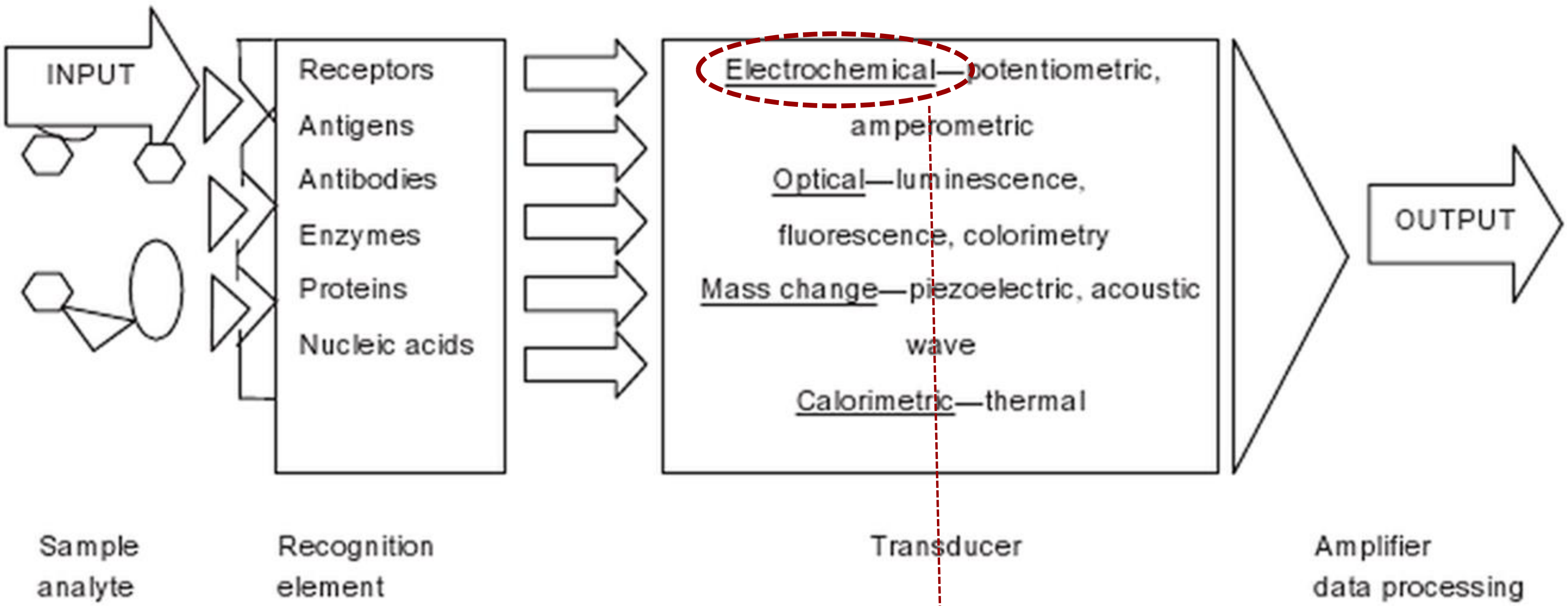
BIO FUEL CELL (BFC) BASED BIOSENSORS:

A subclass of electrochemical biosensors

CLASS of BFC



- ✓Fast
- ✓Sensitive
- ✓Selective
- ✓Label free
- ✓Min. or no sample loss
- ✓Small size

✓ **Biofuelcells Biosensors**

Galvanic principle

Two emerging technologies for the next generation healthcare and allied fields:

BIOFUEL CELLS

BIOSENSORS

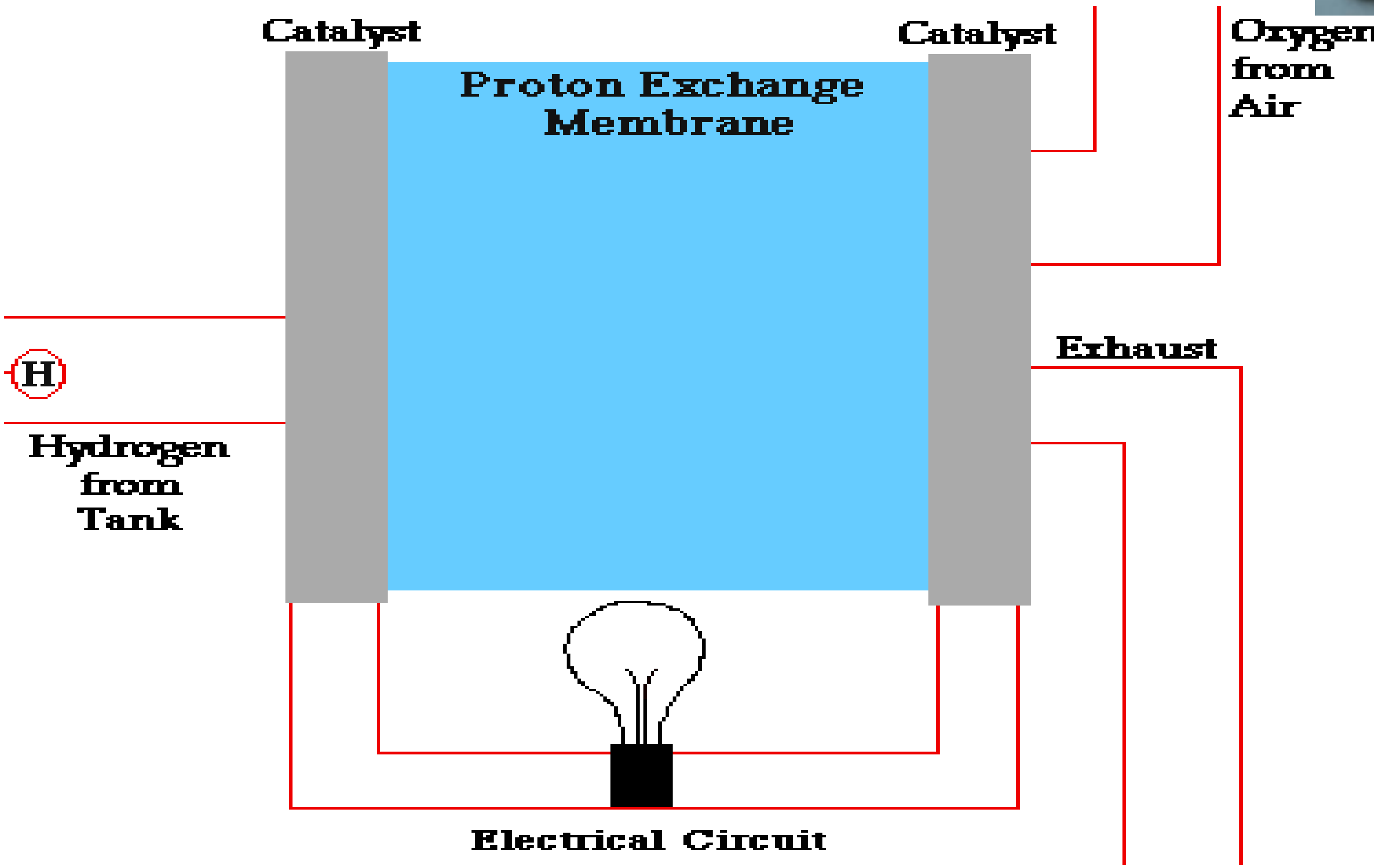
POWER GENERATION

SENSING APPLICATIONS

What is BIOFUEL CELL ?

➢**CELL**：

Electrochemical device that converts **STORED** chemical energy into electrical energy----- **A thermodynamically closed system**



Christian Friedrich Schönbein in the year 1838

http://americanhistory.si.edu/fuelcells/.htm

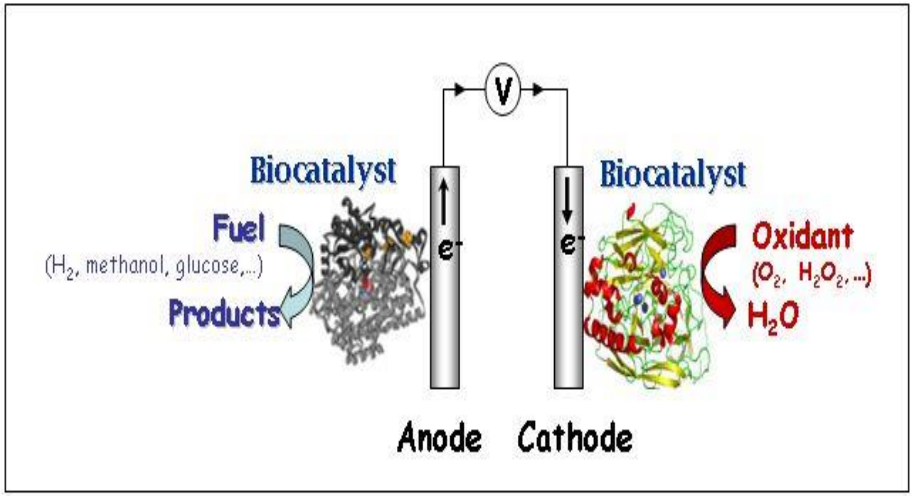
Fuel Cells...applications...advantages ....weaknesses..

