Development of Water Splitting Catalysts Using a Novel Molecular Evolution Approach

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Overview

Timeline
• Start - July 1, 2005
• Finish - June 30, 2009
• 70% Complete

Barriers
• Barriers addressed
  – H. System Efficiency
  – J. Renewable Integration

Budget
• Total Project Funding
  – DOE - $1,200,000
  – Contractor - $300,000
• Funding for FY09
  – $300,000 DOE
  – $75,000 Contractor

Partners
• CombiMatrix Corp., Mukilteo, WA
• Prof. Bill Armstrong, Boston College
Objectives

• Broad Objectives:
  ➢ Develop a novel approach to creating molecular catalysts for redox reactions based on high throughput synthesis on electrodes
  ➢ Mimick Nature’s approach to water splitting
  ➢ Reduce the overpotential by 30%
• Specific Objectives (FY09):
  ➢ Optimize high throughput peptide synthesis on CombiMatrix Arrays
  ➢ Optimize the multielectrode measurements of water splitting on the CombiMatrix Arrays
  ➢ Demonstrate several rounds of optimization for catalytic activity
Significance

• The impact would be an energetically more efficient method for production of hydrogen from renewable electricity sources

• This addresses both System Efficiency and Renewable Integration
General Approach

- Synthesis of 12,000 different peptides directly on electrodes
- Binding of metal ions or metal complex catalysts to the peptides, mimicking PSII water splitting complex
- Direct electrochemical measurement of current due to electrolysis at each electrode
- Analysis of one library of molecules informs the production of the next library
- Iterative optimization should result in an efficient water splitting catalyst
Milestones (FY09)

1. Multi-step patterned synthesis of peptides in an array
2. Verification of synthesis via direct MALDI spectroscopy on the surface
3. Automation of array synthesis
4. Background current measurements on the arrays
5. Comparing currents from peptides with and without Mn on the arrays
6. Iterate synthesis and measurement to result in a sequence optimization

Go/No Go to continue pursuing this approach depends on 1) ability to measure catalytic signal above noise and 2) ability to reproducibly synthesize arrays with multiple variable residues
Summary of Past Accomplishments

1. Tested two platforms, light directed on home-built arrays and electrochemically directed via CombiMatrix arrays: elected CombiMatrix arrays
2. Design, synthesis and characterization of initial Mn binding peptides
3. Partnership formed with Mn-complex chemist
4. Developed MALDI method for measuring products of in situ synthesis directly on the surface
5. Partnered with CombiMatrix to modify sensing equipment to measure currents at 12,500 electrodes
6. Demonstrated ability to perform standard solid phase synthesis on the arrays (by nonpatterned methods)
7. Demonstrated ability to remove blocking groups using patterned electrochemically generated acids and create peptide bonds
Accomplishment: Multistep Synthesis

1. Fmoc-Leu-OH, HBTU/HOBt, DMF, DIPEA

2. 20% Piperidine in DMF

3. Trt-Cl, DIEA in DMF

EGA removes Trt from peptide chains over select electrodes

Ph-NH-NH-Ph

-2e^-

Ph-N=N-Ph + 2H^+

a. Direct MALDI characterization

b. Biotin-SRP-Fluorophore
c. Biotin-SRP-HRP
The major product was a peptide with three of its ten residues patterned by electrochemical synthesis (85% per step yield)
1. Fluidic connection between Pioneer synthesizer and Combimatrix synthesis chamber
2. Software control interface developed between synthesizer and synthesis system
Large, but systematic current variations across electrodes
Accomplishment: Comparing +/- Mn peptides

No significant difference between Mn binding peptide and control

Mn binding Peptide

Control Peptide
1. Multi-step patterned synthesis of peptides in an array ✓
2. Verification of synthesis via direct MALDI spectroscopy on the surface ✓
3. Automation of array synthesis ✓
4. Background current measurements on the arrays ✓
5. Comparing currents from peptides with and without Mn on the arrays ✓
6. Iterate synthesis and measurement to result in a sequence optimization
Key Additional Finding
(Not DOE funded)

Peptide space is smooth and can be searched through iterative mutation

Requires Large Libraries

$10^{26}$ 20mers

Sparse Sampling Effective
Peptides can be used to stabilize or modify activity of existing catalysts
Collaborators

- **CombiMatrix**
  - Industry partner
  - Funded through equipment purchase
  - Provides software/hardware development assistance
  - Outside DOE hydrogen program

- **Professor William Armstrong**
  - Boston University
  - Currently unfunded
  - Will provide Mn-complex catalysts
  - Outside DOE hydrogen program
Future Work

• FY09 is final year of DOE funding (official end June 09, but no cost extension to December granted)

• Perform an Iterative optimization:
  1. Start with one of our peptides known to bind Mn
  2. Select 3-4 residues thought to be key to catalysis
  3. Synthesize array with all possible variants
  4. Measure currents vs. voltage
  5. Pick best
  6. Repeat for 3 additional residues
  7. Etc.
Summary

• After choosing the electrochemical patterning platform, synthesis was optimized to about 85% yield
• Still limited by issues with side chain reactivity
• Using a modified CombiMatrix sensing instrument, have made electrochemical measurements at 12,500 electrodes
• Current Mn binding peptides do not show high enough catalysis to measure on the electrode arrays
• Goal is not to create an array and attempt and optimization in remaining 8 months
The Biodesign Institute at ASU

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- Rapid Vaccine Discovery System
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