MICHIGAN STATE UNIVERSITY

Fuel Cells for Renewable Fuels

Scott Calabrese Barton
Dept. of Chemical Engineering & Materials Science
Michigan State University
scb@msu.edu

MSU RF² Workshop

January, 2013

Fuel Cell Fuels and Applications

MICHIGAN STATE UNIVERSITY

Mobile

- Alcohols
- Hydrogen carriers
- Sugars

horizonfuelcell.com

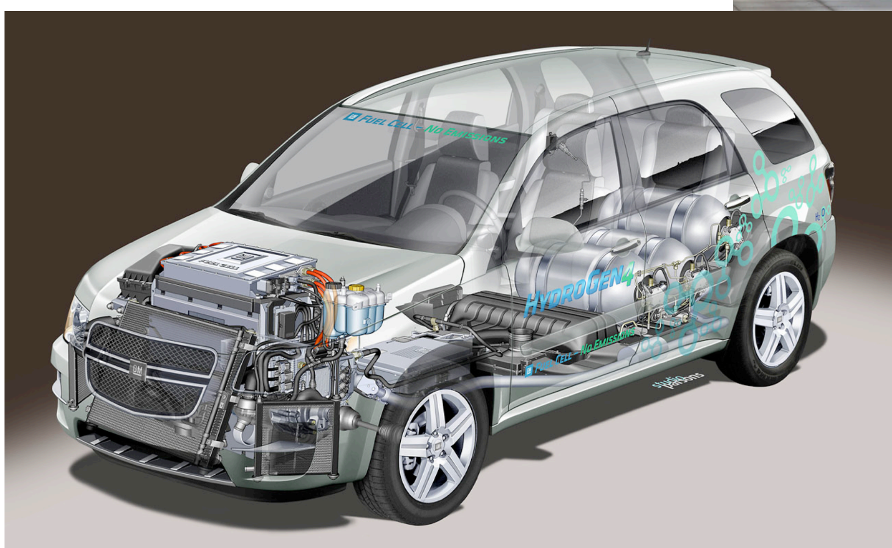
Utility

- NG
- Biogas
- Wastewater

fastcompany.com

Transportation

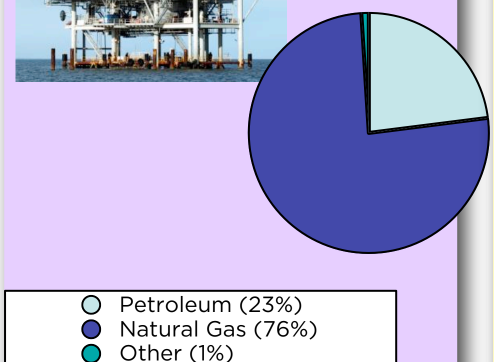
- Hydrogen
- Reformed NG



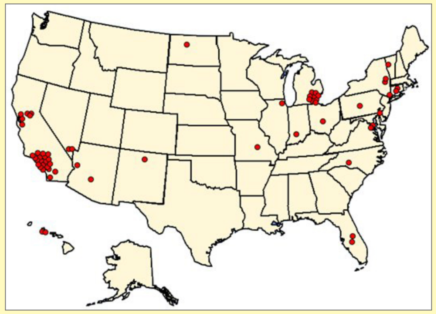
automotiveillustrations.com

Challenge of Automotive Fuel Cells

Hydrogen Production

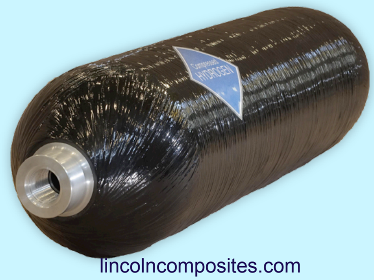


Hydrogen Distribution



64 U.S. stations as of April 2009

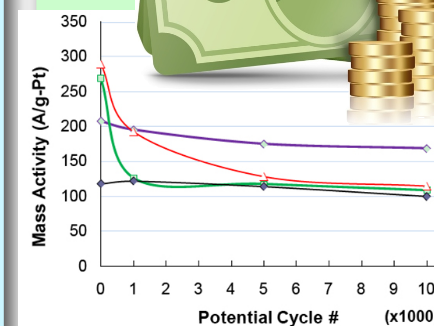
Hydrogen Storage



~5 wt% hydrogen @15,000 psi

Fuel Cell Technology

Cost



Durability

"...you need four significant technological breakthroughs. That makes it unlikely."
-Steven Chu, Technology Review

Opportunities for RF²

MICHIGAN STATE UNIVERSITY

- Fuel sources
  - biohydrogen
  - biogas
  - alcohols
  - sugars
  - waste streams

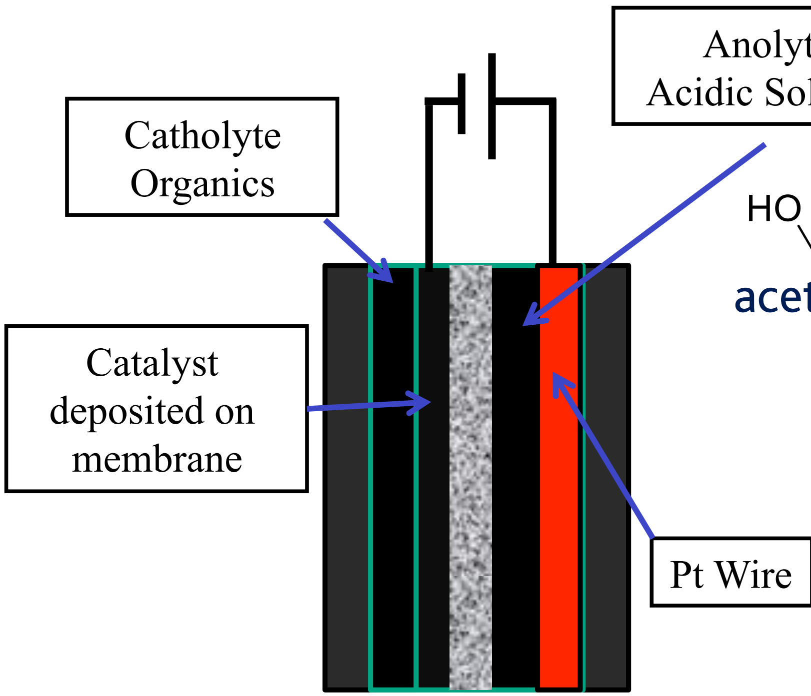
- Electrochemical Conversion
  - CO_2 to fuels
  - renewable fuels
  - value added products

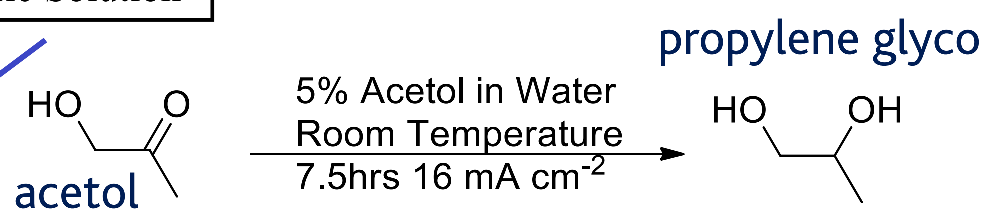
- Fuel Cell Technology
  - electrocatalysis of biofuels
  - non-precious electrocatalysis
    - enzymatic
    - microbial
    - biomimetic
  - new materials
    - electrolytes
    - catalyst supports
    - mediators

J. Jackson

Solid Polymer Electrode

Applications in Organic Reductions





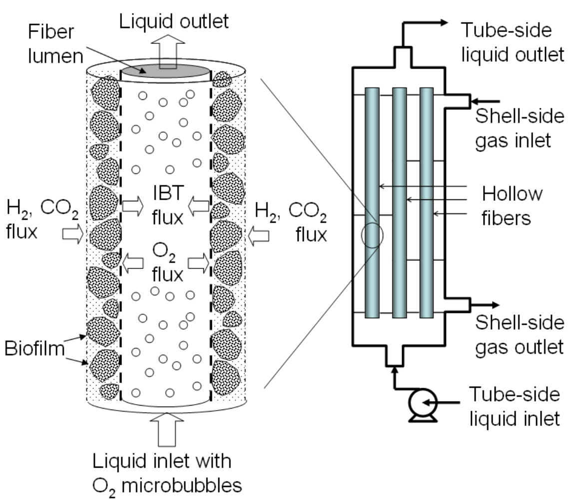
Catalyst	Conversion (%)	C.E. %
No Cat.	13.9	6.0
Cu (1st Use)	47.0	20.2
Cu (2nd Use)	53.9	23.2
Cu (3rd Use)	13.0	5.6
Pt	51.2	22.0
Ru	48.49	28.6

1

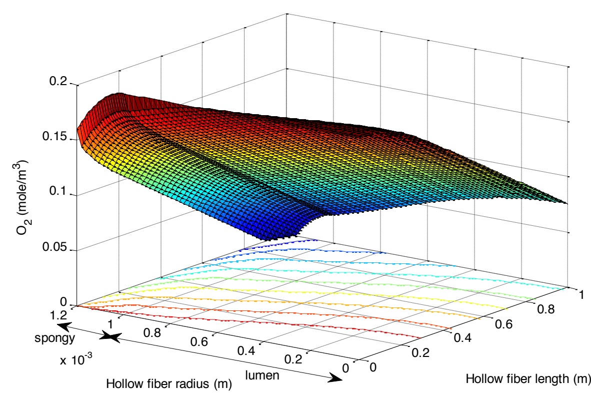
Hydrogen-based electrobiocatalysis

- Gas-intensive electrofuel fermentations
  - Gas mass transfer is rate-limiting factor
  - Improved bioreactor being developed

