Miniature Bio-fuel Cell and Zn-Ag/AgCl Battery in Physiological Condition

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Basics in Electrochemistry, Batteries, Fuel Cells,…

What is electrochemistry?

- **Branch of science relating chemical events and electricity** :
  - Electron transfer or redox reactions through electrodes
  - Conversion between chemical energy and electrical energy
  - Scientific area relating electron transfer with electrical energy, chemical conversion, and electrical signal generation

Chemical Energy, Chemical Transformation → (Galvanic) → Electrical Energy, Electrical Signal

Electrical Energy, Electrical Signal → (Electrolytic) → Chemical Energy, Chemical Transformation

Galvanic - Fuel Cells, Batteries, Corrosions
Electrolytic – Electrolysis, Refining

- **Related fields :**

  Battery, Fuel cells, Sensors, Corrosions, Deposition/Plating/Coating, Display, Solar cells, Electronics, Neurosciences, etc

Meaning of Standard Electrode Potential (E^o)

- **At more negative potential**
  - Easily oxidizable
  - Good electron donor
  - Good reducing agent
  - Good anodic material
- **At more positive potential**
  - Easily reducible
  - Good electron acceptor
  - Good oxidizing agent
  - Good cathodic material
- **Reference potential**
  - H^+/H_2 0.000
- **Compare E^os**
  - Li/Li^+, K/K^+, Na/Na^+
  - F_2/F^-, Cl_2/Cl^-, Br_2/Br^-, I_2/I^-,
  - Au, Ag, Cu

Half-reaction	E^o, V vs. NHE
$Li^+ + e^- \rightarrow Li(s)$	-3.040
$K^+ + e^- \rightarrow K(s)$	-2.924
$Na^+ + e^- \rightarrow Na(s)$	-2.713
$Al^{3+} + 3e^- \rightarrow Al(s)$	-1.676
$Zn^{2+} + 2e^- \rightarrow Zn(s)$	-0.763
$Fe^{2+} + 2e^- \rightarrow Fe(s)$	-0.440
$2H^+ + 2e^- \rightarrow H_2(g)$	0.000
$Cu^{2+} + 2e^- \rightarrow Cu(s)$	+0.340
$I_2(s) + 2e \rightarrow 2I^-$	+0.535
$Ag^+ + e^- \rightarrow Ag(s)$	+0.800
$Br_2(l) + 2e^- \rightarrow 2Br^-$	+1.065
$O_2(g) + 4H^+ + 4e^- \rightarrow 2H_2O$	+1.231
$Cl_2(g) + 2e^- \rightarrow 2Cl^-$	+1.358
$Au^+ + e^- \rightarrow Au(s)$	+1.680
$F_2(g) + 2e^- \rightarrow 2F^-$	+2.866

Battery vs. Fuel Cell

- **Battery**

  - Primary battery – Zn/MnO_2…

  - Secondary attery – Li/Li^+, $Pb/PbSO_4$

  - Chemical form of energy is contained in a case

- **Fuel Cell**

  - H_2/O_2, Classification by the kind of electrolyte -

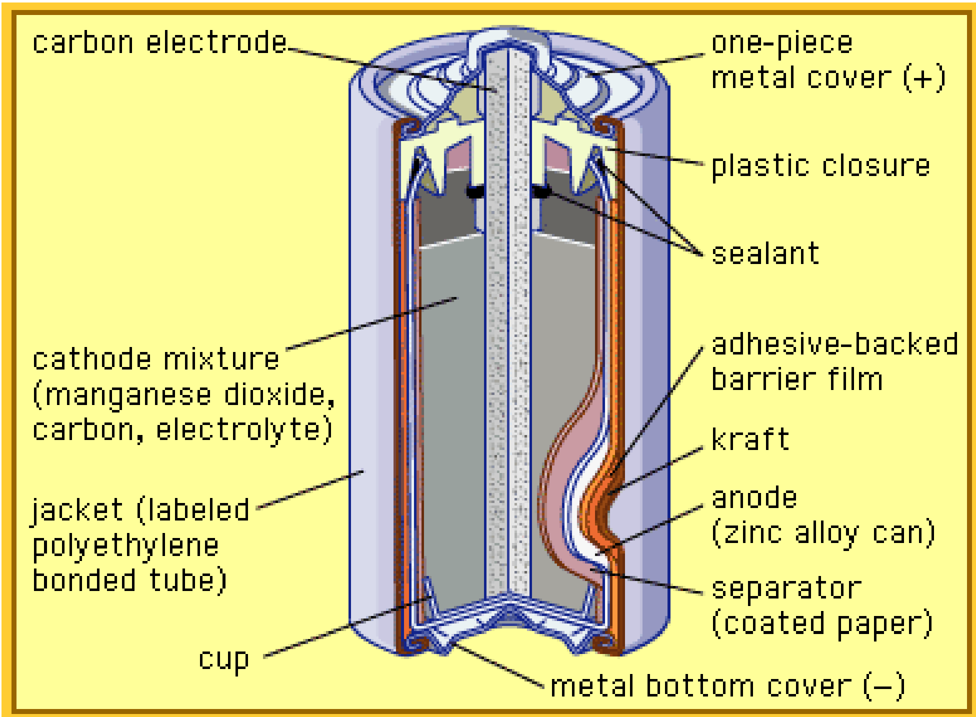
  - Other possible fuels: methanol, hydrocarbon, glucose, organic acids, biomass…

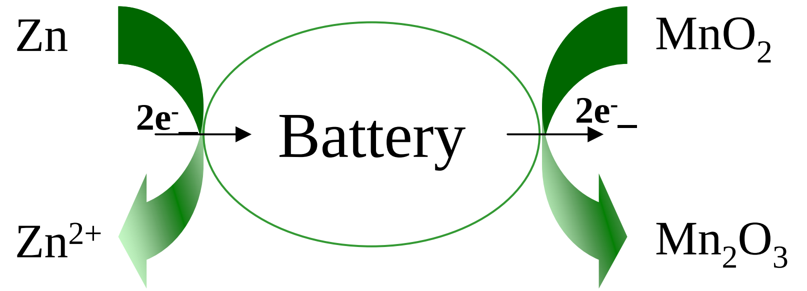
  - Chemical form of energy is supplied from outside

- **Hybrid type**

  - Hybrid type - Al/Air, Zn/Air, …

Zn-MnO_2 Battery – AA, D, …





E_a = - 0.76V

E_c = + 0.79V

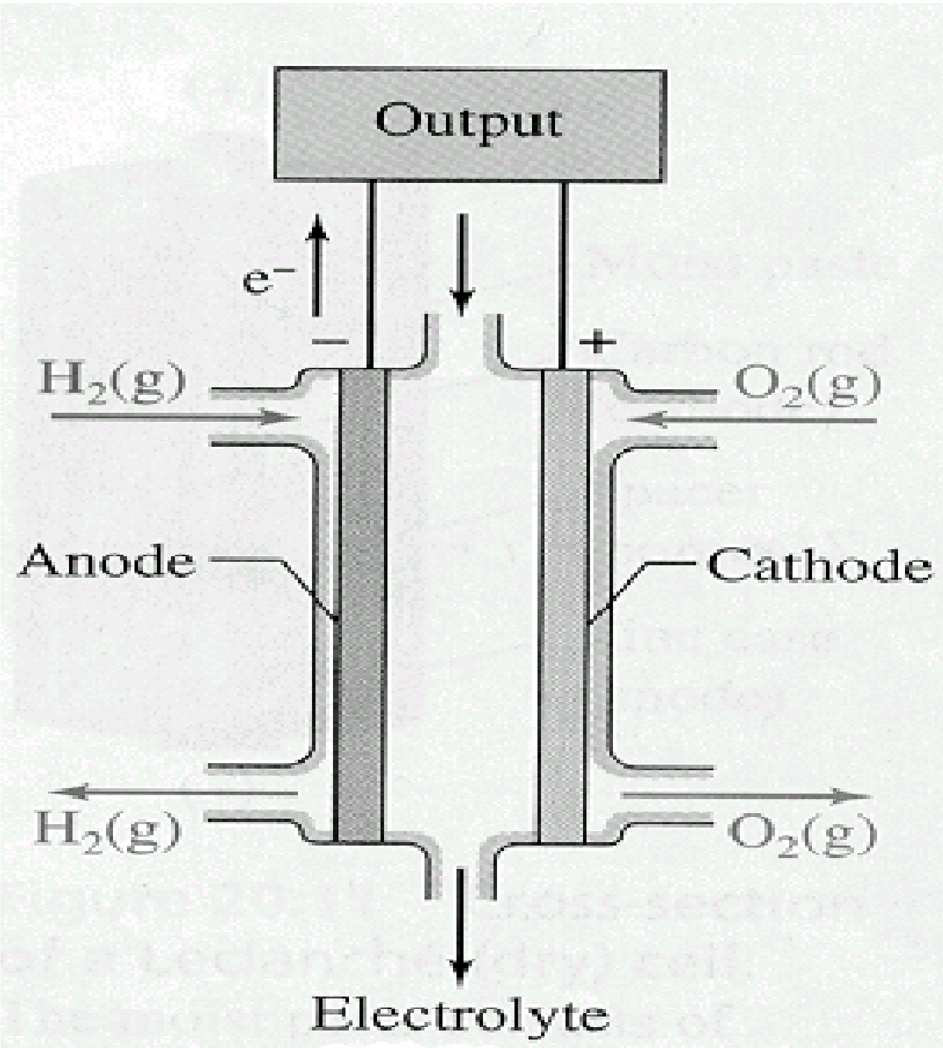
(at pH = 14.0)

