemistry
and
Center for Bioinspired Nanomaterials

MONTANA STATE UNIVERSITY

DOE Project ID#: PDP3

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

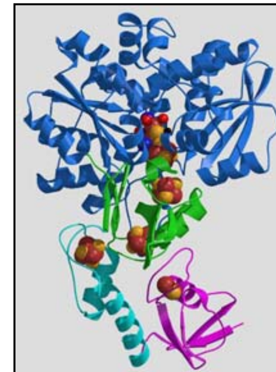
Partners

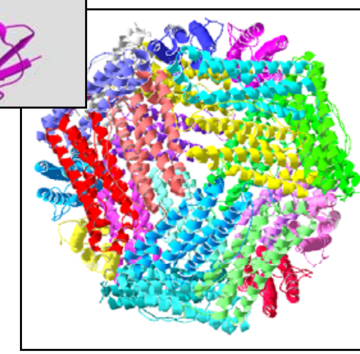
- Montana State University

DOE Project ID#: PDP3

Approaches

Couple Different Catalyst Systems for Light Driven Hydrogen Generation





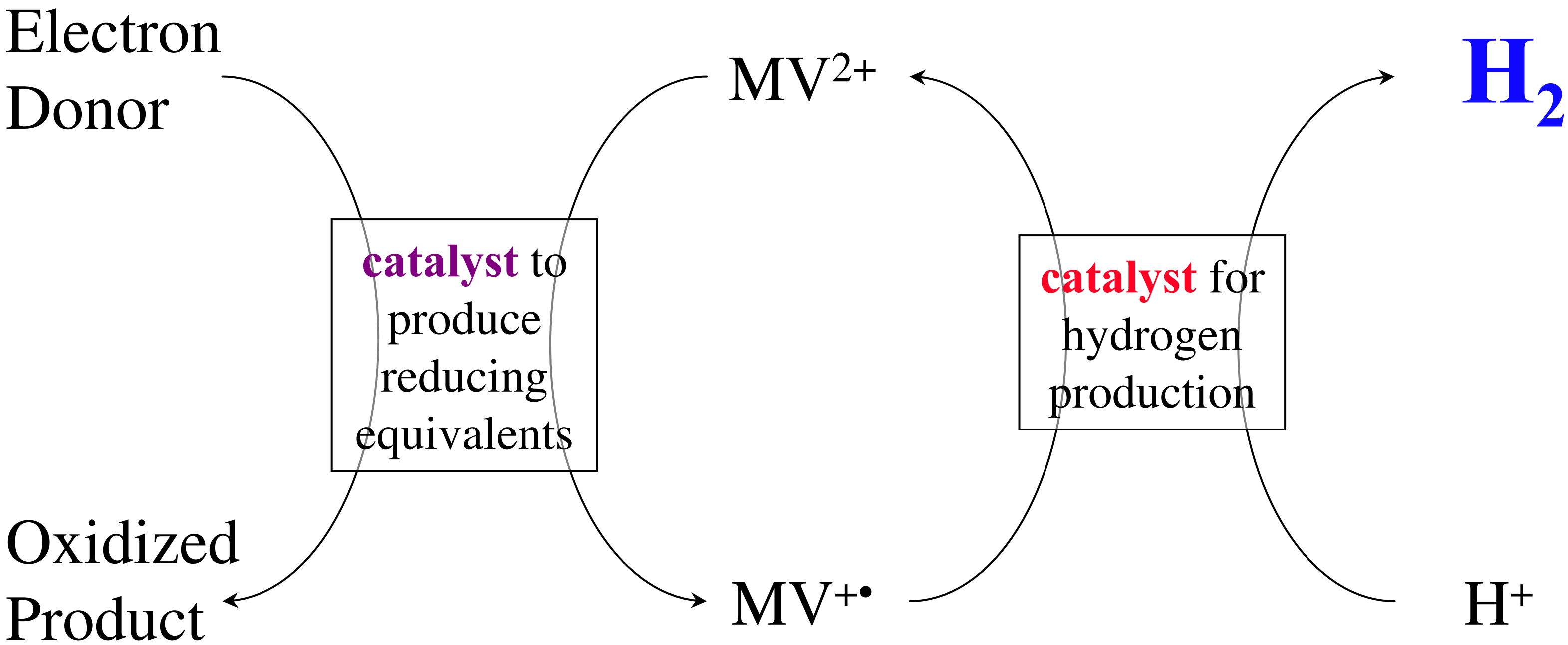
Biological catalysts (Hydrogenases)

