

2007 DOE Hydrogen Program Combinatorial Development of Water Splitting Catalysts Based on the Oxygen Evolving Complex of Photosystem II

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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

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.

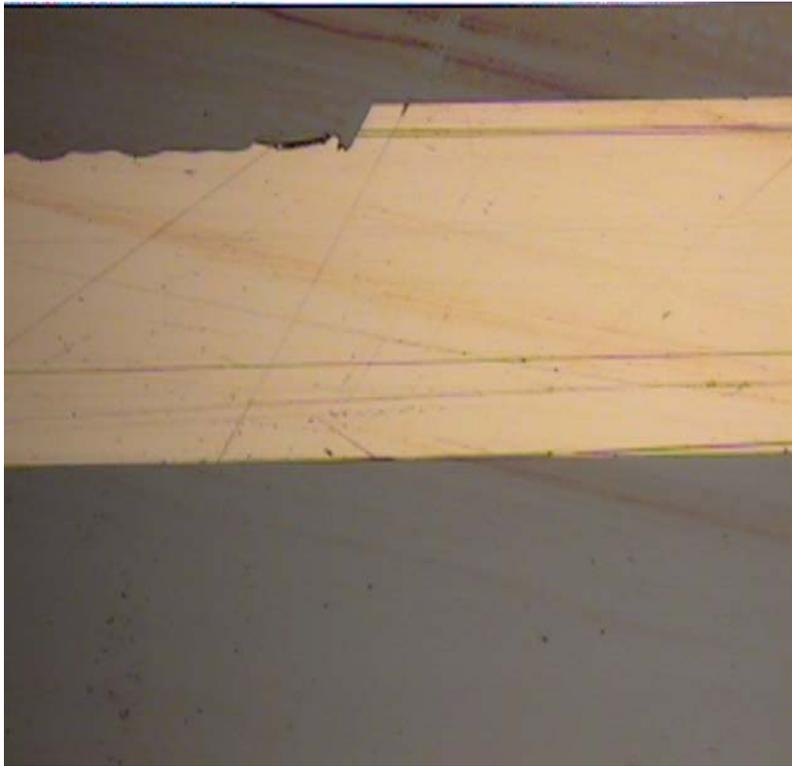
Approach: Optically Directed Evolution

- 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.

Technical Accomplishments

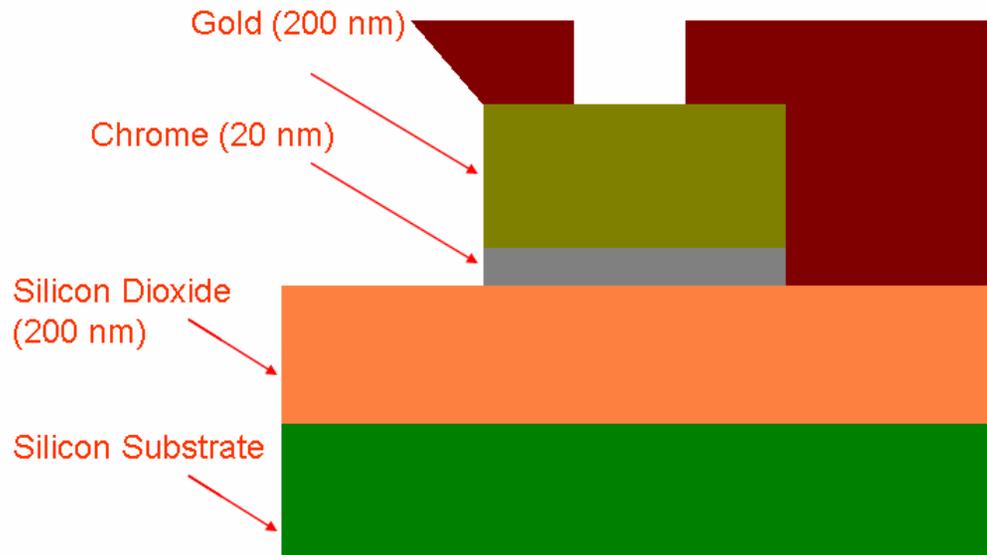
- Electrode Fabrication
- Light Directed Peptide Synthesis
- Electrochemically Directed Peptide Synthesis
- Metal-Binding Peptide Design