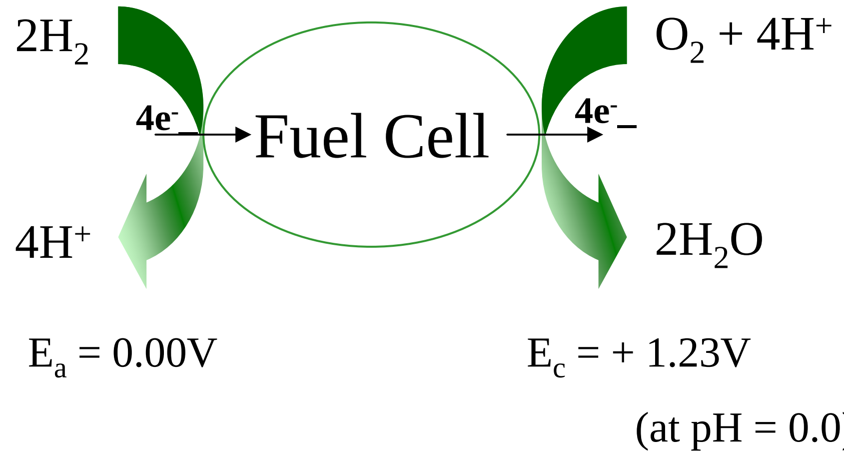
$$Zn(s) + 2OH^-(aq) \rightarrow Zn(OH)_2(s) + 2e^- \qquad E_a = -0.76\ V$$

$$2MnO_2(s) + H_2O(l) + 2e^- \rightarrow Mn_2O_3(s) + 2OH^- \qquad E_c = +0.79\ V$$

$$Zn(s) + 2MnO_2(s) + H_2O(l) \rightarrow Zn(OH)_2(s) + Mn_2O_3(s) \qquad E_{rxn} = 1.55\ V$$

H_2-O_2 Fuel Cell





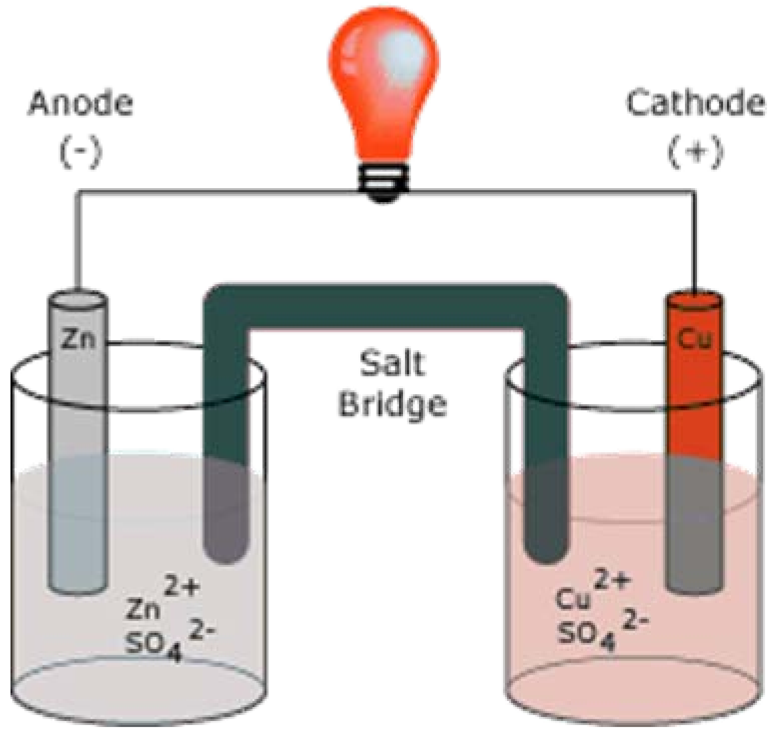
$2 \times (H_2 \rightarrow 2H^+ + 2e^-)$	$E_a = \quad 0.00\ V$
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	$E_c = +\ 1.23\ V$
$2H_2 + O_2 \rightarrow 2H_2O$	$E_{rxn} = +\ 1.23\ V$

Basic Components of Electrochemical Cells

- ❑ **Components of the cell**

  - Electrodes
    - Anode
    - Cathode
  - Solution
    - Electroactive species
    - Supporting electrolyte
    - Solvent
  - Separator
  - Wire
  - Case

(Note!) Electron transfer (or redox reaction) always accompanies ion transfer.



Daniel Cell

$Zn(s)/ZnSO_4(1\ M)//CuSO_4(1\ M)/Cu(s)$

Redox Potentials of Biologically Important Reagents and Enzymes

Redox Couple (Ox/Red)	E°' (mV vs. NHE, pH = 7.0)	Redox Couple (Ox/Red)	E°' (mV vs. NHE, pH = 7.0)
Succinate+CO_2 / α-KG	- 670	FAD / $FADH_2$	- 220
Acetate / Acetaldehyde	- 600	Pyruvate / Lactate	- 190
CO_2/formate	- 580	FMN / $FMNH_2$	- 190
CO_2/CO	- 520	Dehydro-/Ascorbate	+ 80
Gluconate/Glucose	- 440	Cytochrome c	+ 220
$2H^+$ / H_2	- 414	O_2/H_2O_2	+ 281
CO_2/CH_3OH	-380	*p*-Phenylenediamine (PPD)	+ 356
Cystine/Cysteine	- 340	L-DOPA	+ 380
$NAD(P)^+$ / NAD(P)H	- 320	Ferri / Ferrocyanide	+ 430
CO_2/acetate	- 290	ABTS (-N=N-)	+ 677
CO_2/CH_4	- 240	Laccase (*P. versicola*)	+ 780
		O_2 / H_2O	+ 820

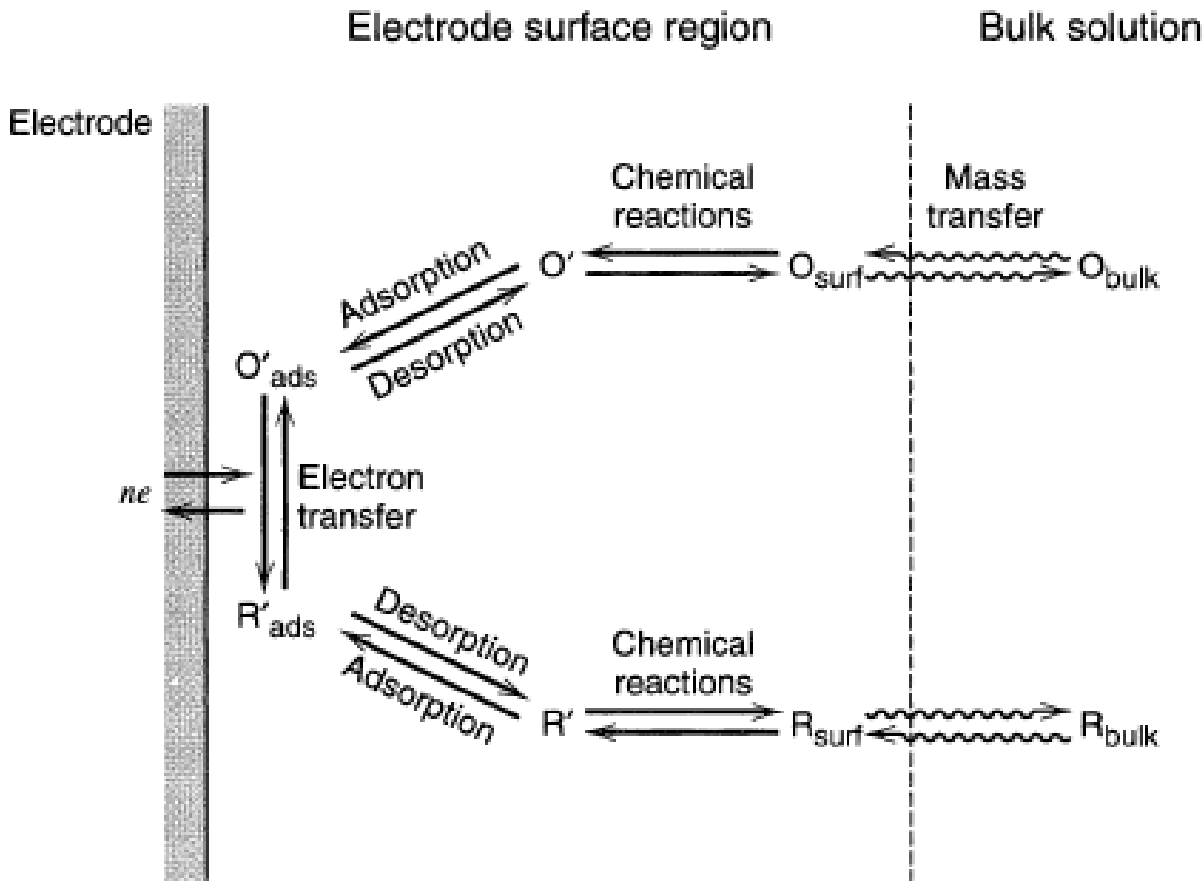
$P\ (W) = E_{cell}\ (V) \times I\ (A)$

- Power ($W = J/s = V \cdot I$)
- $E_{cell} = E_c - E_a$: Choice of E_a and E_c
- I : Electron transfer reaction rate

  (Fast ET, MT, Increase Area)

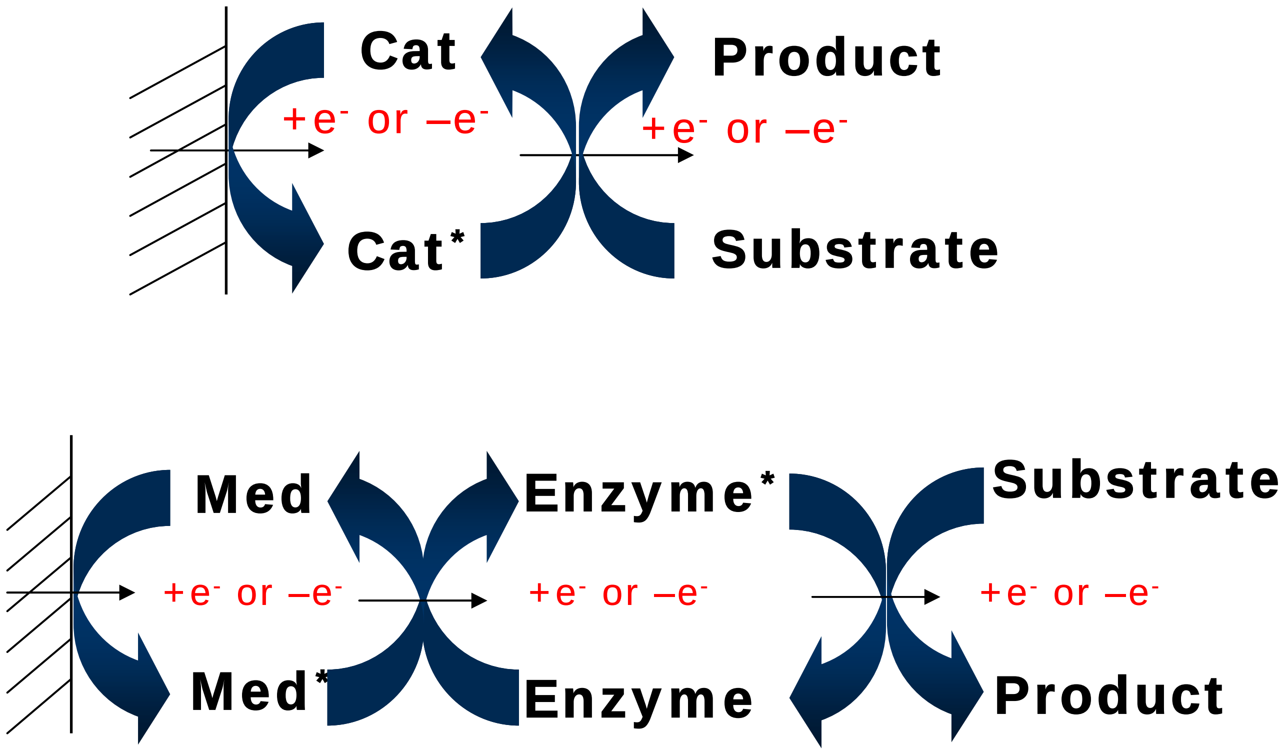
Factors Affecting Electrode Reaction Rate, i.e. Current