✓Capable of producing power anywhere in the 1 W to 10 MW ...can be applied to → stationary power supply & vehicle (1kW - 100kW)

✓Energy efficiency: 40% to 60%.....goes upto 85% when its waste heat is used to heat a building in a co-generation system.

✓Reduces the design complexity of a vehicle...greatly reduce the number of moving parts in the car → reduce the likelihood of failure…….run silent…………..low emission

BIO-FUEL CELL (BFC)



✓*Catalyst*: Biocatalysts…..Enzymes, organelles, microorganisms etc.

✓*Fuel*: Renewable>>>carbohydrate, alcohol, & non-renewable

✓*Operating temperature*: 20 to 40 ºC, usually at room temperature

✓*Working pH*: Around neutral pH

Green technology……

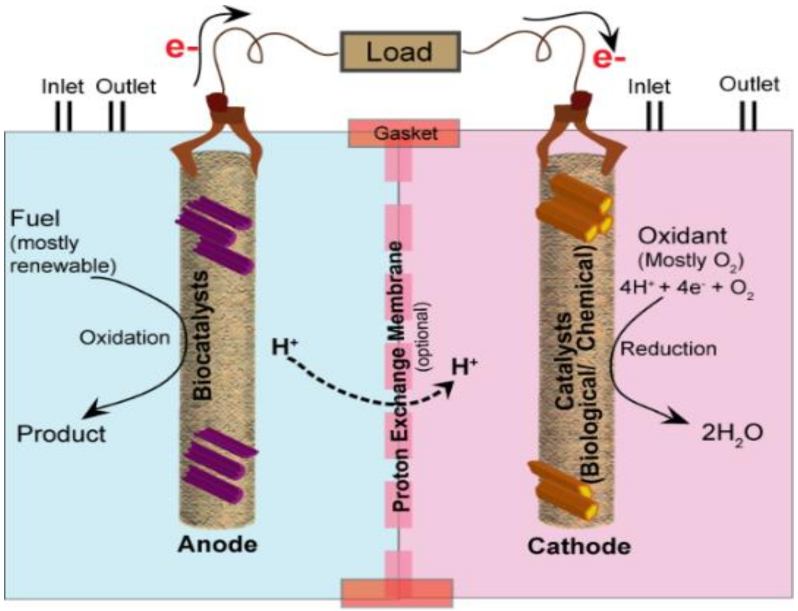
- **Microbial BFC**
- **Enzymatic BFC**

Bacteria:
Potter, M.C. (1911: Univ Durham). Electrical effects accompanying the decomposition of organic compounds. *Proceedings of the Royal Society*, B, 84.

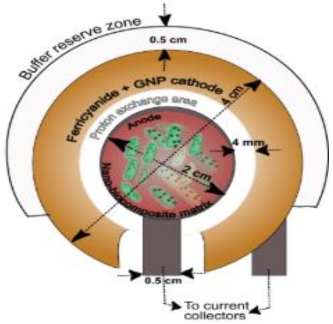
Enzyme:
Yahiro, et. al. (**1964**) : Enzyme utilizing bio-fuel cell studies. *Biochimica et Biophysica Acta* **88**.

Space-General Corporation, Calif. U.S.A.

BFC design for sensing applications



Scaling down

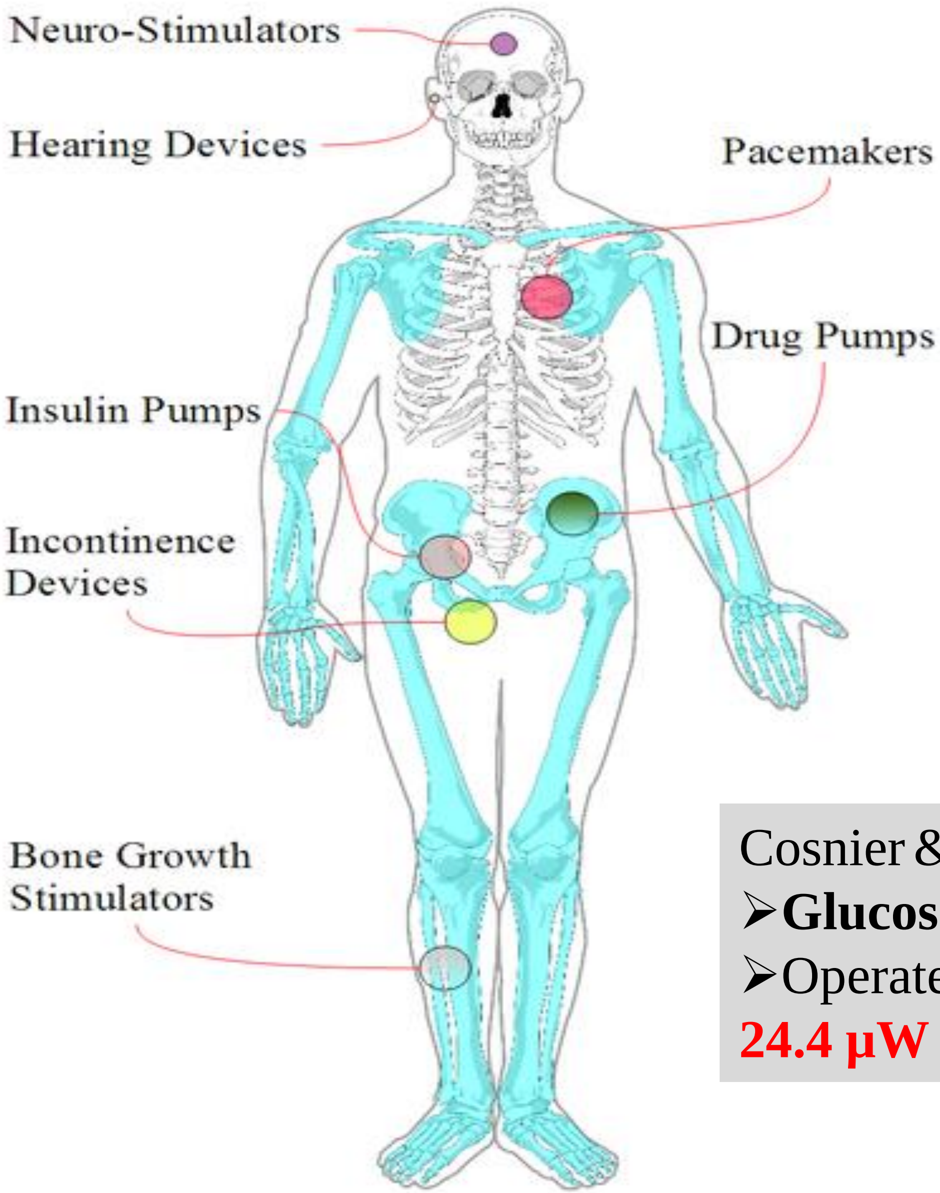


Kaushik & Goswami *ACS Appl. Mat. Interface* (2018)

- ❑ Ohmic resistance decreases
- ❑ Sensitivity increases
- ❑ Response time decreases

Advantage for sensor application**: Stand-alone operation (**Self-powered)

Application of BFCs : **Powering implant devices**



- Glucose can provide up to 16 kWs/g
- Oxygen level in blood ~200 µmol L^{-1}
- No battery leakage poisoning

Cosnier & his group (***PLoS One***. 2010: 5: e10476)

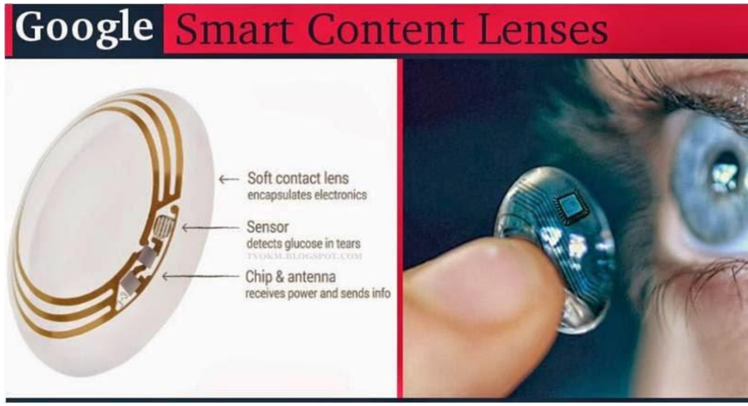
➢ **Glucose BFC** implanted in a rat.