Nanoparticle Mimetic catalysts

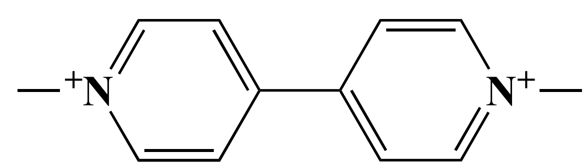
Objectives

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 H_2 production

Coupled Reactions to generate hydrogen



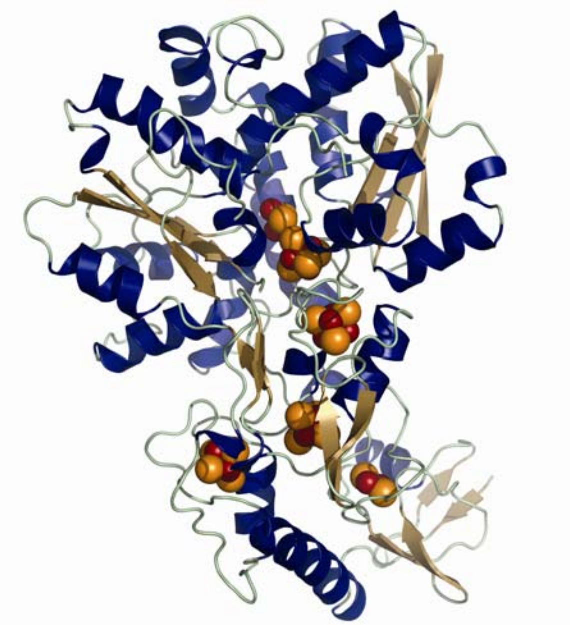
GOAL: use a **catalyst** to reduce an electron mediator (methyl viologen, MV^{2+}) with a variety of sacrificial electron donors. Hydrogenase and mimetic catalysts then use $MV^{+\bullet}$ to produce H_2.



methyl viologen, MV^{2+}

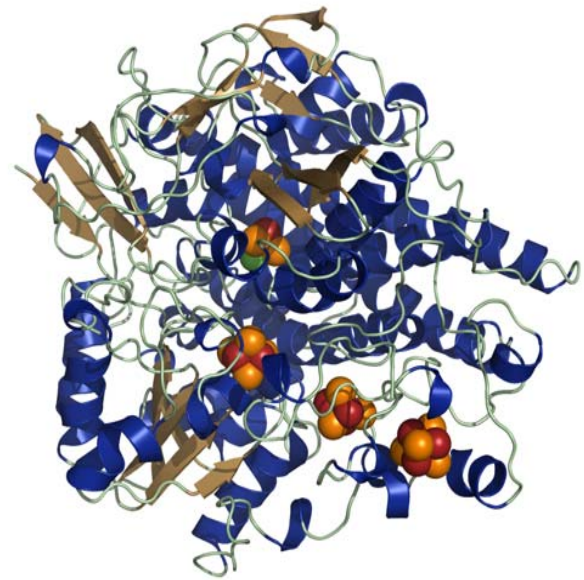
Hydrogenases: Highly evolved finely tuned catalysts for *hydrogen oxidation and proton reduction (hydrogen production)*

C. pasteurianum



$$H_2 \leftrightarrows 2H^+ + 2\ e^-$$

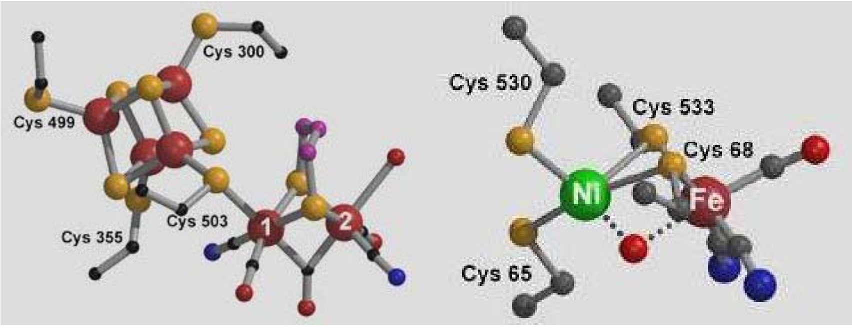
Desulfovibrio gigas



Cellular location

Membrane Associated
Soluble
Periplasmic
Cytoplasmic

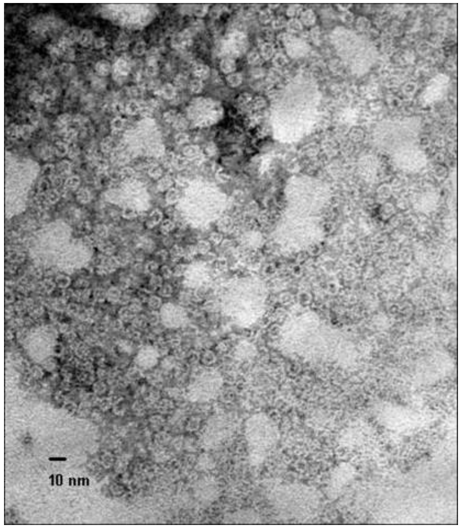
"H Cluster" **NiFe Cluster**



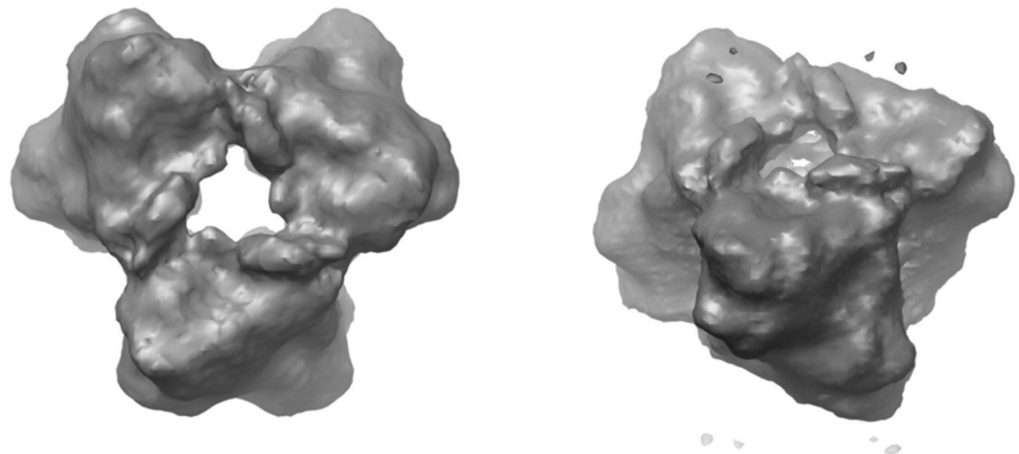
Microorganisms:

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

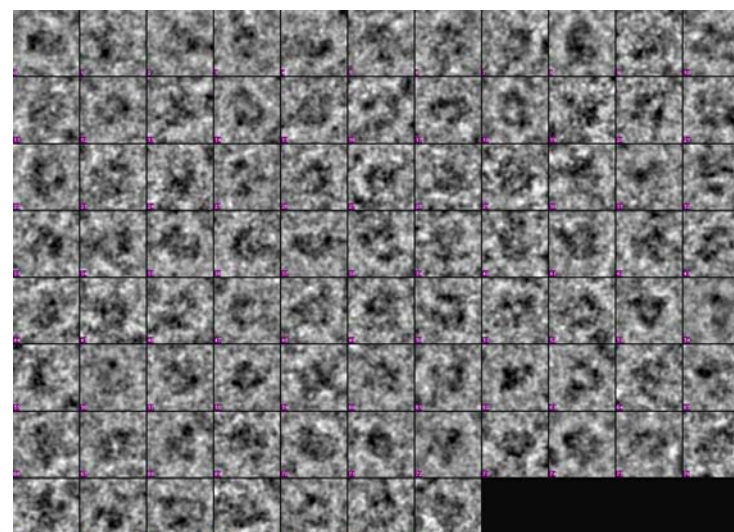
Stable NiFe hydrogenase from purple sulfur bacteria form supermolecular structures



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

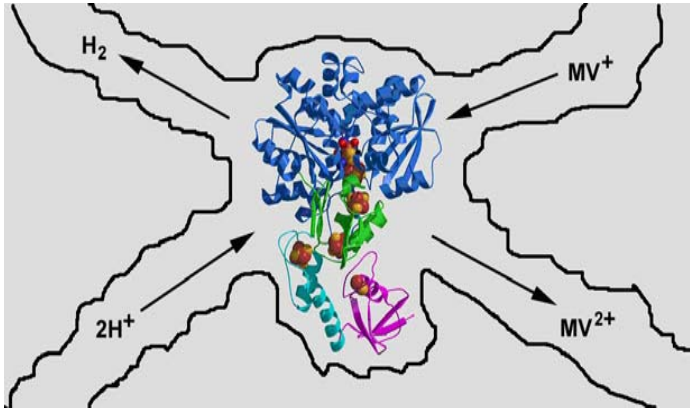


Cryo reconstruction of hydrogenase from *T. roseopersicina* at ~33 Å.



Properties	***Thiocapsa roseopersicina***
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”

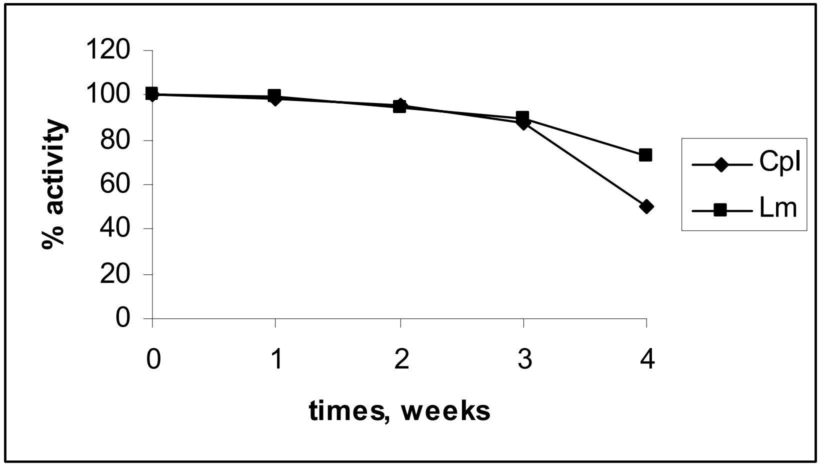
Recovery of hydrogenase activity* encapsulated in Sol-Gel

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

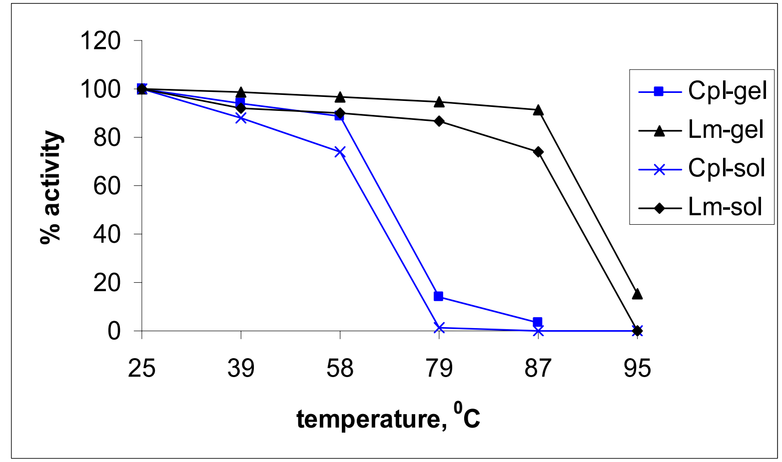
•Activity measure at 25º C indicated in nmol/min/mg protein. Values represent average rate over a four-hour period.