Electron Transfer **(Chemical Reactions)** **Mass Transfer**

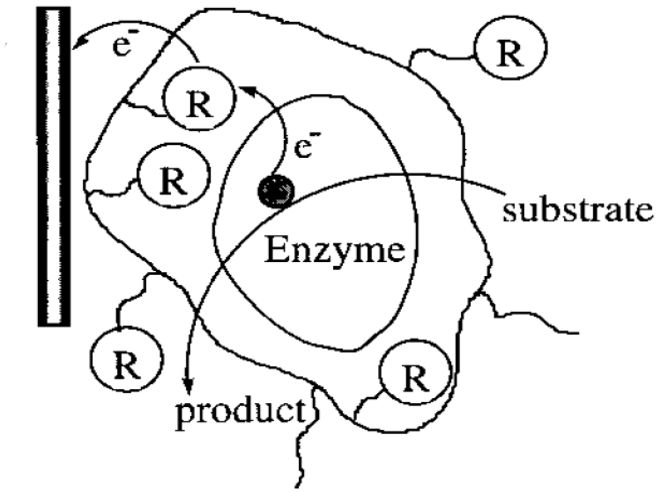


Bard & Faulkner, “Electrochemical Methods” **2000**, p. 23.

Mediated Electron Transfer (MET) vs. Direct Electron Transfer (DET)



Electrical Communication between Electrode and Enzyme - Mediated Electron Transfer by Osmium Redox Polymer



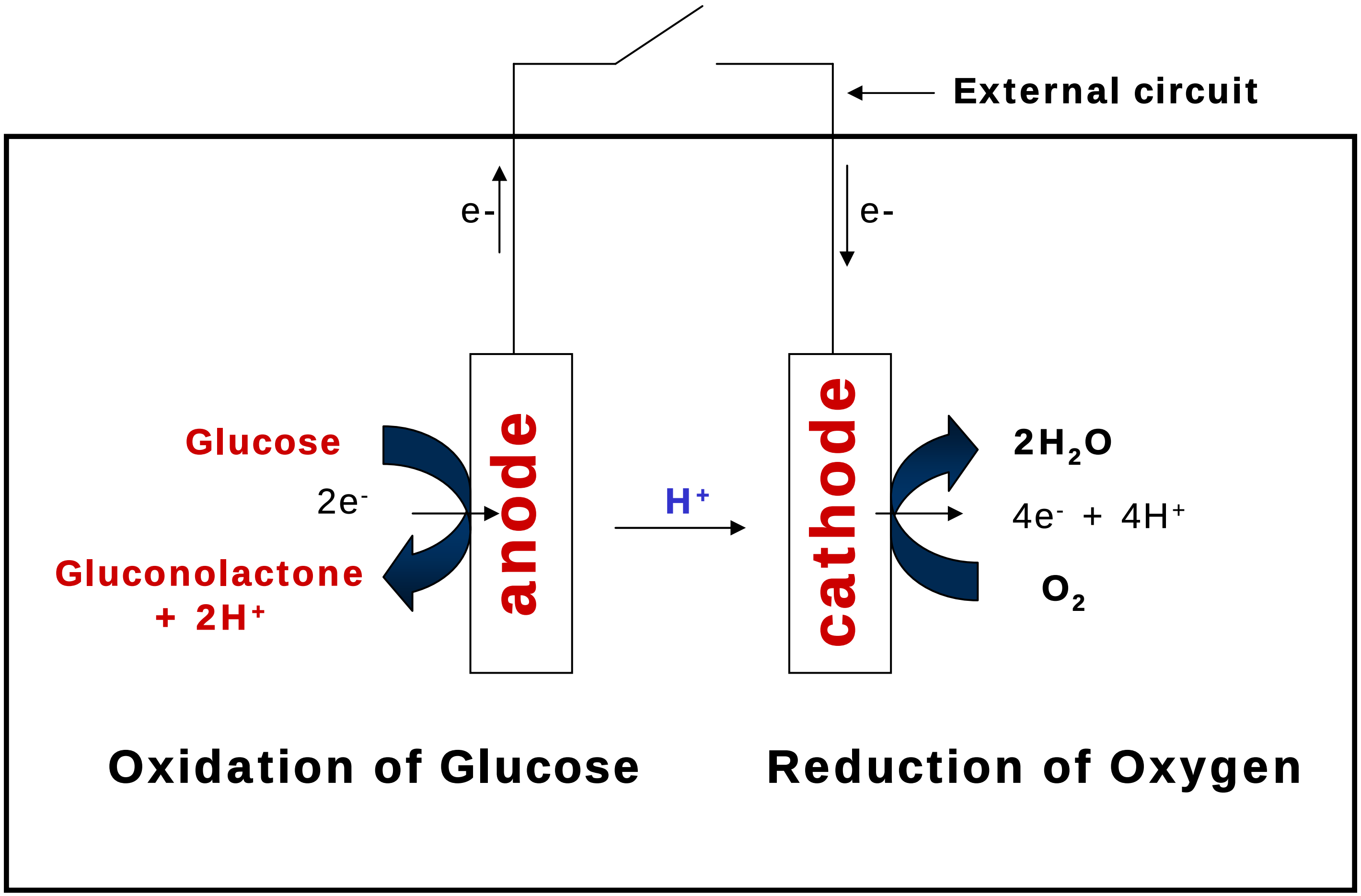
Polymer	E^0 (mV Ag / AgCl)
PVI-[Os-(diamine-bpy)$_2$Cl]	- 170
PAA-PVI-[Os(dme-py)$_2$]	+ 100
PAA-PVI-[Os(bpy)$_2$Cl]	+ 200
PVI-[Os(bpy)$_2$Cl]	+ 200
PAA-PVP-[Os(bpy)$_2$Cl]	+ 300
PAA-PVI-[Os(dCl-bpy)$_2$Cl]	+ 350
PVI-[Os(dCl-bpy)$_2$Cl]	+ 350
PVP-[Os(dCl-bpy)$_2$Cl]	+ 400
PVI-[Os(tpy)(dme-py)]	+ 550

A redox-enzyme electrically 'wired' to an electrode surface by flexible polymer chains functionalized with redox-mediator groups and surrounding the enzyme at the electrode surface.

Heller, *Acc. Chem. Res.* **1991**, *23*, 128-134.
Gao, Z.; Heller, A. *et. al.* *Angew. Chem. Int. Ed.* **2002**, *41*, 810- 813.

