DOE Hydrogen Program

2007 DOE Hydrogen Program

Combinatorial Development of Water Splitting Catalysts Based on the Oxygen Evolving Complex of Photosystem II

Neal Woodbury, Pallav Kumar, Nicolas Yakubchak, Matt Greving, Zbigneiw Cichacz, Loren Howell, Bharath Takulpalli, James Allen, JoAnn Williams, Trevor Thornton

Arizona State University, Departments of Electrical Engineering and Chemistry and Biochemistry and the Biodesign Institute (Contact: NWoodbury@asu.edu)

April 13, 2007

THE biodesign INSTITUTE AT ARIZONA STATE UNIVERSITY

PDP35

Overview

Timeline

- Start - July 1, 2005
- Finish - June 30, 2009
- 50% Complete

Budget

- Total Project Funding
  - DOE - $1,200,000
  - Contractor - $300,000
- Funding for FY07
  - $130,000 DOE
  - $0 Contractor

Barriers

- Barriers addressed
  - H. System Efficiency
  - J. Renewable Integration

Partners

- CombiMatrix Corp., Mukilteo, WA
- Prof. Bill Armstrong, Boston College

THE biodesign INSTITUTE AT ARIZONA STATE UNIVERSITY

Objectives: Hydrogen Evolution Catalysts

- Develop a library-based solid-phase synthetic method for molecular evolution of a catalyst for electrolysis
- Evolve such a catalyst using metal binding peptide libraries based on photosynthetic complexes.
- Optimize the catalyst for minimum overpotential.

THE biodesign INSTITUTE
AT ARIZONA STATE UNIVERSITY

Approach: Optically Directed Evolution

- Using a photosynthetic model system for oxygen evolution, design a peptide library
- Synthesize the library using photolithographic or electrochemical solid phase synthesis methods directly on an array of electrodes
- Measure the voltage/current characteristics of each catalyst, model the best, and design a new library, etc.

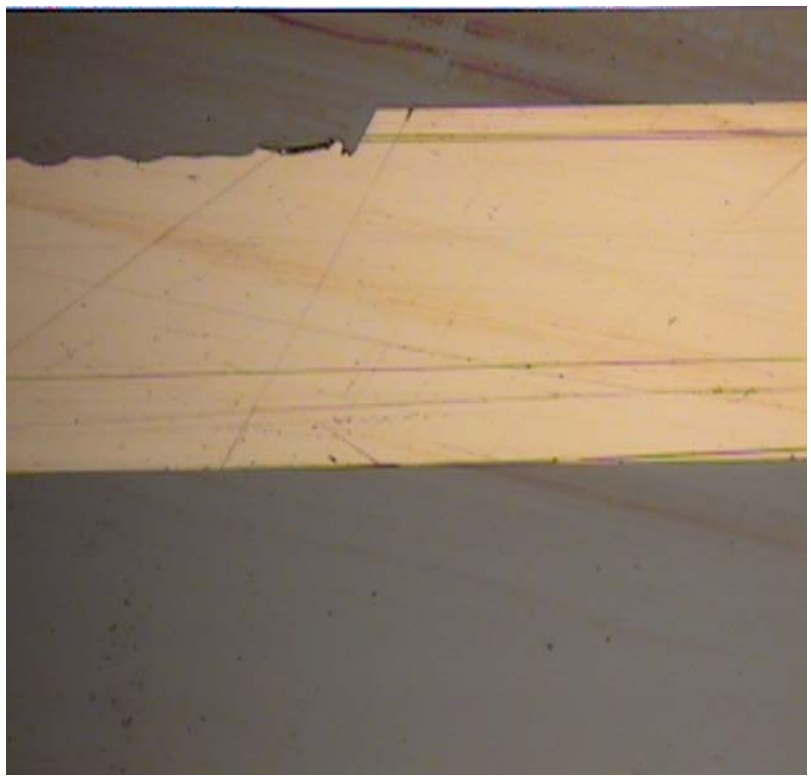
THE biodesign INSTITUTE
AT ARIZONA STATE UNIVERSITY

Technical Accomplishments

- Electrode Fabrication
- Light Directed Peptide Synthesis
- Electrochemically Directed Peptide Synthesis
- Metal-Binding Peptide Design