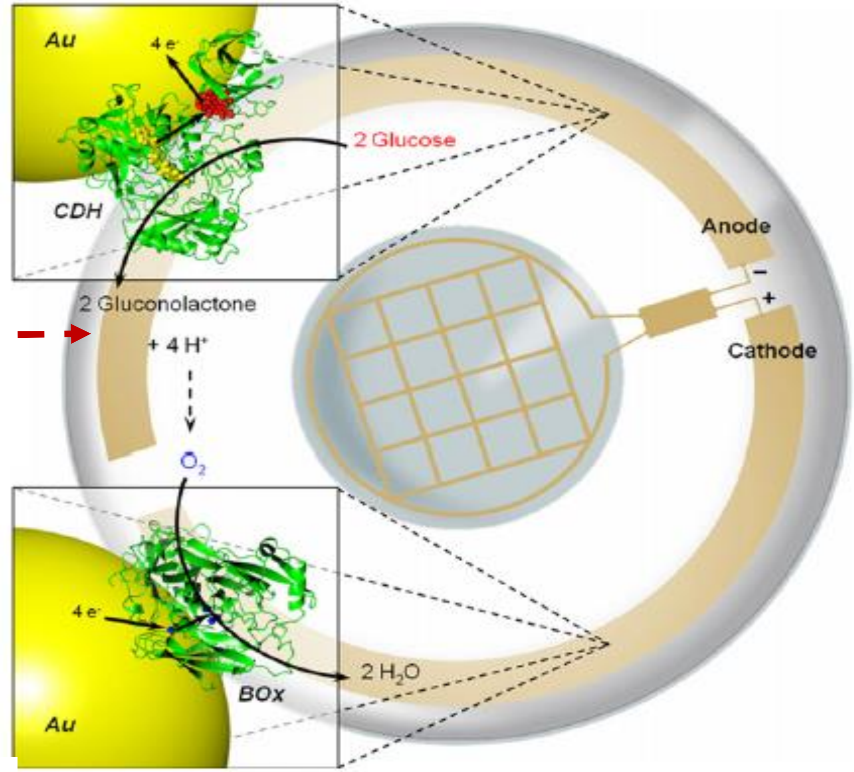
➢ Operated for 11 days with no ill effects.

24.4 µW mL^{-1}, which is suitable for pacemakers

Barton *et al. Chem Rev.* 104 (2004).

Wearable Biosensors





Ocular BFC

Fuel from lachrymal fluid: 1 mWcm^2 at 0.5 V.
Can be used to power sensors or other electronic devices (via the wireless technology RFID etc).

Falk et al. ***Biosens. Bioelectron. 37, (***2012)

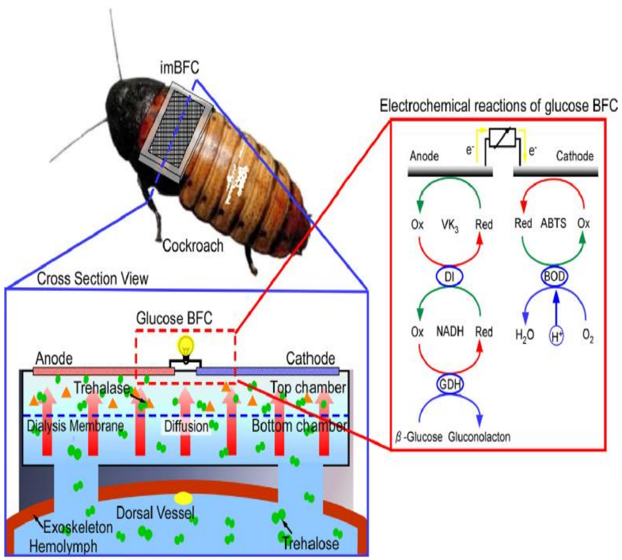
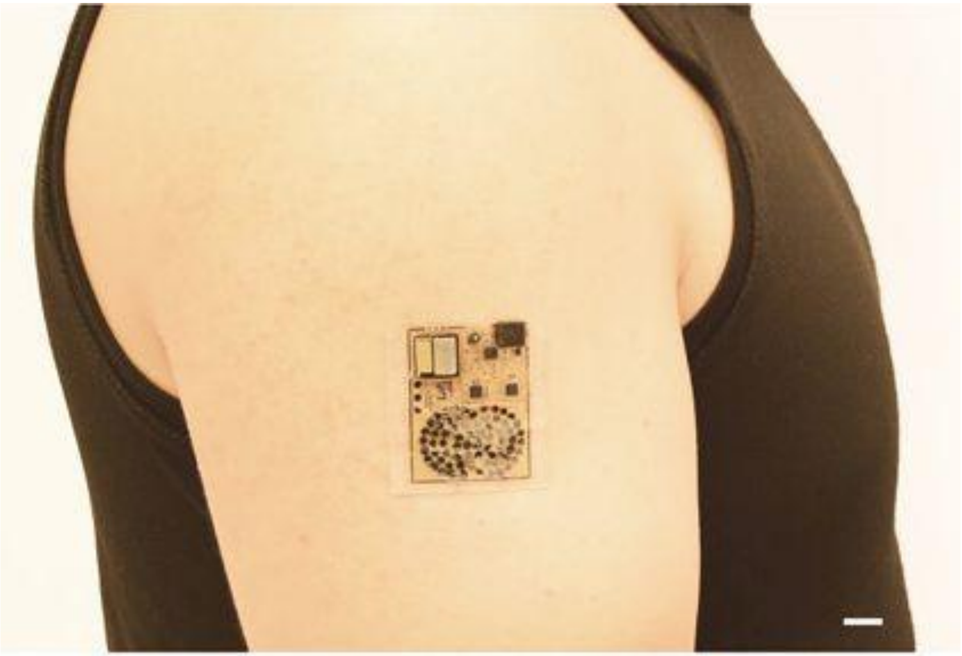
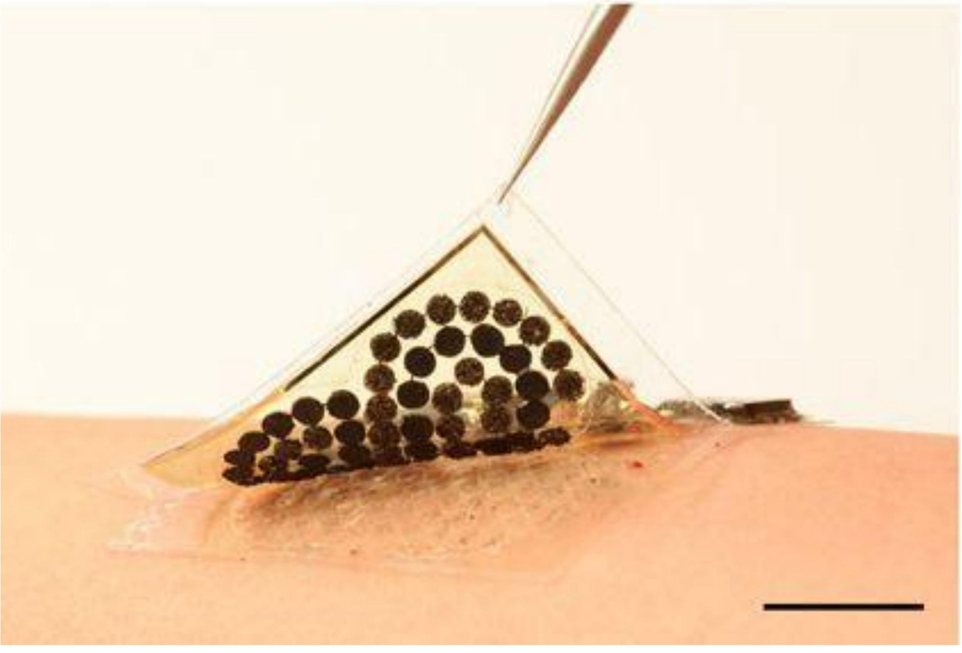