R.M.Worden



Novel *Bioreactor for Incompatible Gases*



Design challenges for new bioreactor

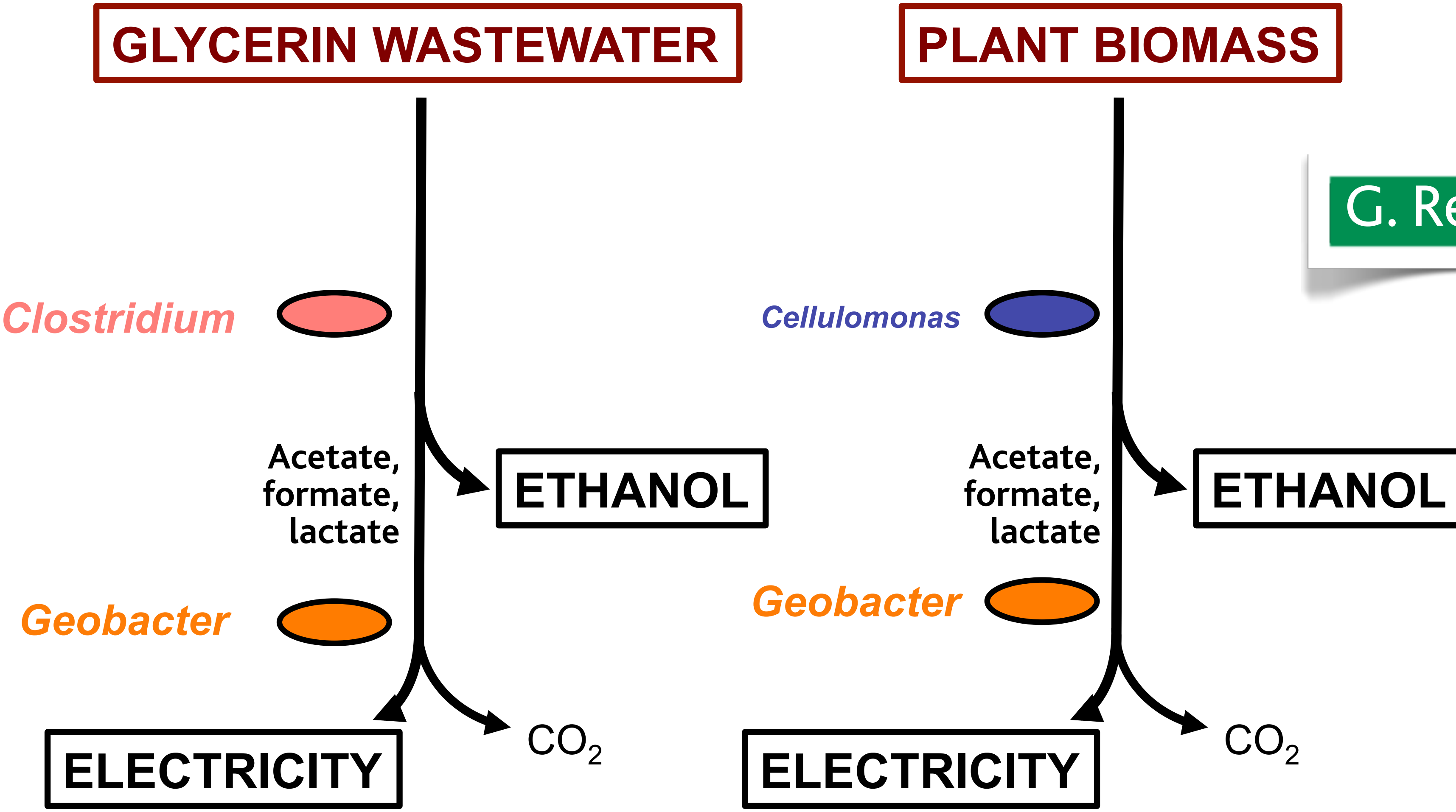
Partnership with Michigan Biotechnology Institute

Microbial Fuel Cell Pathways

MICHIGAN STATE UNIVERSITY

Crops to fuels and electricity

G. Reguera

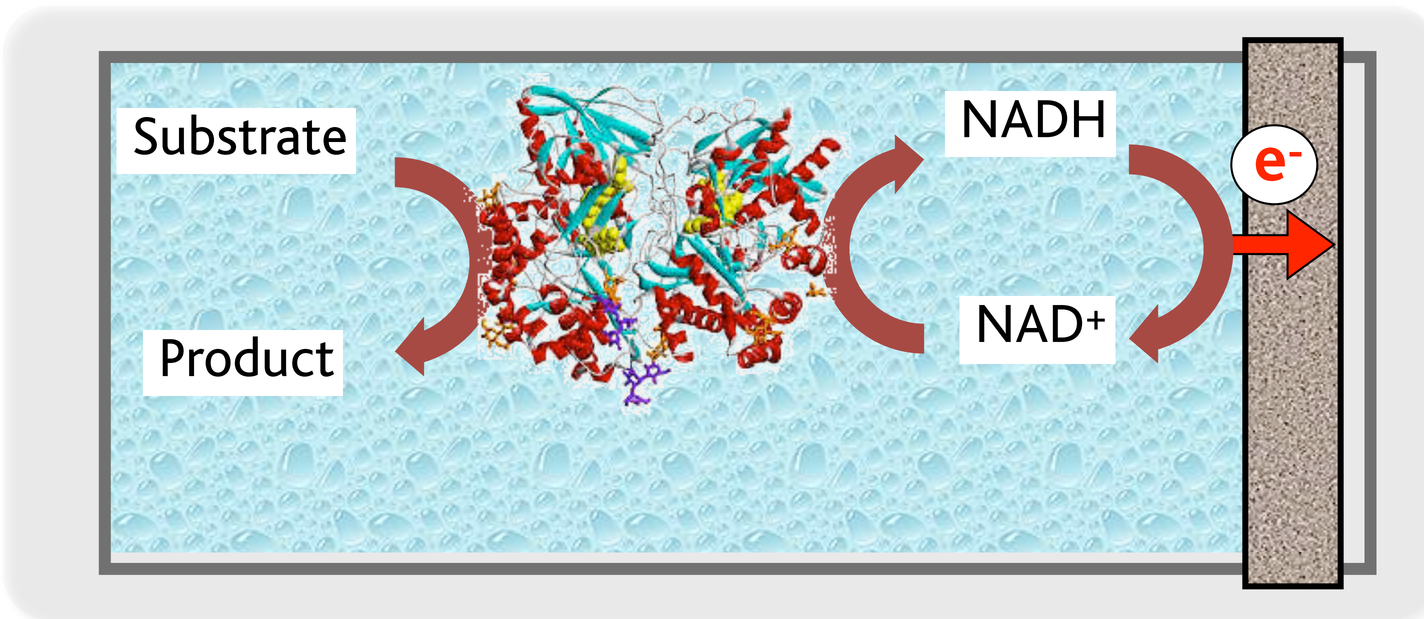


Cofactor Regeneration in Bioelectrocatalysis

MICHIGAN STATE UNIVERSITY

Malate
Alcohol
Glycerol
…

Oxaloacetate
Aldehyde
DHA
…

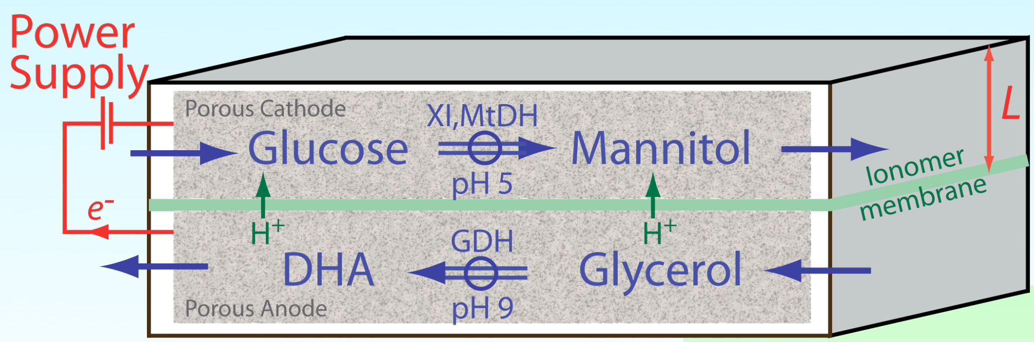


Rate Limiting Step

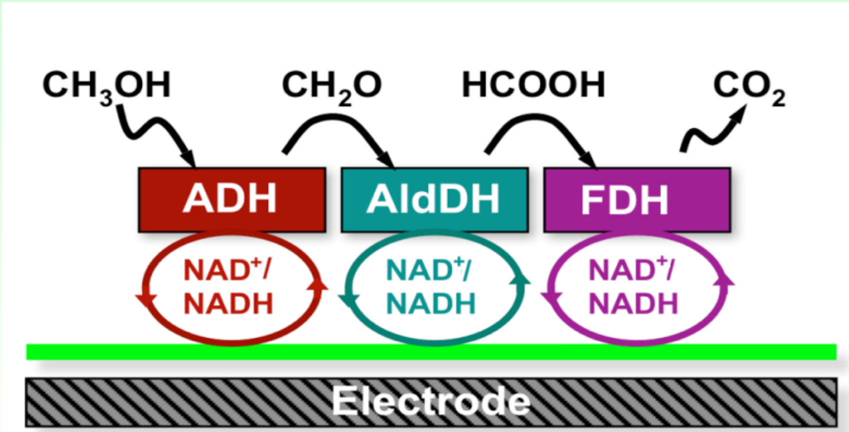
Dehydrogenase-based electrochemical conversion