THE biodesign INSTITUTE
AT ARIZONA STATE UNIVERSITY

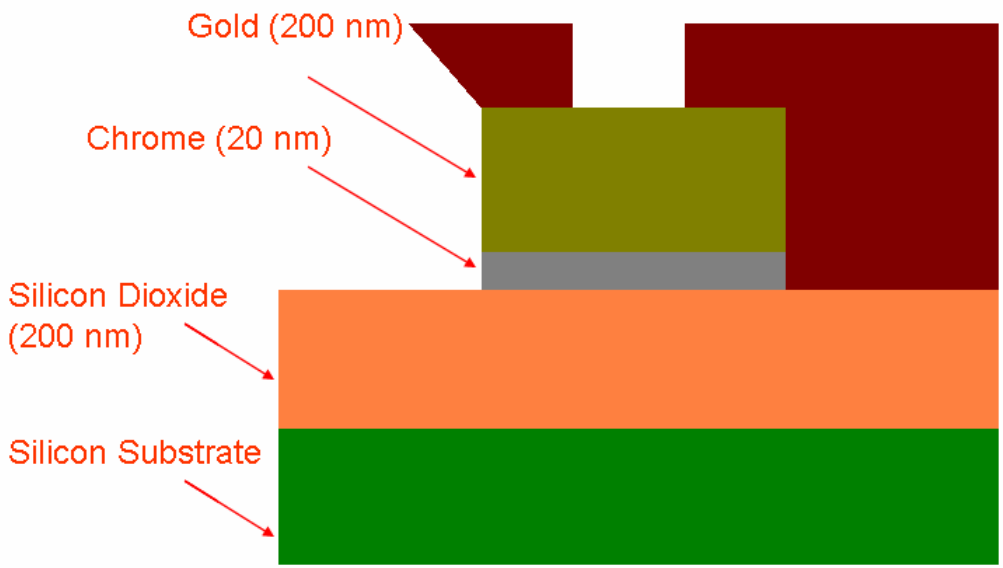
Electrode Fabrication



- Problem: original design not stable – gold layer peeling due to O_2 production under edges during electrolysis

THE biodesign INSTITUTE
AT ARIZONA STATE UNIVERSITY

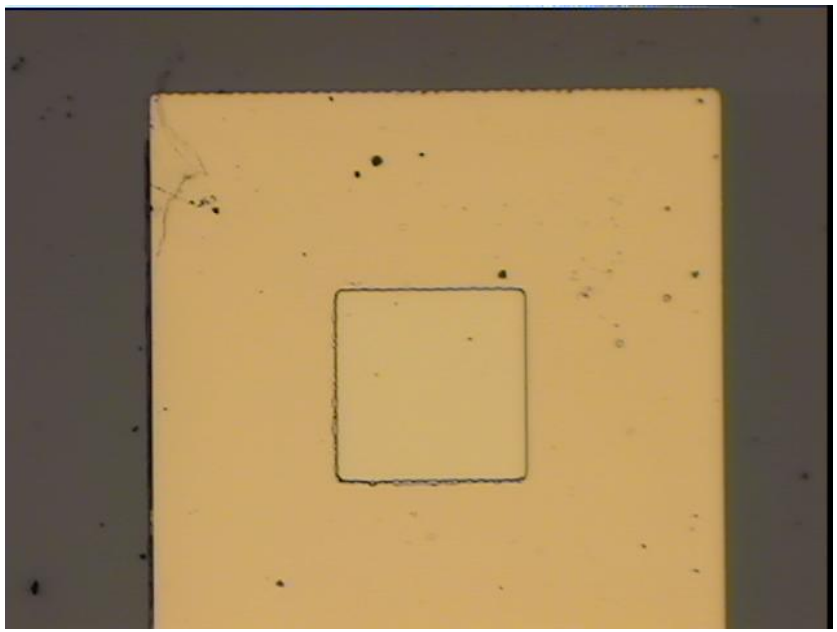
New Electrode Design



- New Design employs an SU-8 mask over the gold (red at left) to protect from solvent seeping under gold layer