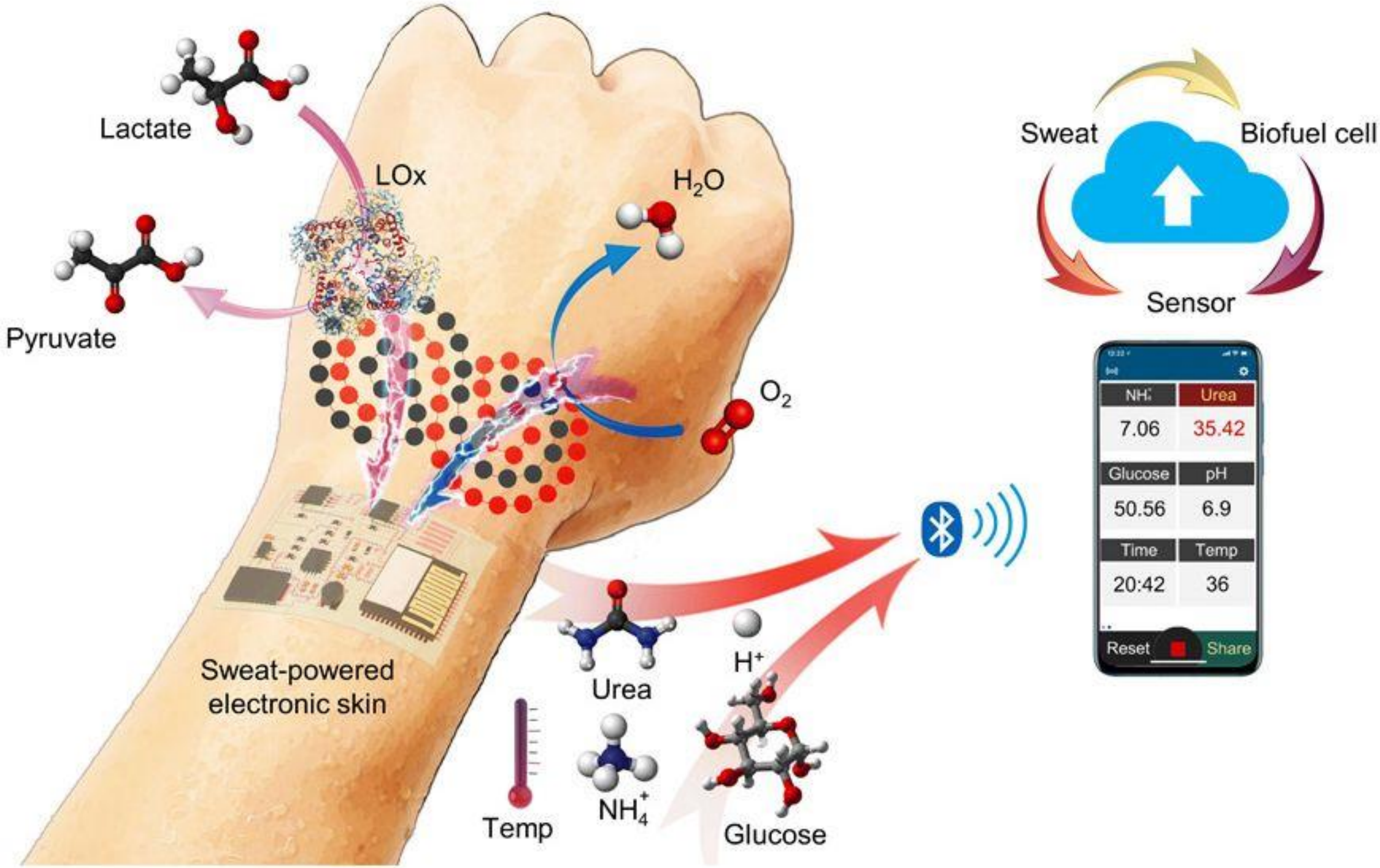
Fig. 1. Schematic illustration of the imBFC. Trehalose in insect hemolymph diffuses from the insect body to the chamber. Then, the trehalose is decomposed to glucose enzymatically. Finally, electric power is generated by the glucose BFC. The inset shows the electrochemical reaction of the glucose BFC consisting of theVK3/DI/NADH/GDH anode and the ABTS/BOD cathode.

BFC backpacked for wireless sensing
Shoji et al. *Biosensors Bioelectronics* 78 (2016)



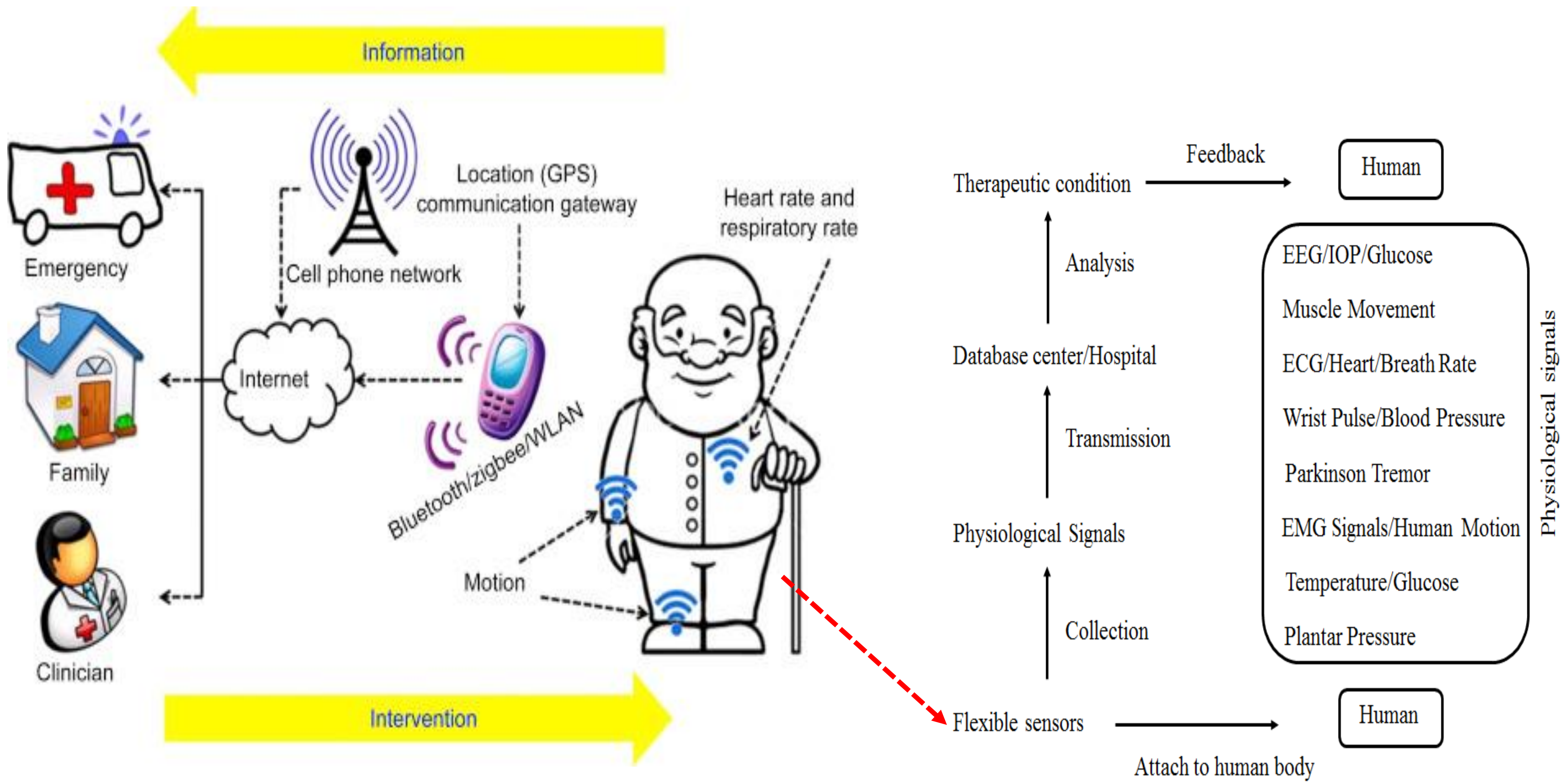


Sweat-powered metabolic sensors



Battery-free, biofuel-powered e-skin that harvests energy from the human body, performs multiplexed biosensing, and wirelessly transmits data to a mobile user interface through Bluetooth.