Glucose / O_2 Bio-fuel Cell

Glucose / O_2 Bio-fuel Cell

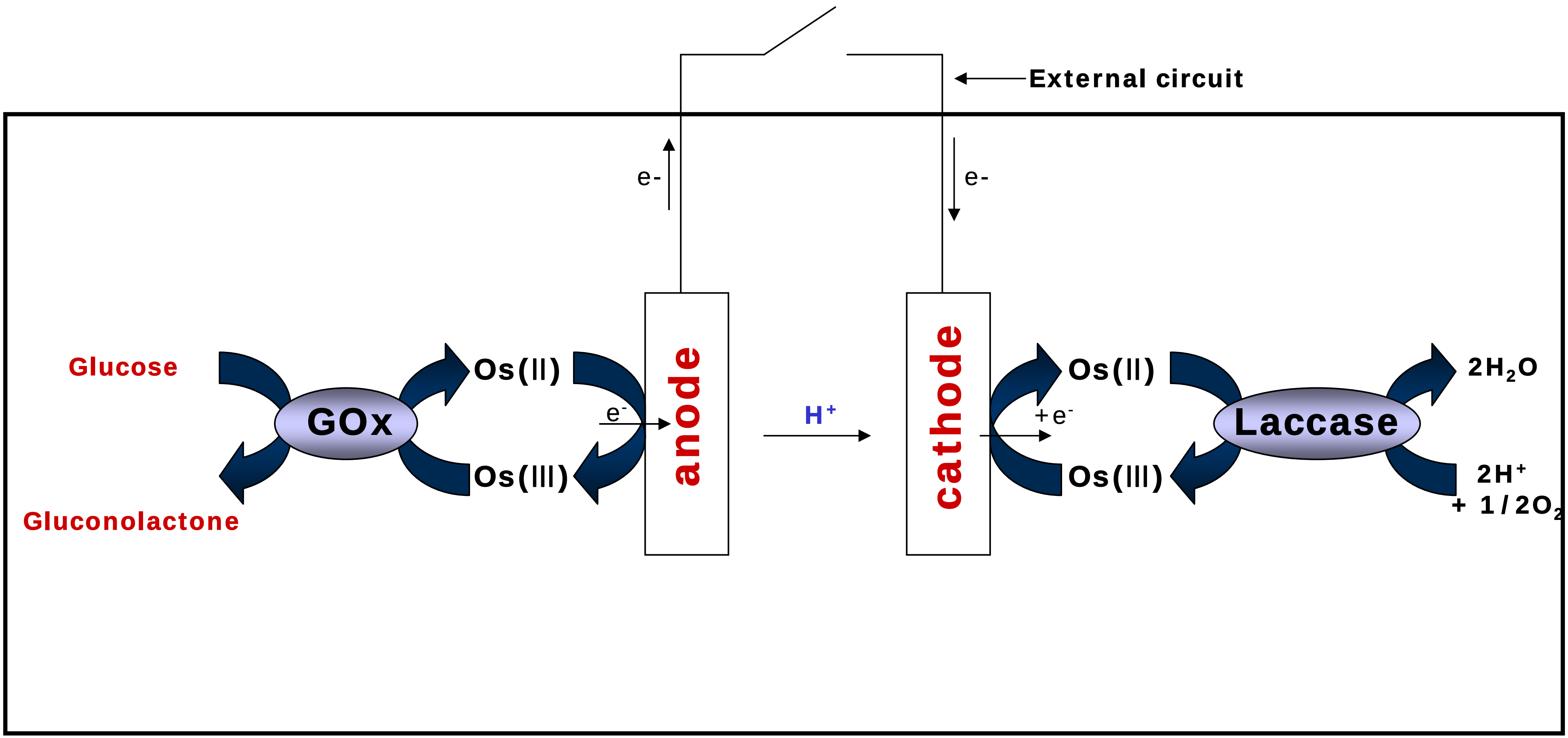


$$2 \times (\text{Glucose} + H_2O \rightarrow \text{Gluconolacone} + 2H^+ + 2e^-) \quad E_a = -0.44 \text{ V vs. NHE}$$

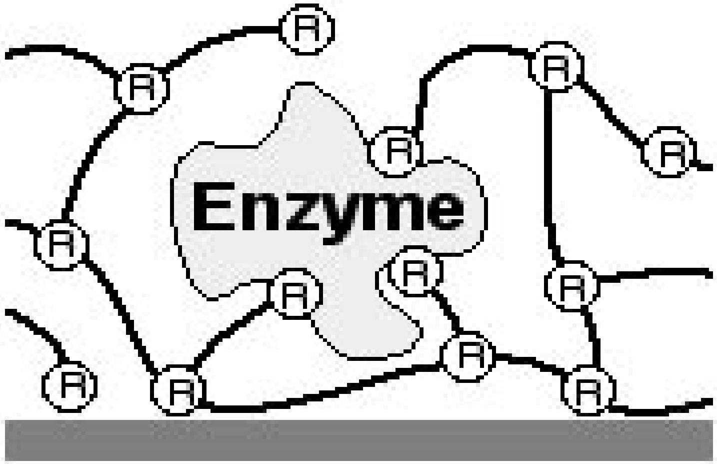
$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad E_c = +0.82 \text{ V vs. NHE}$$

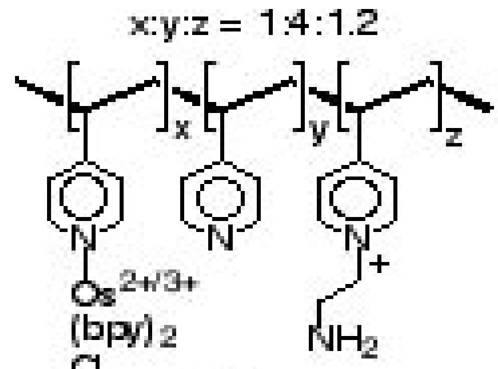
$$2 \text{ Glucose} + O_2 \rightarrow 2 \text{ Gluconolactone} \quad E_{cell} = 1.26 \text{ V}$$

Enzymes and Mediators Are Essential for Bio-fuel Cell



→ Membraneless, Caseless Possible





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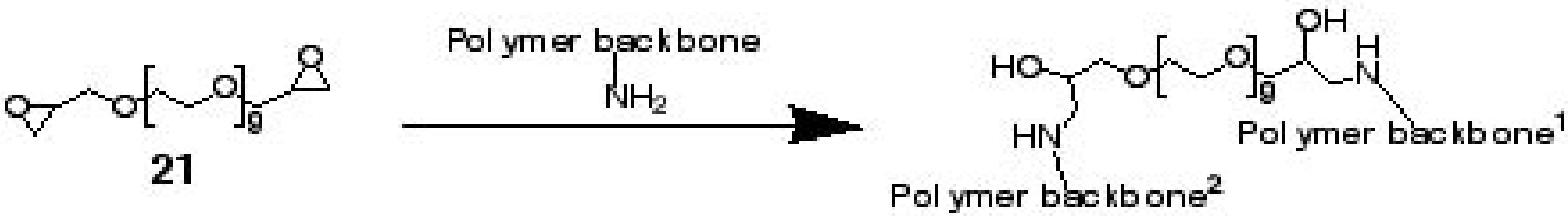
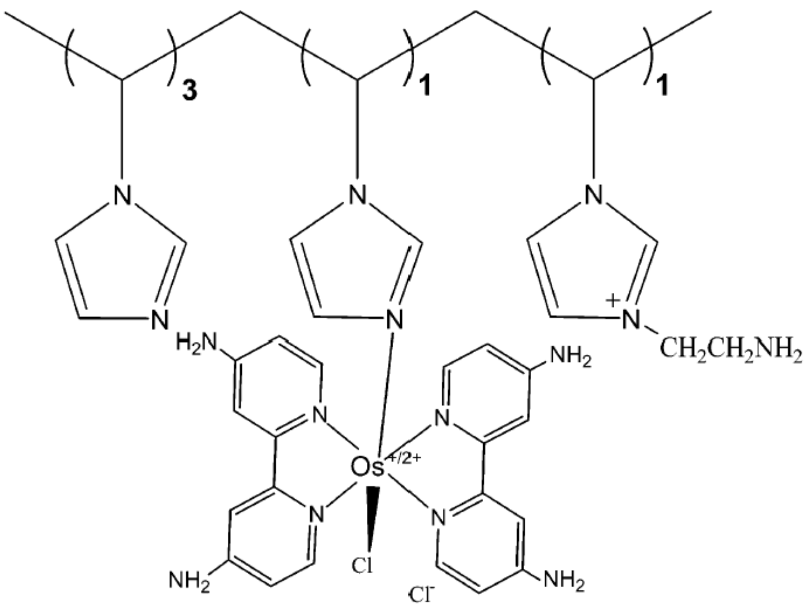


A redox-enzyme electrically 'wired' to an electrode surface by flexible polymer chains functionalized with redox-mediator groups and surrounding the enzyme at the electrode surface.