Electrode Fabrication



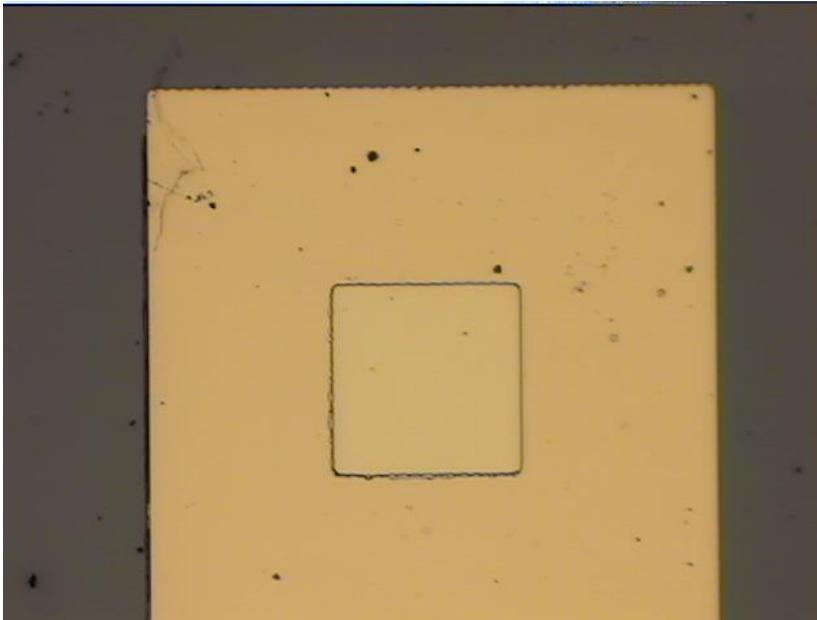
- Problem: original design not stable – gold layer peeling due to O_2 production under edges during electrolysis

New Electrode Design



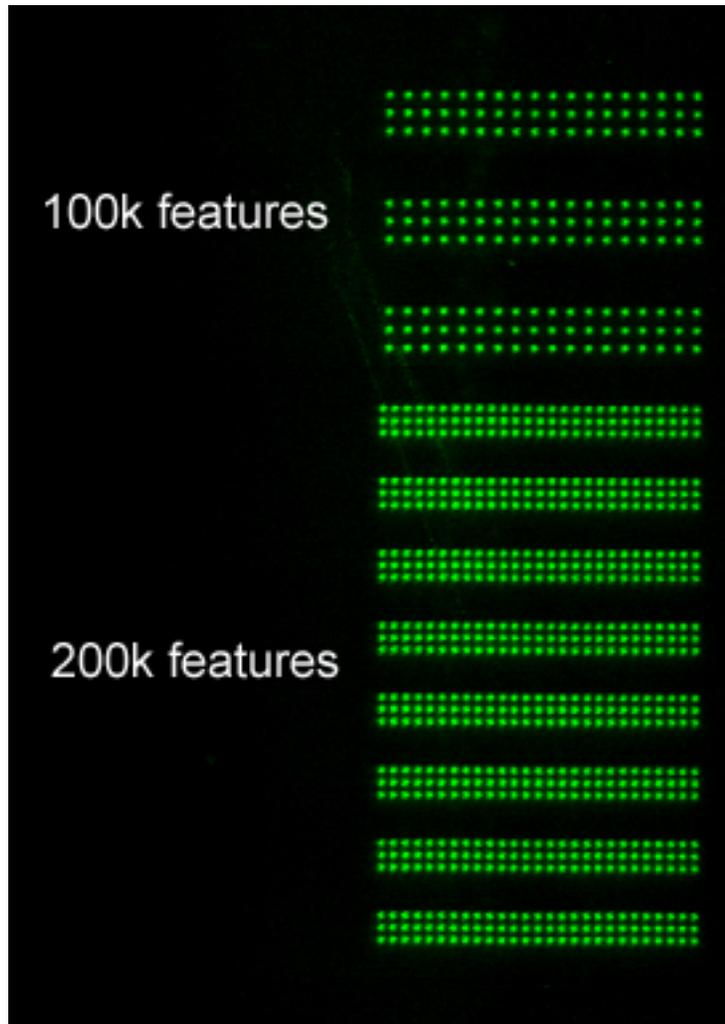
- New Design employs an SU-8 mask over the gold (red at left) to protect from solvent seeping under gold layer