Hydrogenase stability can be enhanced by encapsulation

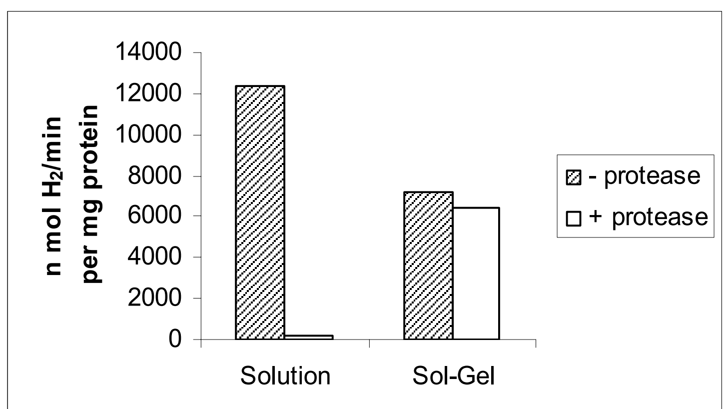
Increased half-life and increased temperature stability



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

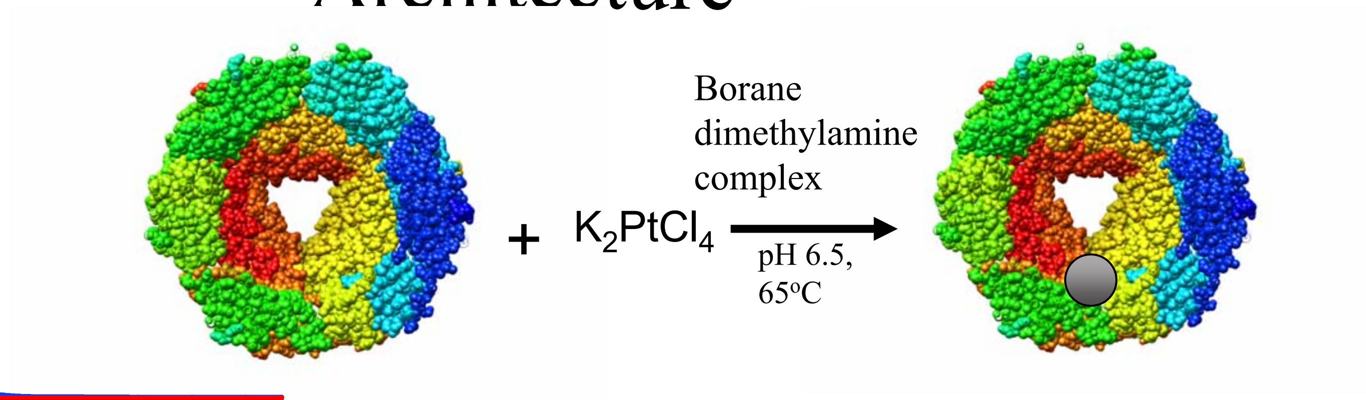


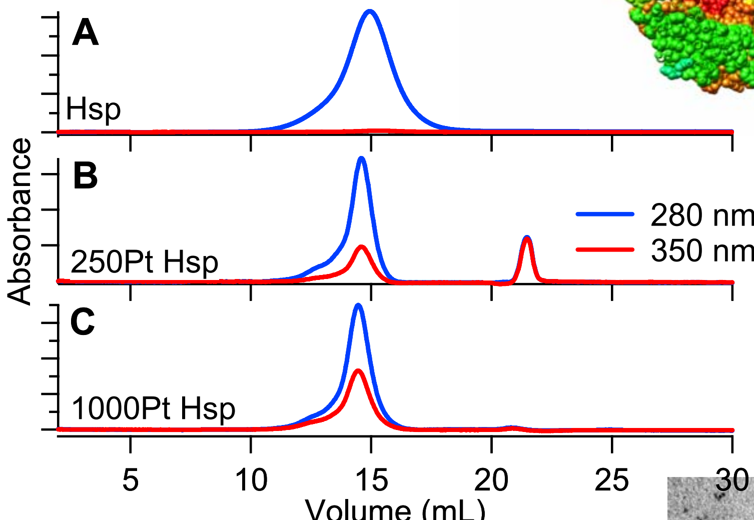
Stability of hydrogen production activity of CpI and Lm hydrogenases enhanced when encapsulated

