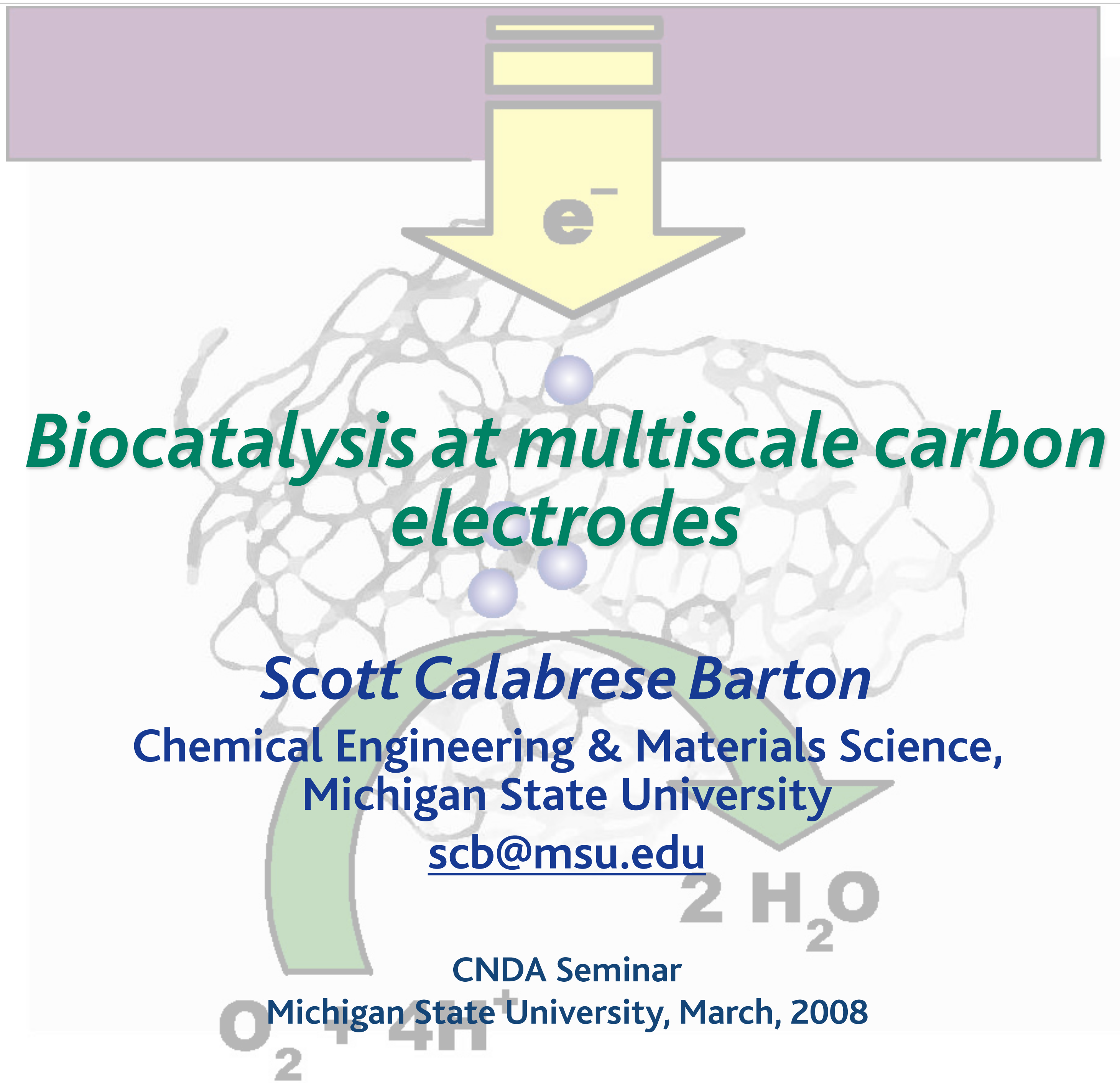

Biocatalysis at multiscale carbon electrodes

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Michigan State University

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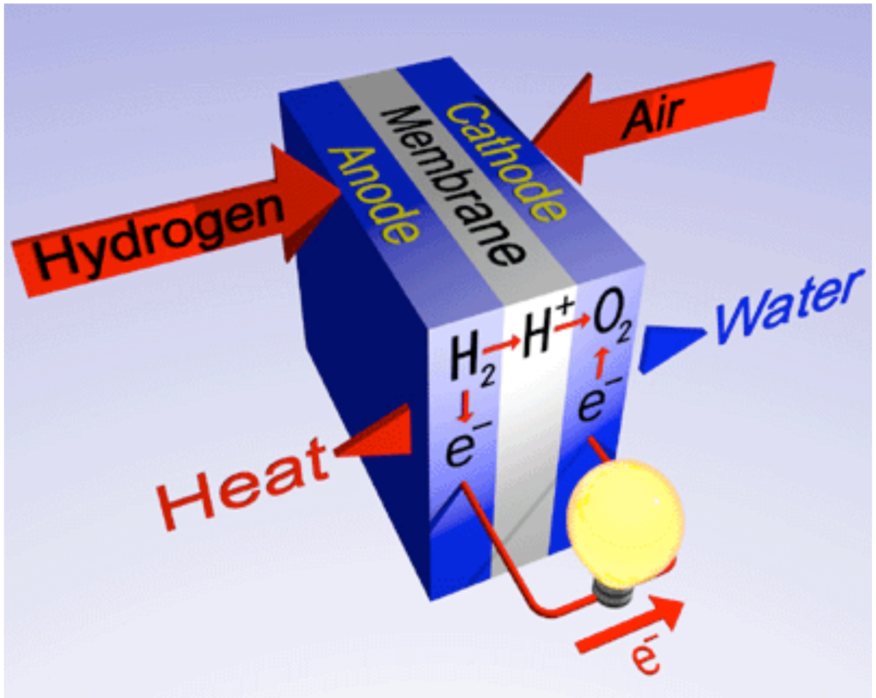
CNDA Seminar

Michigan State University, March, 2008

Outline

- Introduction
- Mediated oxygen cathodes
- Multiscale carbon supports for glucose anodes
- Mixed-feed biofuel cell performance.

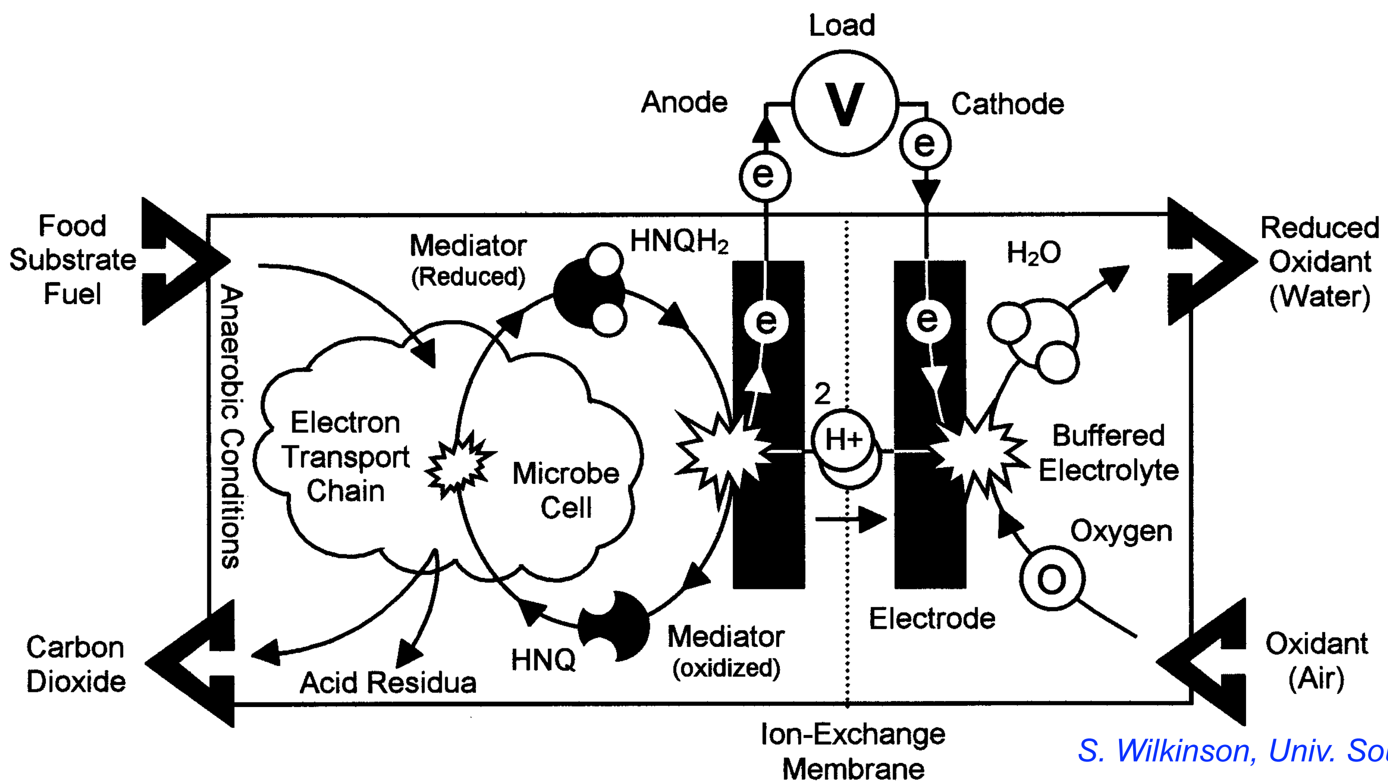
What is a Fuel Cell?



http://www.fuelcelltoday.com

- Converts externally-supplied fuel to electricity.
- Can be continuously or intermittently refueled.
- Reactions at both electrodes rely on
  - Catalysis,
  - Interfacial (heterogeneous) electron transfer
  - Reactant species transport

Microbial Biofuel Cells



S. Wilkinson, Univ. South Florida

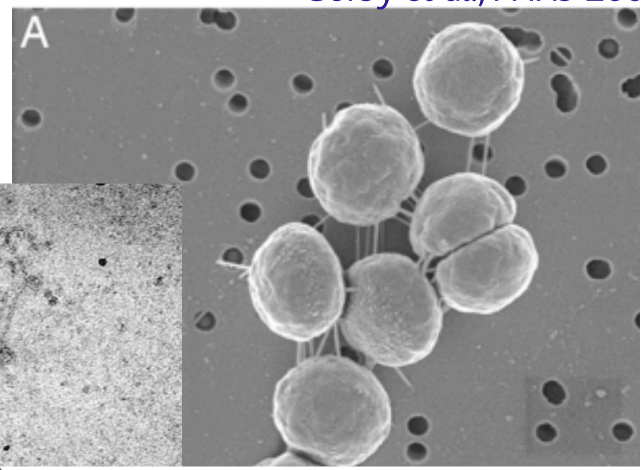
★Multi-step oxidation of fuels

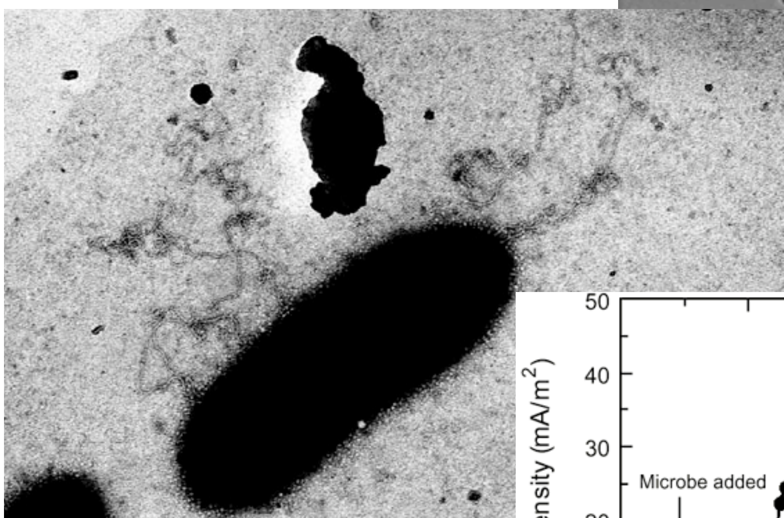
★Higher stability?