THE biodesign INSTITUTE
AT ARIZONA STATE UNIVERSITY

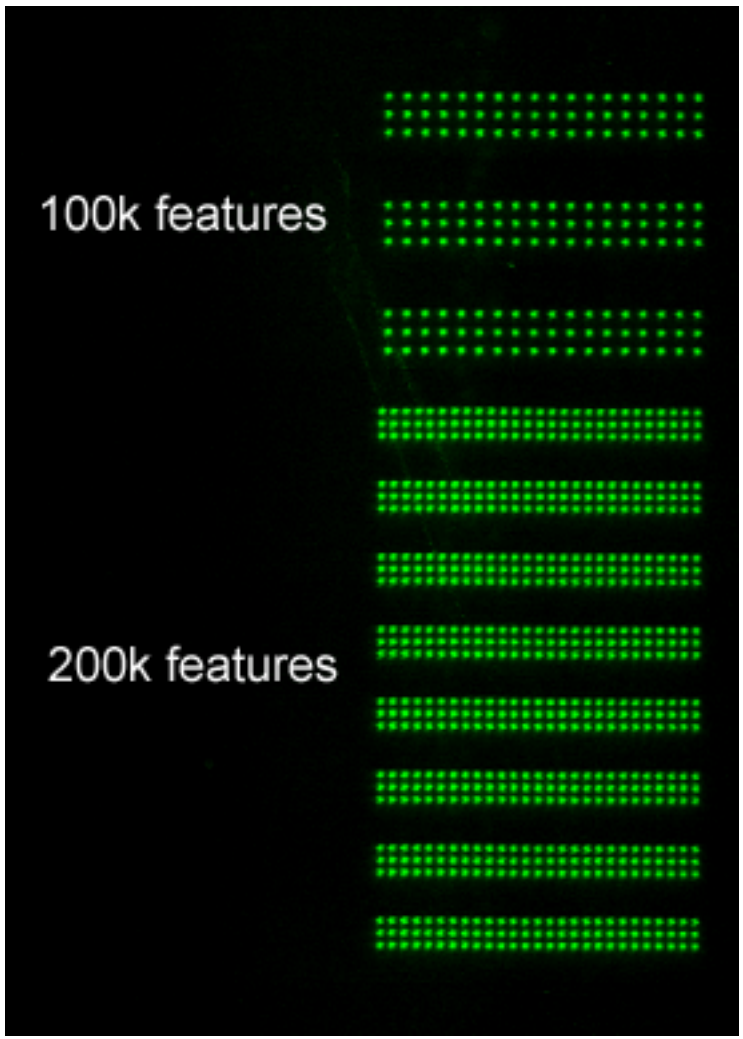
More stable surface



- All the gold outside of the box is covered (sealed) by SU-8. The exposed gold is more stable to repeated electrolysis measurements, though we are still improving the design

THE biodesign INSTITUTE
AT ARIZONA STATE UNIVERSITY

Light Directed Peptide Synthesis



- Last year, 10,000 peptides per slide were possible. This year we have made up to 200,000 peptides per slide.

THE biodesign INSTITUTE
AT ARIZONA STATE UNIVERSITY

Couple to New High Resolution Electrochemical Scanner

- New collaboration initiated with Prof. Joseph Wang (Electrochemist, Biodesign Institute)
- Light directed peptide synthesis on a conductive surface
- Electrochemical Scanner will be used to read current at specific voltages (either detecting electrolysis current or oxygen)
- This is an alternative to the CombiMatrix approach described below