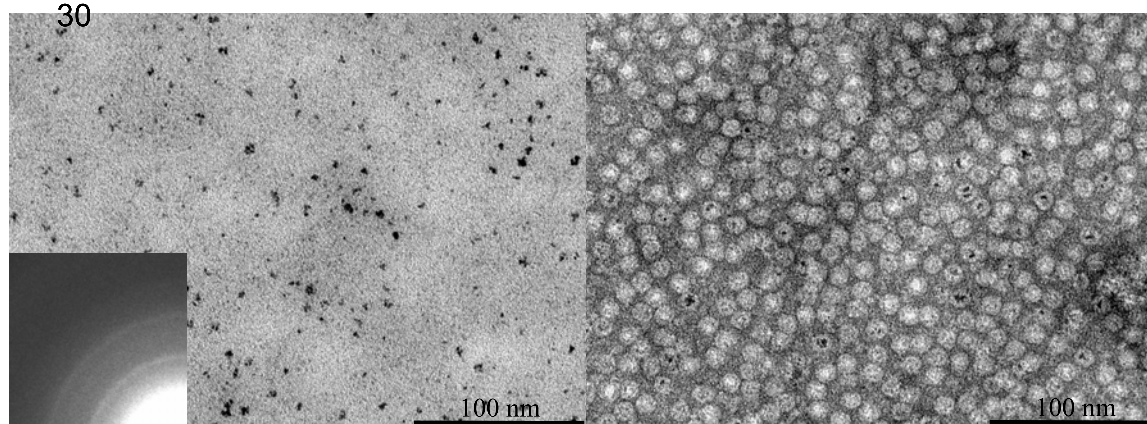


Encapsulated hydrogenases are insensitive to proteases.

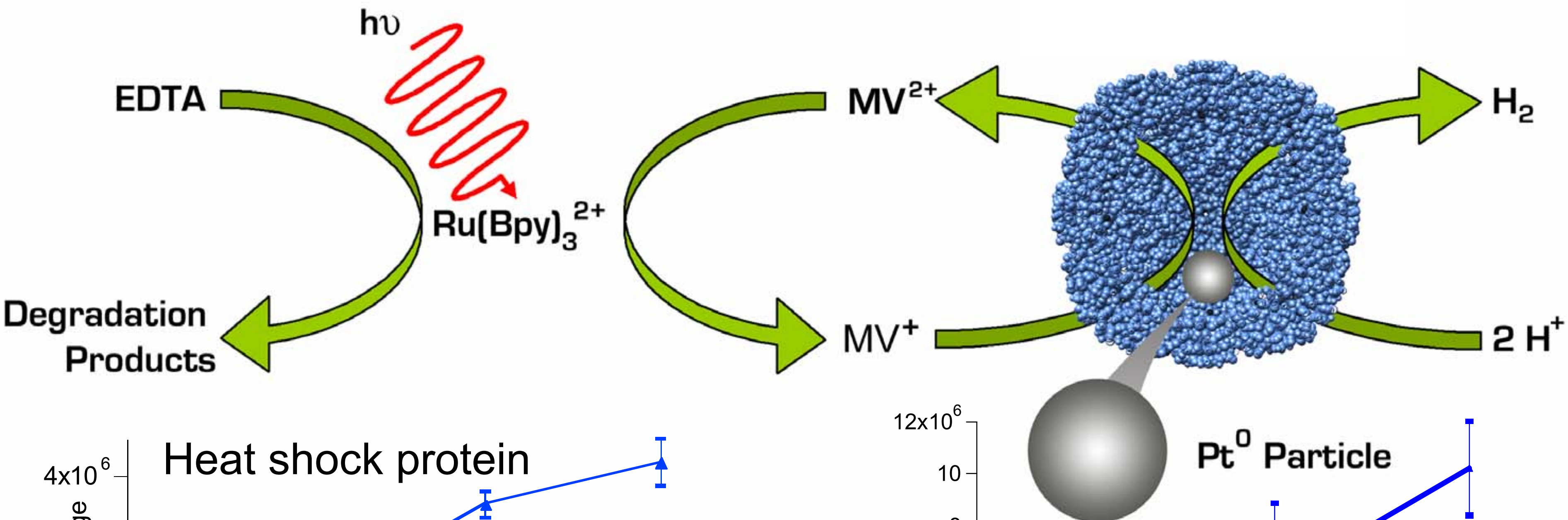
Synthesis of Pt^0 inside of Protein Cage Architecture