✕ Low power (< 5 μW/cm²)

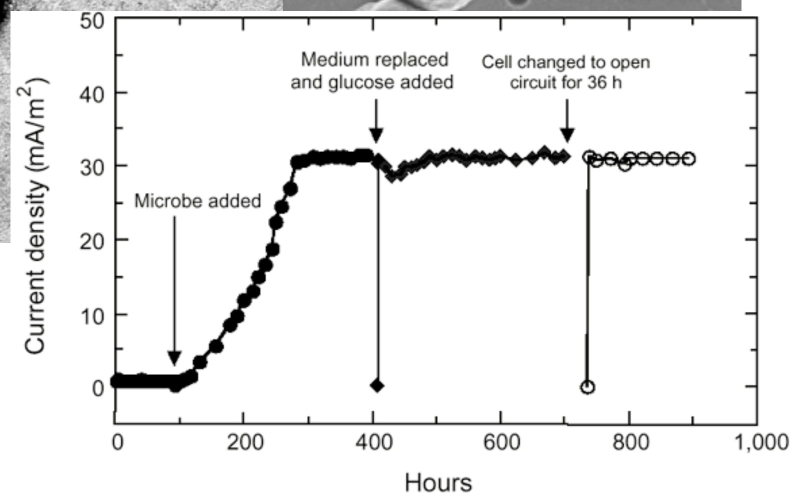
Electron Conduction by Bacterial Nanowires

Gorby et al., *PNAS* **2006**, *103*, 11358.



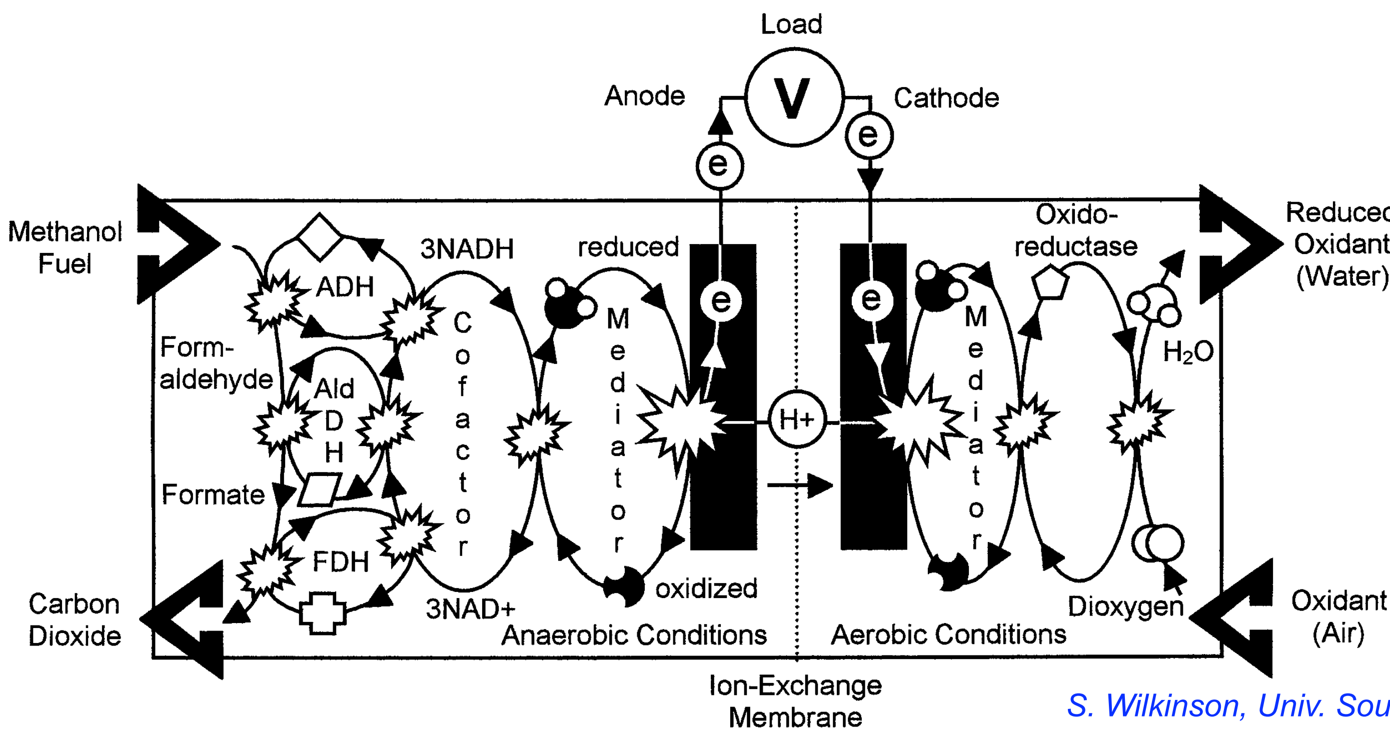


Reguera et al, *Nature* **2005**, *435*, 1098.



Chaudhuri and Lovley, *Nat. Biotechnol.* **2003**, 21, 1229.

Enzymatic Biofuel Cells



S. Wilkinson, Univ. South Florida

★Higher power (< 10 mW/cm²)

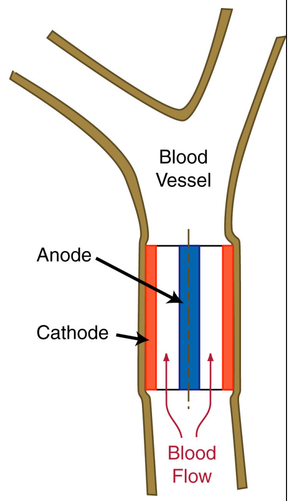
✕1- or 2-step oxidation

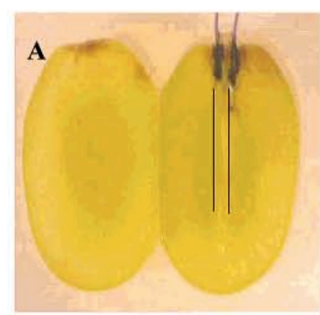
✕Low Stability

Applications

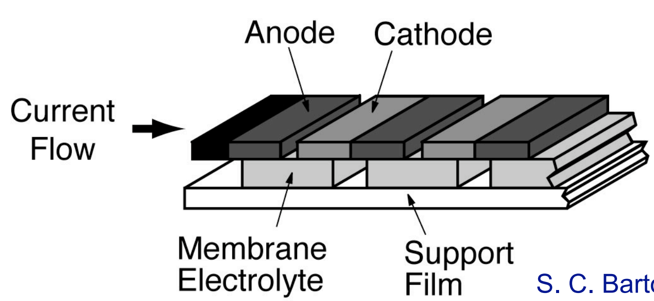
S. A. Calabrese Barton, J. Gallaway, and P. Atanassov, *Chemical Reviews*, **November, 2004**.

- Implantable power
  - » Relies on physiologically ambient glucose and oxygen
  - » Chemical/temperature sensor/telemeter (<1 W/L, short term)
  - » Muscle actuator (1-10 W/L, long-term)
- Distributed power from ambient fuels
  - » Relies on ambient sugars and air
  - » Sugars other than glucose must be bioreformed.
    - – Multi-enzyme electrodes or external bioreformer.
- Methanol micro fuel cells
  - » Multistep, complete oxidation of methanol.
  - » High-potential reduction of airborne oxygen.





N. Mano, et al, *JACS,* 125, 6588 (2003)



S. C. Barton et al., *J. Power Sources*, **96**, 329-336 (2001).

Volumetric Current Density Comparison

O_2 Cathode Catalysts

...the activity of a costless cathode catalyst (per unit *volume* of supported catalyst, *i.e.*, A/cm^3) for automotive applications needs to be no less than 1/10th of the current industrial Pt activity...

Gasteiger et al., Applied Catalysis B: Environmental 2005, 56, 9.

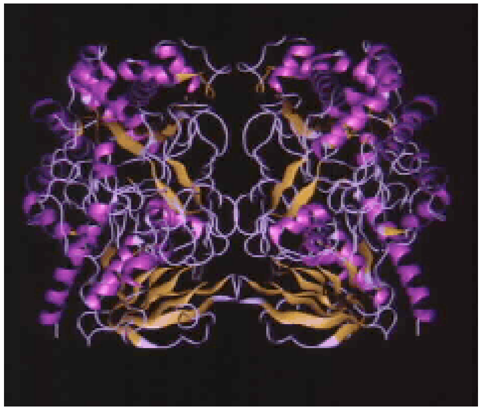
Catalyst	T (°C)	Potential (V/RHE)	TOF (e^-/site·s)	S.D./10^{20} (site/cm^3)	A/cm^3	W/cm^3
47% Pt/C[1]	80	0.8	25	3.2	1300	1000
Ideal Laccase	40	1.11	200	0.1	160	180
Mediated Laccase	40	0.7	200	0.01	32	22.4

➡ Biocatalysts not <u>yet</u> a challenger for automotive fuel cell catalysis (power density driven).

➡ Biocatalysts are better positioned for micro-scale and portable electronics (energy density driven).

Typical Enzyme Details

Property	Glucose Oxidase	Laccase
Source	*Aspergillus niger*	*Coriolus hirsutus*
Molecular weight	80,000	65,000
Redox Center	$FADH_2/FAD$	$Cu^{+/2+}$
Redox potential (re: SHE)	-0.13	+0.82
Ideal pH:	4-7	3
Natural Substrates	Glucose, Oxygen	Lignin, Oxygen



Glucose Oxidase

Laccase

Other enzymes (e.g. O_2-reducing copper oxidases)

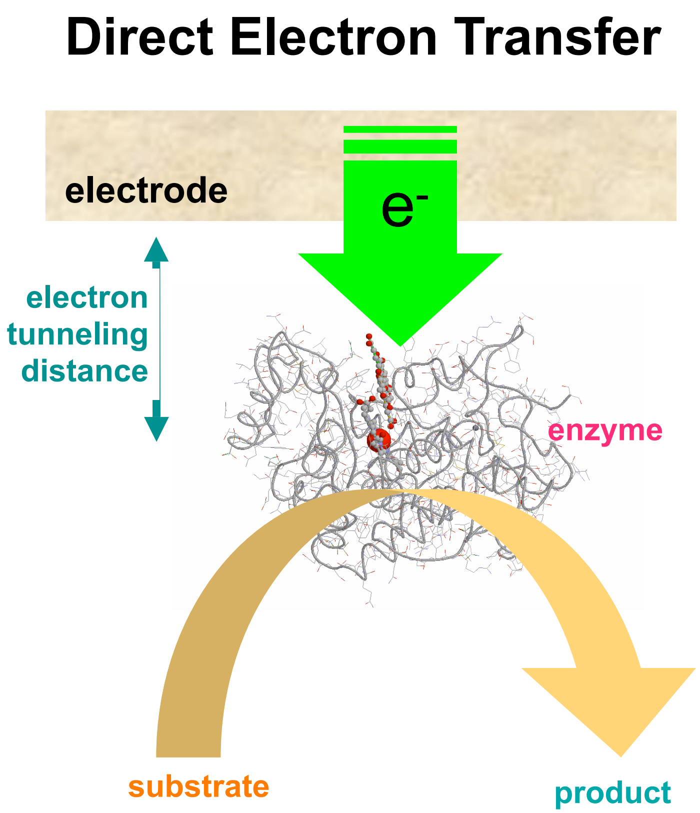
Table 1. Redox Potentials of T1 Copper Site in Some Copper-Containing Enzymes (E^0 in mV vs SHE) and the pH at Which It Was Estalished[92]

enzyme	E^0, mV (pH)	enzyme	E^0, mV (pH)
Laccases		Ascorbate Oxidase	
Polyporus versicolor	775−785 (pH 4.0)	*Cucurbita pepo medullosa*	344 (pH 7.4)
Polyporus pinsitus	760−790 (pH 4.0)	*Cucumis sativus*	350 (pH 7.4)
Coriolus hirsutus	750−850 (pH 4.0)		
Rhizoctonia solani	680−730 (pH 4.0)	Ceruloplasmin	
Trametes versicolor	780−800 (pH 4.0)	human I	490−580 (pH 7.4)
Pycnoporus cinnabarinus	740−760 (pH 7.0)	bovine	370−390 (pH 7.4)
Myrothecium verrucaria	480−490 (pH 7.4)		
Scytalidium thermophilum	480−530 (pH 7.0)	Bilirubin Oxidase	
Rhus Vernicifera	394−434 (pH 7.0)	*Myceliophthora thermophila*	450−480 (pH 7.0)