THE biodesign INSTITUTE
AT ARIZONA STATE UNIVERSITY

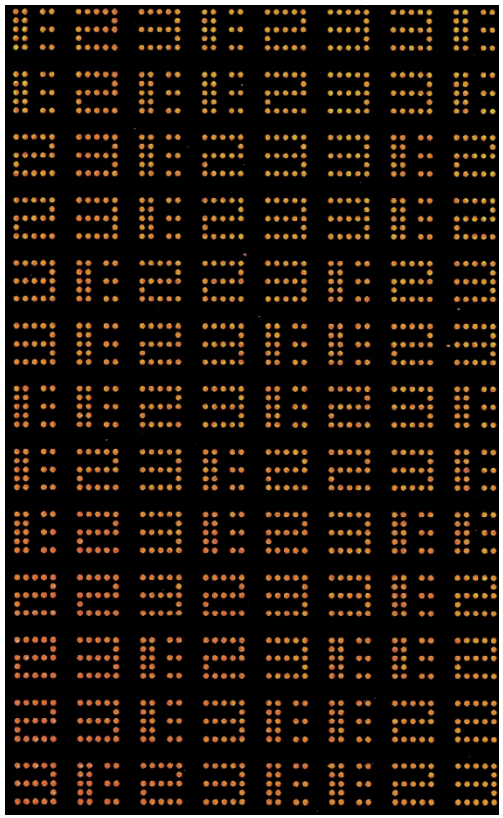
Electrochemically-Directed Peptide Synthesis

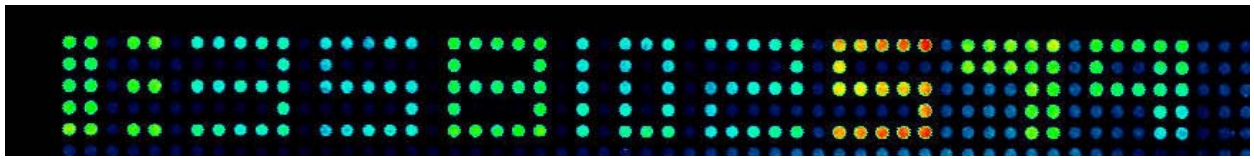
COMBIMATRIX

- Last year, we had just set up the instrument from CombiMatrix for performing electrochemical synthesis on 12,500 electrodes

THE biodesign INSTITUTE
AT ARIZONA STATE UNIVERSITY

High Yield Array Synthesis Demonstrated





- Now we have demonstrated the ability to synthesize peptides of up to 10 amino acids long with stepwise yields of about 94%
- The arrays shown here are peptides electrochemically synthesized onto an electrode array with a biotin attached to the terminal amino acid. These were then bound to fluorescent streptavidin.

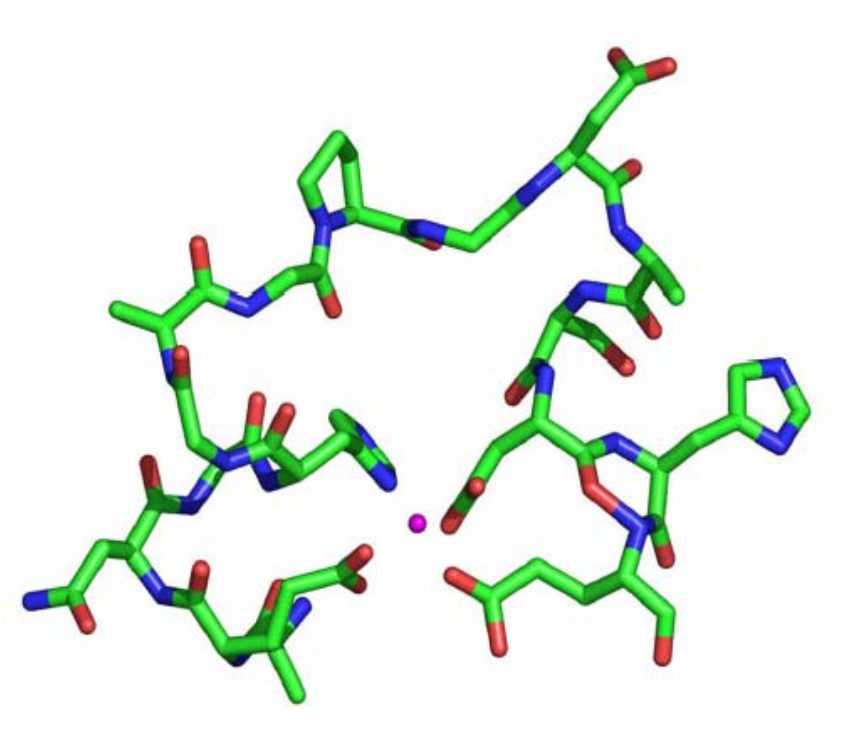
THE biodesign INSTITUTE
AT ARIZONA STATE UNIVERSITY