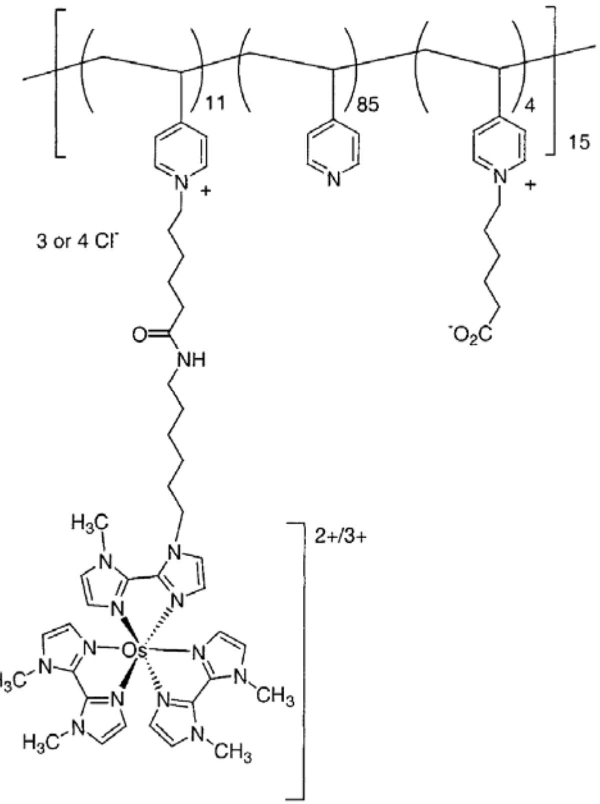
Osmium Polymers for GOx



For GOx

PVI-[Os-(diamine-bpy)$_2$Cl]$^{+/2+}$

E^0 = -170 mV vs. Ag/AgCl

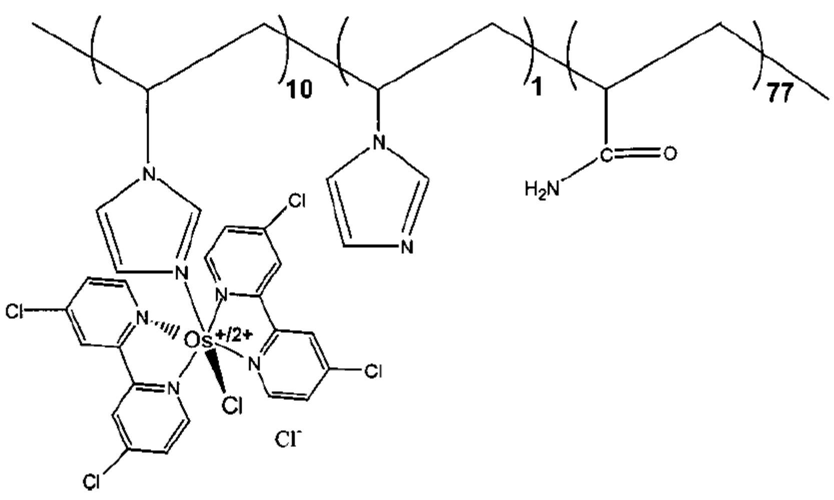


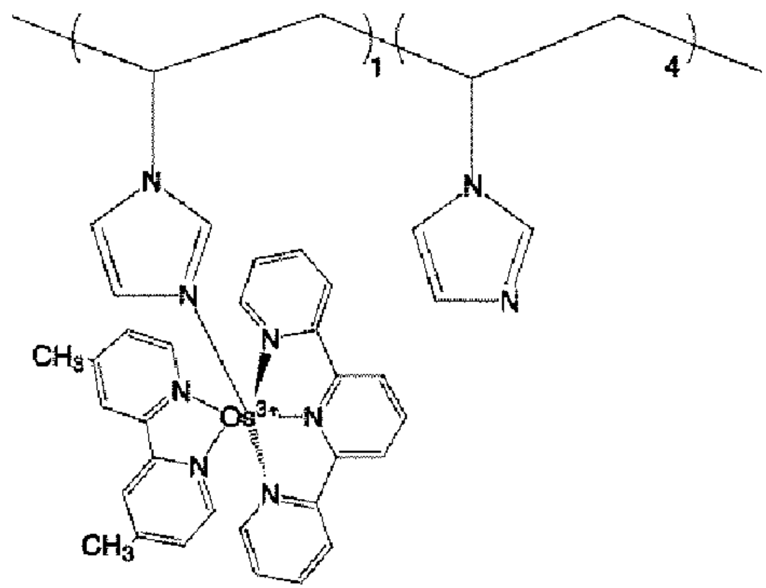
For GOx

PVP-[Os-(dimethyl-bis-imidazole)$_2$Cl]$^{2+/3+}$

E^0 = -190 mV

Osmium Polymers for BOD and Laccase





For BOD

PAA-PVI-[Os(dCl-bpy)$_2$Cl]$^{+/2+}$

E^0 = +350 mV

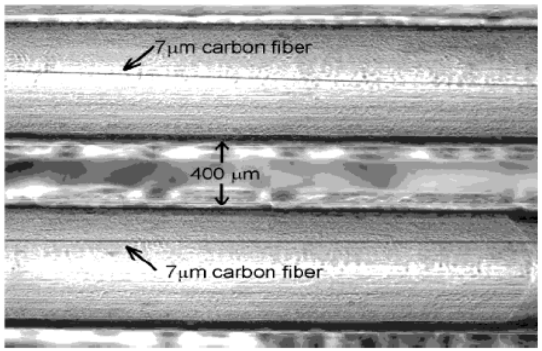
For Laccase

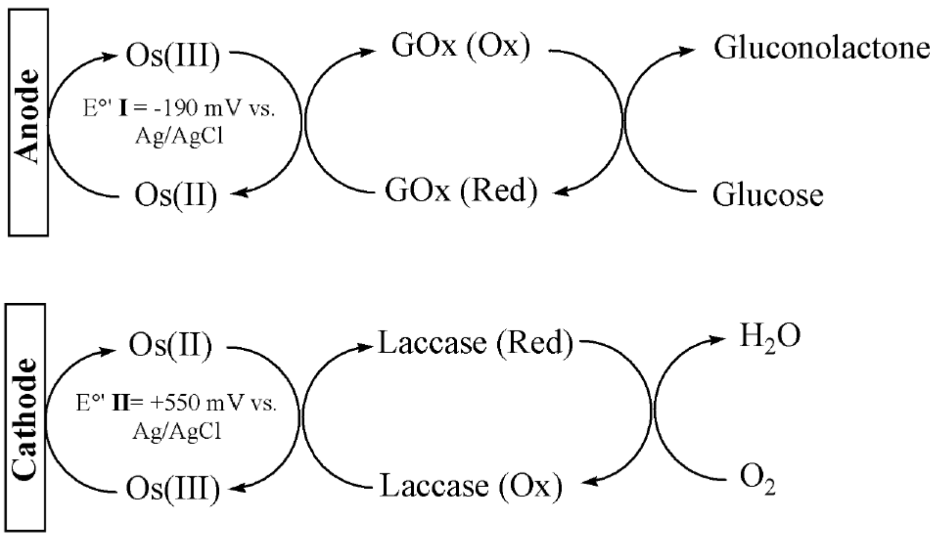
PVI-[Os(tpy)(dme-py)]$^{2+/3+}$

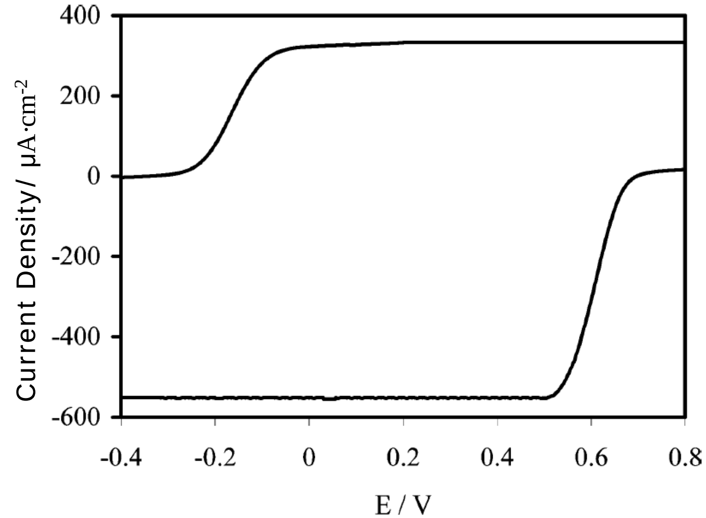
E^0 = +500 mV

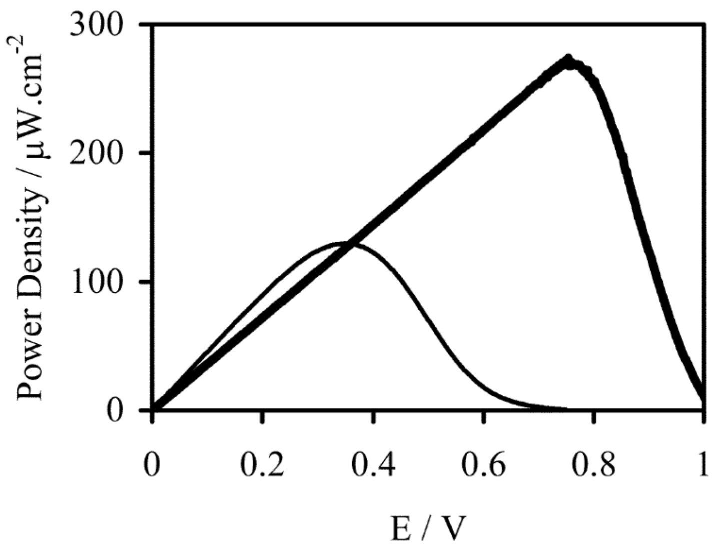
Glucose / O_2 Miniature Bio-fuel Cell – under Air, GOx / Lc

7 µm C-fiber – 2 cm each



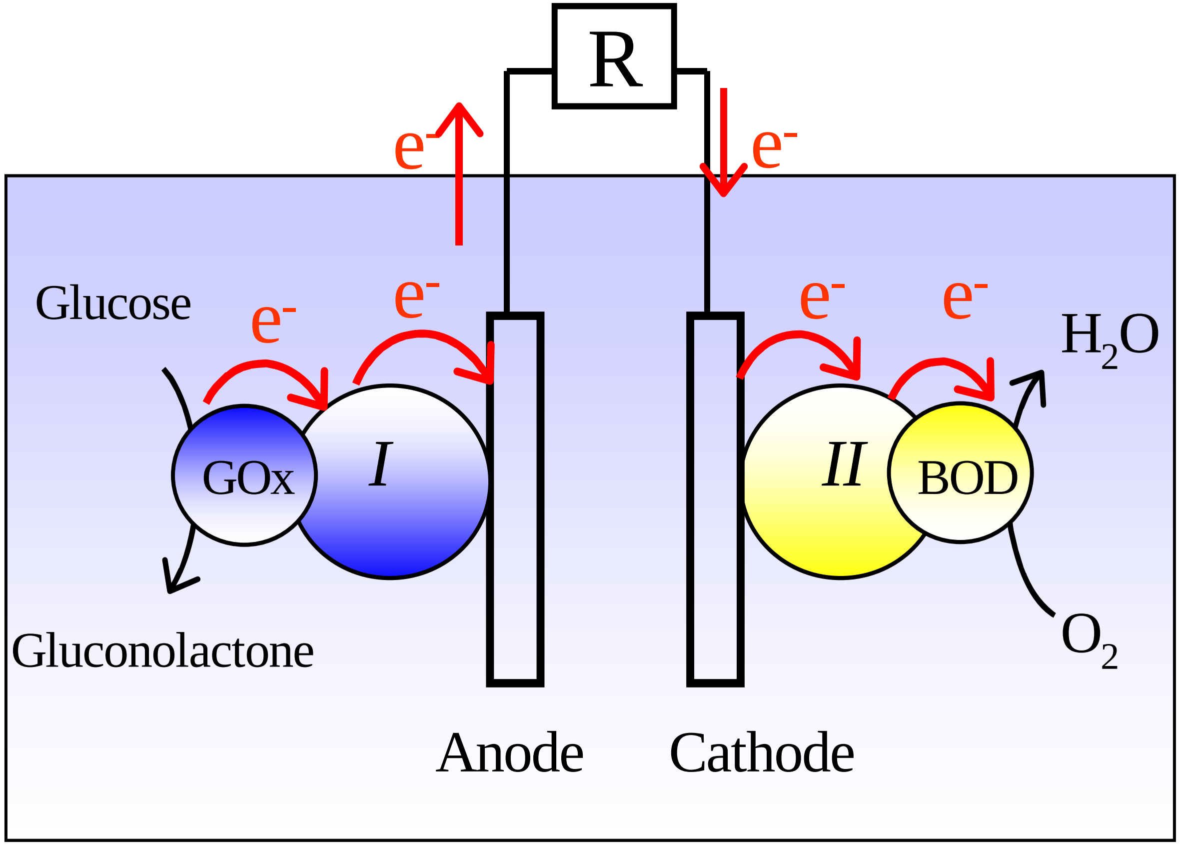






Mano, N.; Mao, F.; Shin, W.; Chen, T.; Heller, A. *Chem. Comm.* **2003**. *4*, 518

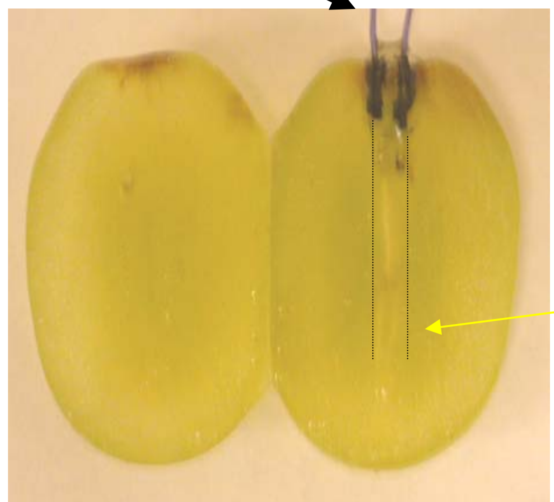
The "Wired" Enzyme Glucose-O_2 Biofuel Cell