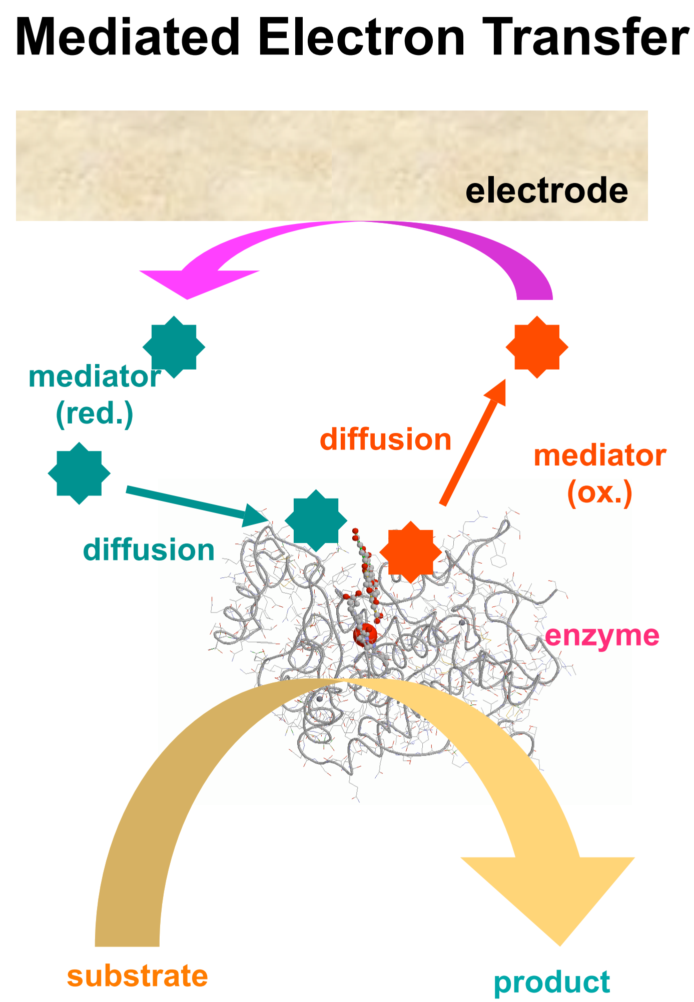
E. I. Solomon, U. M. Sundaram and T. E. Machonkin, Chem. Rev., 96, 2563-2605 (1996).

Mediated oxygen cathodes

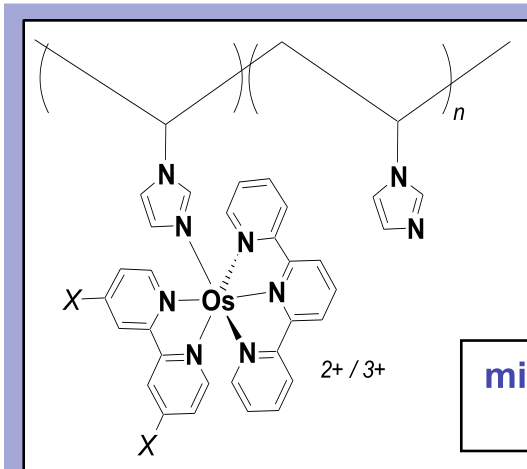
Electron Transfer Mechanisms



A. L. Ghindilis et al., *Electroanalysis* **1997**, *9*, 661.



Redox polymer mediators



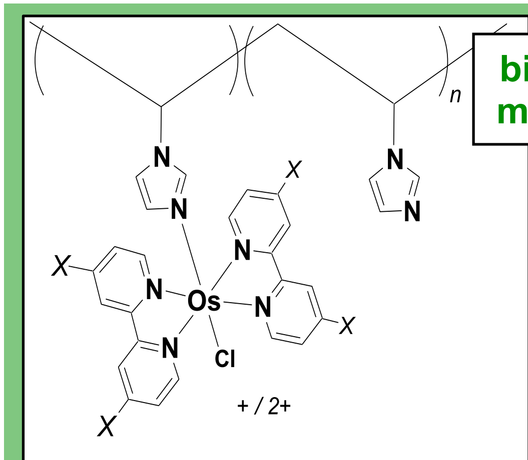
mixed chelate, bivalent

2D ***X* = Cl** 5.5% Os
$E_{1/2}$ = 0.95 V (*SHE*) (theoretical)

2C ***X* = H** *n* = 15, 9.2% Os
$E_{1/2}$ = 0.823 V (*SHE*)

2B ***X* = CH_3** *n* = 22, 6.6% Os
$E_{1/2}$ = 0.775 V (*SHE*)

2A ***X* = OCH_3** *n* = 28, 5.6% Os
$E_{1/2}$ = 0.687 V (*SHE*)



bis chelate, monovalent

1D ***X* = Cl**
$E_{1/2}$ = 0.54 V (*SHE*) (theoretical)

1C ***X* = H** 11% Os
$E_{1/2}$ = 0.43 V (*SHE*)

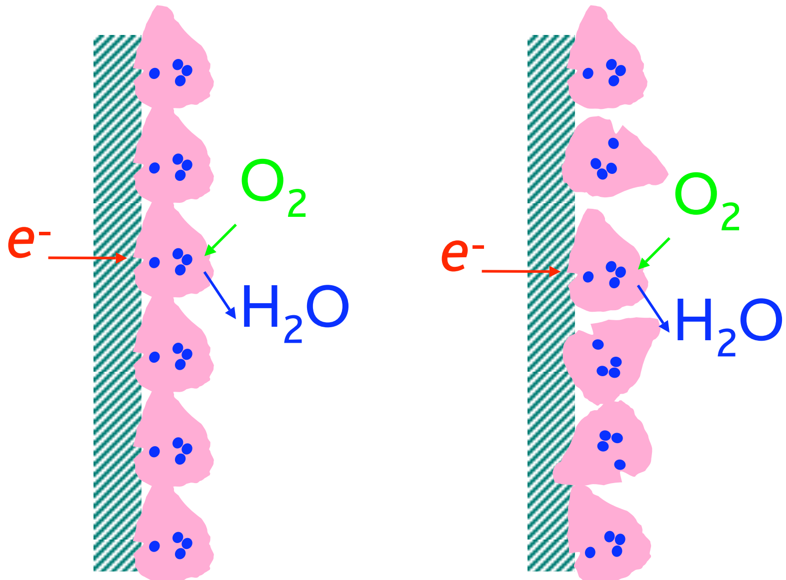
1B ***X* = CH_3** *n* = 24, 6.5% Os
$E_{1/2}$ = 0.41 V (*SHE*)

1A ***X* = OCH_3** 2.6% Os
$E_{1/2}$ = 0.11 V (*SHE*)
Partially quaternized

High Potential

Low potential

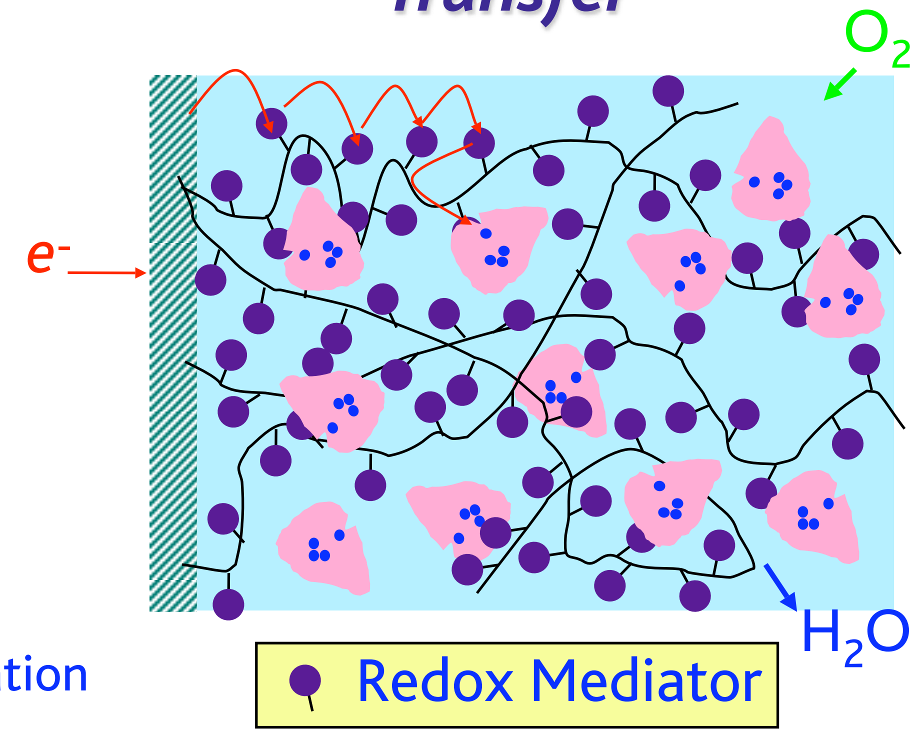
Direct Electron Transfer



Uniform Orientation (Active)

Random Orientation (Less Active)