MICHIGAN STATE UNIVERSITY

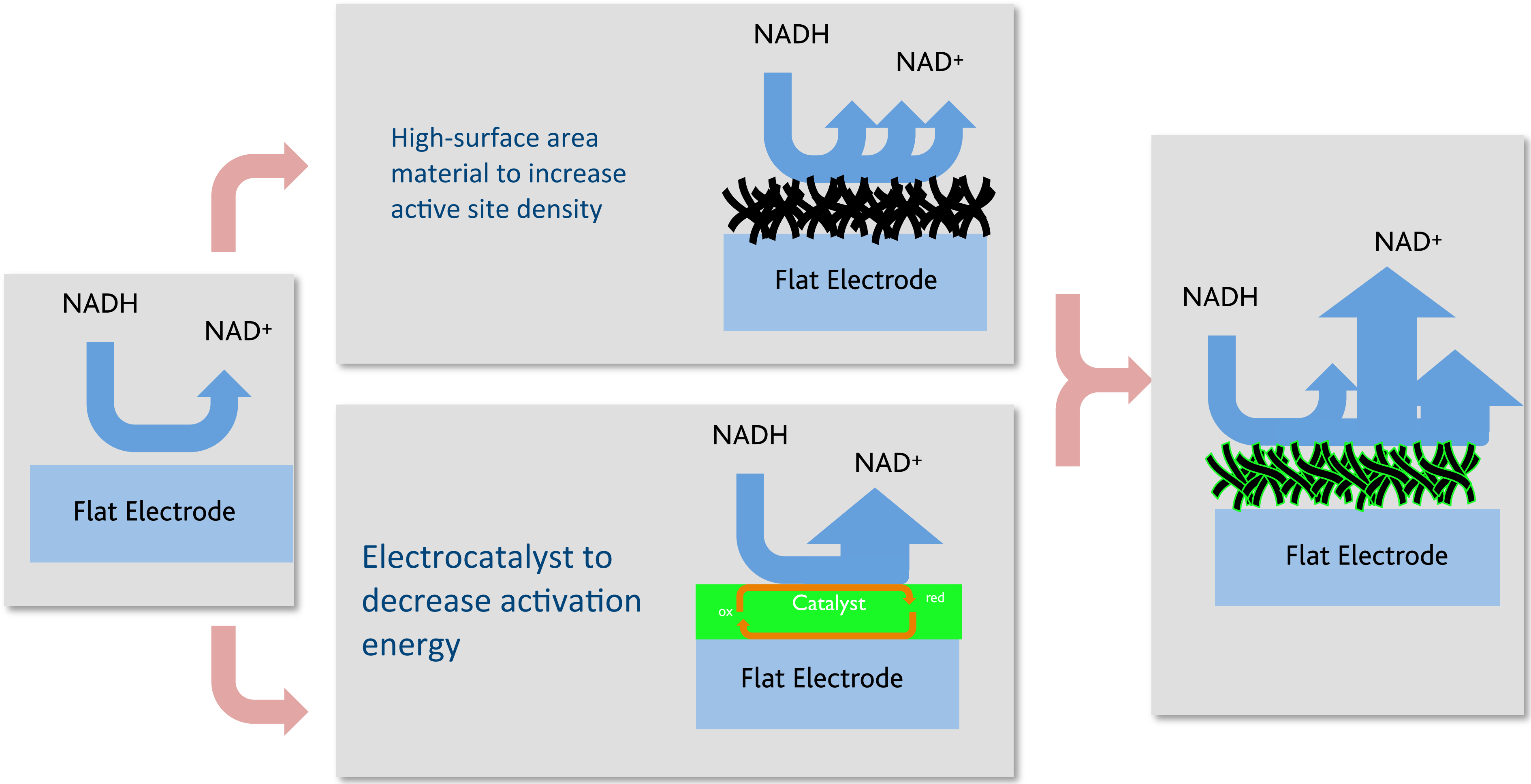
Bioreactors



Biofuel Cells



Electrode Modification for NADH oxidation

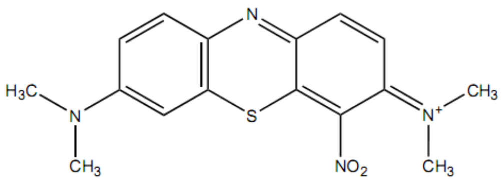


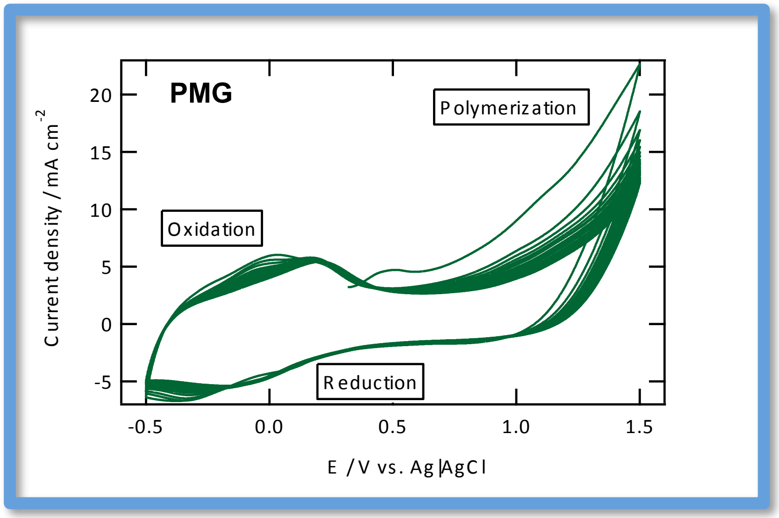
Li, H.; Wen, H.; Calabrese Barton, S. *Electroanalysis* ***2012, 24, 398.***

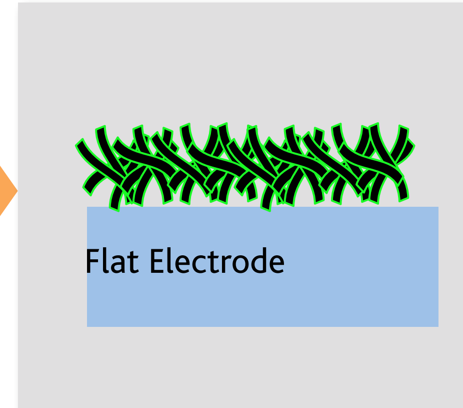
Electrocatalyst Deposition

MICHIGAN STATE UNIVERSITY

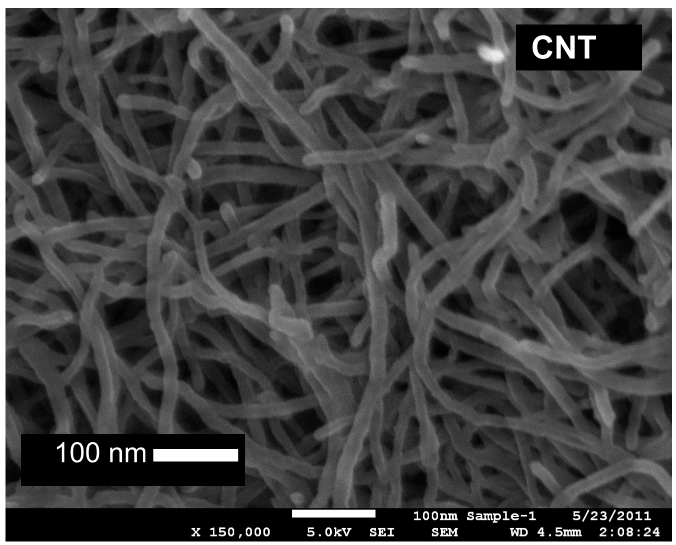
Azine: Methylene Green (MG)

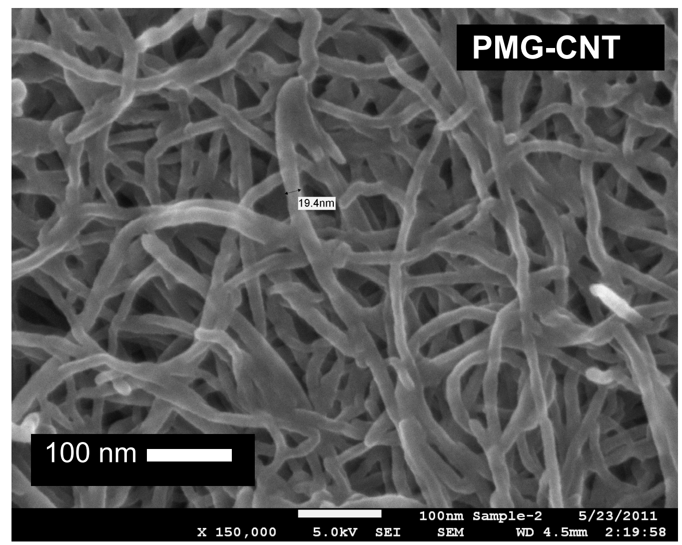






Cyclic voltammograms on 0.85 mg cm^{-2} CNT-coated GC, 20 cycles, 50 mV/s, 0.4 mM TBO, 0.01 M borate buffer pH 9.1, 0.1M $NaNO_3$, 30 C

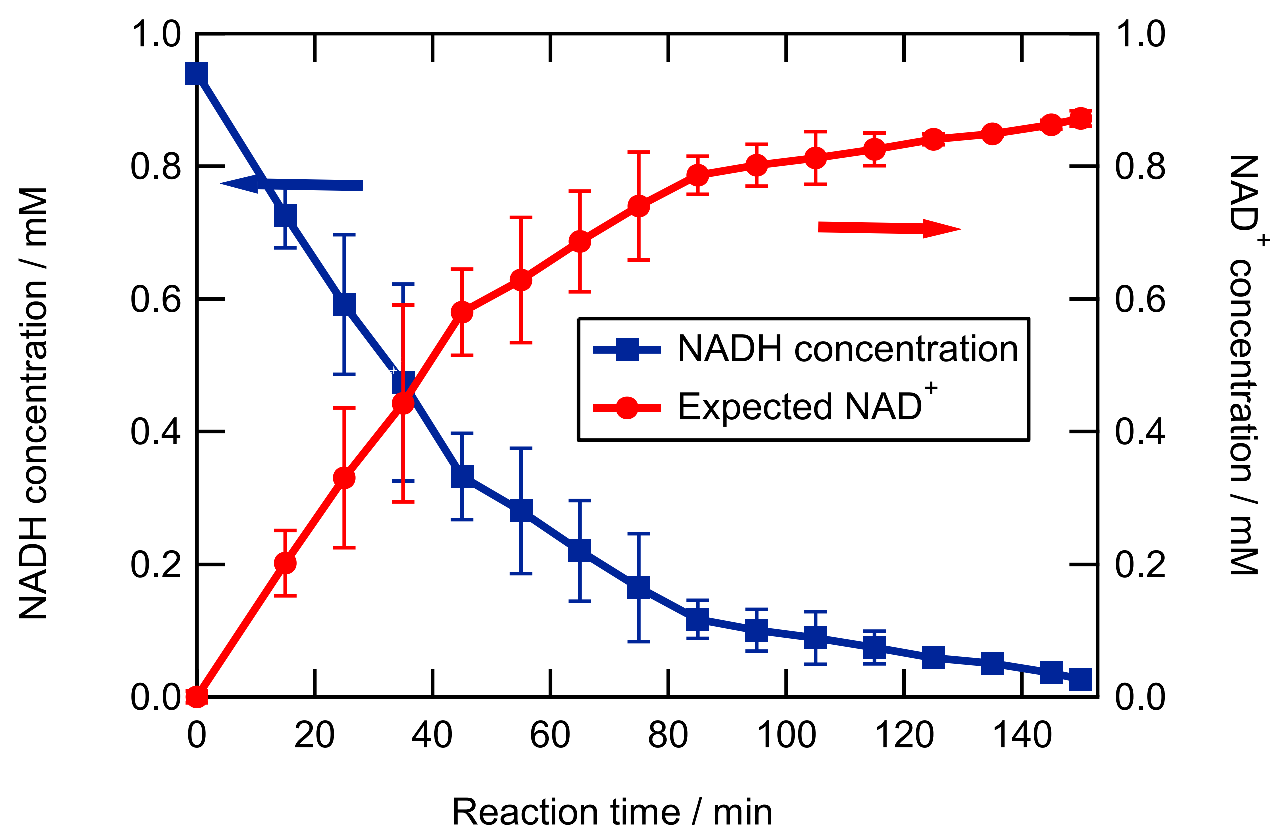




1. Karyakin, A. A.; Karyakina, E. E.; Schuhmann, W.; Schmidt, H. L. *Electroanalysis* **1999, 11, 553.**
2. Zeng, J.; Wei, W.; Wu, L.; Liu, X.; Liu, K.; Li, Y. *Journal of Electroanalytical Chemistry* **2006, 595, 152.**