Fully Automated Synthesis

- More recently, we have hooked the CombiMatrix electrochemical electrode array up to a peptide synthesizer
- Now peptide array synthesis is automated

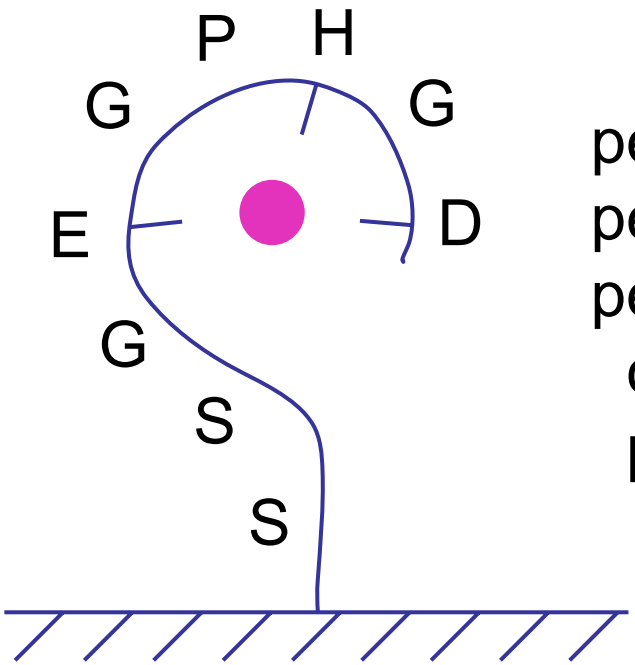
THE biodesign INSTITUTE
AT ARIZONA STATE UNIVERSITY

Design and Analysis of Mn-Binding Peptides



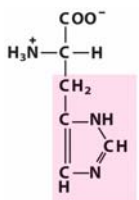
- Designed an initial set of Mn-binding peptides. Last year, showed that they bound Mn

Initial Peptides Tested

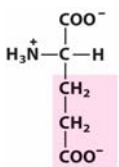


peptide 1: E G H P G E G Y S
peptide 2: E G H P G E S S S
peptide 3: D G H P G E G S S
control: N G H P G Q G S S
polyHis: H H H H H H H S S