Mediated Electron Transfer

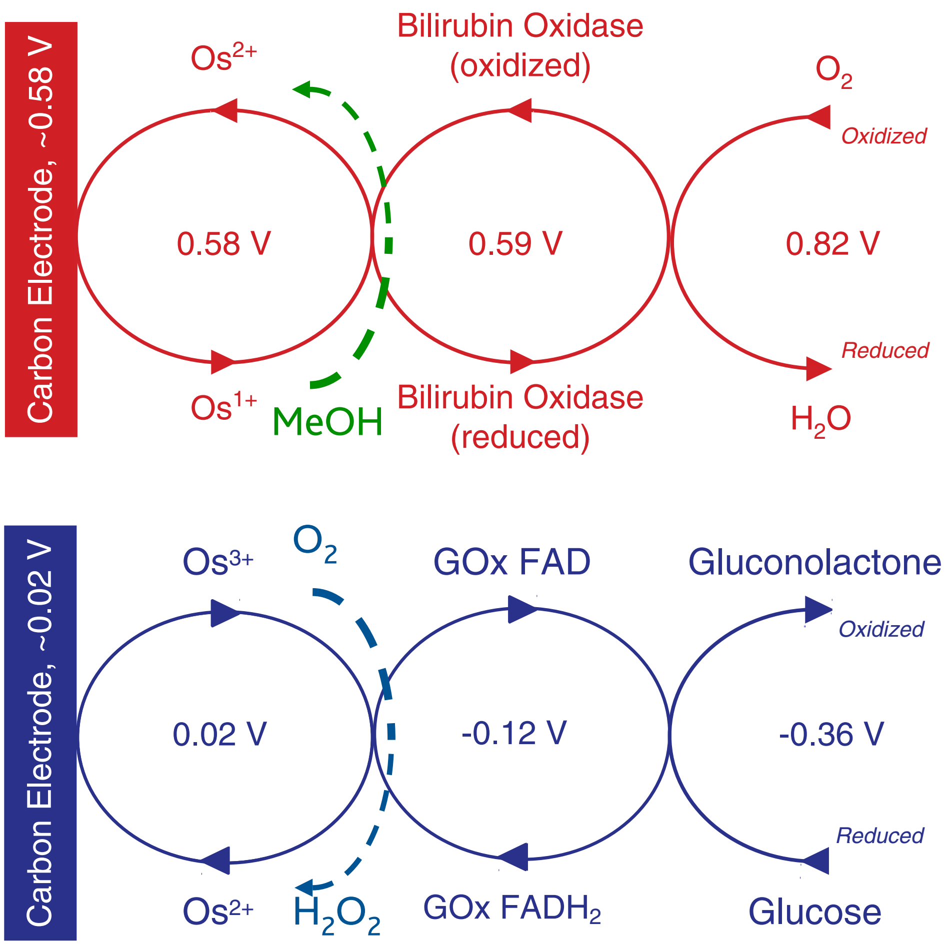


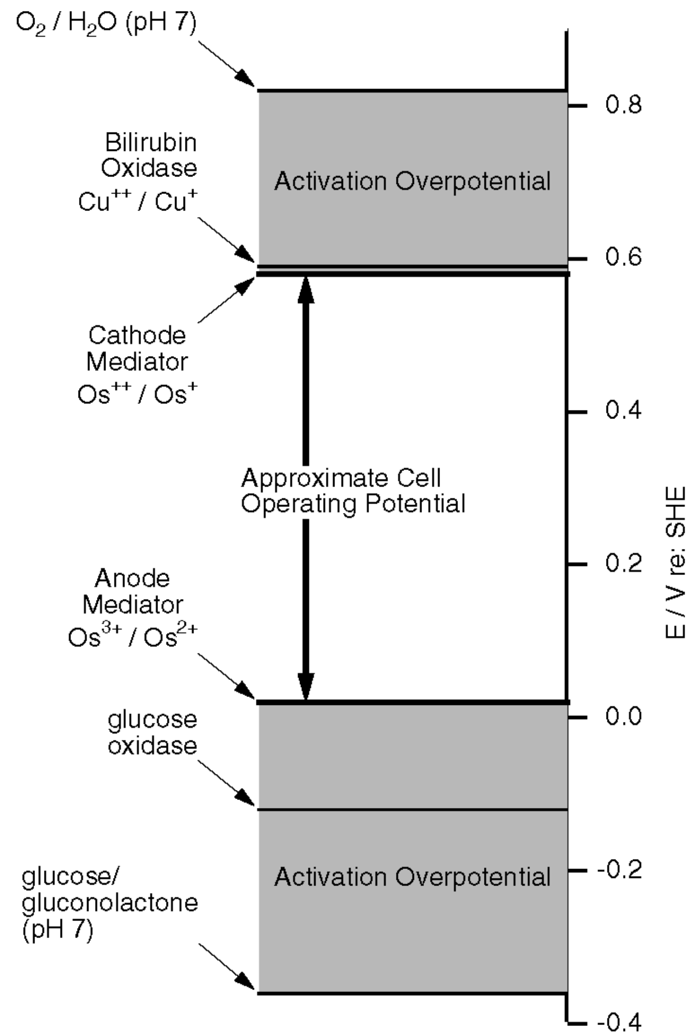
- Orientation independent
- Transport limited
  - » Electrons
  - » Substrate (O_2).

Structure of a laccase*

*Hakulinen N, et al., Nature Struct. Biol. **9** (2002) 601-605.

Effect of Mediator Redox Potential



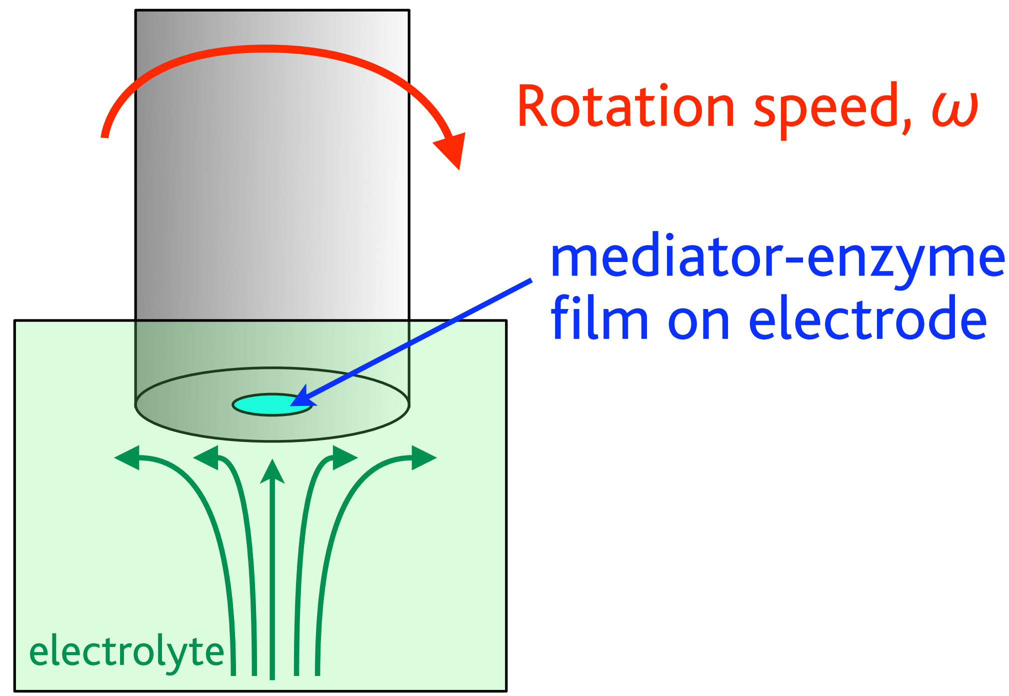


S. A. Calabrese Barton, J. Gallaway, and P. Atanassov, *Chemical Reviews*, **November, 2004**.

Rotating Disk Electrode (RDE) Studies

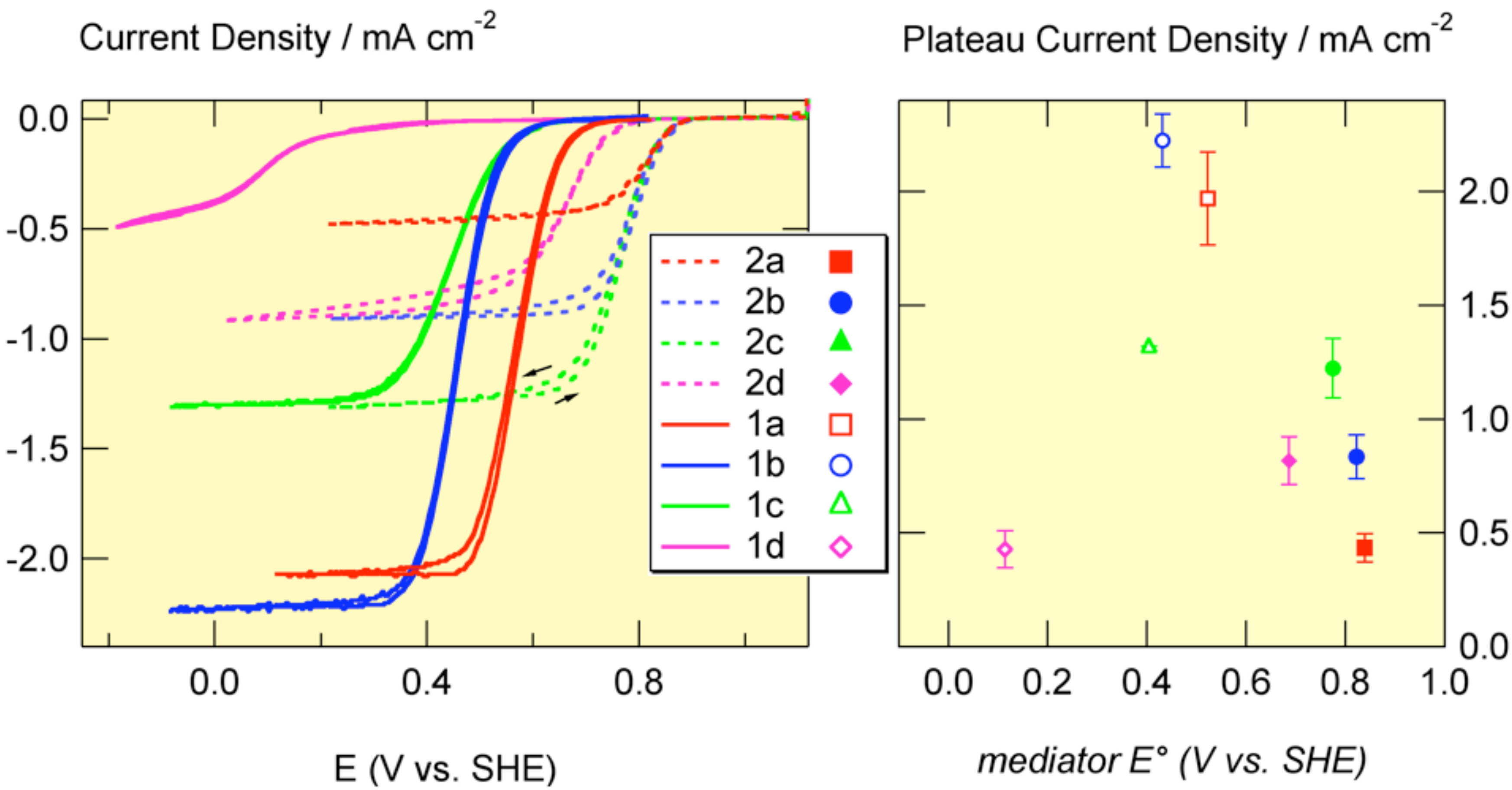
- Allows control of mass transfer in bulk electrolyte ($i_{lim} \propto \omega^{1/2}$)
- Film kinetics, i_{kin} can be isolated by

$$\frac{1}{i_{obs}} = \frac{1}{i_{kin}} + \frac{1}{i_{lim}}$$



"Steady-State" Polarization

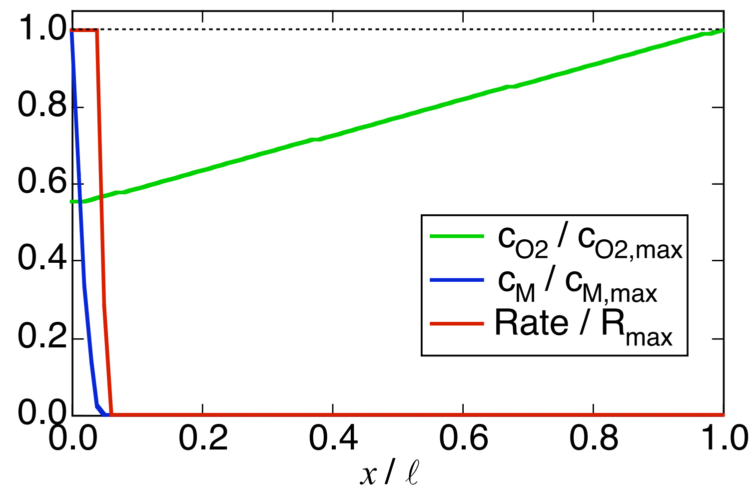
1 mV/s scan rate, 100 mM pH 4 citrate buffer, O_2-saturated, 40°C , 900 rpm rotation



Transport Model of Enzyme-Mediator Film

- Reaction rate within film limited by
  - mediator electrode kinetics
  - electron transport (mediated)
  - reactant (O2) transport.
  - Enzyme kinetics

$$R = \frac{k_{cat}E}{1 + \frac{K_M}{M_{red}} + \frac{K_S}{S}}$$



- Experimentally obtain mediator transport parameter (D_{app})
- Use 1D reaction-diffusion model to extract kinetic parameters (k_{cat}/K_M)

P. N. Bartlett, and K. F. E. Pratt, *J. Electroanal. Chem.* 1995, 397, 61-78.

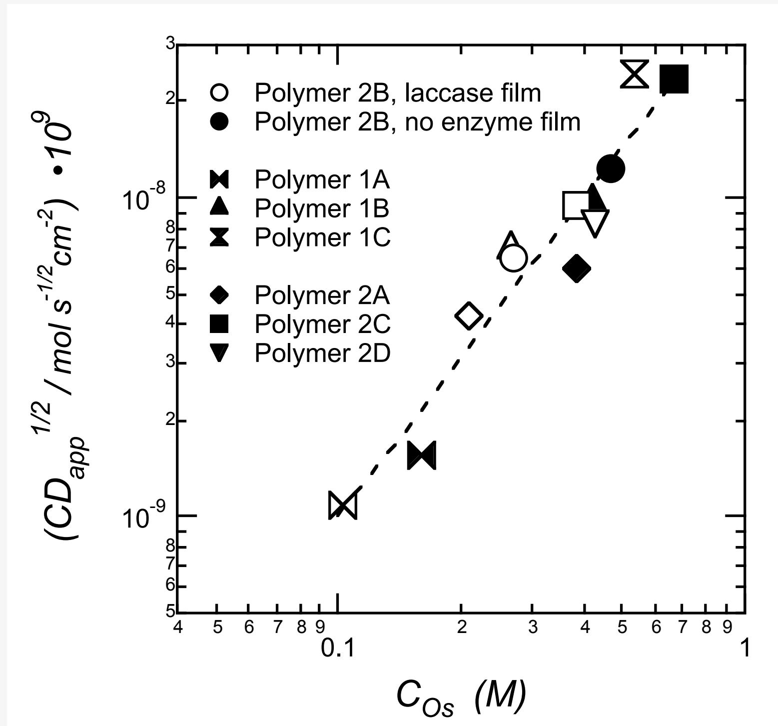
Osmium Loading and Charge Transport via Diffusion

Expression for charge transport when redox species are bound to supramolecular structure, yet not strictly immobile (*bounded diffusion model*):

$$D_{app} = \frac{1}{6} k_{ex} (\delta^2 + 3\lambda^2) C$$

For the redox polymer series, osmium loading determines charge transport.