NADH Oxidation in Batch Reactor

MICHIGAN STATE UNIVERSITY

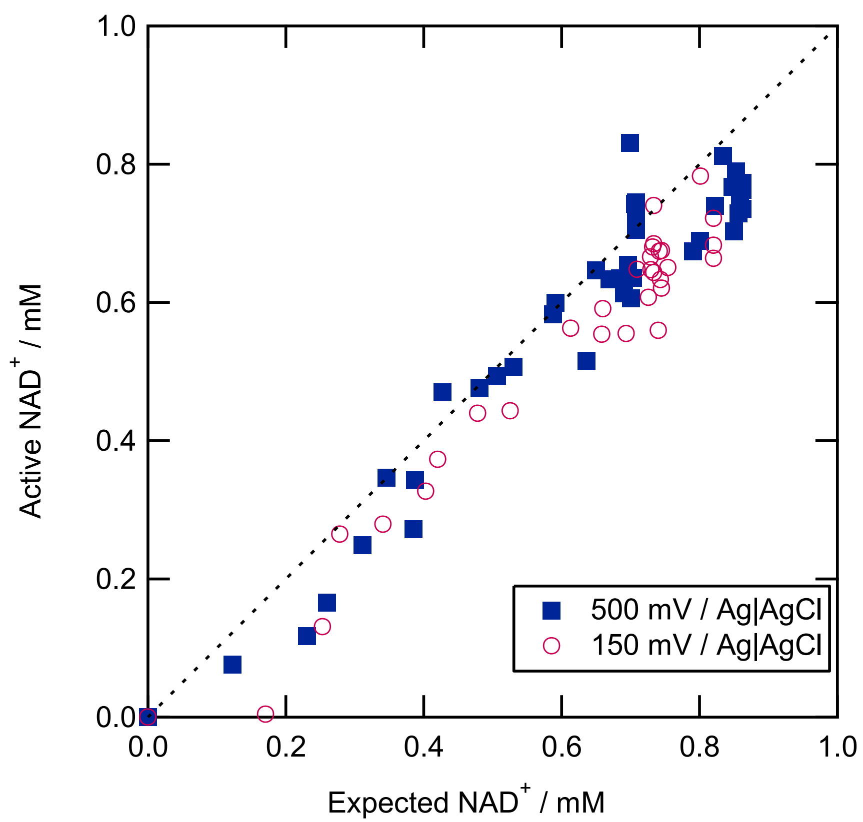


Li, H., et al, *ACS Catalysis*. doi:10.1021/cs3004598

Bioactivity of Electrogenerated NAD+

MICHIGAN STATE UNIVERSITY

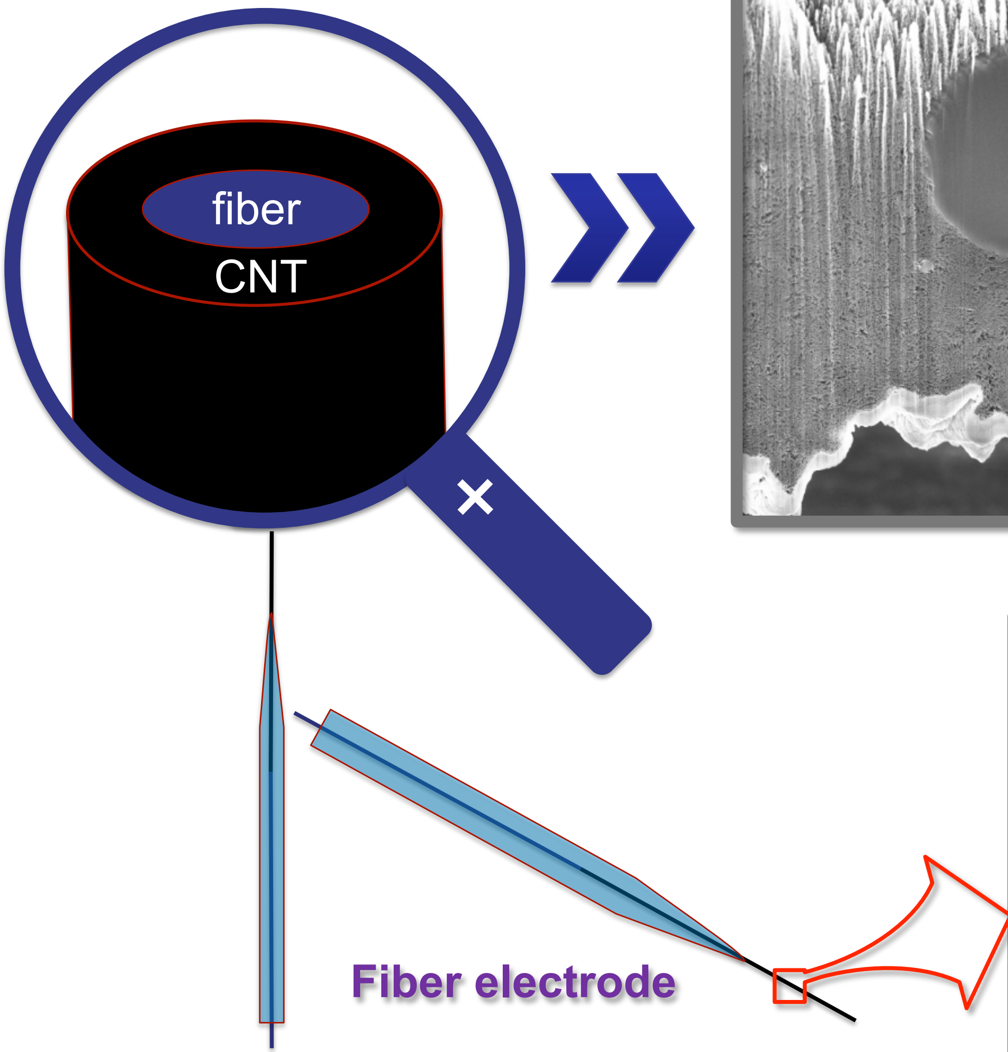
Assessed by EnzyChrom™ Assay

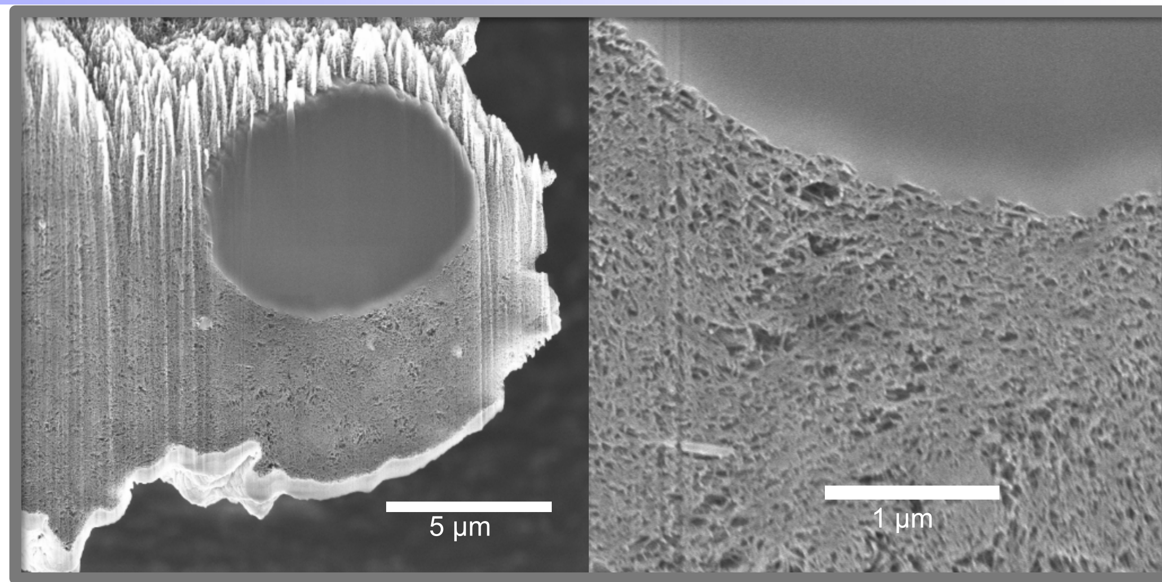


Electrode Potential / mV	150	500
Yield / %	87 ± 8	93 ± 6

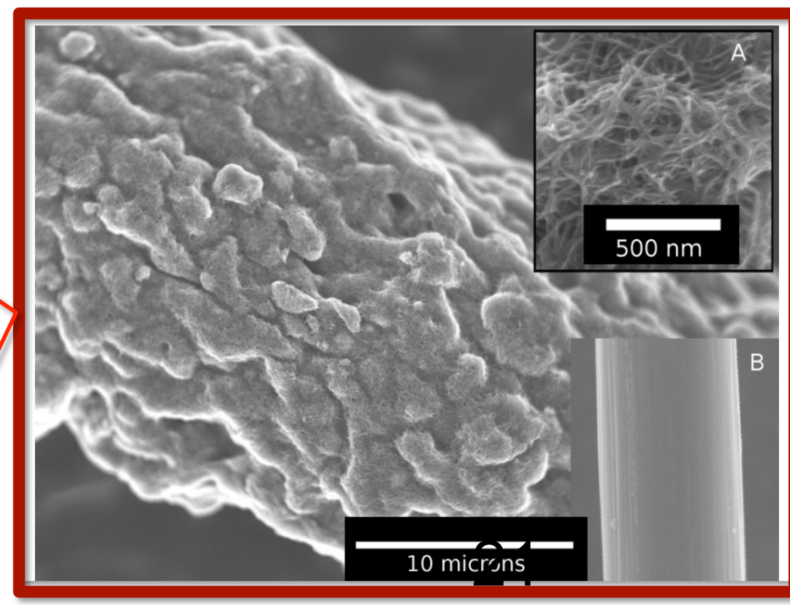
Li, H., et al, *ACS Catalysis*. doi:10.1021/cs3004598