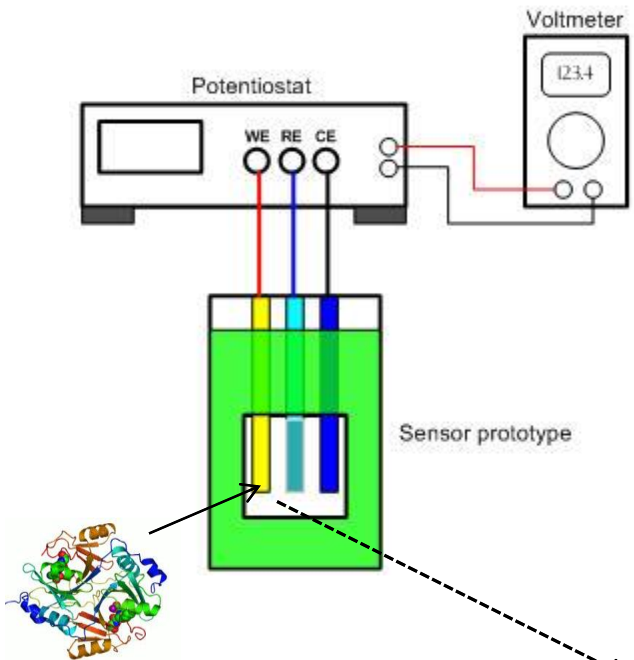
Wearable sensors for elderly care



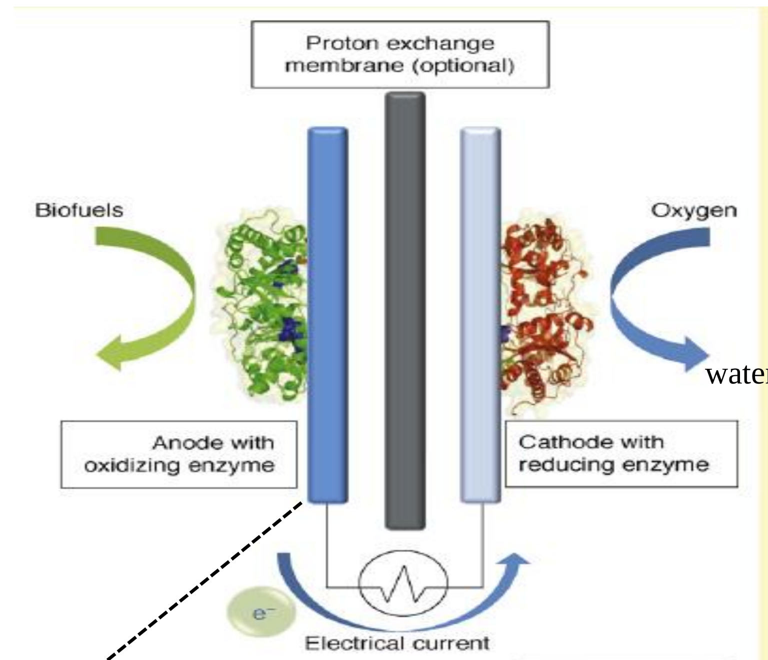
Internet of Things (IoT) is the network of interconnected things/devices which are embedded with sensors, software enabling to collect and exchange data making the system responsive without human intervention.

Zhu et al. Medical Biosensors for PoC applications 2017

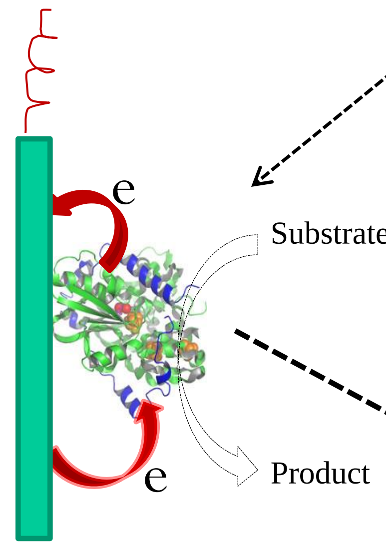
DEVELOPMENT OF BIOELECTRODES



Amperometric & voltammetric devices



BIOFUELCELL



Bioelectrode

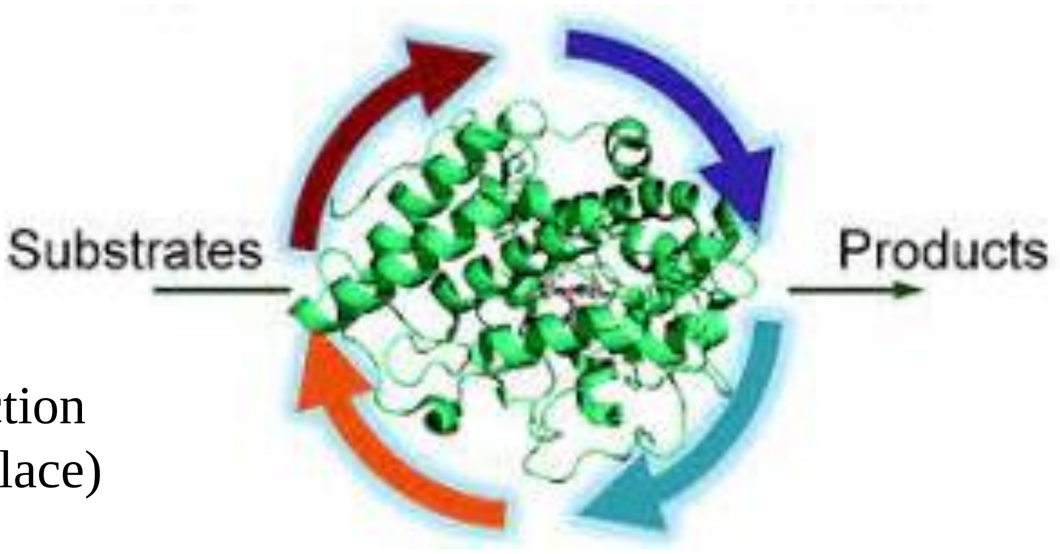
<u>Common requirements:</u>

➢Facile electron exchange between electrode and reaction

------- **high sensitivity/low activation overpotential**

Electrical current from *biologically active* materials :