$CD_{app}^{1/2}$ determined by Cottrell Potential Step Experiments

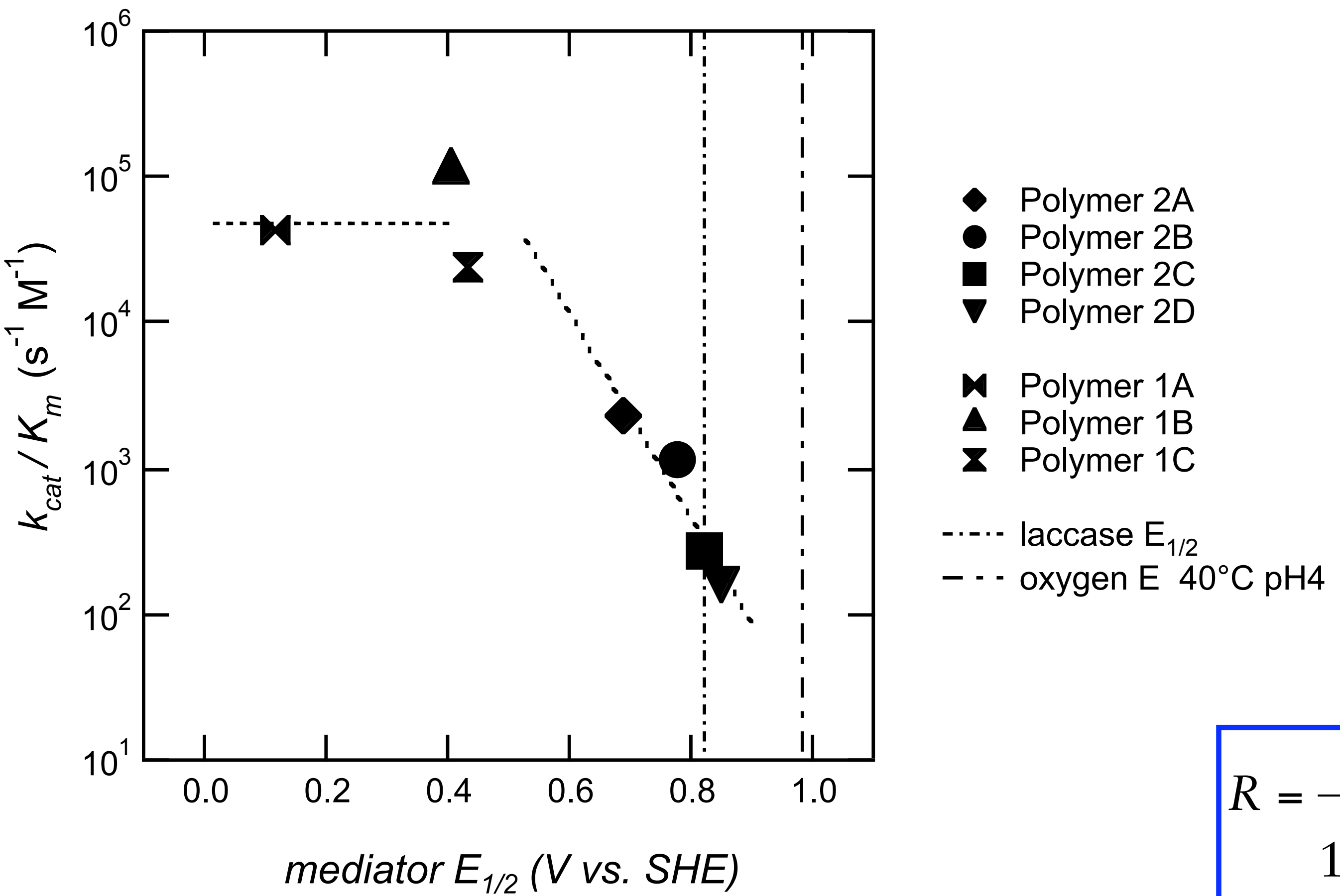


Blauch, D.N., et al. *J Am. Chem. Soc.* 1992, 114, 3323-3332.

Expected concentration dependence

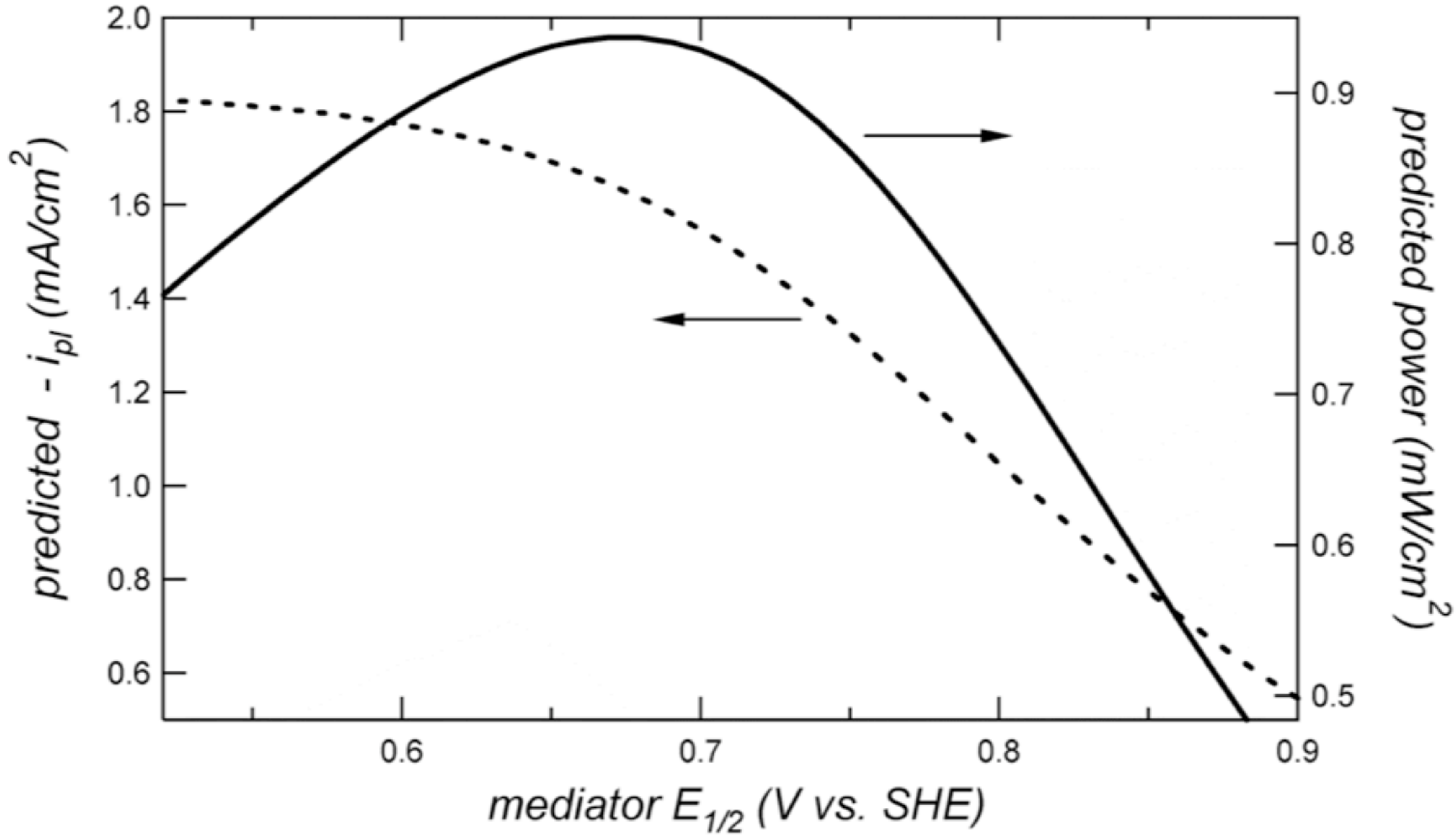
Kinetics of Mediated Electron Transfer

Study of the Kinetic Mechanism of Mediator/Enzyme Interactions



$$R = \frac{k_{cat}E}{1 + \frac{K_M}{M_{red}} + \frac{K_S}{S}}$$

Mediator Potential and Cell Power
(SHE anode assumed)

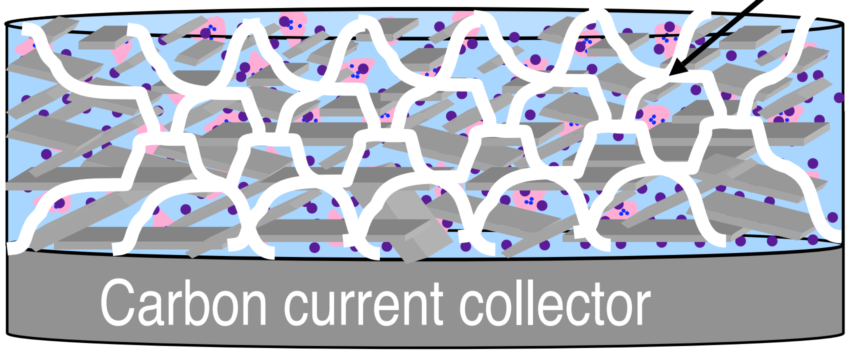


Mediator Summary

- Key parameters in redox polymer hydrogel mediator design
  - » Redox potential
  - » Redox center loading
  - » Polymer charge
- Raw catalytic current density controlled significantly by mediated electron transport in turn controlled by redox center loading.
- Kinetics of electrocatalyzed oxygen reduction controlled by mediator redox potential
  - » relatively low overpotential (~200 mV) required for maximum catalytic rate.