Carbon Fiber / CNT Electrode





Focused Ion Beam Cut Cross Section

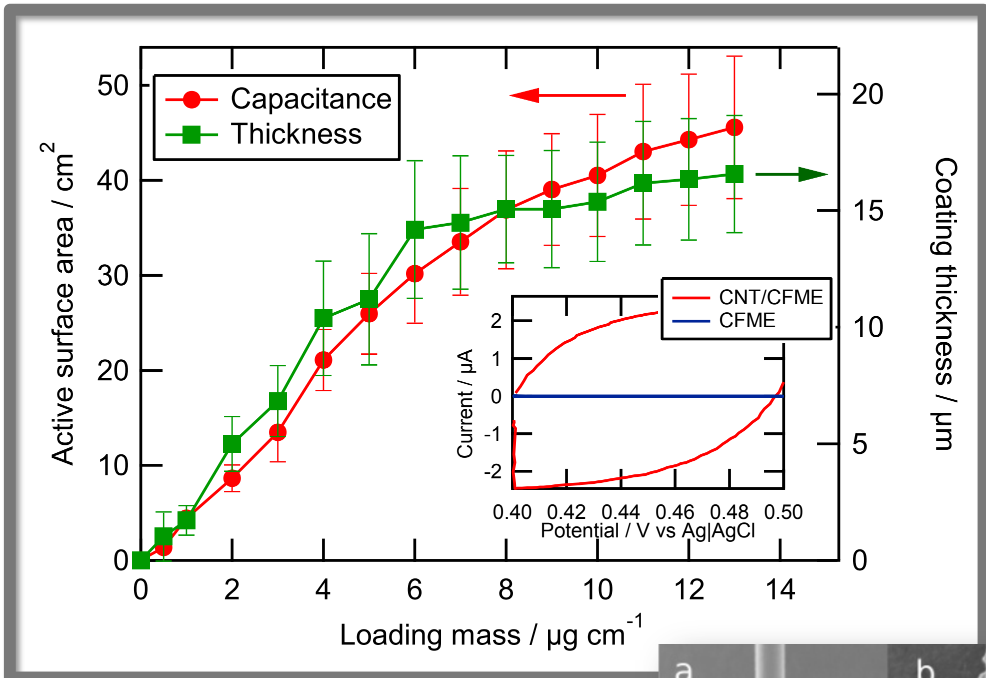


SEM Side View

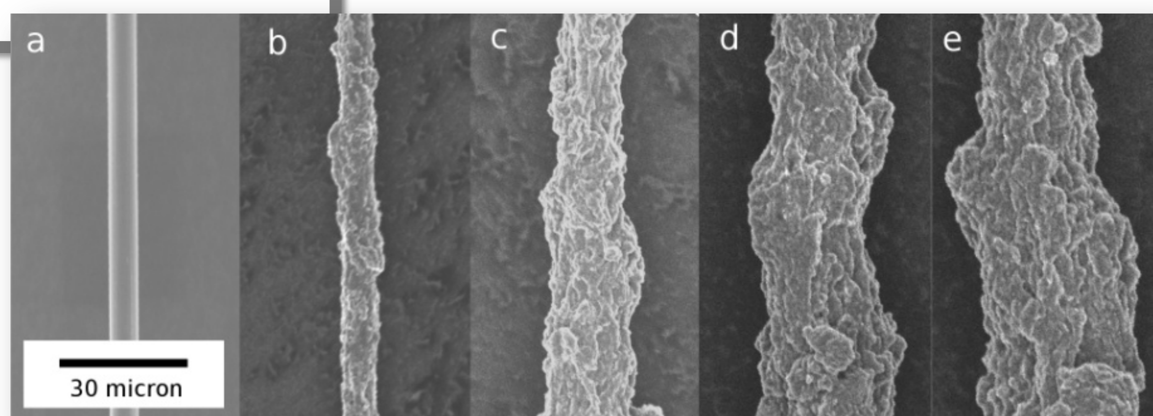
MICHIGAN STATE UNIVERSITY

AFOSR

Thickness & Capacitance



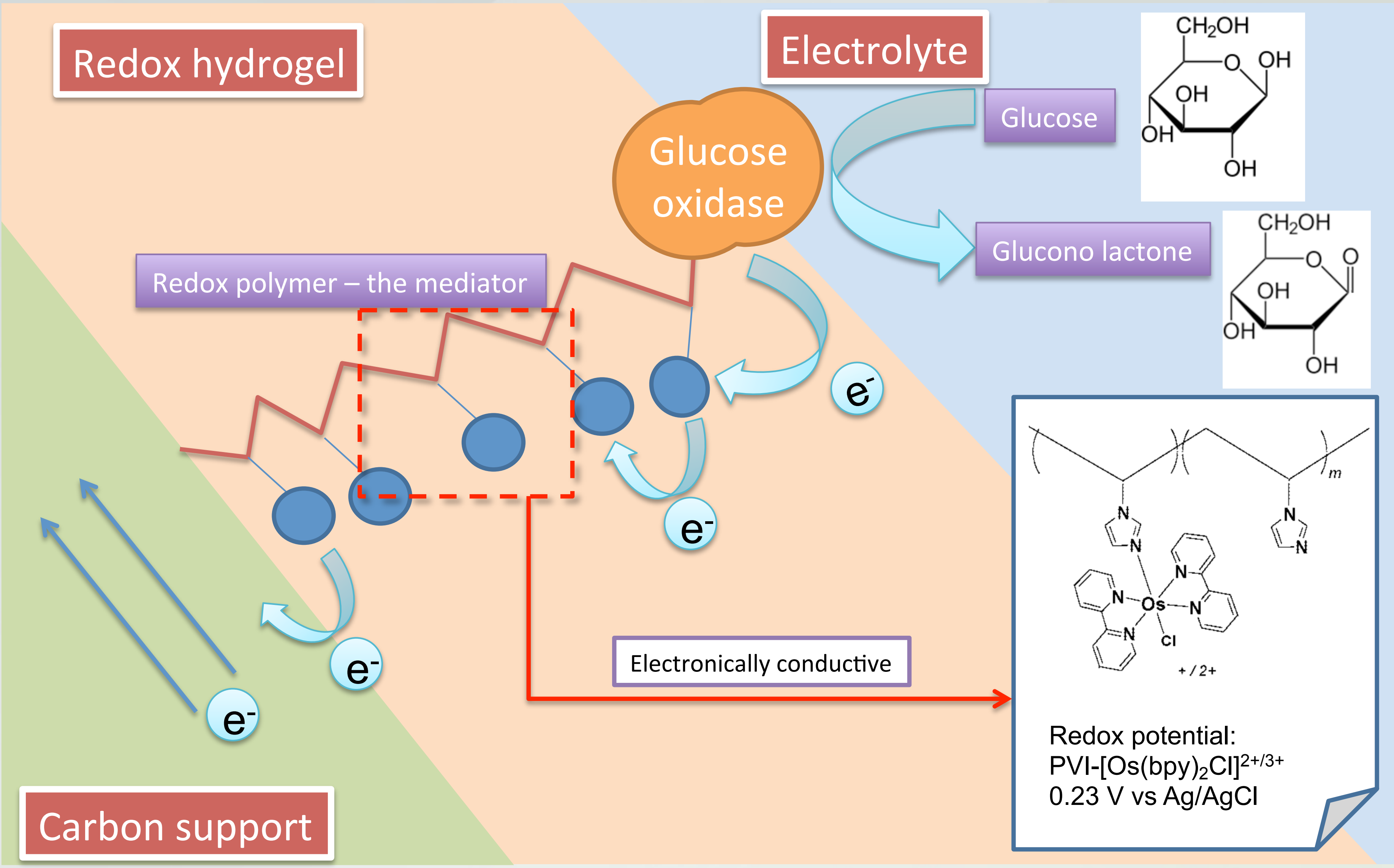
- Capacitance measured in 20 mM PBS solution with 0.1 M NaCl.
- The coating thickness was measured digitally by optical micrograph.
- Surface area conversion factor: 1.5 µF/cm^2