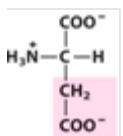
H Histidine



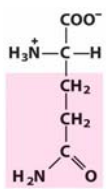
E Glutamate



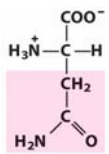
D Aspartate



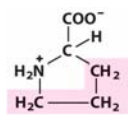
Q Glutamine



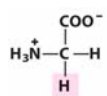
N Asparagine



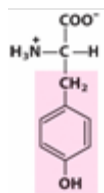
P Proline



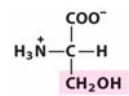
G Glycine



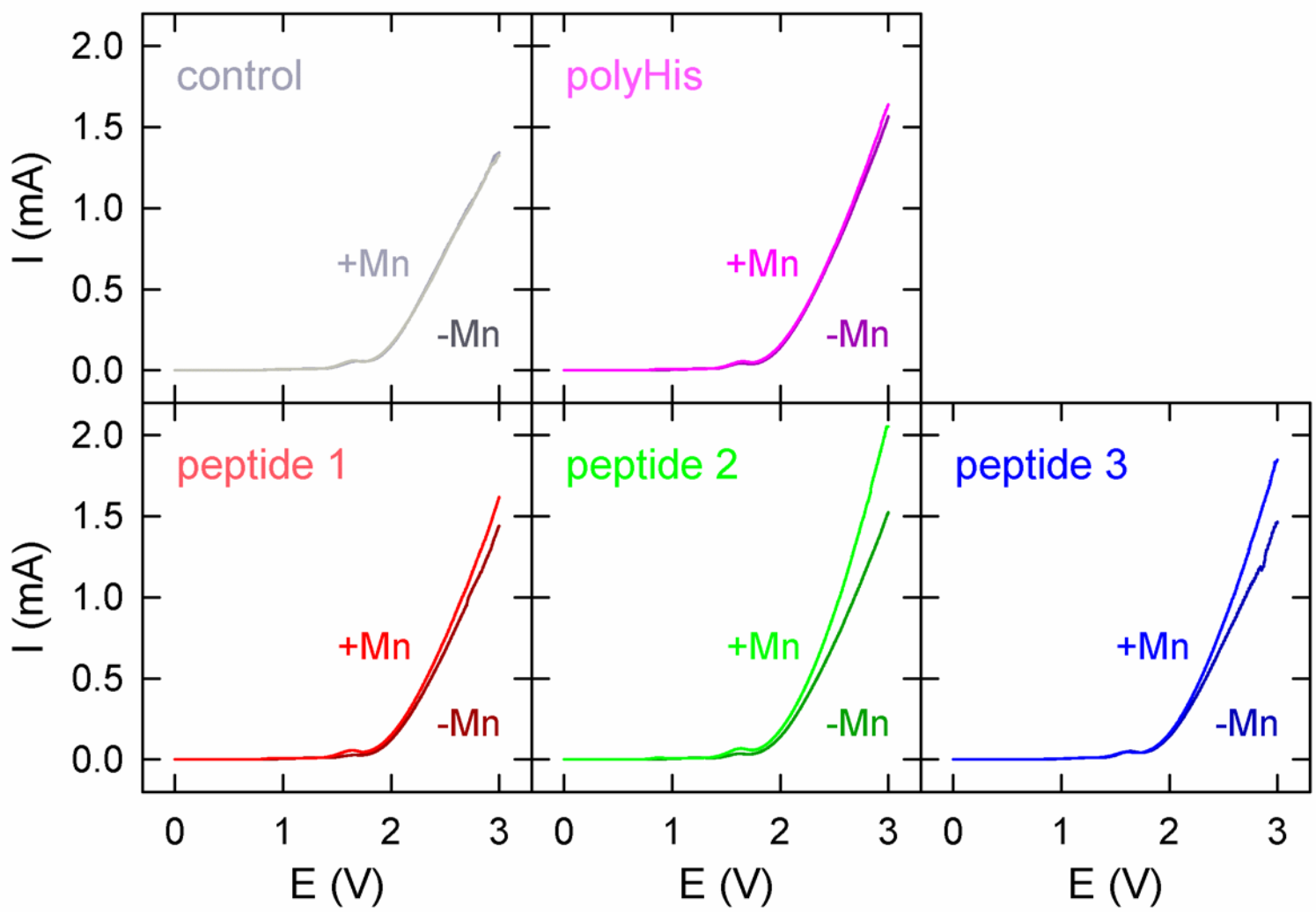
Y Tyrosine



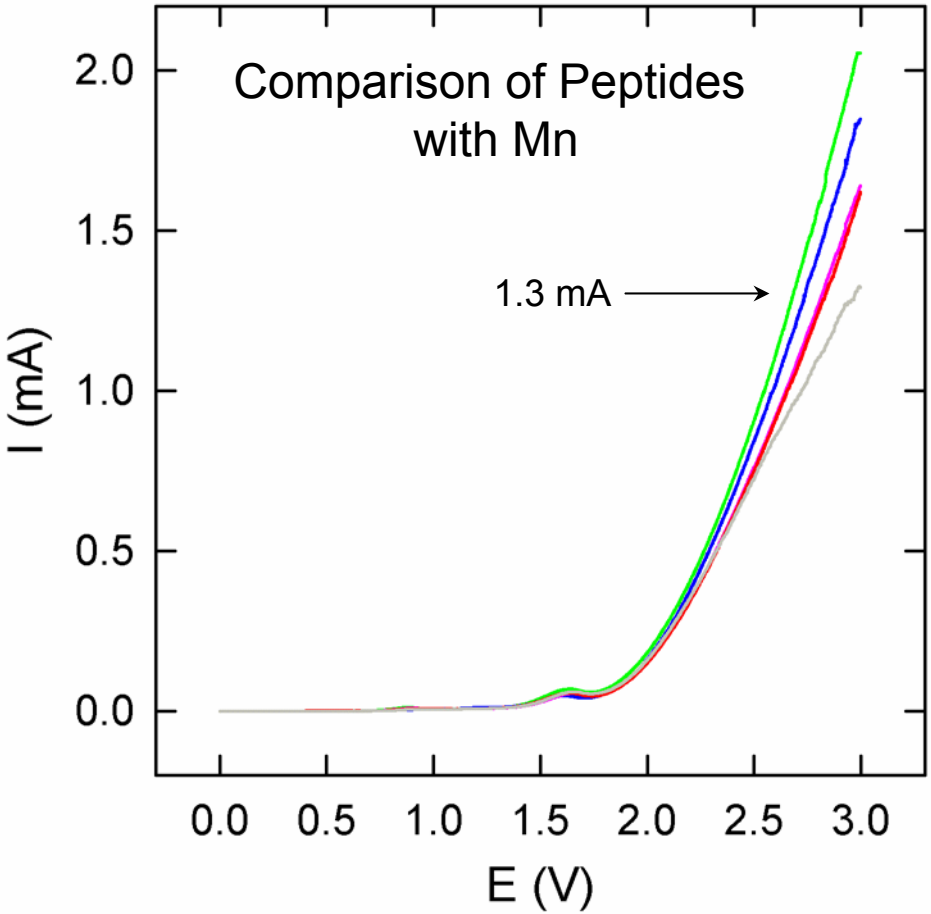
S Serine



Results of Peptides w/ and w/o Mn



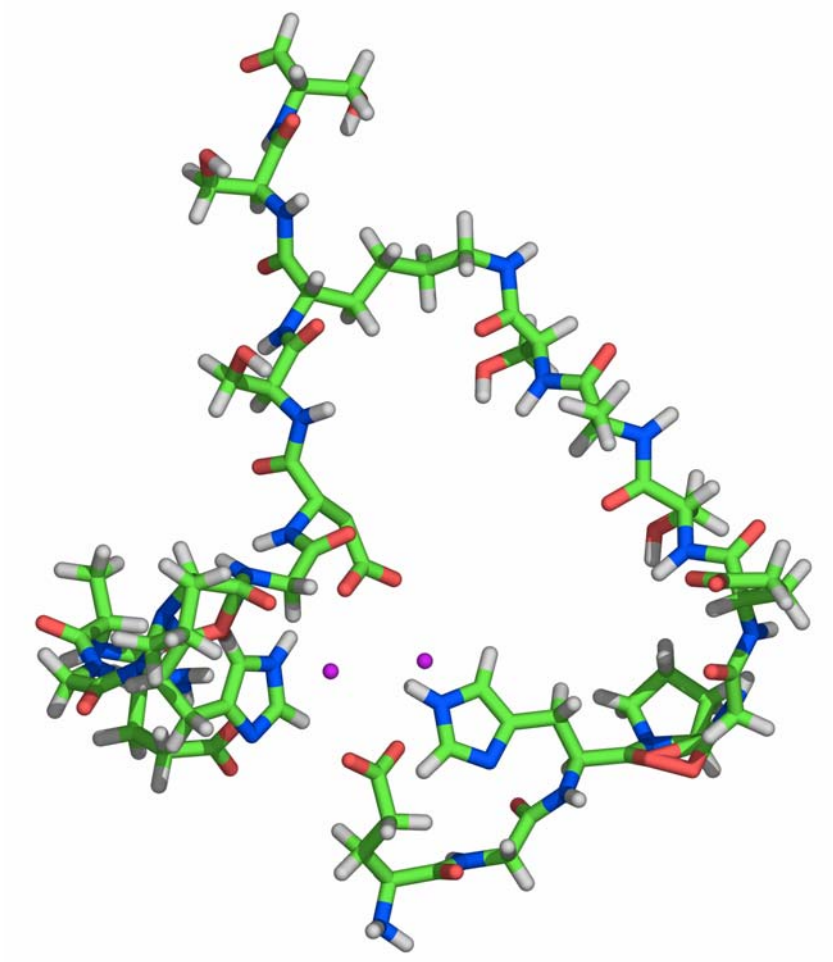
Comparison of Electrolysis Currents



Change in potential at 1.3 mA compared to control (V)	
peptide 2	-0.29
peptide 3	-0.23
polyHis	-0.15
peptide 1	-0.13
control	-