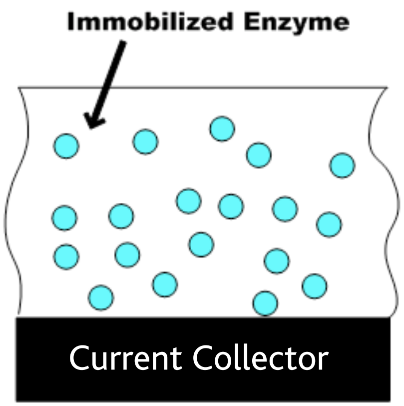
Paths to higher power density

- Enhanced electron transport
  - ★ Mediator design
  - ★ Carbon supports
- Enhanced species transport
  - » Gas diffusion

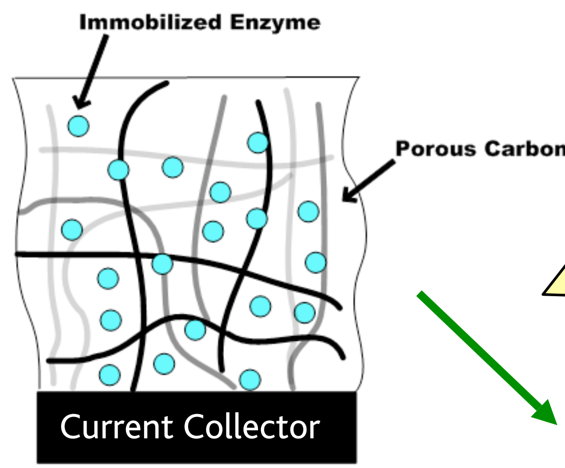


Multiscale Carbon Supports

Glassy carbon film



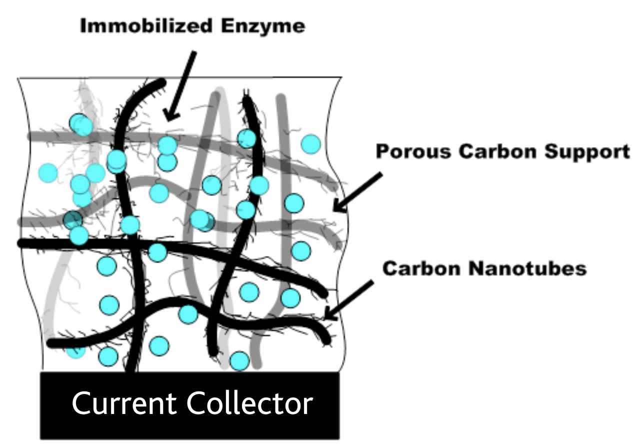
Carbon paper composite



This work:
100x increase in surface area
10x increase in current density vs. carbon paper†

50x increase in electrode surface area, 5x increase in current density compared to glassy carbon.

S.C. Barton et al., JACS 123, 5802 (2001).
S.C. Barton et al., J Phys Chem B 105, 11917 (2001).



Multiscale carbon composite

†S. Calabrese Barton, Y. Sun, B. Chandra, S. White, and J. Hone, *Electrochem. Solid State Letts*. **10**(5) (2007).

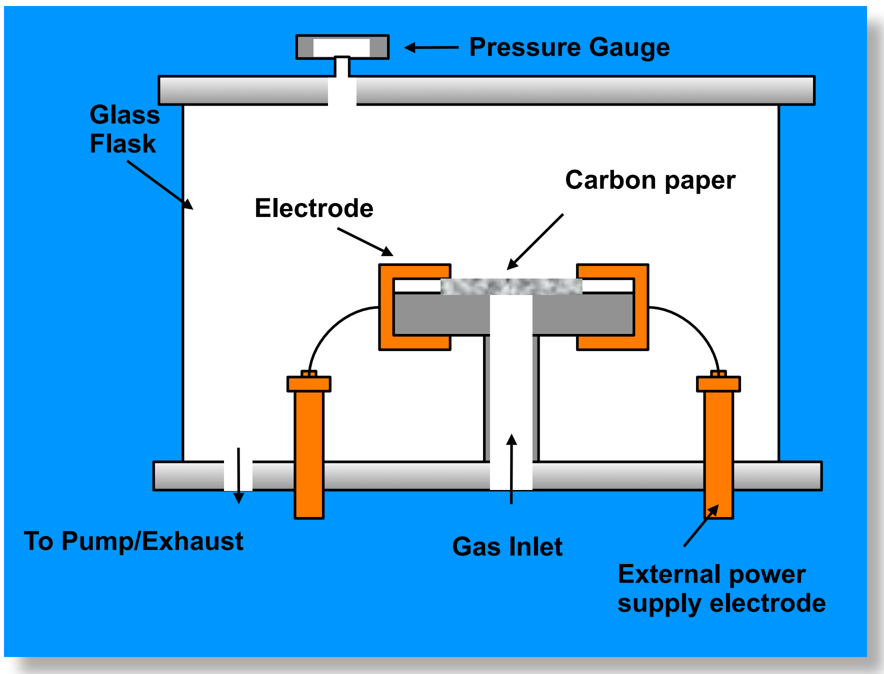
Multiscale Carbon Supports

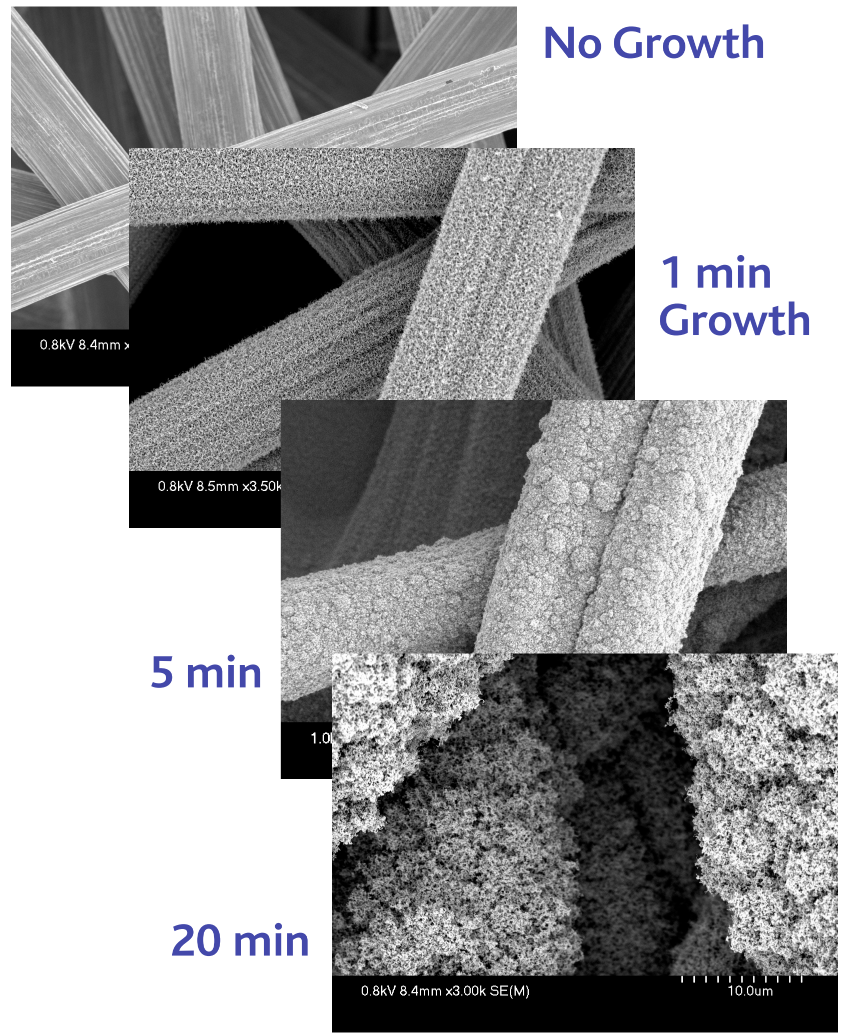
Material	Carbon paper	Nanotubes
Surface area	Low	High
Sizes of pores and fibers	Large	Small
Structural stability	Excellent	Poor

Opportunity: Create multiscale carbon structures to obtain **combination** of

★catalytic activity (nanoscale)
★species transport (macroscale).

Multiwall Nanotube Growth by CVD on Ohmically-heated Carbon Paper





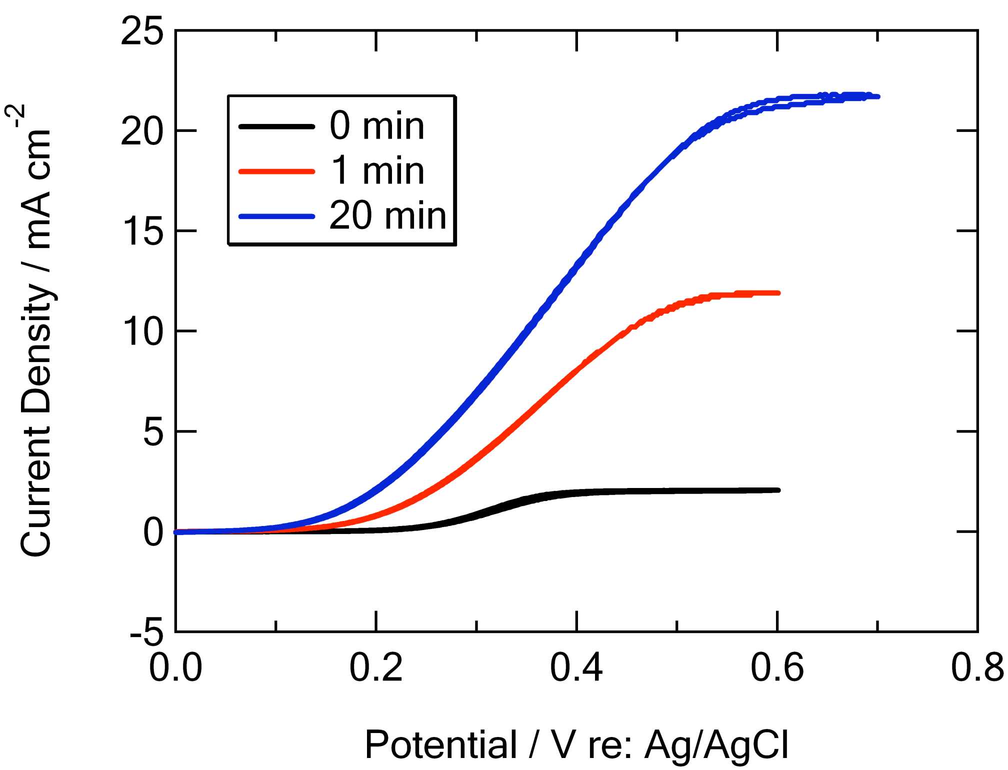
Feed: CO, H_2

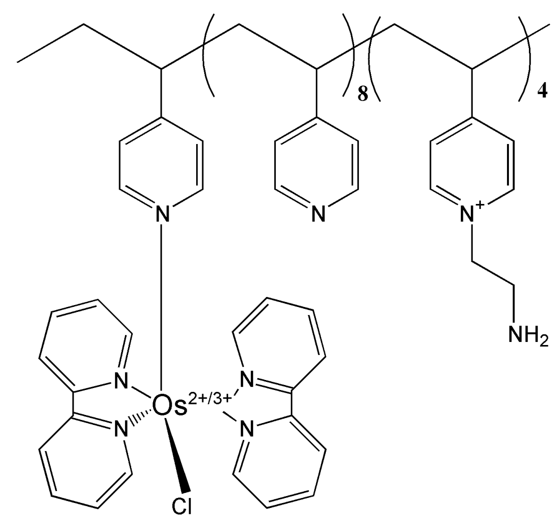
Catalyst: Fe nano-particle (diameter 1-5 nm)