MICHIGAN STATE UNIVERSITY

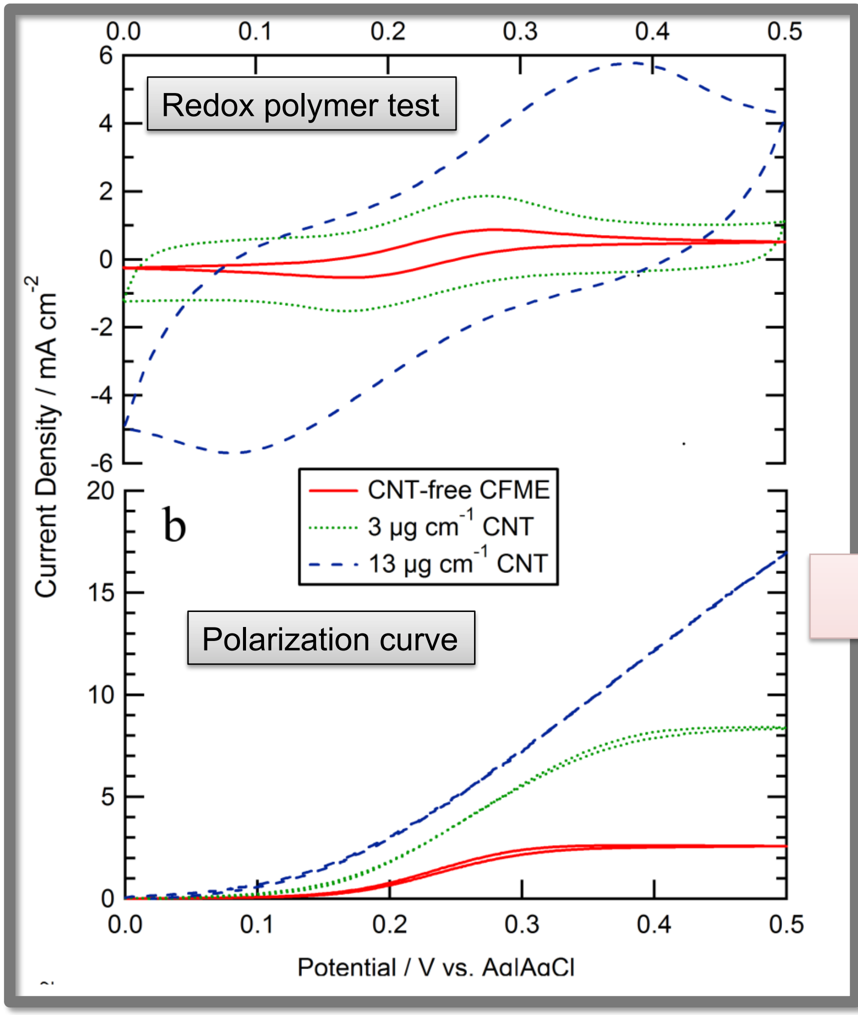
AFOSR

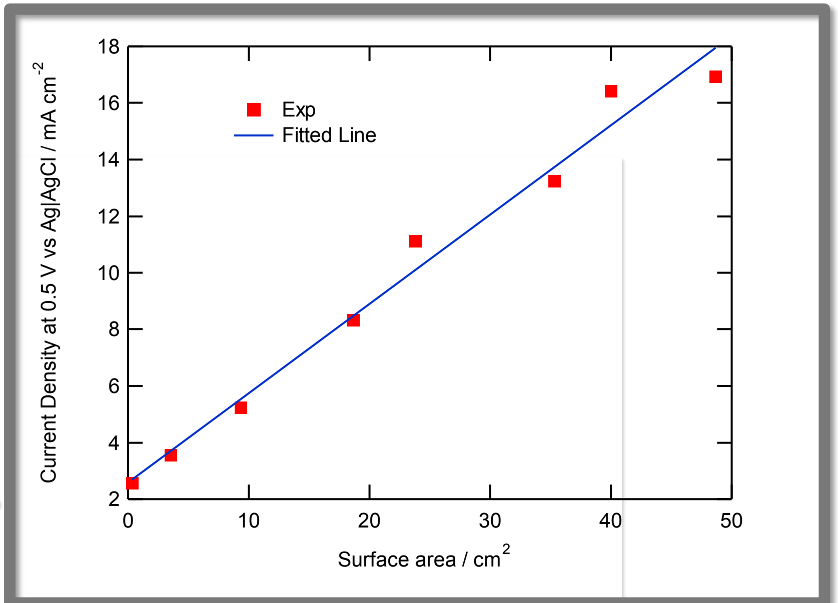
Biocatalyst Test System



B. Gregg and A. Heller, J. Phys. Chem. 95, 5970 (1991).

CFME/CNT/Hydrogel Performance





Performance summary

6.4 fold increase of current density

50 mM glucose, 20 mM phosphate buffer solution, 0.1 M NaCl as supporting electrolyte, 37.5 ⁰C, 150 rpm stirring bar, nitrogen saturated.

H. Wen, V. Nallathambi, D. Chakraborty, and S. Calabrese Barton, *Microchimica Acta* **2011**, *175*, 283-289.

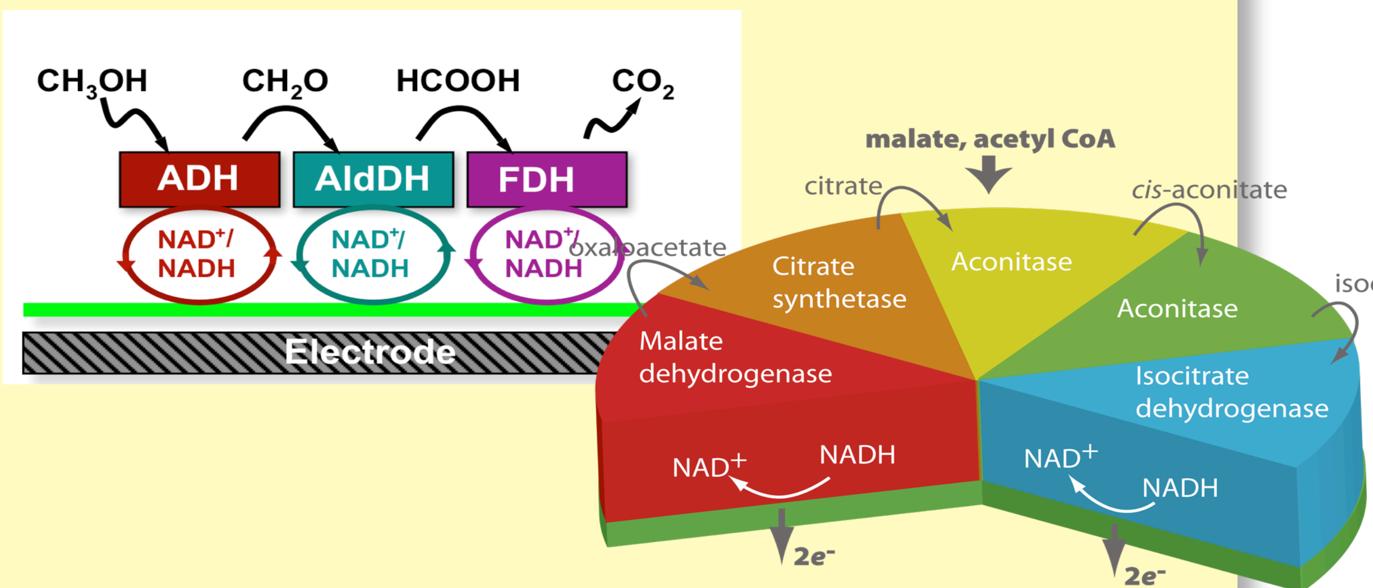
MICHIGAN STATE UNIVERSITY

AFOSR

Modeling of Multistep Bioelectrochemical oxidation

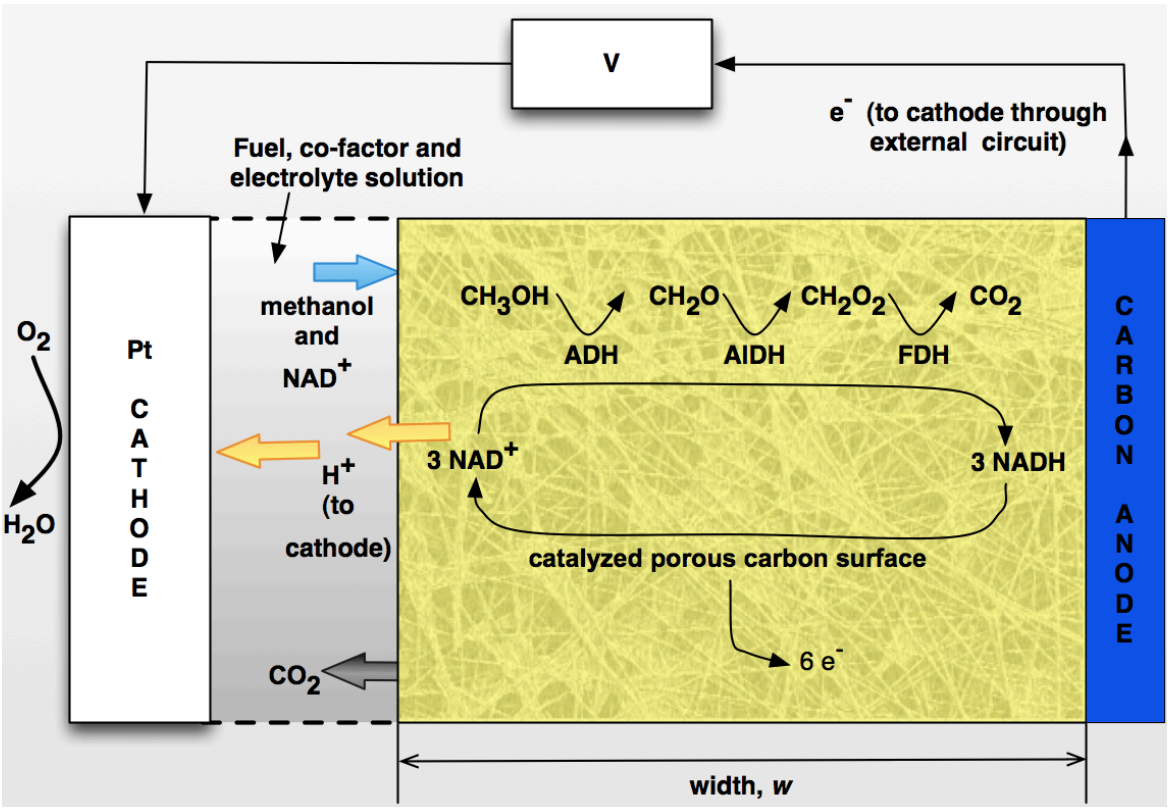
- Develop predictive and quantitative models for electrode performance.
- Evaluate system parameters (materials, kinetics, transport) to improve model accuracy.

Simulation of Multistep Electro-oxidation



Model of Methanol Biofuel Cell

P. Kar, H. Wen, H. Li, S. D. Minteer, and S. C. Barton, *J. Electrochem. Soc.* **2011**, *158*, B580-B586.



Enzymes are encapsulated within TBAB modified Nafion

Oxidation of CH_3OH to CO_2 on the surface of poly(methylene green) by the three-step enzymatic reaction

Co-enzyme / co-factor:

NAD^+ --- *Nicotinamide Adenine Dinucleotide*

NAD^+ dependent Enzymes:

ADH --- *Alcohol Dehydrogenase*

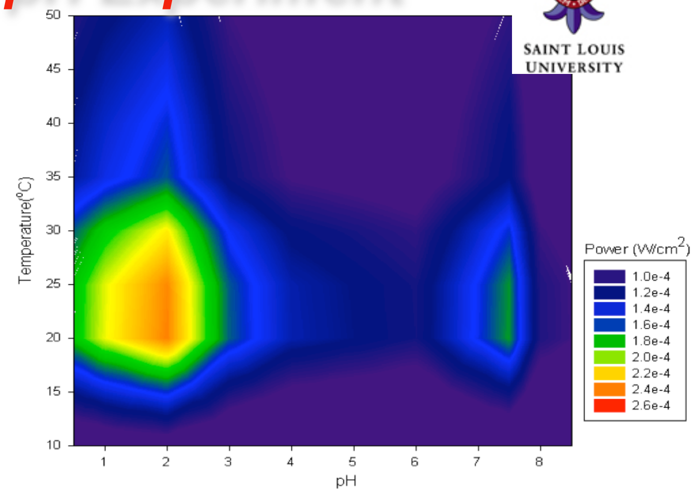
AIDH --- *Formaldehyde Dehydrogenase*

FDH --- *Formate Dehydrogenase*

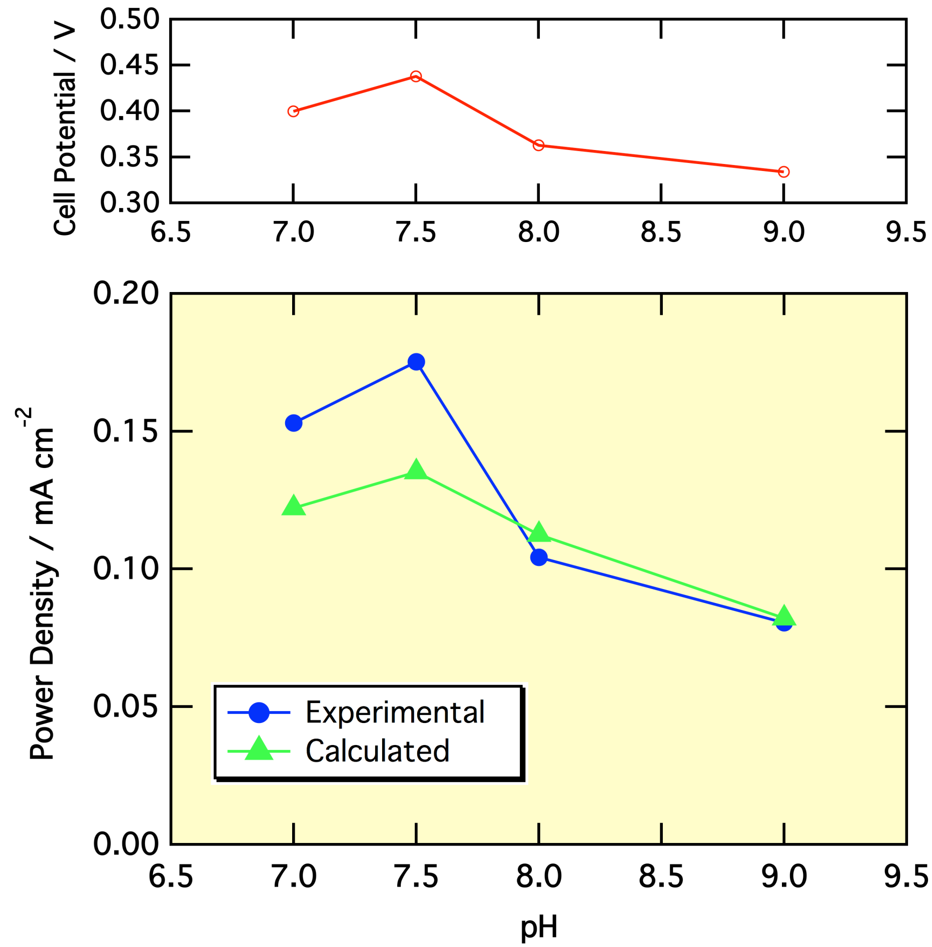
P. Kar, H. Wen, H. Li, S. D. Minteer, and S. C. Barton, *J. Electrochem. Soc.* **2011**, *158*, B580-B586.

Comparison to Experimental Power Density

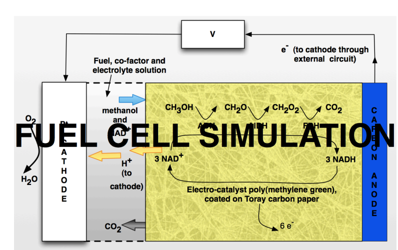
pH Experiment



Addo, P. K.; Arechederra, R.; Minteer, S. Electroanalysis 2010, 22, (7-8), 719



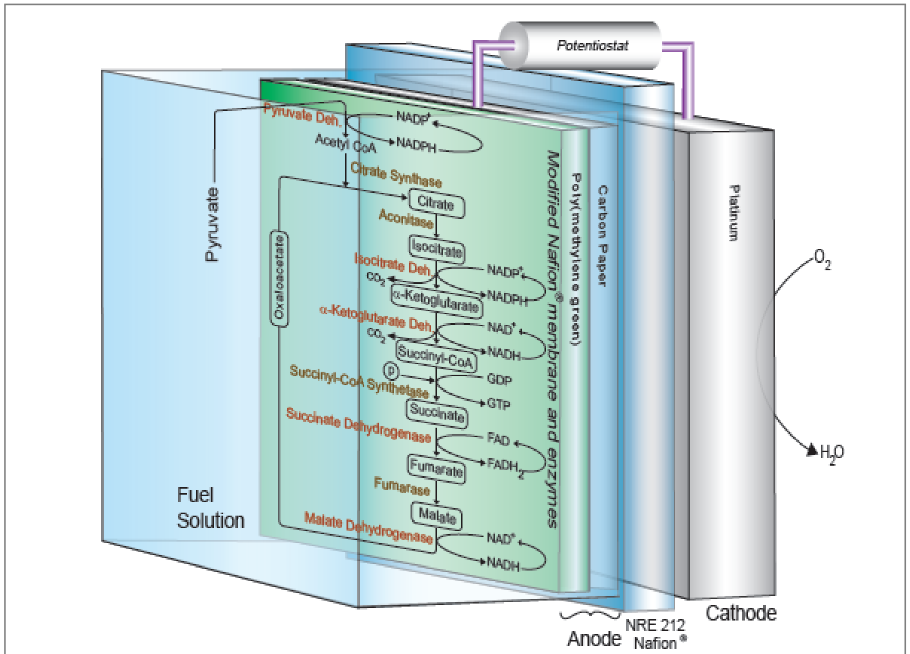
P. Kar, H. Wen, H. Li, S. D. Minteer, and S. C. Barton, *J. Electrochem. Soc.* **2011**, *158*, B580-B586.



MICHIGAN STATE UNIVERSITY

AFOSR

Pyruvate Electrode



Scheme 1. Enzyme cascade reaction of the complete oxidation of pyruvate in an enzymatic biofuel cell.[1]

D. Sokic-Lazic, and S. D. Minteer, *Electrochemical and Solid State Letters* **2009**, *12*, F26-F28.

Glycerol Electrode

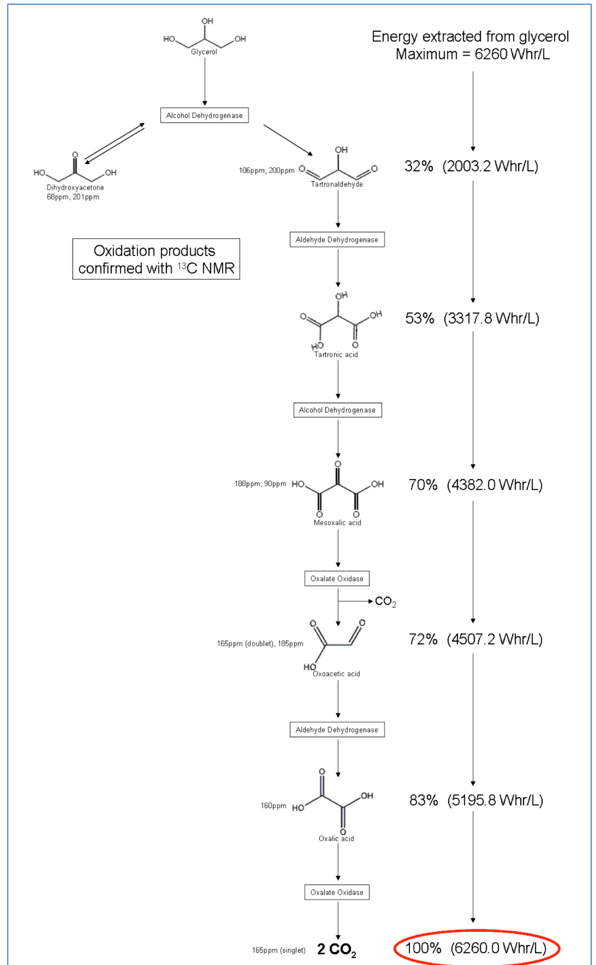


Figure 2. Enzyme cascade reaction of the complete oxidation of glycerol.

R. L. Arechederra, and S. D. Minteer, *Fuel Cells* **2009**, *9*, 63-69.

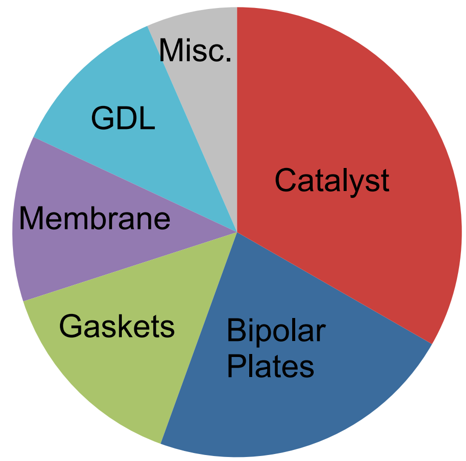
State of the art platinum electrocatalysts

- Commercial catalysts for low temperature fuel cells: Pt supported on carbon black[1]

  Total Pt loading 0.1 to 0.2 mg/cm^2 (2015)

- For an 80 kW PEMFC, Pt costs ~**$3000** ($1545 / troy ounce)[2]
- Platinum reserve issues

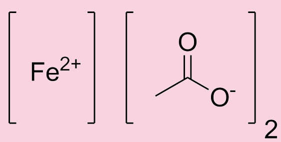
[3]2015 PEMFC Stack cost
$21/kW$_{net}$, $1711



[1]http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/dti_80kwW_fc_system_cost_analysis_report_2010.pdf
[2]http://platinumprice.org/

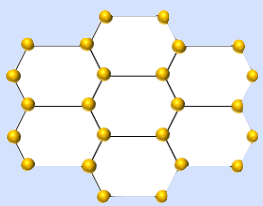
High pressure pyrolysis synthesis approach