Redox polymers *I* and *II* respectively "wire" glucose oxidase (GOx) and bilirubin oxidase (BOD), selective and non-leachable electrocatalysts

2.4 μW Power from a "Wired" Enzyme Glucose- O_2 Micro-fuel Cell Operating in a Grape

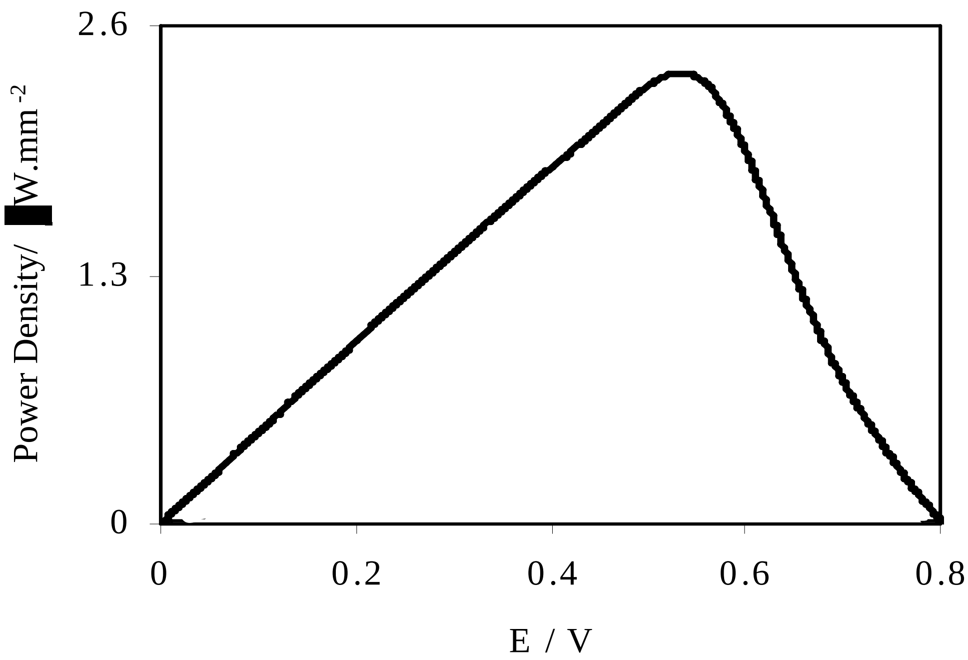
Contacts



7 μm carbon fibers. Drawn, as the fibers are too fine to be photographed

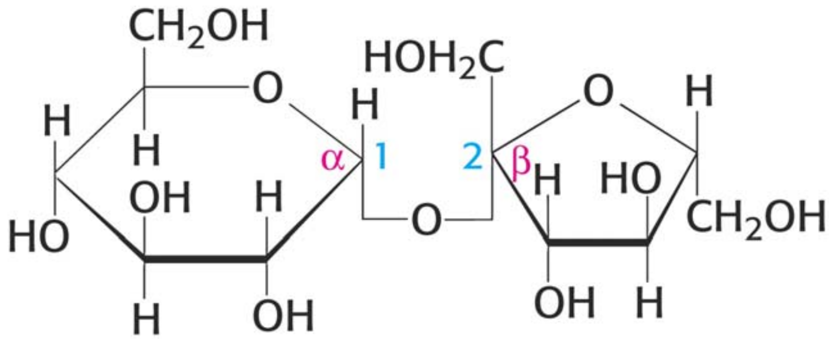
N. Mano, F. Mao A. Heller ***J. Am. Chem. Soc***., 2003, *125*, 6588

Dependence of the Power Output on the Operating Potential in a Grape



* The cell consists of two 13 µm diameter, 2 cm long, “wired” enzyme-coated carbon fibers. Their combined footprint is 0.53 mm^2 and their combined volume is 0.0052 mm^3

- **Possible Candidates of Fuels from Body:**
  - **Sugar:** Sucrose, Glucose, Fructose,…
  - **Organic Acids:** Formic, Acetic, Citric,…



Sucrose
(α-D-Glucopyranosyl-(1 → 2)-β-D-fructofuranose

$HCOOH$

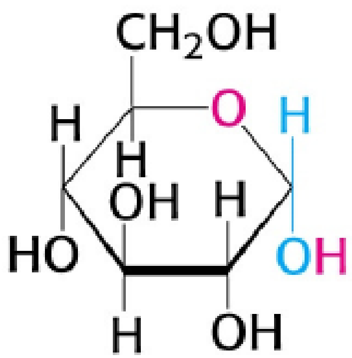
CH_3COOH

Citric Acid

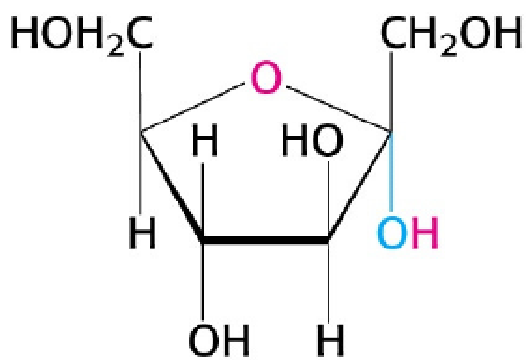
$(HOOCCH_2C(OH)(COOH)CH_2COOH)$

CH_3OH

,…



α-D-Glucopyranose



α-D-Fructofuranose
(a cyclic form of fructose)

Zn Anode for Miniaturized Power Source in Physiological Conditions

$$Zn(s) \rightarrow Zn^{2+} + 2e^- \qquad E_a = -0.76\ V\ vs.\ NHE$$

$$AgCl(s) + e^- \rightarrow Ag(s) + Cl^- \qquad E_c = +0.20\ V\ vs.\ NHE$$

$$Zn(s) + 2\ AgCl(s) \rightarrow Zn^{2+} + Ag(s) + Cl^- \qquad E_{rxn} = 0.96\ V$$

Physiological Condition

PBS (Phosphate Buffered Saline):

20 mM phosphate buffer, pH = 7.4, 0.15 M NaCl

Serum

PBS + others (proteins, ascorbate, urate,...)

Motivation - Anodic Potential Limit of Glucose / O_2 Bio-fuel Cell

$E^{o'}$ (glucose / gluconate) = -0.64 V vs. Ag / AgCl

(at pH=7)

$E^{o'}$ ($FADH_2$ / FAD) = -0.42 V

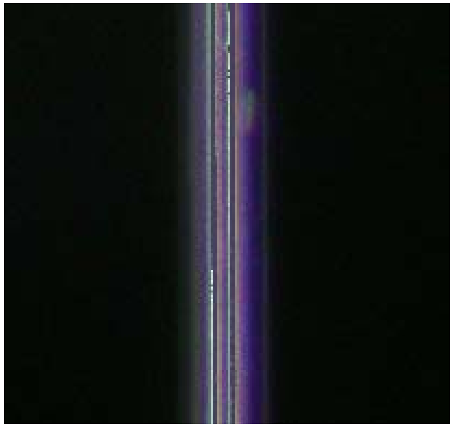
$E^{o'}$ (GOx) = -0.2 ~ -0.4 V

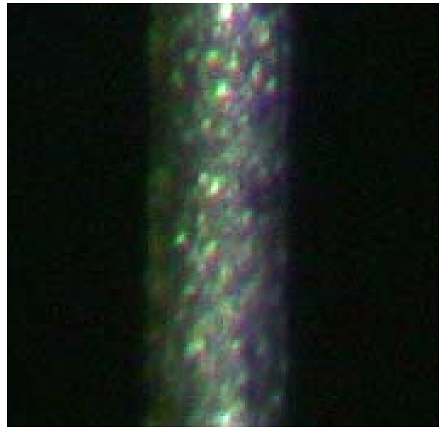
$E^{o'}$ (mediator or polymer) = 0.0 ~ -0.2 V

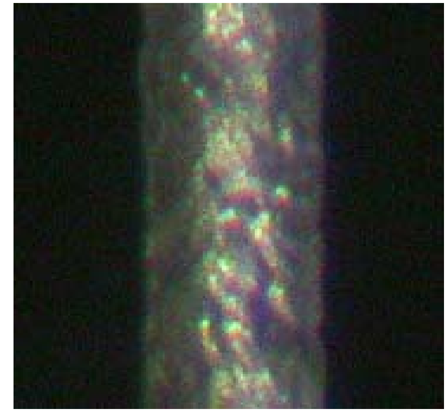
cf. $E^{o'}$ (Zn/Zn^{2+}) = -0.963 V vs. Ag / AgCl

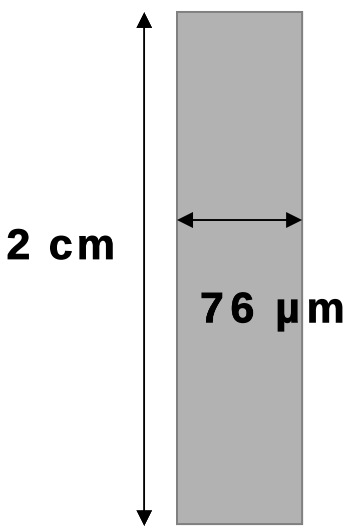
Preparation of Zn Anode

- Zinc deposition and Nafion coating on 2 cm long, 76 µm diameter Pt wire electrode