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

Light Directed Peptide Synthesis

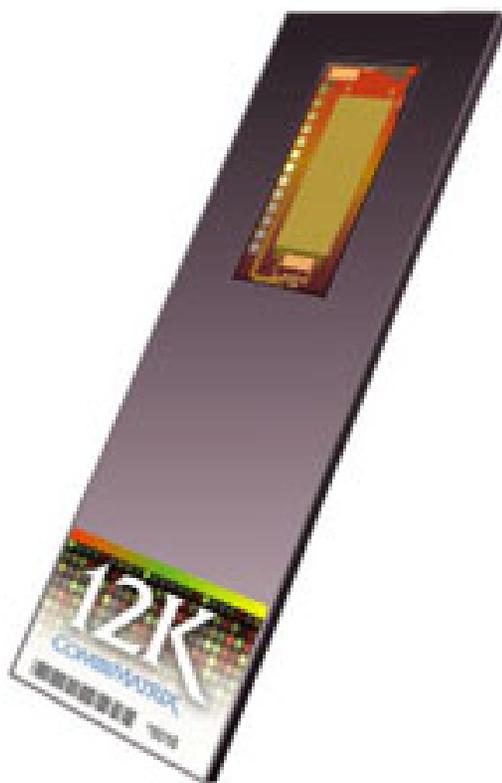


- Last year, 10,000 peptides per slide were possible. This year we have made up to 200,000 peptides per slide.

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

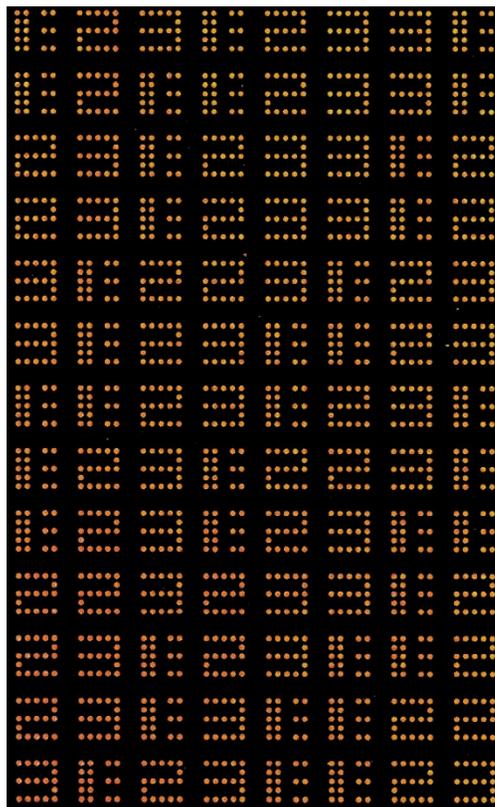
Electrochemically-Directed Peptide Synthesis