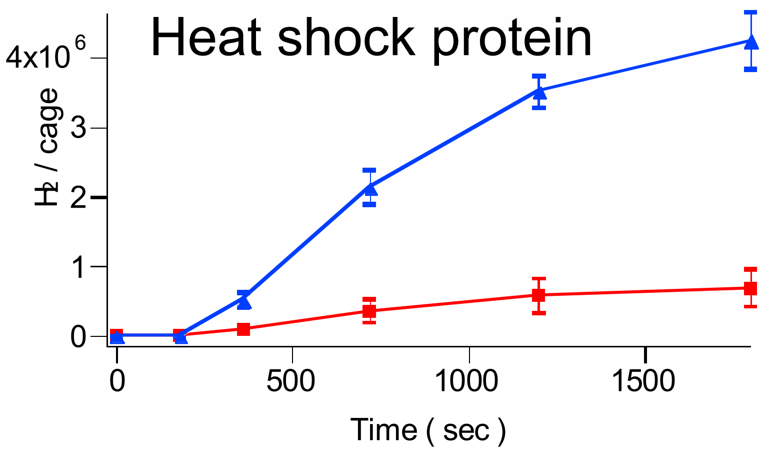


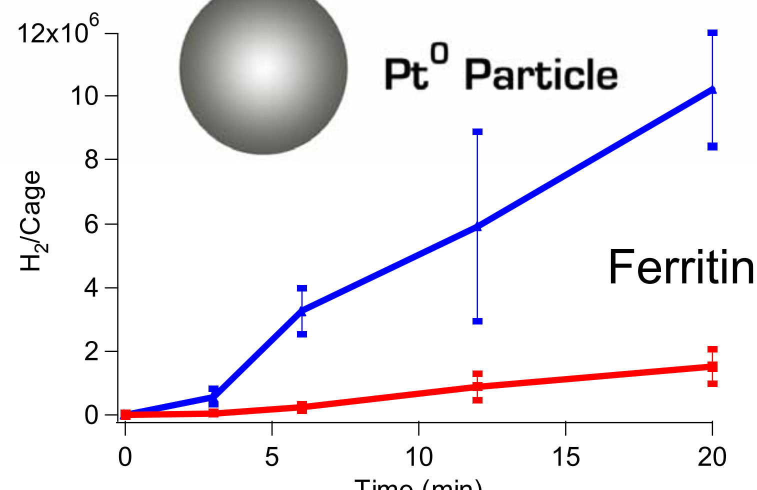


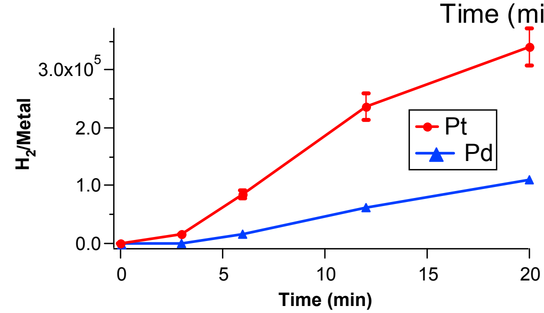


Coupled Photocatalysis for H_2 Production









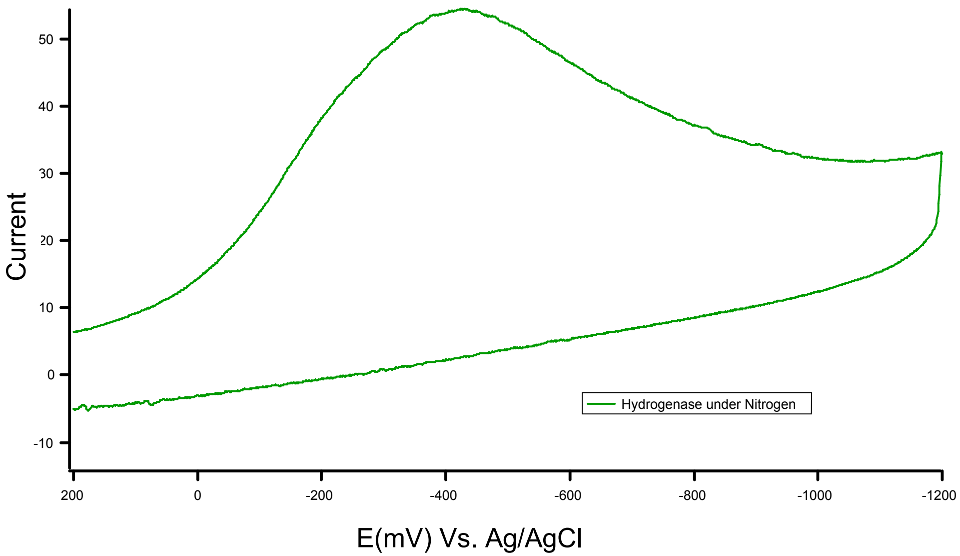
Pd particles show significantly lower activity than Pt

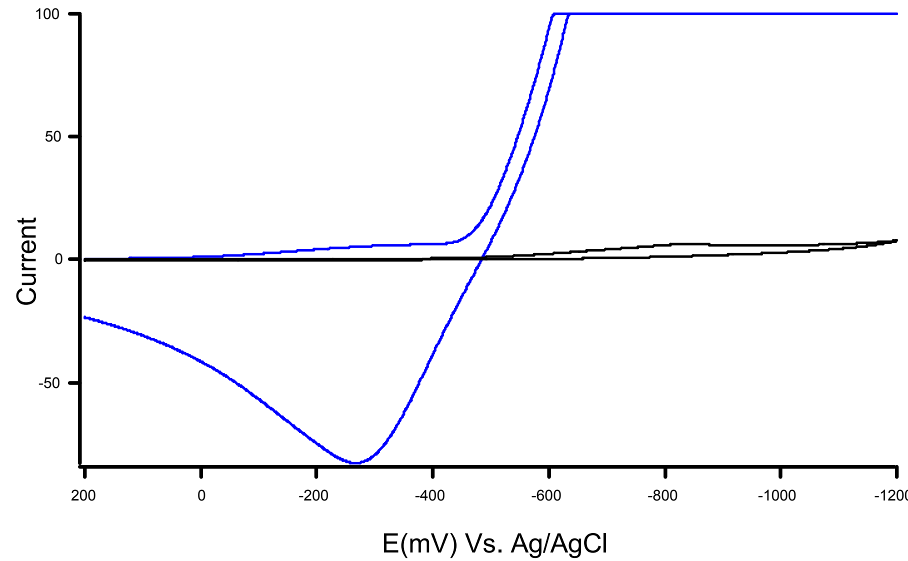
Initial rates (Pt): 4.47×10^3 H_2/sec/Hsp