R. Kothandaraman et al, *Appl. Catal. B*, **92** 209 (2009).



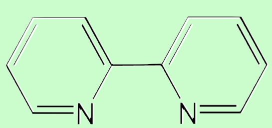
Metal source

+

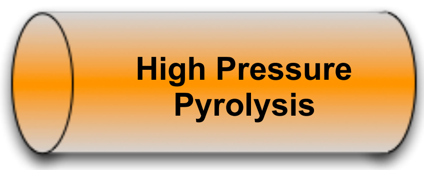


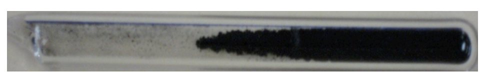
Porous carbon support

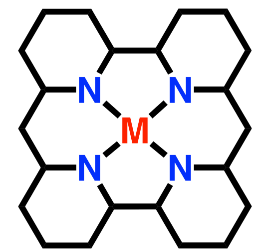
+



Nitrogen source







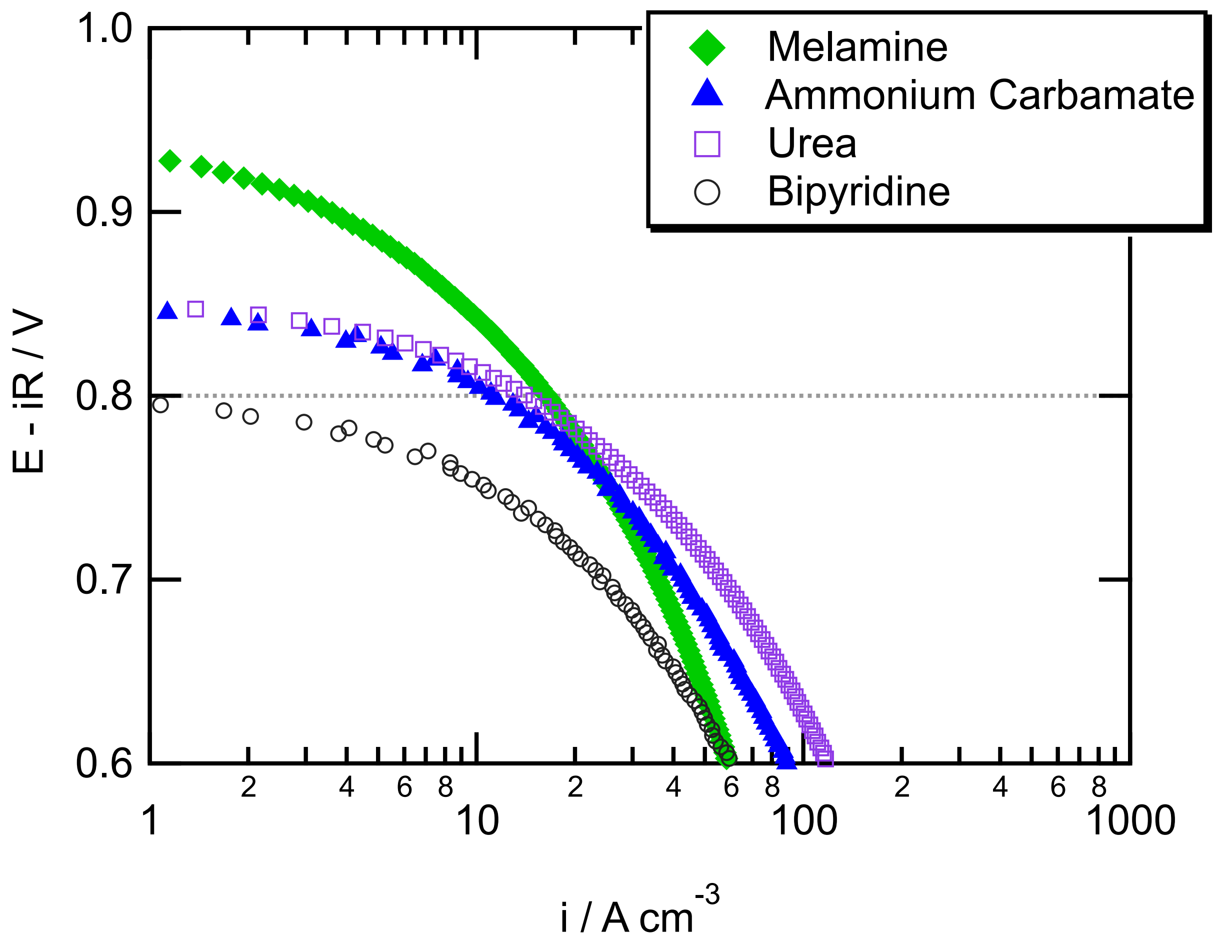
MNC catalyst

Autogenic pressure due to N precursor evaporation & decomposition:

- retains N precursor
- increases N activity

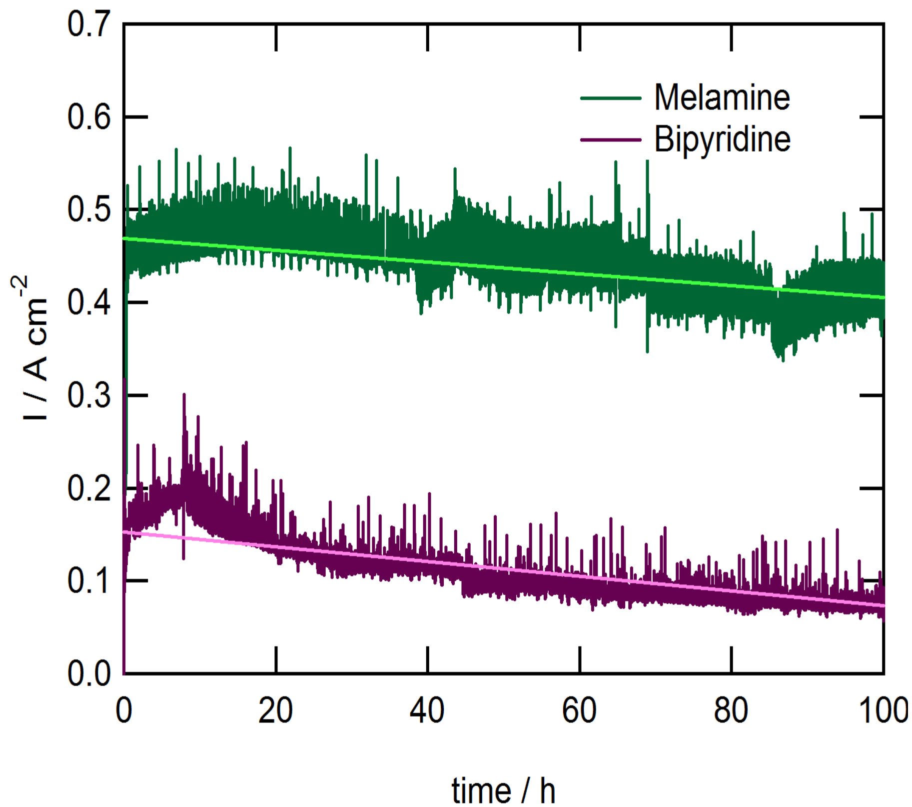
R. Kothandaraman, V. Nallathambi, K. Artyushkova and S. C. Barton, *Applied Catalysis B: Environmental*, **92**, 209 (2009).

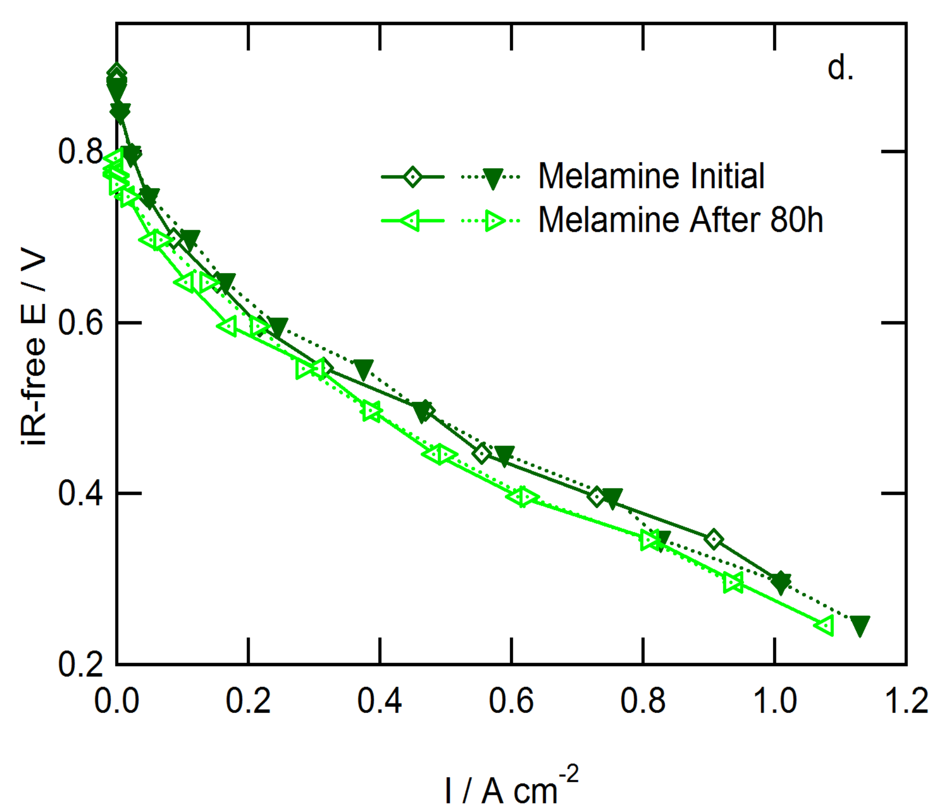
Fuel cell characterization



- Cathode : MNC 1.4 mg cm^{-2}
- Anode : 20 % Pt / C 0.4 mg cm^{-2}
- T_{cell} : 80^{o}C
- Nafion 112
- 100% Humidity
- Feed : H_2/O_2
- Back pressure : 1 bar gauge
- Area : 5 cm^2

Fuel cell durability





- Cathode : MNC 1.3 mg cm^{-2}
- Anode : 20 % Pt / C 0.4 mg cm^{-2}
- T_{cell} : 80°C, Nafion 112, 100% Humidity
- Feed : H_2/O_2
- Back pressure : 1 bar gauge
- Area : 5 cm^2

Simulations of hydrocarbon membrane PEMFCs

using combined Quantum and Classical Mechanical Simulations

R. Cukier

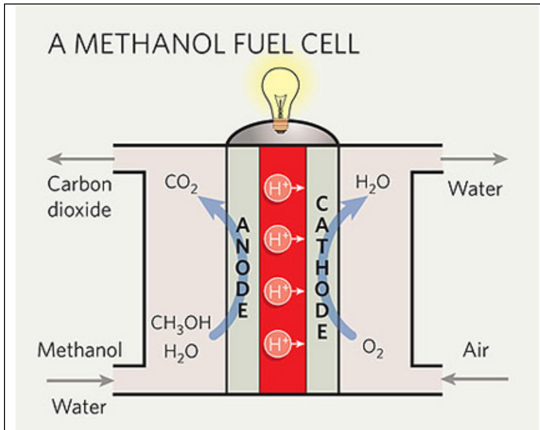


Fig. 1. (from from soultek.com)

Schematic methanol Fuel Cell. Anodic input CH_3OH Cathodic input O_2. The polymer electrolyte membrane provides the medium for proton conduction from anode to cathode. The circuit being completed externally with electron flow to produce EMF.

$CH_3OH+H_2O \rightarrow CO_2 + 6H^+ + 6e^-$ (anode)
$3/2\ O_2+6H^+ +6e^- \rightarrow 3H_2O$ (cathode)
$CH_3OH+3/2O_2 \rightarrow CO_2 + 2H_2O$ (overall)

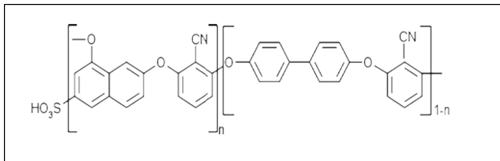


Fig. 8. Molecular structure of m-SPAEEN Sulfonated poly(arylene ether ether nitrile) (m-SPAEEN) copolymers. n/1-n provides the ratio of the polymer repeating unit; e.g. m-sPAEEN 60 denotes a 60:40 ratio.
Figure taken from reference [1]

- roles of polymer chain length and conformation,
- backbone hydrophobicity, and water content in the hydrophilic regions
- proton transport and methanol transport

[1] T. Ohkubo, Y. Iwadate, Y.S. Kim, N. Henson and Y.K. Choe, Understanding properties of copoly(arylene ether nitrile)s high-performance polymer electrolyte membranes for fuel cells from molecular dynamics simulations, Theor Chem Acc 130 (2011) 555-561.