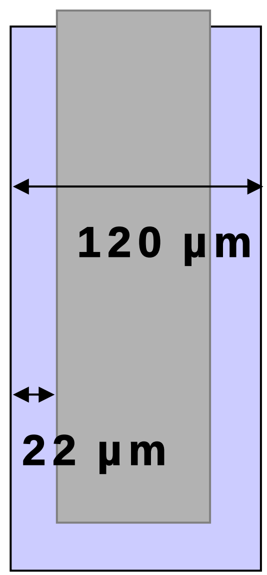




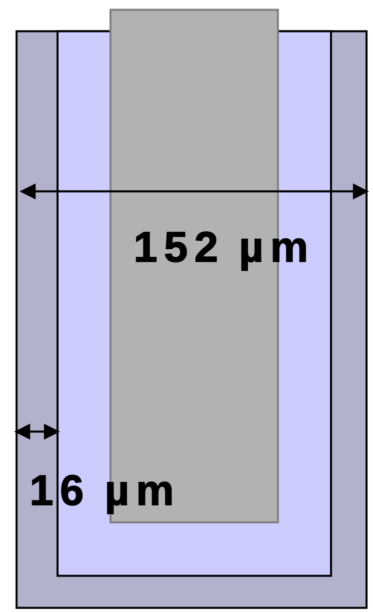




Pt wire



Zn on Pt

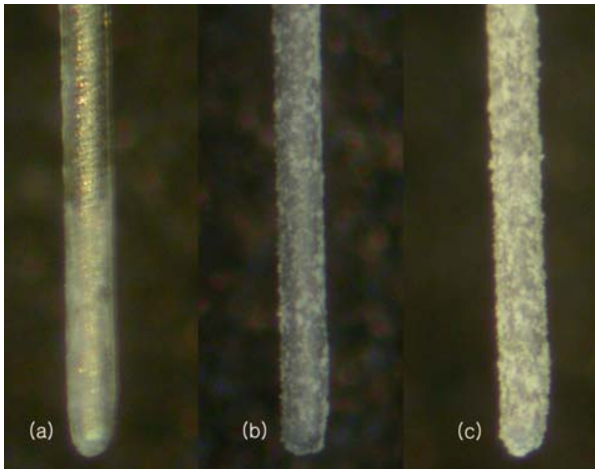


Nafion-Zn on Pt

Zn Anode for Implantable Power Source

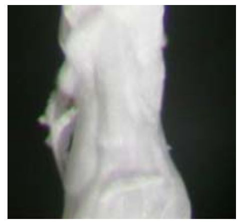
Hopeite Growth on Nafion coated Zn anode

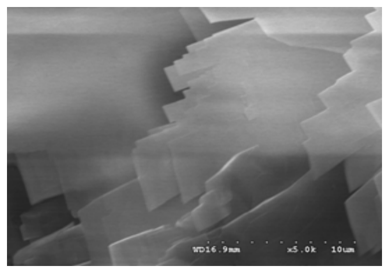
Initial stages of discharge



4 mC 250 mC 430 mC

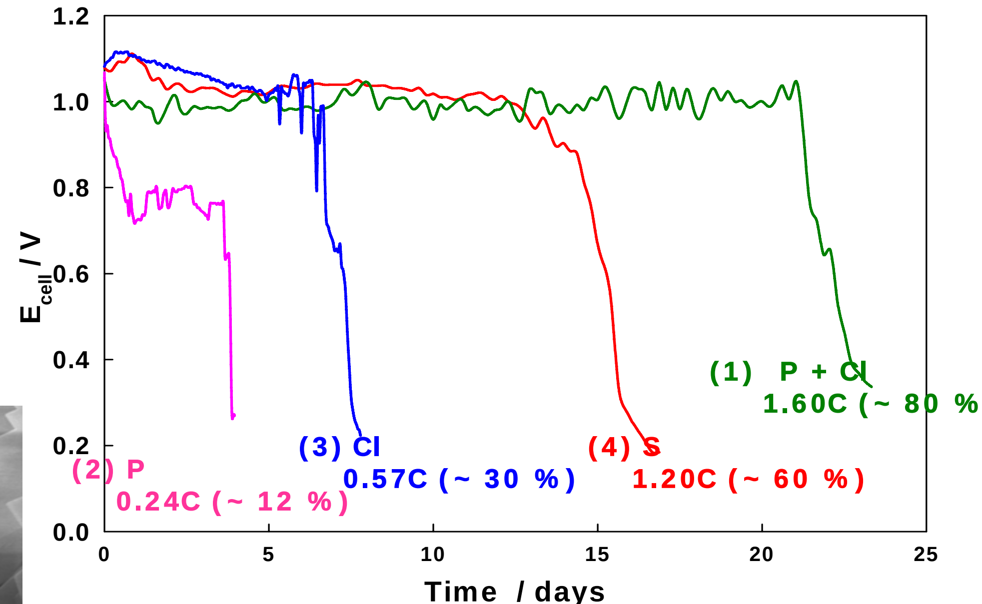
After completion of discharge (1.6 C)





Formation of highly Zn^{2+} conductive and O_2 blocked layer formation upon discharging in PBS condition
→ Made Zn anode working in neutral solution

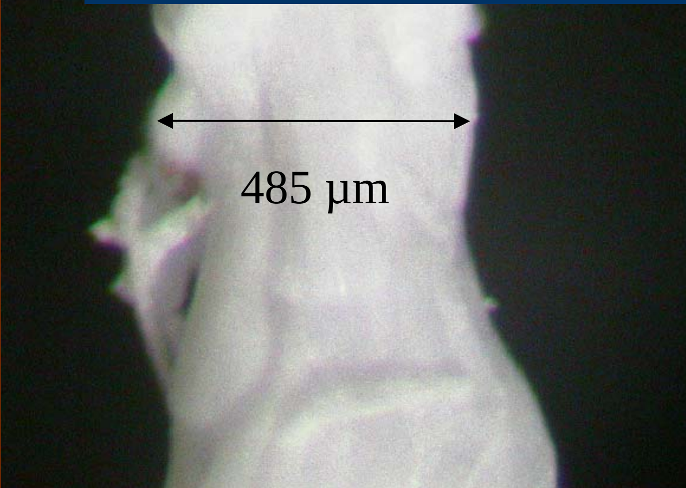
Discharge Curves (13 mA·cm-2



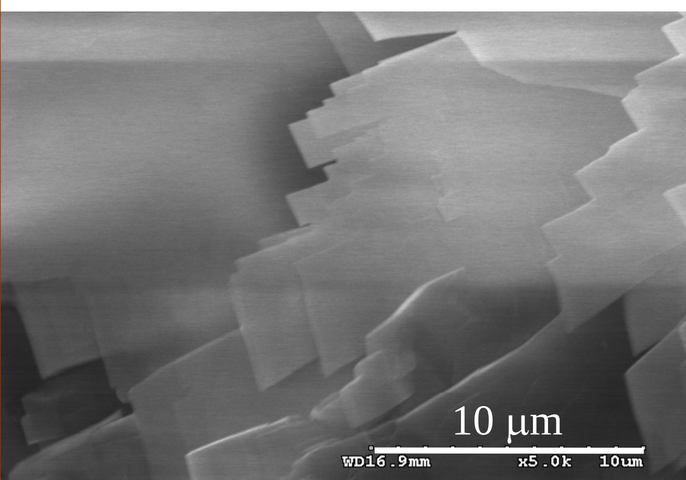
(1) in pH 7.4, 20 mM phosphate buffer + 0.15 M NaCl
(2) in pH 7.4, 20 mM phosphate buffer
(3) in 0.15 M NaCl solution
(4) in serum

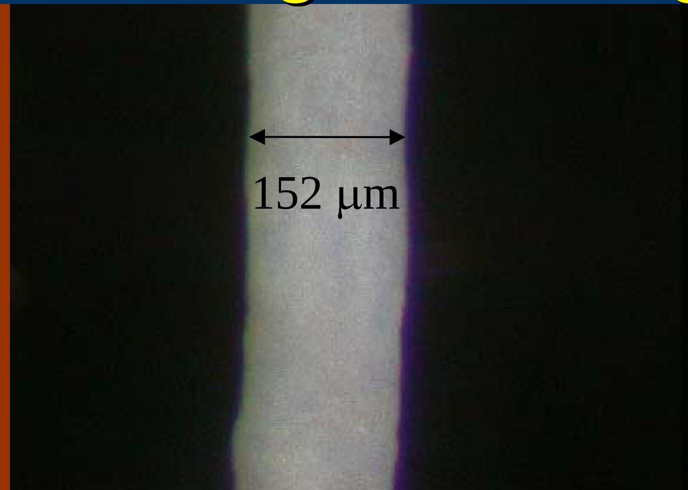
Shin, W; Lee, J.; Kim, Y.; Steinfink, H.; Heller, A, *J. Am. Chem. Soc.* **2005**, *127*, 14590.
Heller, A; Shin, W., US Pat. 20070125644

Microscopic and SEM Images after Finishing Discharge

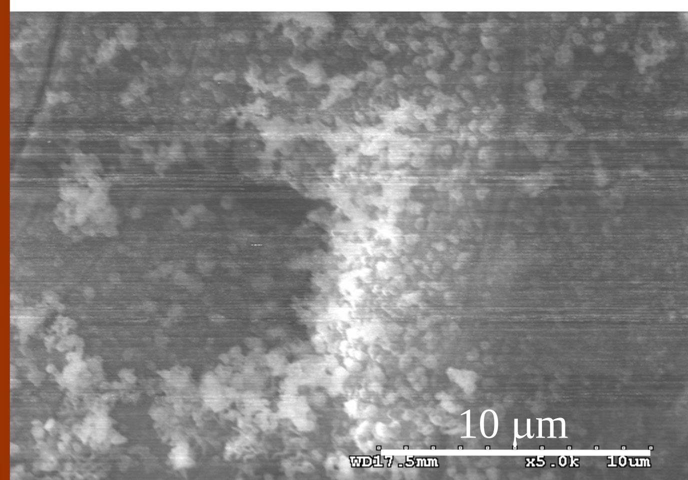


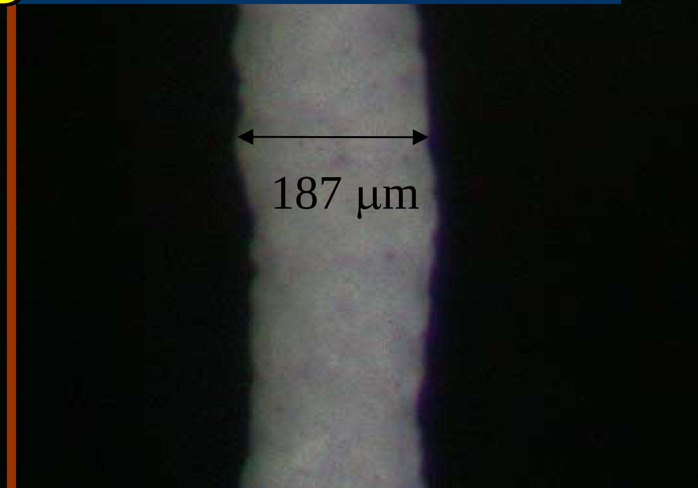
pH 7.4, 20 mM phosphate buffer (containing 0.15 M NaCl)