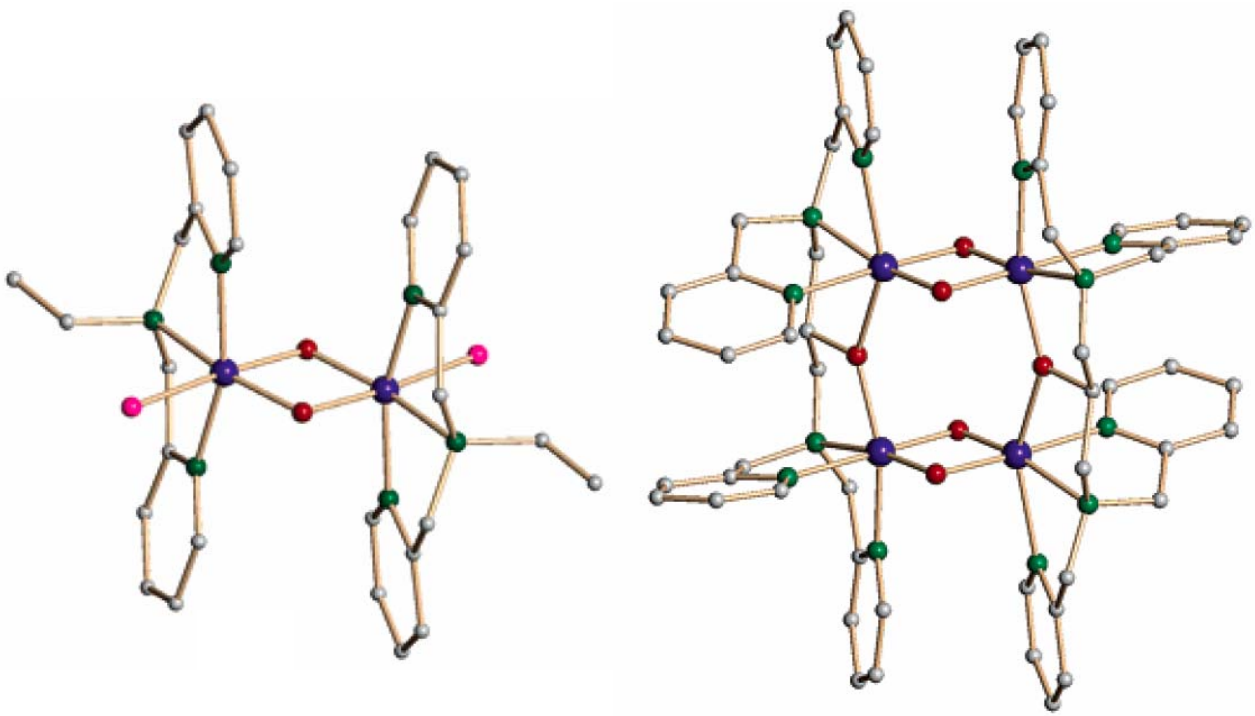
In terms of efficiency, one can see that it is possible with peptide 2 to get the same current (same rate of hydrogen production) at 2.7 V that would require 3.0 V with the control peptide. This is a 10% power reduction in that voltage range.

Future Work – Branched Peptides



- Create branched peptides with multiple Mn

Future Work – Multi-Mn clusters



Through collaboration with Bill Armstrong, insert multi-Mn clusters into peptide complexes

Future Work – Electrochemical Array Measurements

- Working with CombiMatrix, set up electrochemical measurements of thousands of potential metal-binding peptide catalysts
- In collaboration with Prof. Joe Wang, set up spatially resolved electrochemical scanning methods for measuring electrocatalysis on gold surfaces with thousands of candidate catalysts.
- Scan and analyze electrolysis currents at specific voltages for many thousands of possible peptide structures, starting with the peptides that have shown some catalysis and iteratively optimize.

Summary

- Improved density of light directed synthesis by 20 fold in a fully automated format that can be used with scanning electrochemcial detection
- Demonstrated electrochemical synthesis of 10 amino acid peptides on 12,500 electrodes (CombiMatrix platform)
- Fully automated the electrochemical synthesis of peptide arrays
- Improved design and stability of measurement electrodes
- Characterized a set of initially designed peptides showing two peptides with significant catalytic activity and up to 10% power reduction in the 3V range