COMBIMATRIX

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

High Yield Array Synthesis Demonstrated

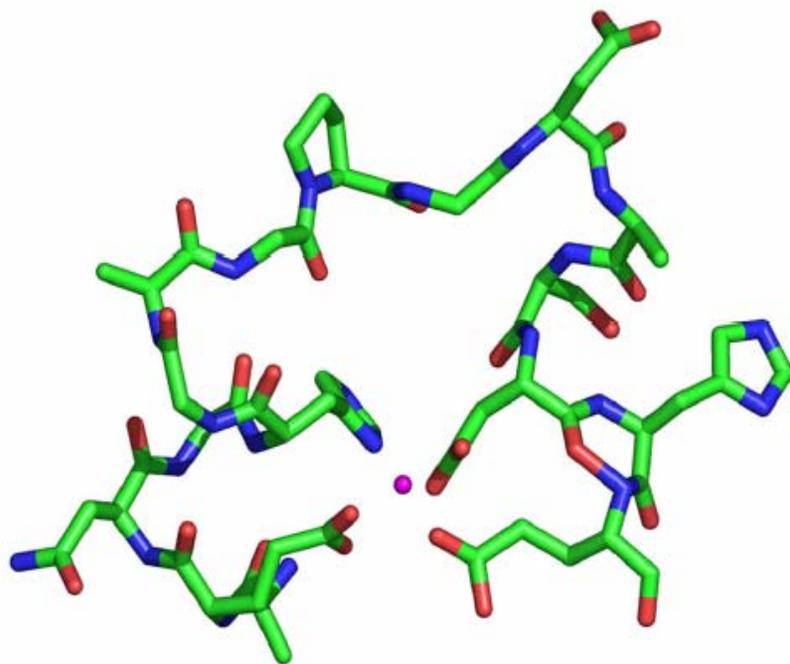


- Now we have demonstrated the ability to synthesize peptides of up to 10 amino acids long with stepwise yields of about 94%
- The arrays shown here are peptides electrochemically synthesized onto an electrode array with a biotin attached to the terminal amino acid. These were then bound to fluorescent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

Fully Automated Synthesis

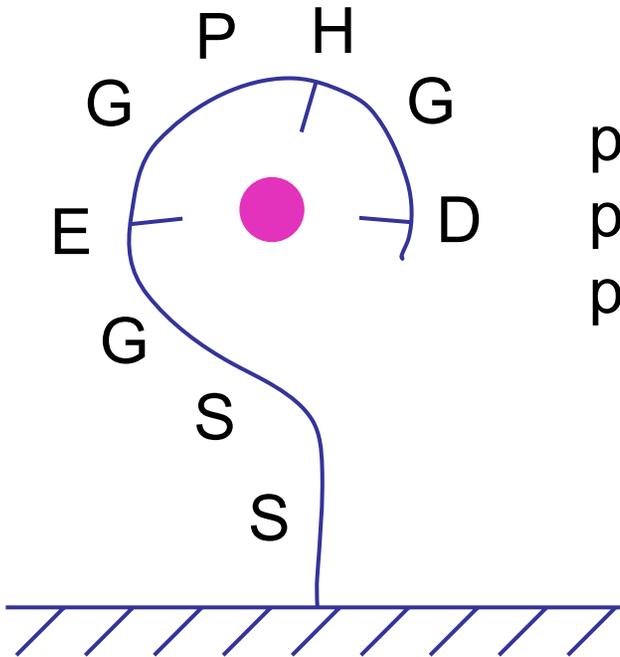
- More recently, we have hooked the CombiMatrix electrochemical electrode array up to a peptide synthesizer
- Now peptide array synthesis is automated

Design and Analysis of Mn-Binding Peptides

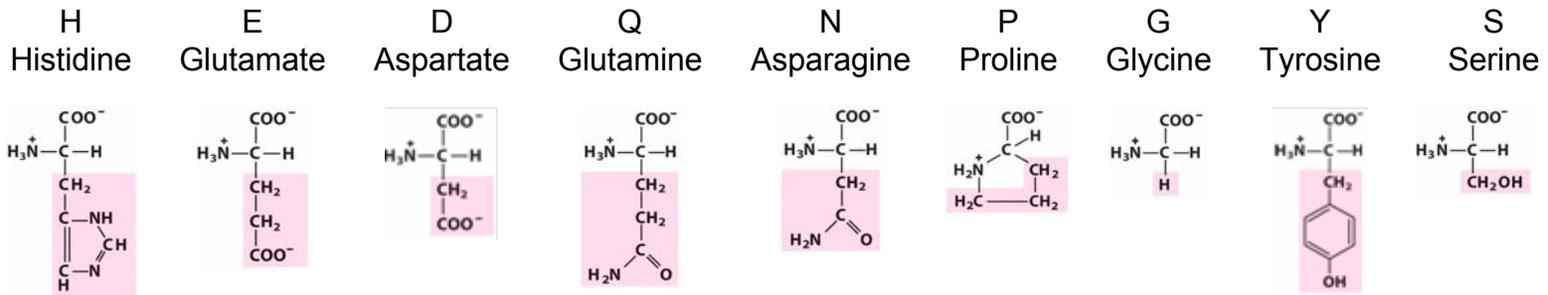


- Designed an initial set of Mn-binding peptides. Last year, showed that they bound Mn