LIVING MICROORGANISMS



Redox enzymes

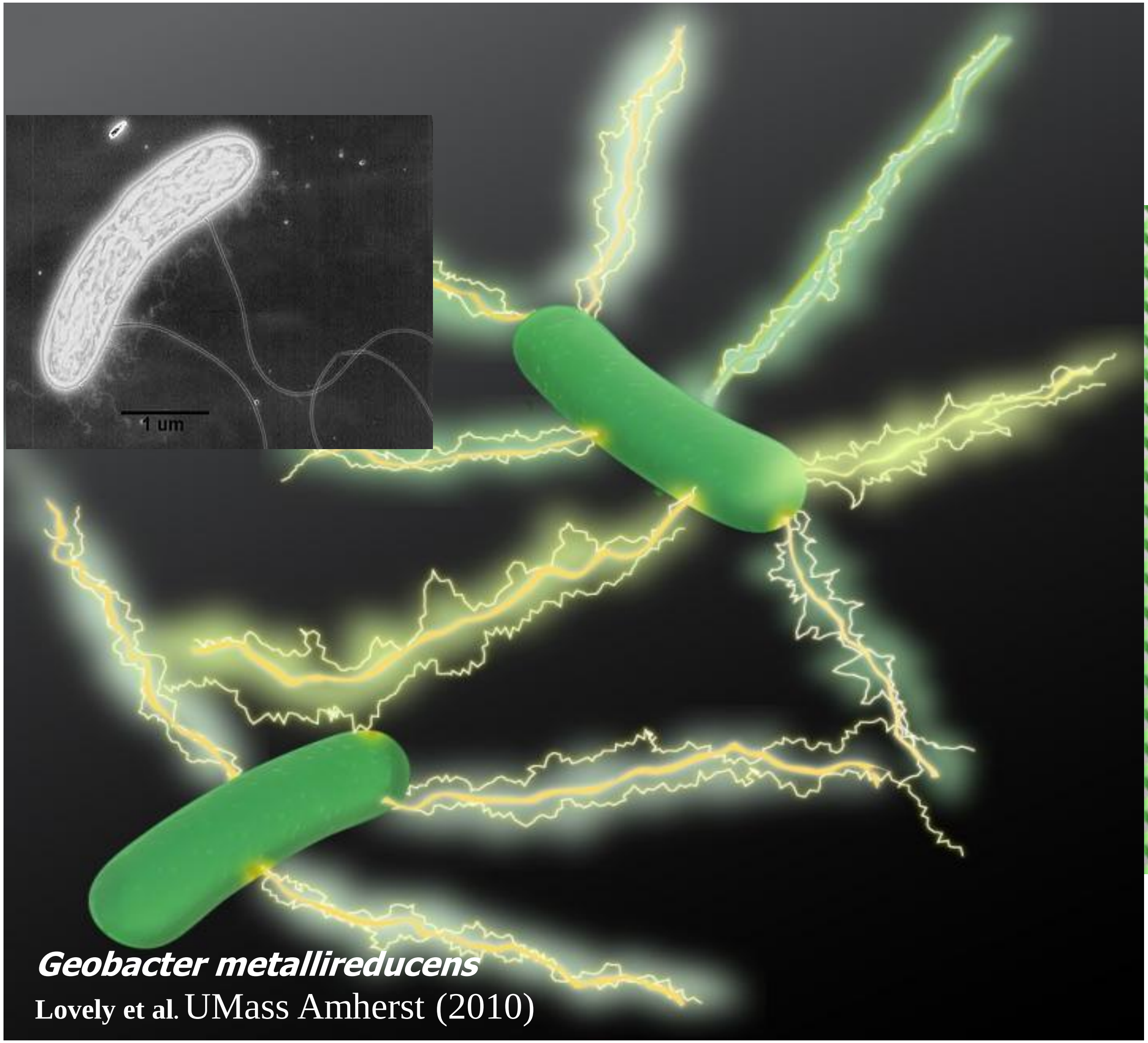
Catalyses reduction or oxidation reaction
(where exchange of electrons takes place)

CATALYSIS

INSPIRATION FROM NATURE

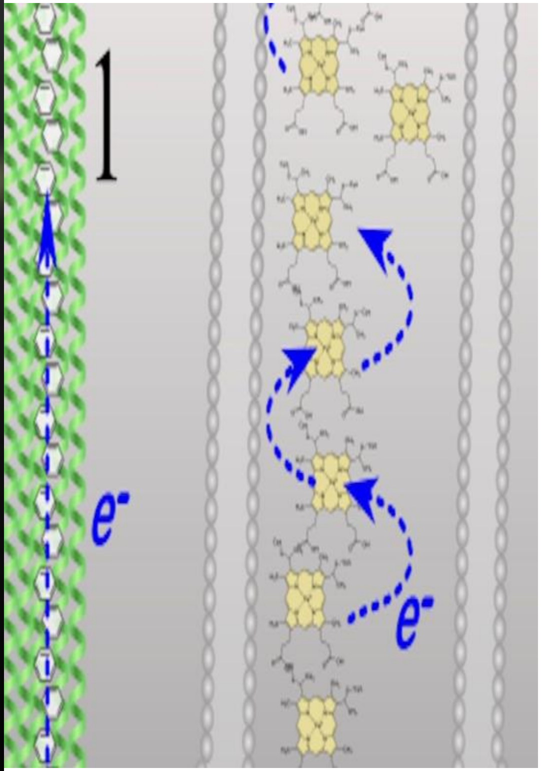
Electrogenic bacteria

Bacteria:
Potter, M.C. (1911: Univ Durham). Electrical effects accompanying the decomposition of organic compounds. *Proceedings of the Royal Society*, B, 84.



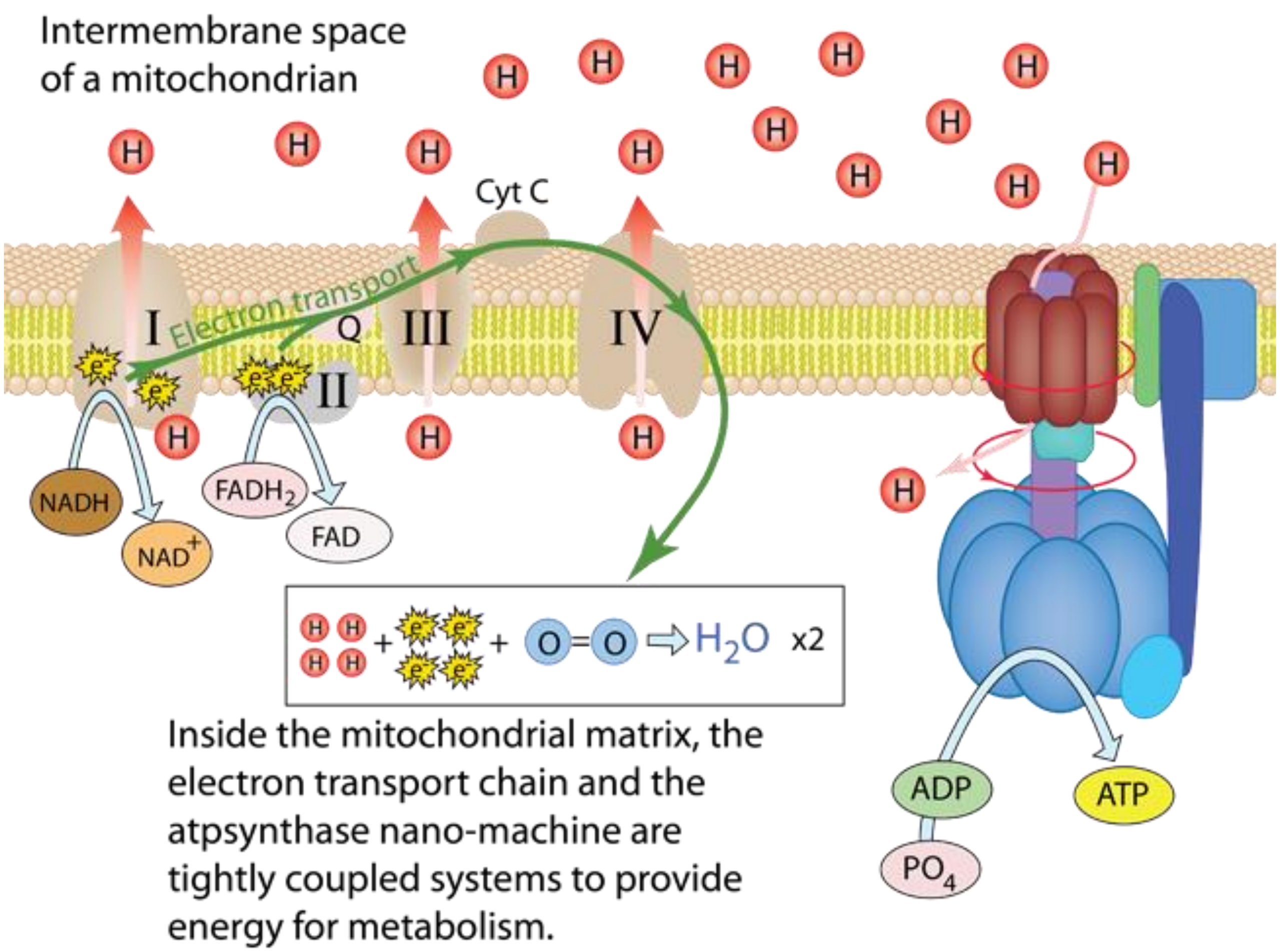
Geobacter metallireducens

Lovely et al. UMass Amherst (2010)