1.5×10^4 H_2/sec/ferritin

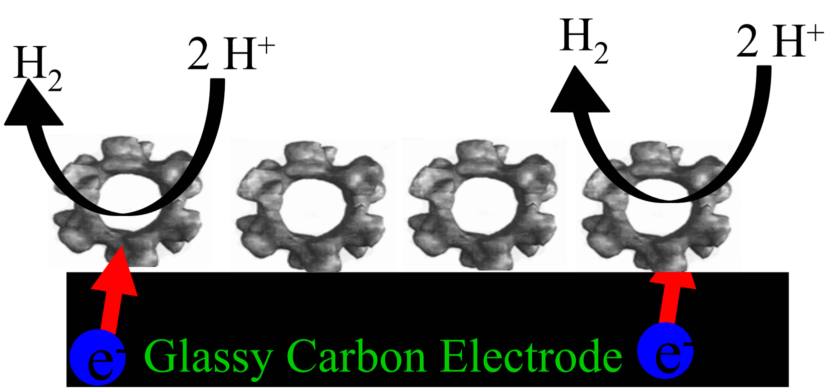
(Hydrogenase => $6 \times 10^3 H_2$/sec/hydrogenase)

Cyclic Voltammetry

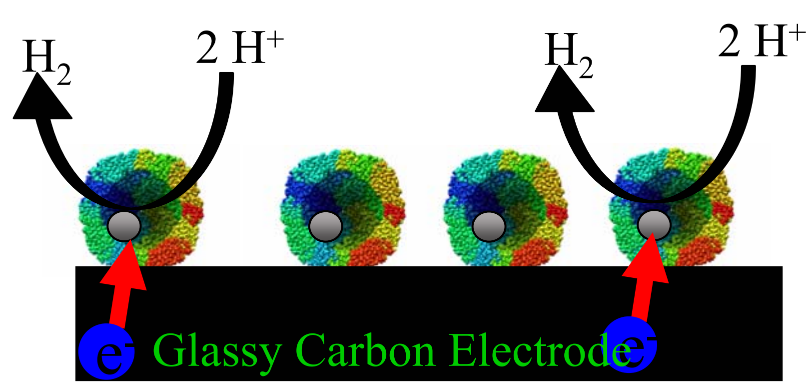




Hydrogenase



Synthetic Mimic



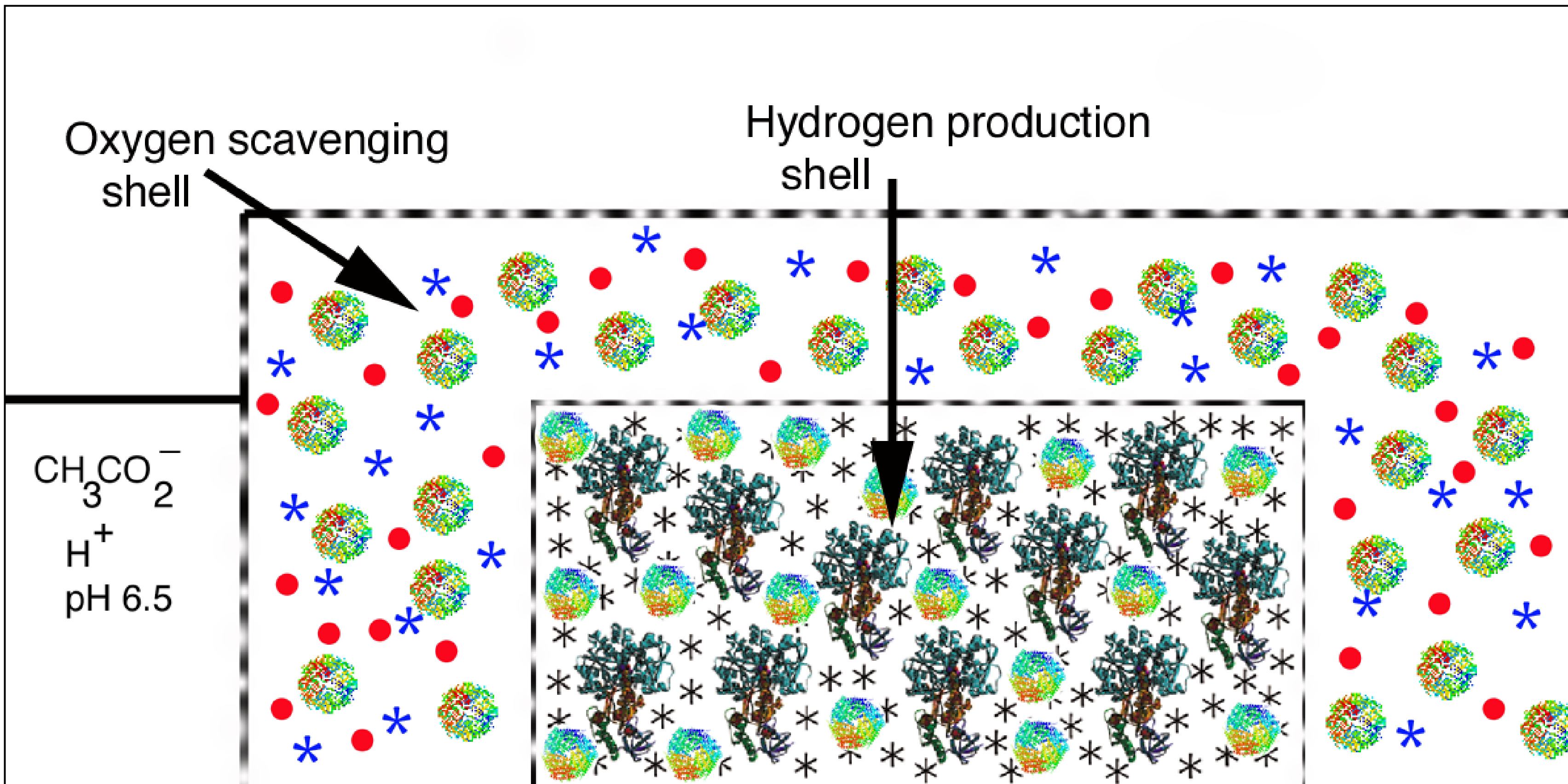
Current properties in the context of technical targets