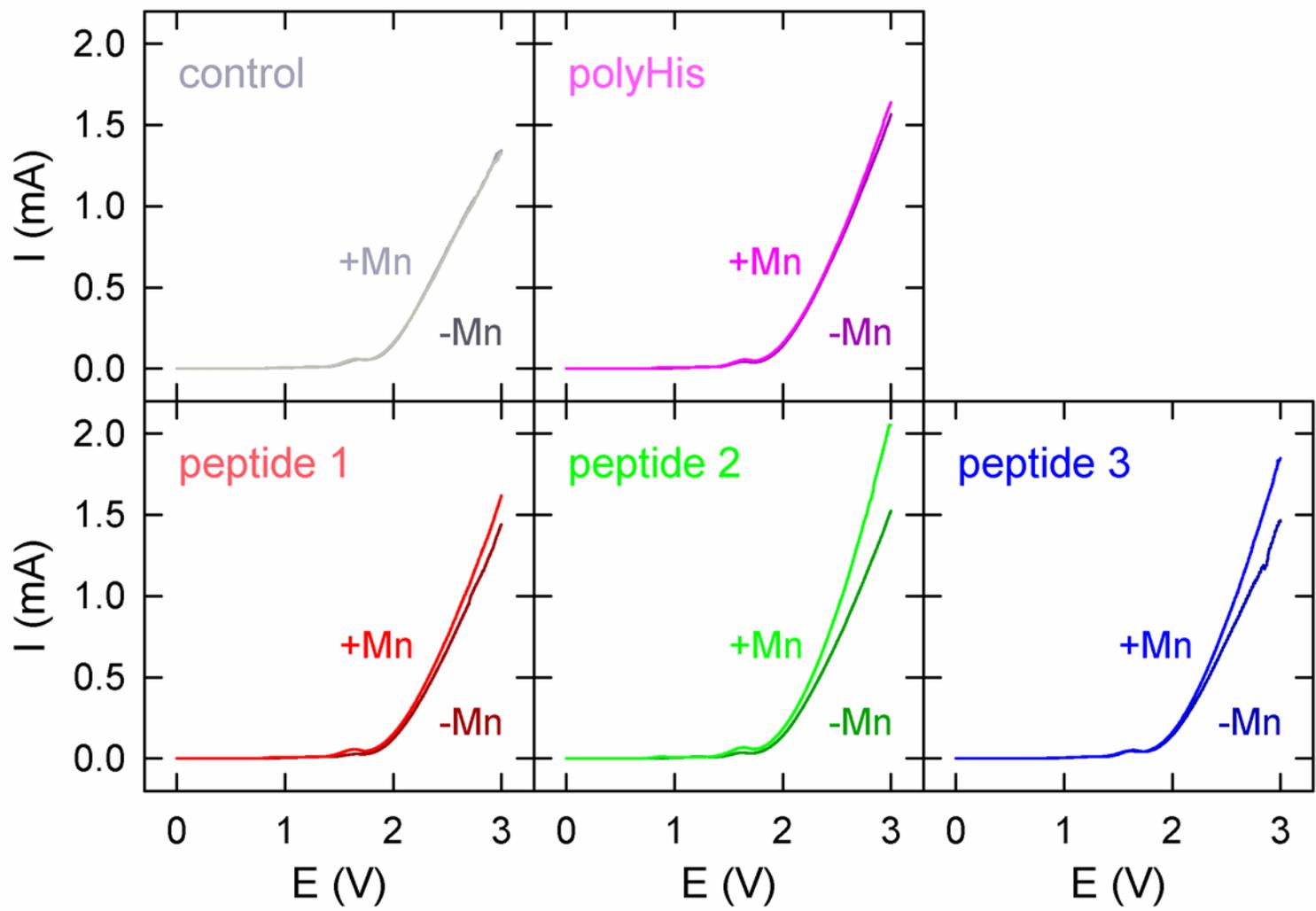
Initial Peptides Tested



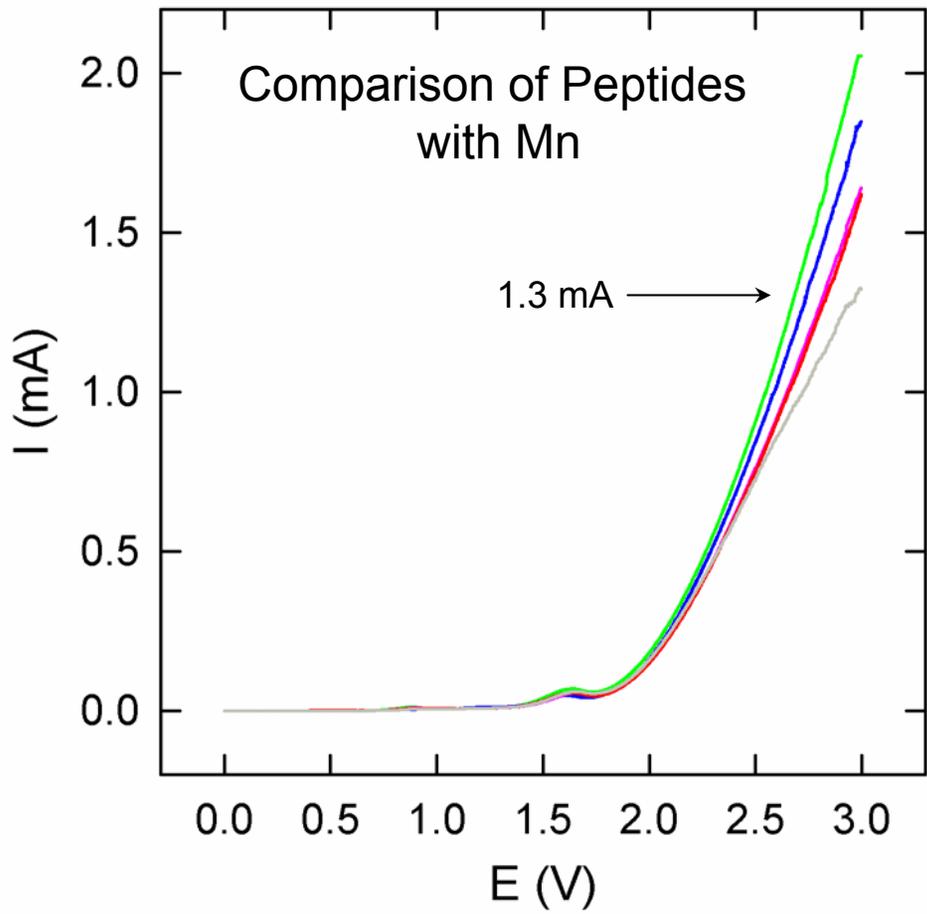
peptide 1: E G H P G E G Y S
 peptide 2: E G H P G E S S S
 peptide 3: D G H P G E G S S
 control: N G H P G Q G S S
 polyHis: H H H H H H H S S