Pi stacking of hemes

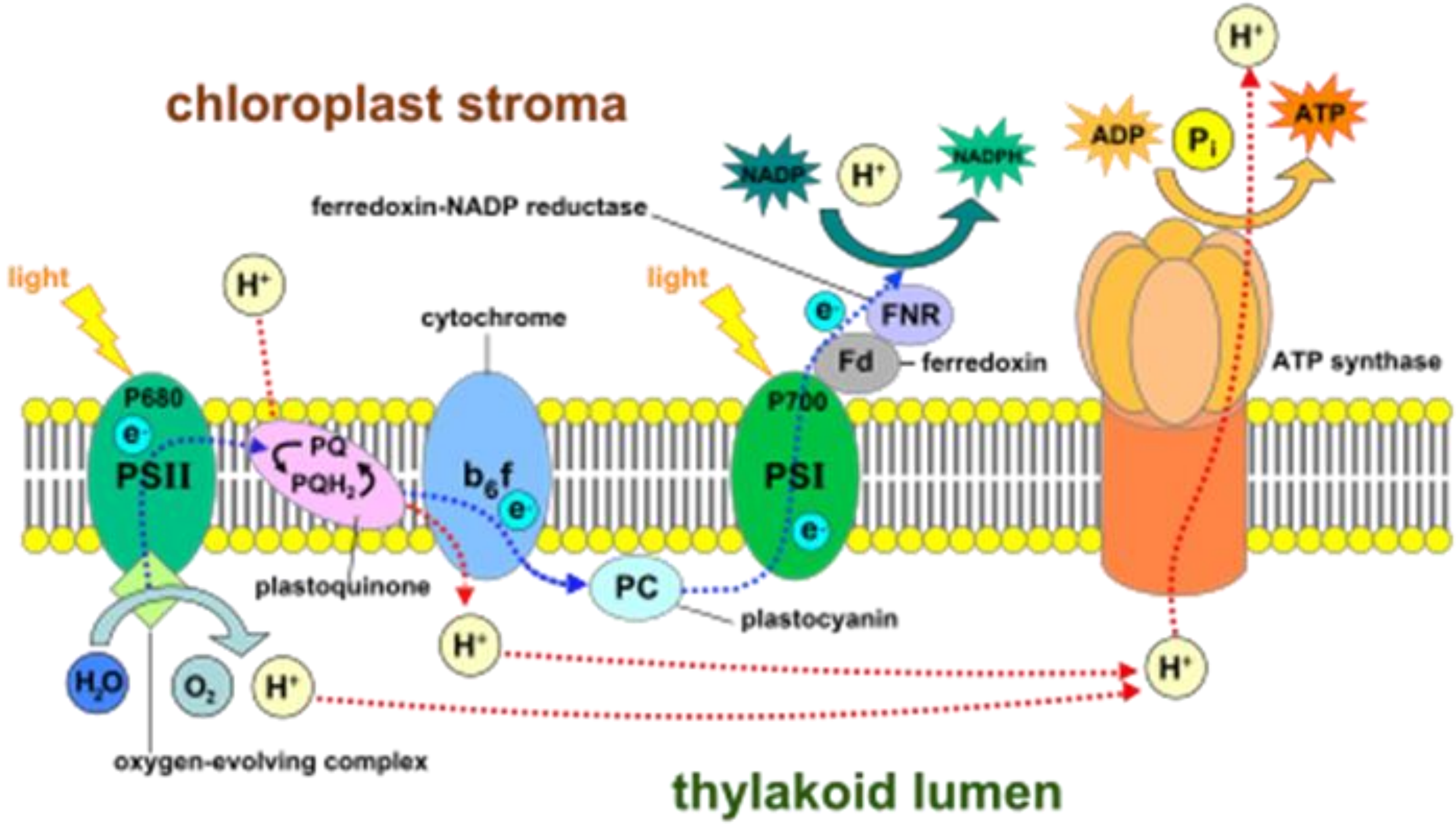
Internal electrical circuit in living systems



The ETC proteins:
complex I,
complex II,
coenzyme Q,
complex III,
cytochrome C,
complex IV

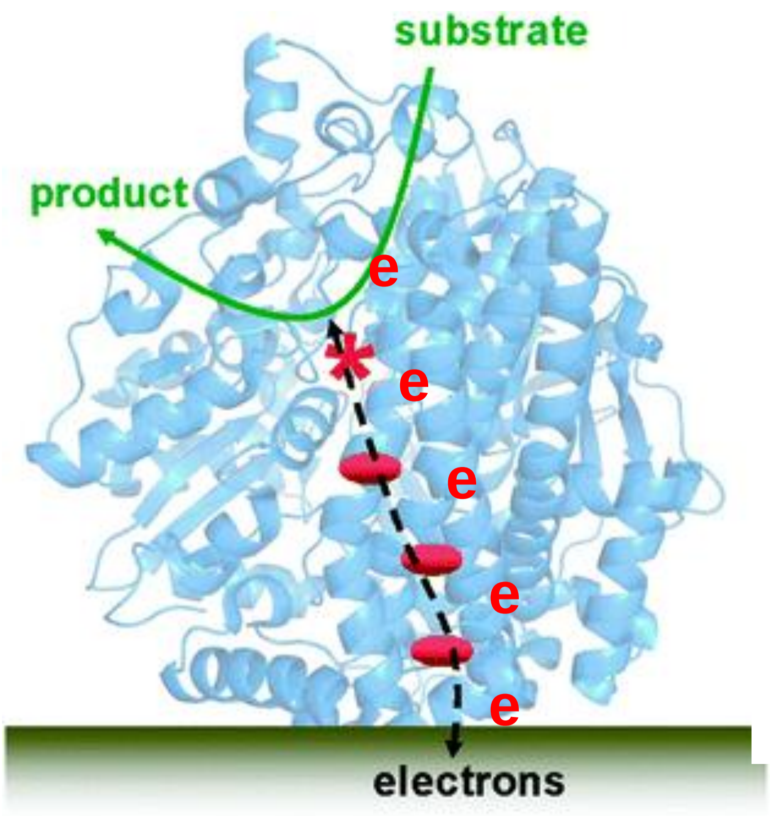
Edge to edge distance for haem-haem electron transfer chain system 25 to 35 A°

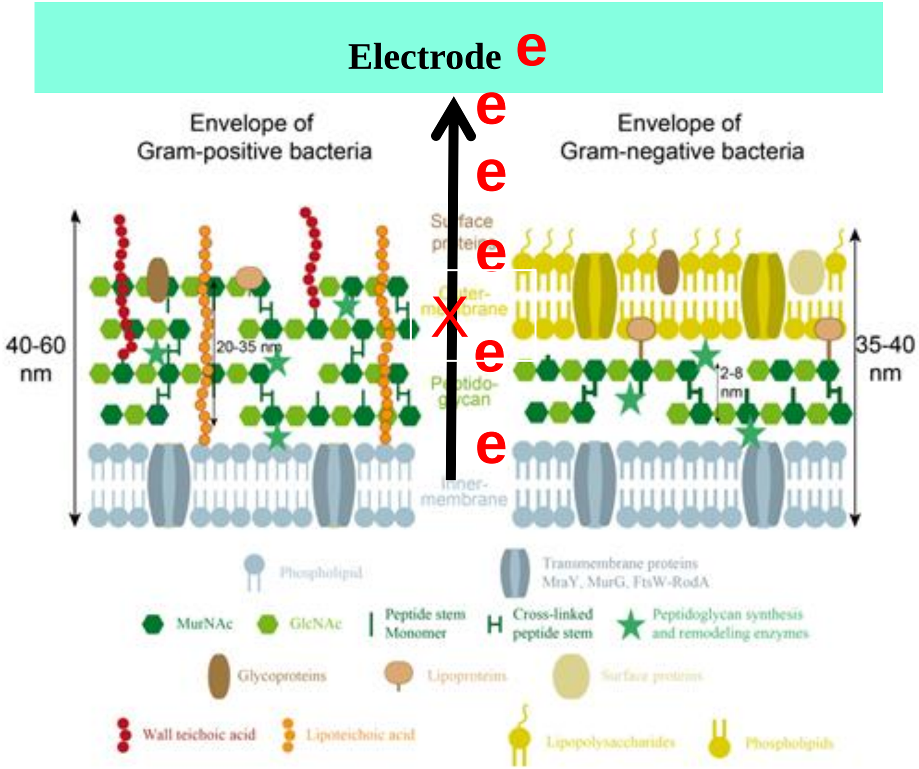
http://hyperphysics.phy-astr.gsu.edu/hbase/Biology/etcatps.html



chloroplast stroma
H+
ADP
Pi
ATP
NADP
H+
NADPH
ferredoxin-NADP reductase
light
H+
cytochrome
light
e-
FNR
Fd
ferredoxin
ATP synthase
P680
e-
PSII
PQ
PQH2
b6f
e-
P700
PSI
e-
PC
plastoquinone
plastocyanin
H+
H+
H2O
O2
H+
oxygen-evolving complex
thylakoid lumen