J. Hone, M. Llaguno, M. Biercuk, A. Johnson, B. Batlogg, Z. Benes, J. Fischer, *Applied Physics A*, **74** (2002), 339.

X. Sun, B. Stansfield, J. Dodelet, and S. Desilets, *Chemical Physics*, **363** (2002), 415.

Polarization of a Glucose Oxidase Anode





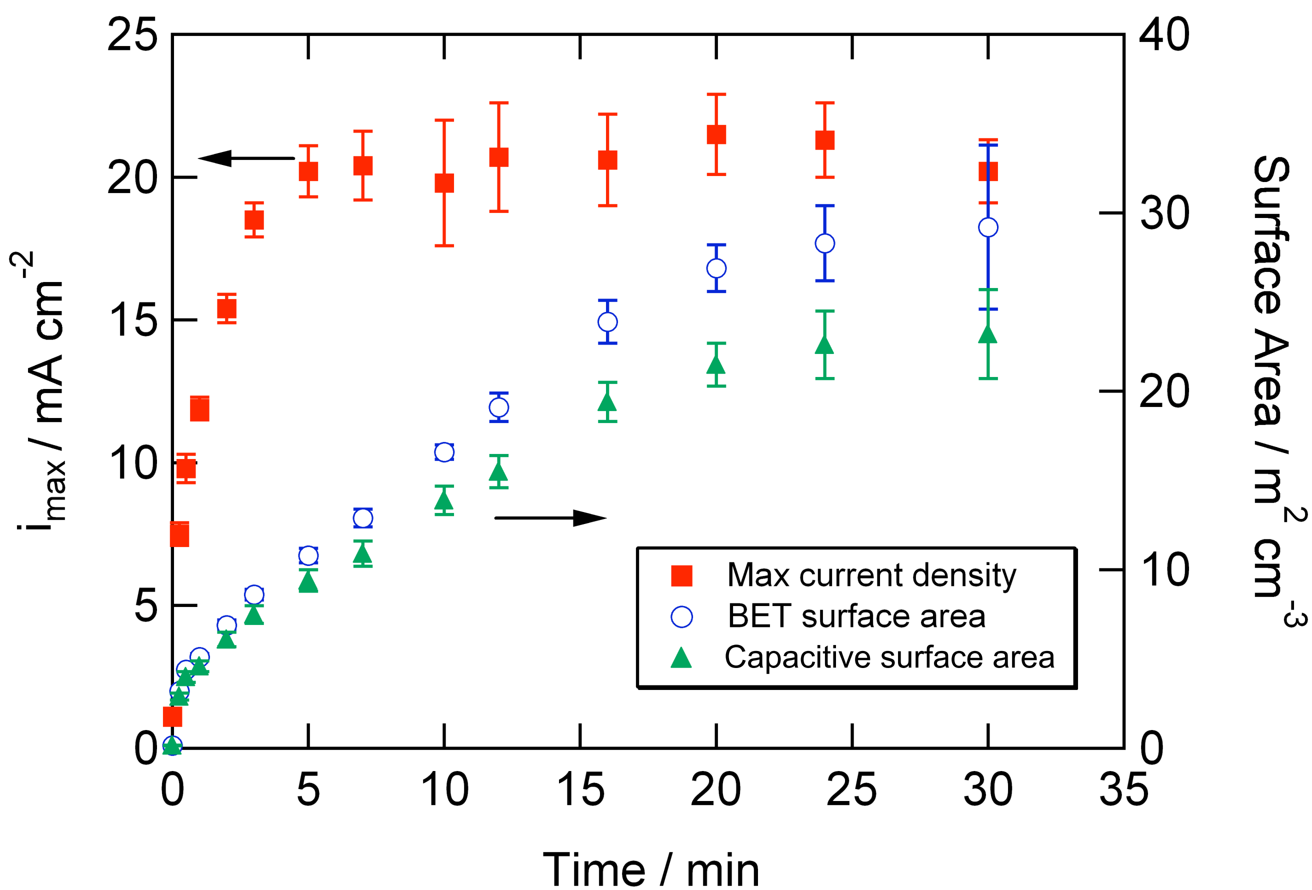
PVP-$[Os(bpy)_2Cl]^{+/2+}$,

Redox potential 0.29 V re: Ag/AgCl

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

50 mM glucose, in pH 7.1 PBS buffer at 37.5 °C under N_2, rotation speed 4000 rpm, 1 mV/s scan rate.

Effect of NT Growth Time

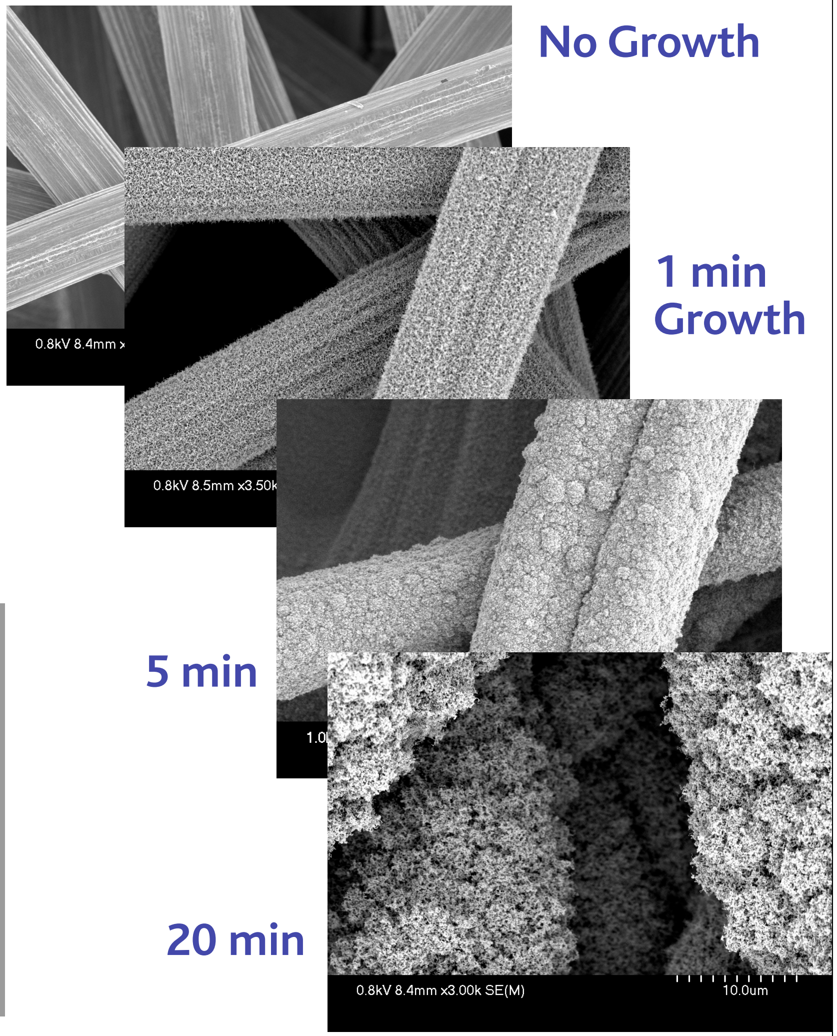


NT growth catalyzed with ohmic heating 90 μm thick carbon paper substrate.

Limitations to Multiscale Approach

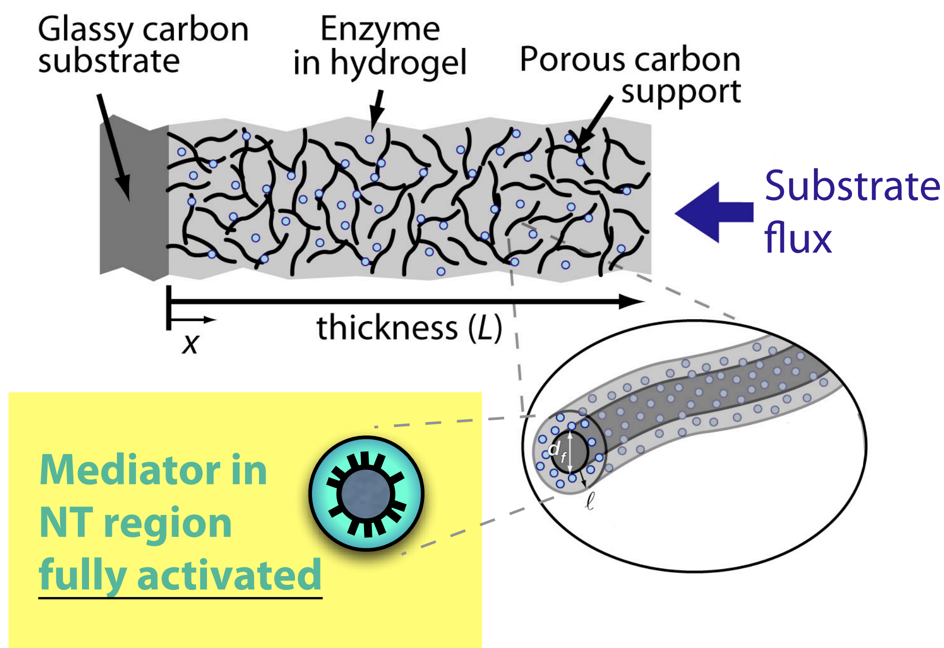
- **Catalyst Loading:**
  - Maximum loading of mediator and enzyme within NT layer controls utilization.
  - NT pore size of ~20 nm comparable to enzyme size.
  - Current **plateau** expected at large growth time.

- **Reactant Transport:**
  - NT growth reduces micron-scale porosity of carbon paper, inhibiting reactant transport.
  - Current **maximum** expected at large growth time.



Composite electrode model

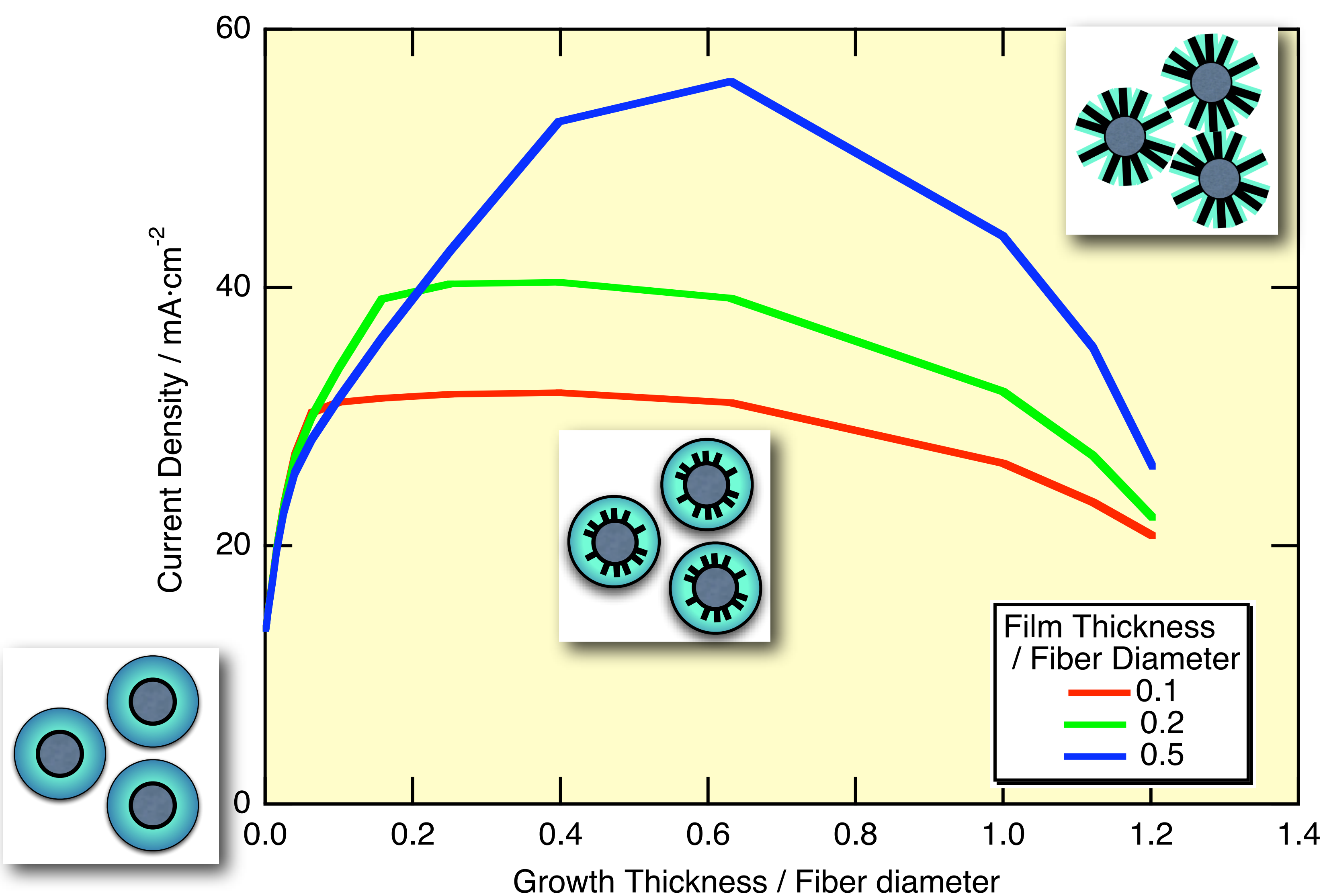
- Based on 1-D film model.[1]
- Modifications for
  - » Porous composite (solute diffusion)
  - » Reactive film (gas diffusion)[2]
- Key Geometric parameters
  - » Thickness, volume fraction, fiber diameter (SDE)
  - » Gas-phase volume fraction (GDE)



$$R = \frac{k_{cat}E}{1 + \frac{K_M}{M_{red}} + \frac{K_S}{S}}$$

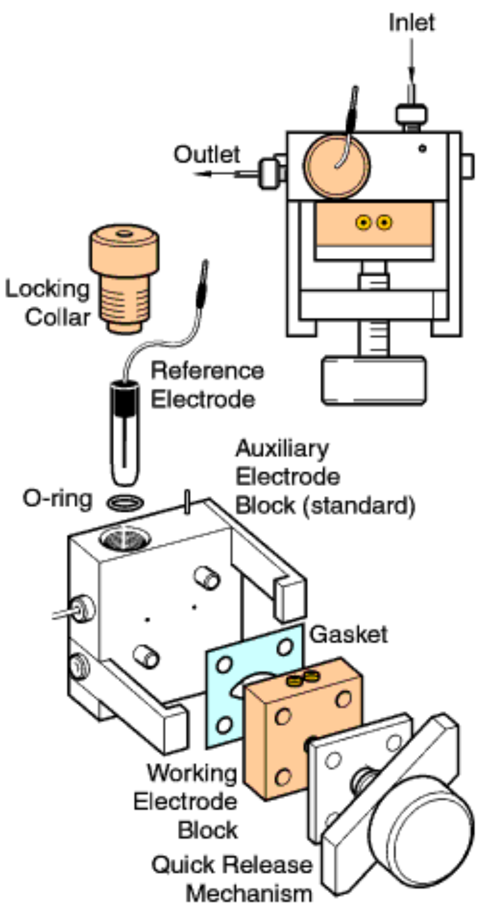
1. P. N. Bartlett and K. F. E. Pratt, *J. Electroanal. Chem.*, **397**, 61-78 (1995).
2. J. Giner and C. Hunter, *J. Electrochem. Soc.*, **116**, 1124-1130 (1969)
3. S. Calabrese Barton, Electrochim. Acta, **50**, 2145-2153 (2005).