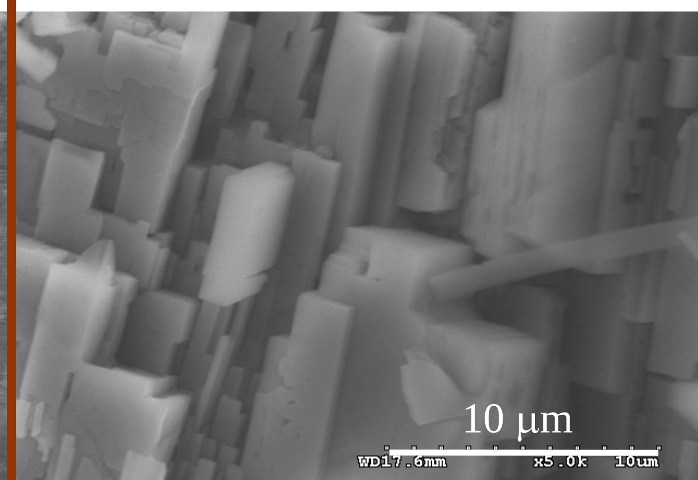


0.15 M NaCl solution



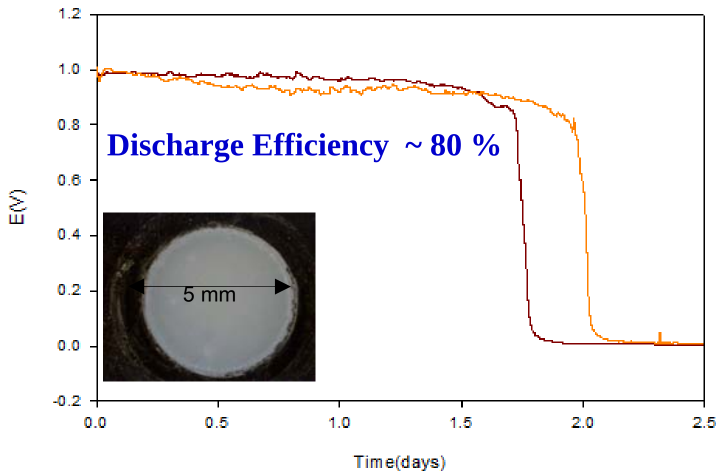


pH 7.4, 20 mM phosphate buffer

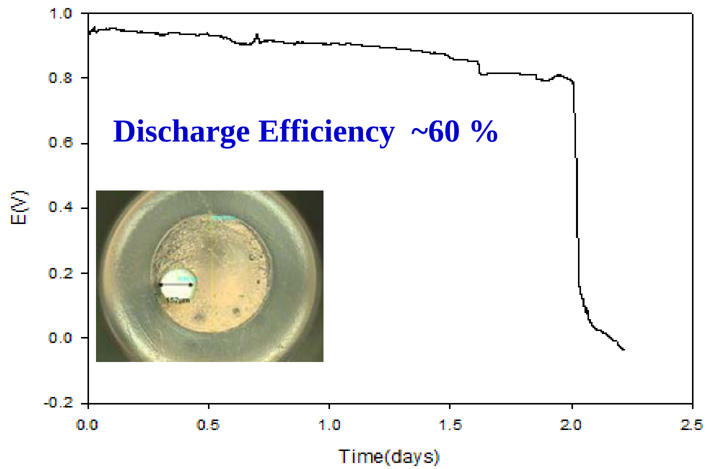


Miniaturization of Zn Anode

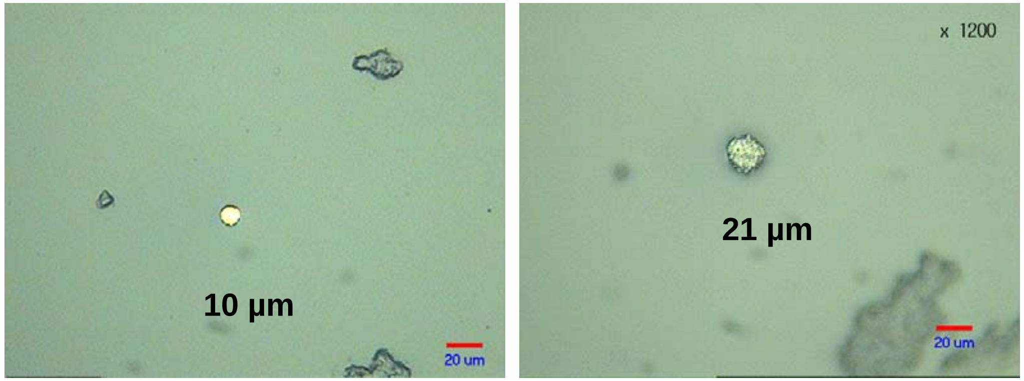
5 mm disc: R = 50 kΩ, I = 20 μA



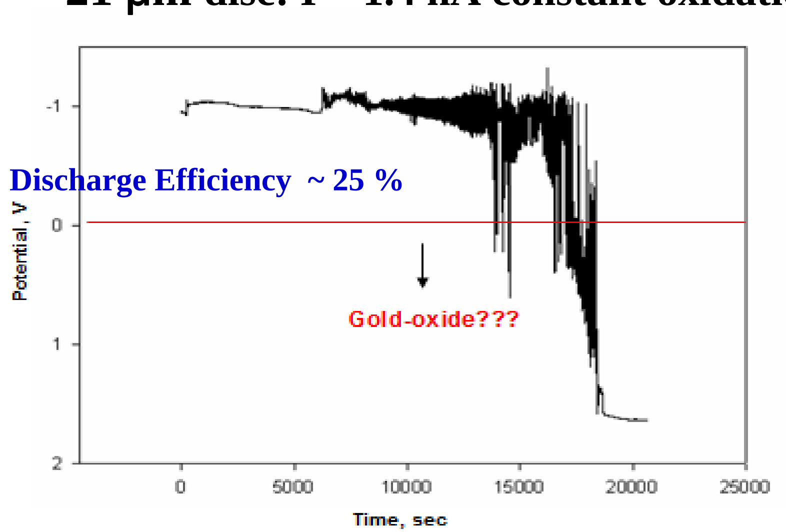
152 μm disc: R = 48 MΩ, I = 20 nA



Electrodeposition on 10 μm disk 9.9 x 10^{-6} C (50 nA x 1980 s)



21 μm disc: I = 1.4 nA constant oxidation



1.4 nA x 1.0 V = 1.4 nW

Shin, W; Lee, J.; *Unpublished*.

The Potentially Implantable Zn–AgCl Cell

Projected scheme

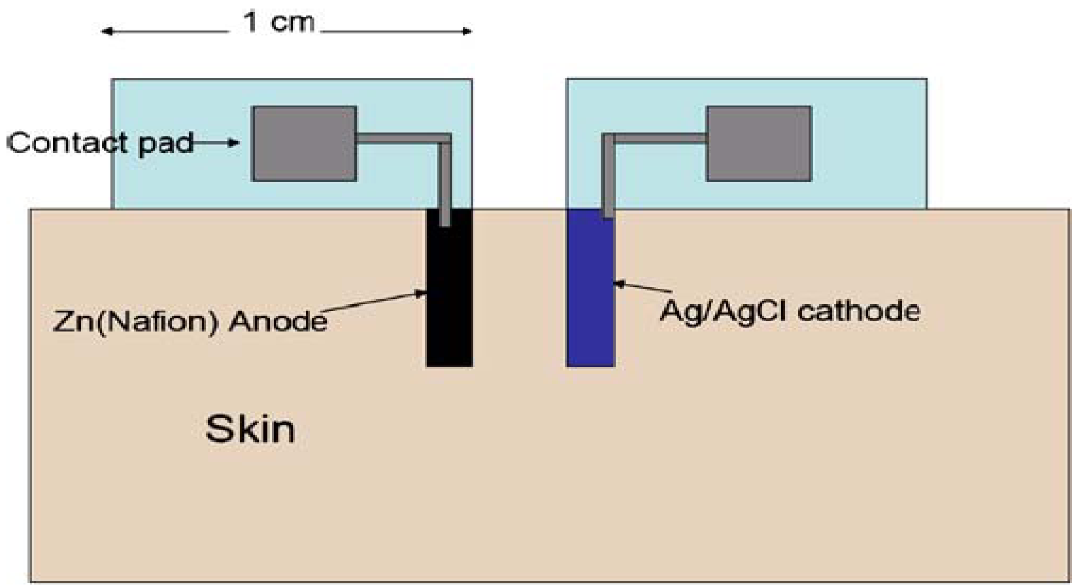


Fig. Schematic diagram of a caseless miniature Zn(Nafion)–AgCl battery operating in the subcutaneous interstitial fluid

Ag/AgCl cathode-coated with biocompatible hydrogel allowing the out-diffusion of Cl-

->should be safe to implant

Heller, A.; *Anal Bioanal Chem* (2006) 385: 469–473
Shin W, Lee J, Kim Y, Steinfink H, Heller A (2005) J Am Chem Soc 127:14590–14591

Actual characteristics of small commercially available batteries and projected characteristics of potentially implantable microcells

Cell	Li-MnO_2	Zn-air	Zn-MnO_2	Zn-AgCl (proj.)	Zn-O_2 (proj.)	Glucose-air (proj)
Availability	Now	Now	Now	Lab	Lab	Lab
Case	Steel	Steel	Steel	None	None	None
Electrolyte	Organic	KOH	KOH	Serum	Physiological	Physiological
Min. size, mm^3	200	50	200	0.1	0.05	0.01
W/L	300	150	200	50	10	1
Wh/L	650	1800	600	500	5000	50,000
Life at 37°C*	3 years	1 month	1 year	1 month	2 weeks	2 weeks

Heller, A.; *Anal Bioanal Chem* (2006) 385: 469–473