Results of Peptides w/ and w/o Mn



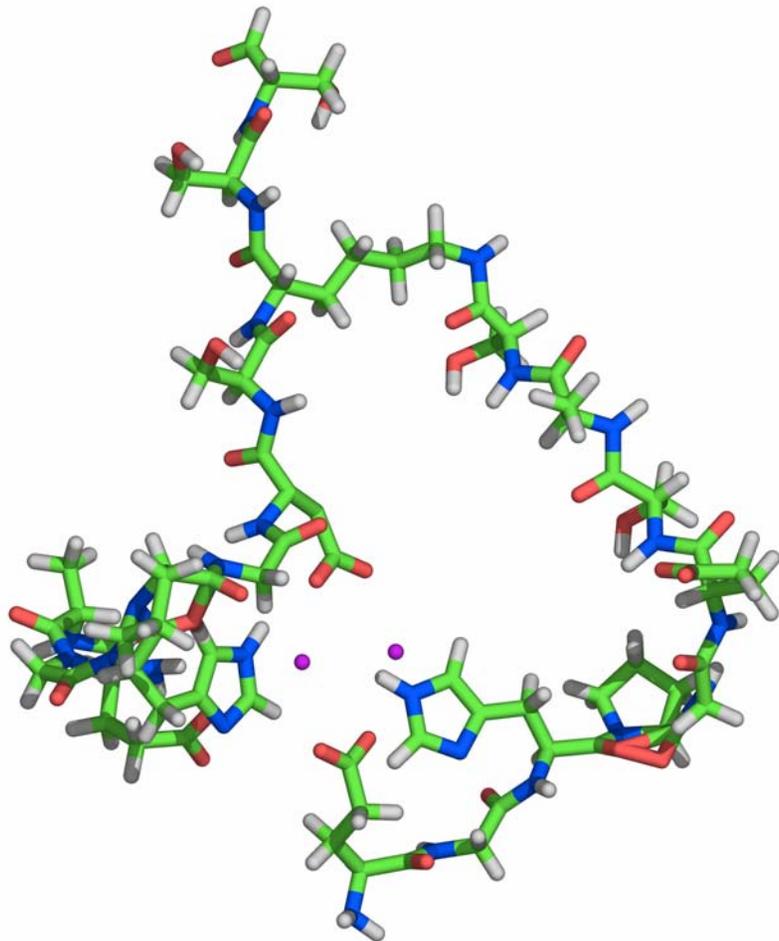
Comparison of Electrolysis Currents



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	-

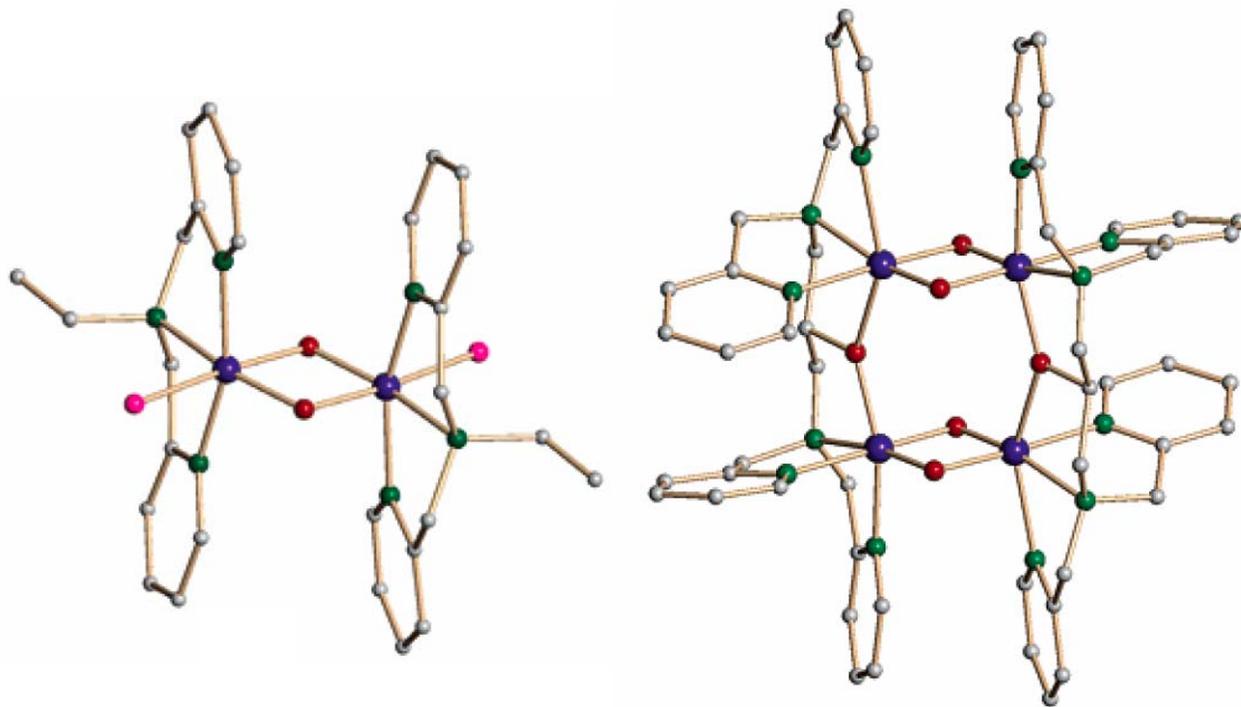
In terms of efficiency, one can see that it is possible with peptide 2 to get the same current (same rate of hydrogen production) at 2.7 V that would require 3.0 V with the control peptide. This is a 10% power reduction in that voltage range.

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. 20

Summary

- Improved density of light directed synthesis by 20 fold in a fully automated format that can be used with scanning electrochemical 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