Simulation of growth effect on electrode performance



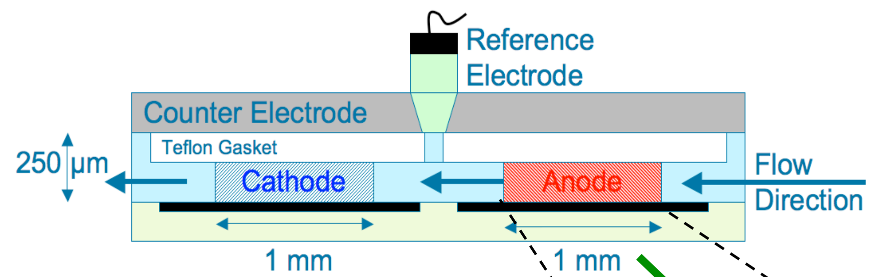
Complete Mixed-feed biofuel cell

Flow Through Biofuel Cell (BASI LCFC Flow Cell)

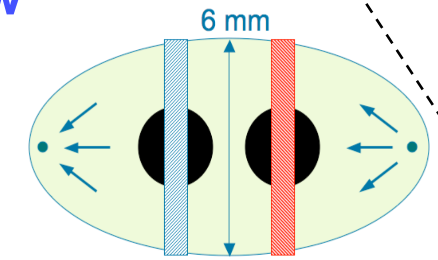


Bioanalytical Systems Inc., www.bioanalytical.com

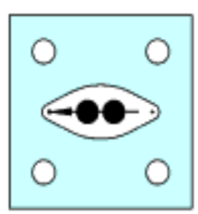
Cross Section



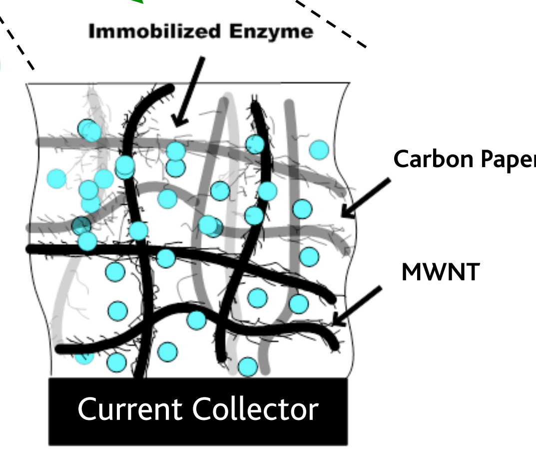
Plan View



b.

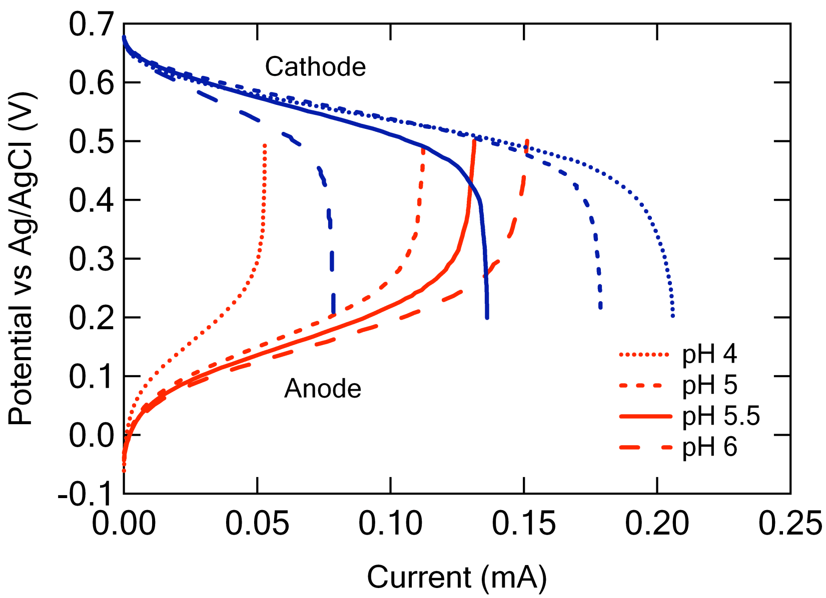


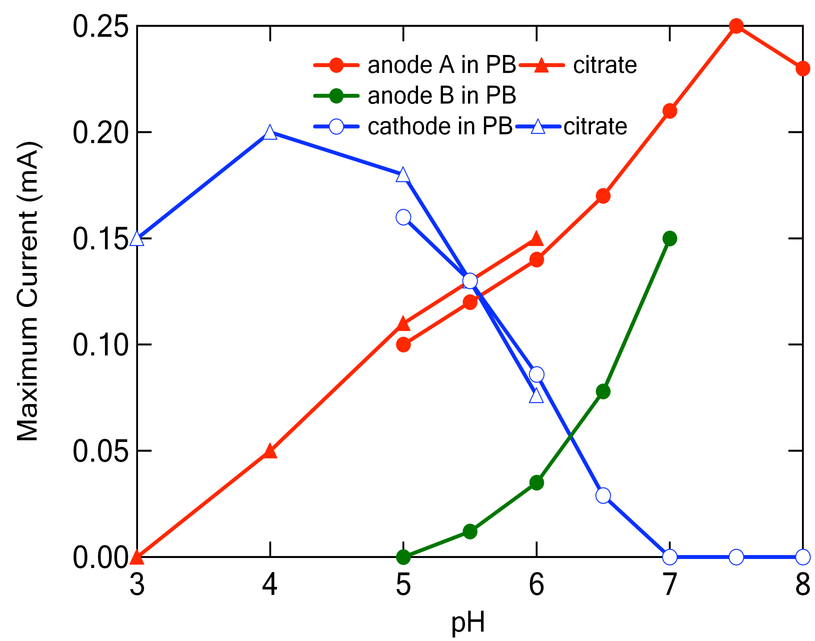
Dual, Series Crossflow



Multiscale carbon composite

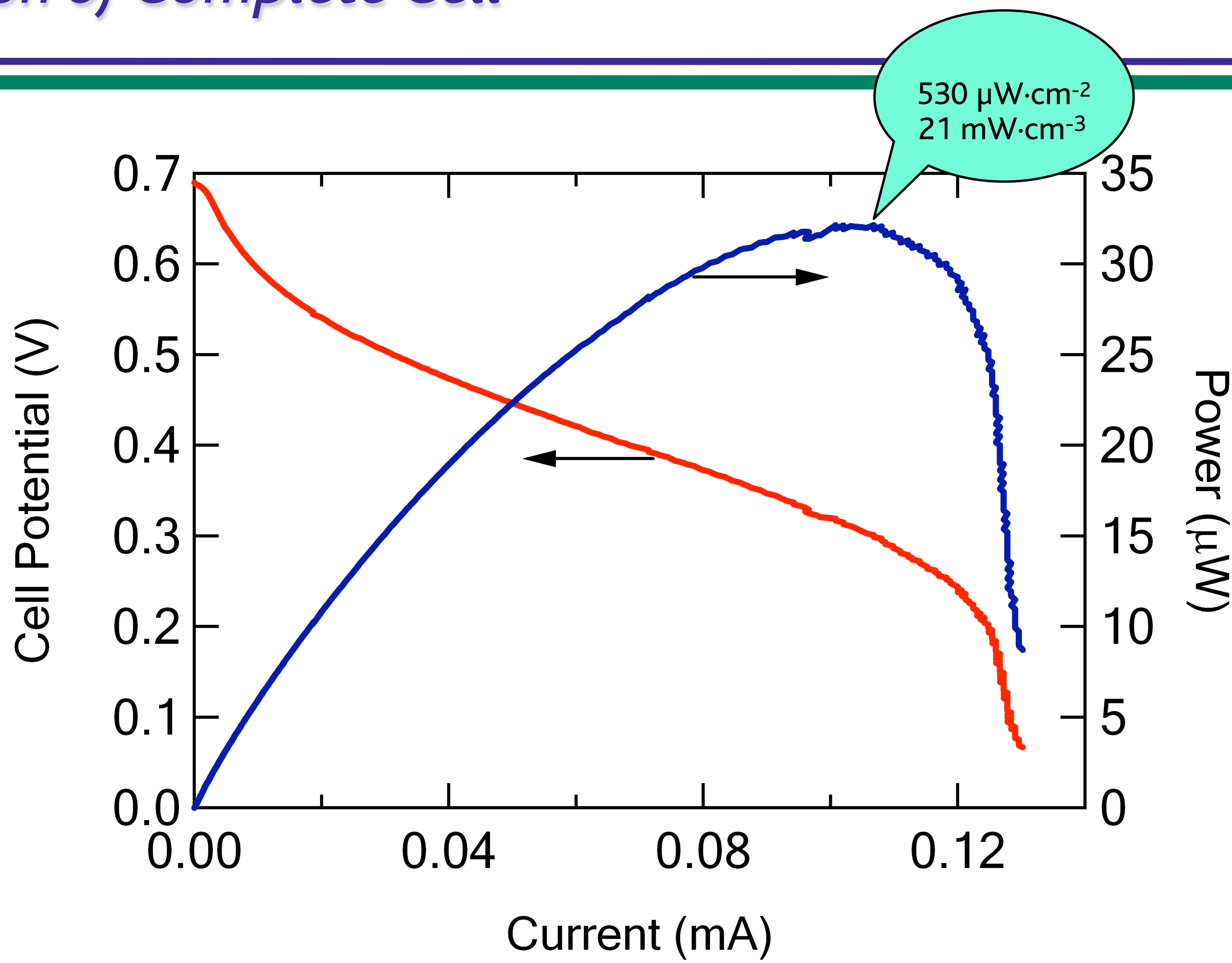
pH Dependence of Anode and Cathode





50 mM glucose, in 0.15 M buffer at 37.5 °C under air, flow rate 16 mL/min.

Polarization of Complete Cell



50 mM glucose, in 0.15 M, pH 5.5 citrate buffer at 37.5 °C under air, flow rate 16 mL/min. 6 mm × 1 mm × 0.25 mm electrode.

Conclusions

- Biofuel cells are candidate power supplies in applications where low cost, activity to ambient fuels, and selectivity can be exploited.
- Major technical hurdles (<u>activity</u>, stability) can be overcome through biochemical and <u>materials</u> approaches.
- At present, electrochemical mediators lead to systems of maximum power but introduce complicating factors.

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