	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 $Ru(bpy)_3^{2+}$ photoreduction of MV^{2+} 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 H_2 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 H_2 level below 3%
- Vent gases in fume hood
- Keep away from open flame and flammable chemicals
- Keep quantity of H_2 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

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

15% Complete	**Task 1: Porous Metal Substrate Development** •Evaluate metal powder for free form fabrication •Develop various substrate models •Create sintering schedule •Fabricate substrates •Determine substrate porosity	**0% Complete**	**Task 3: Plate Membrane onto Substrate** •Develop plating procedure •Complete membrane plating on substrate •Evaluate plating effectiveness
10% Complete	**Task 2: Palladium Based Membrane Development** •Evaluate palladium and palladium alloys •Determine application method (electroless plating, chemical vapor deposition, etc.) •Assess substrate surface treatment	**10% Complete**	**Task 4: Separation Module Testing** •Design and fabricate testing apparatus with safety emphasis •Test membrane integrity (density) •Test hydrogen separation effectiveness •Test operating condition durability

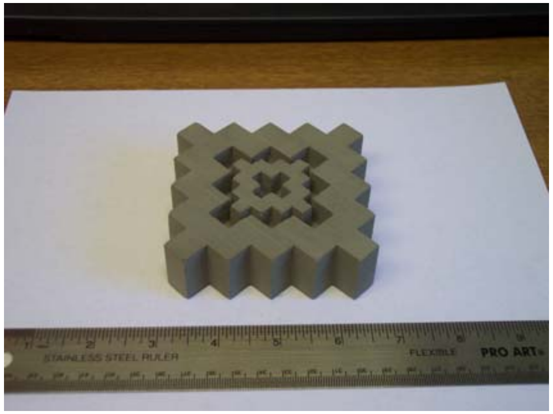
Technical Accomplishments

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

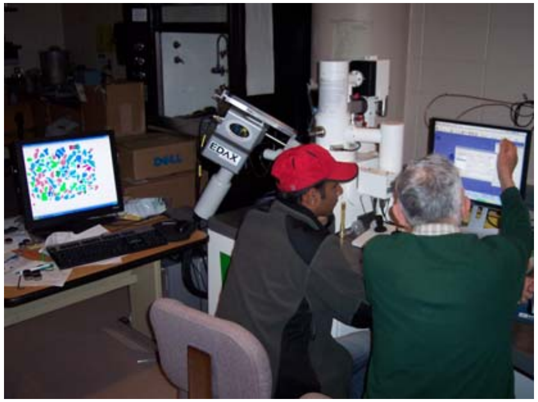
- It has been determined that a Prometal R2 3D Printer can be used to perform the free form fabrication of the metallic substrate. This machine is manufactured by Ex-One of Irwin, Pennsylvania.
- Test piece using 30 **m**m stainless steel powders has been successfully fabricated.
- Montana Tech / CAMP 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

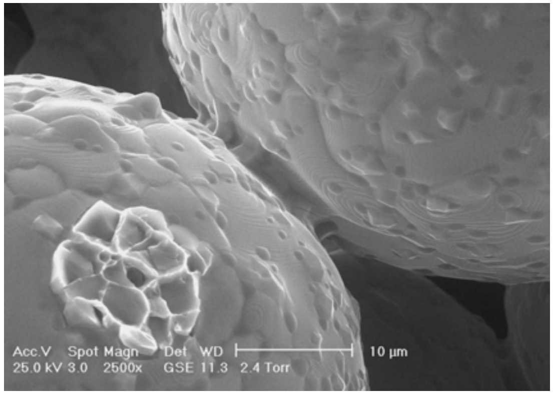
Prometal R2 3D Printing Machine at Montana Tech / CAMP



Un-sintered test piece fabricated with Prometal R2 and 30**m**m 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 than 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.