Challenges of extracting electrical signal/current from biological system





➢Redox enzymes : **hydrodynamic dia. 50 to 100s of A°**

➢Typically, the protein environment allows electron tunneling within a **separation of 5 to 20 Å**

Lovely et al. Nature **435, 1098-1101 (2005)**

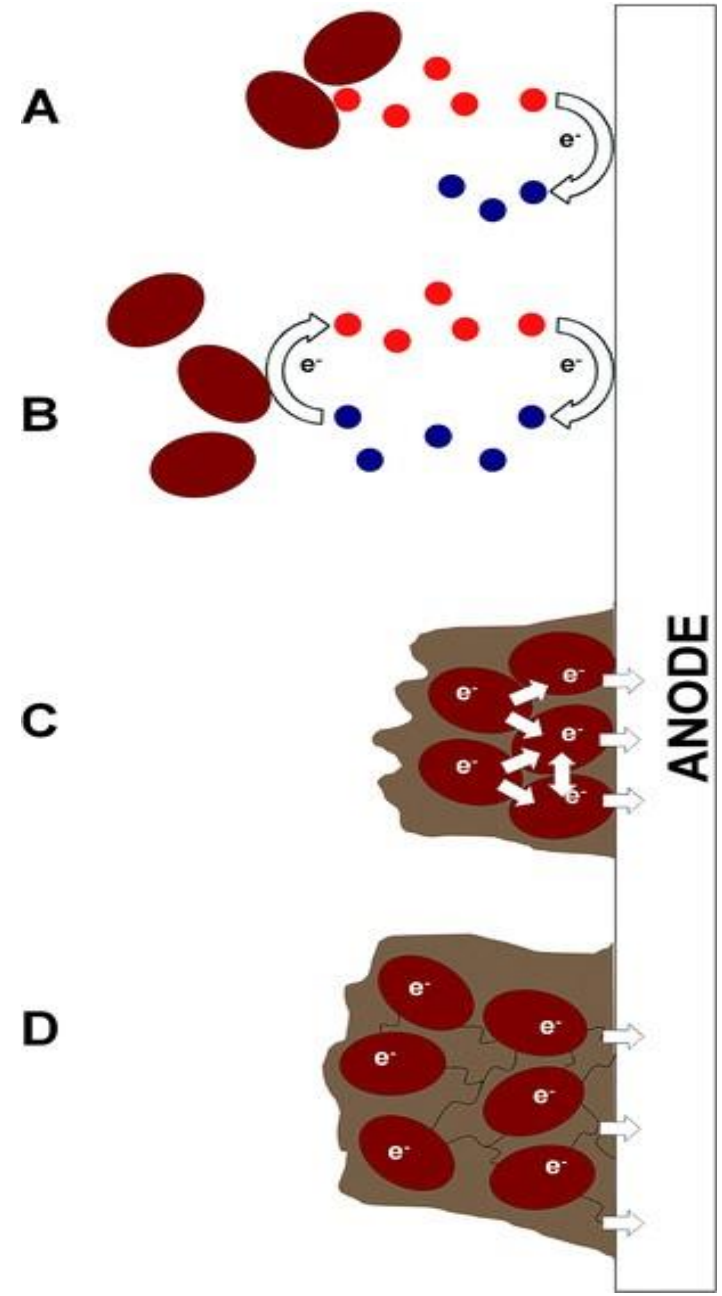
Shuttle electrons to electrodes:

(A) Indirect extracellular electron transfer without recycling.

(B) Indirect extracellular electron transfer with redox cycling.

(C) Direct extracellular electron transfer.

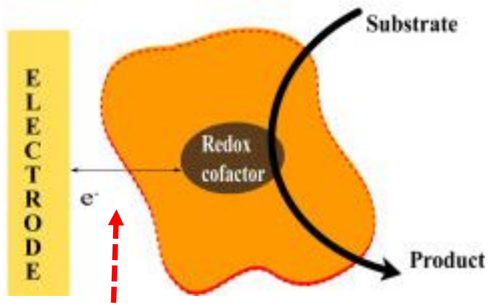
(D) Direct contact by nanowire appendages.



(McCormick et al. 2015)

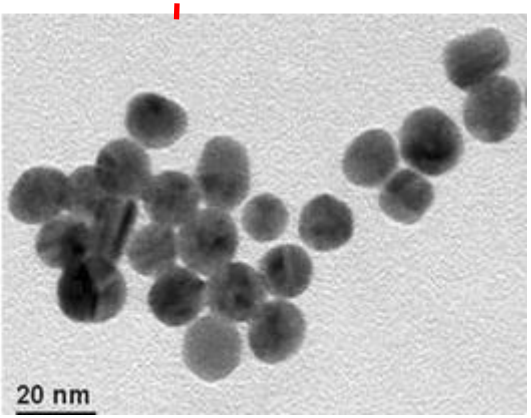
Advantages of 3G bioelectrodes

- ✓ DET goes hand-in hand with turnover numbers.
- ✓ Low polarization potential offers high specific currents and biosensor sensitivity.
- ✓ Higher operational stability of the device (no issue such as, mediator leaching).
- ✓ Suitable in open environment/body integrated system (as no toxic mediators are used).



3G Bioelectrode

Direct Electron Transfer



sensors & Bioelectron. 79 (2016).

When the overall reaction of a BFC is thermodynamically favorable, electricity is generated. The concept may be defined by the following equation:

$$\Delta G_r = - E_{emf} * nF$$

where ΔGr (J) is the Gibbs free energy, nF is the charge transferred in the reaction with n representing the number of electrons per reaction mol, and F is Faraday's constant (96485 C/mol).

The electromotive force E (emf) generated in the fuel cell is due to the difference between the cathodic (E_{cat}) and anodic (E_{an}) potential, as shown later, and can be calculated from the Gibbs free energy change for the anodic and cathodic reactions.

$$E_{\mathrm{emf}} = E_{\mathrm{cat}} - E_{\mathrm{an}}$$

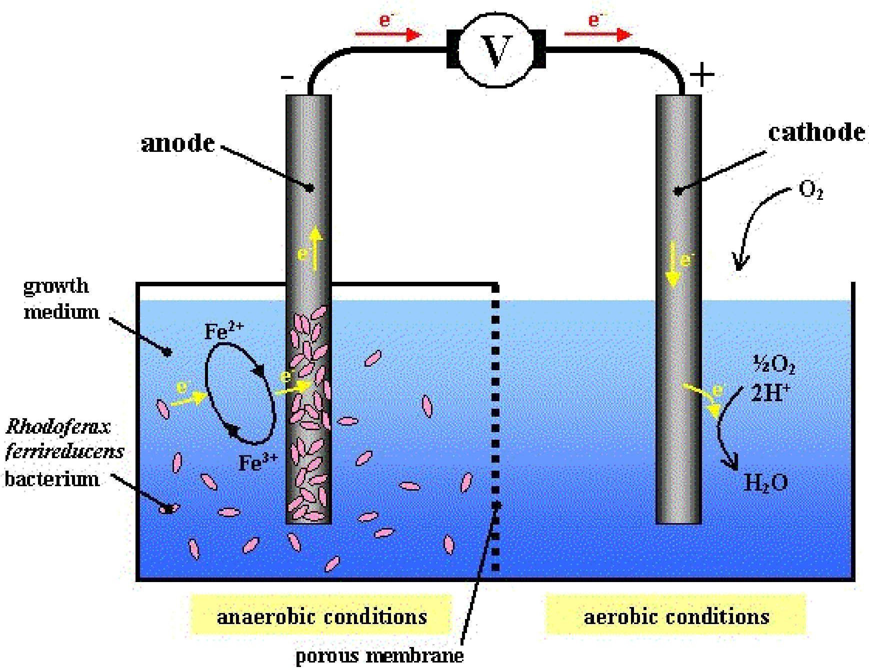
Theoretical cell voltage, $E_{cell} = E°'_{ox} - E°'_{fuel}$

Actual cell voltage, $\mathbf{V_{cell} = E_{cell} - \eta}$

Where η (Over voltage) $= \Delta\eta_{act} + \Delta\eta_{ohm} + \Delta\eta_{con}$

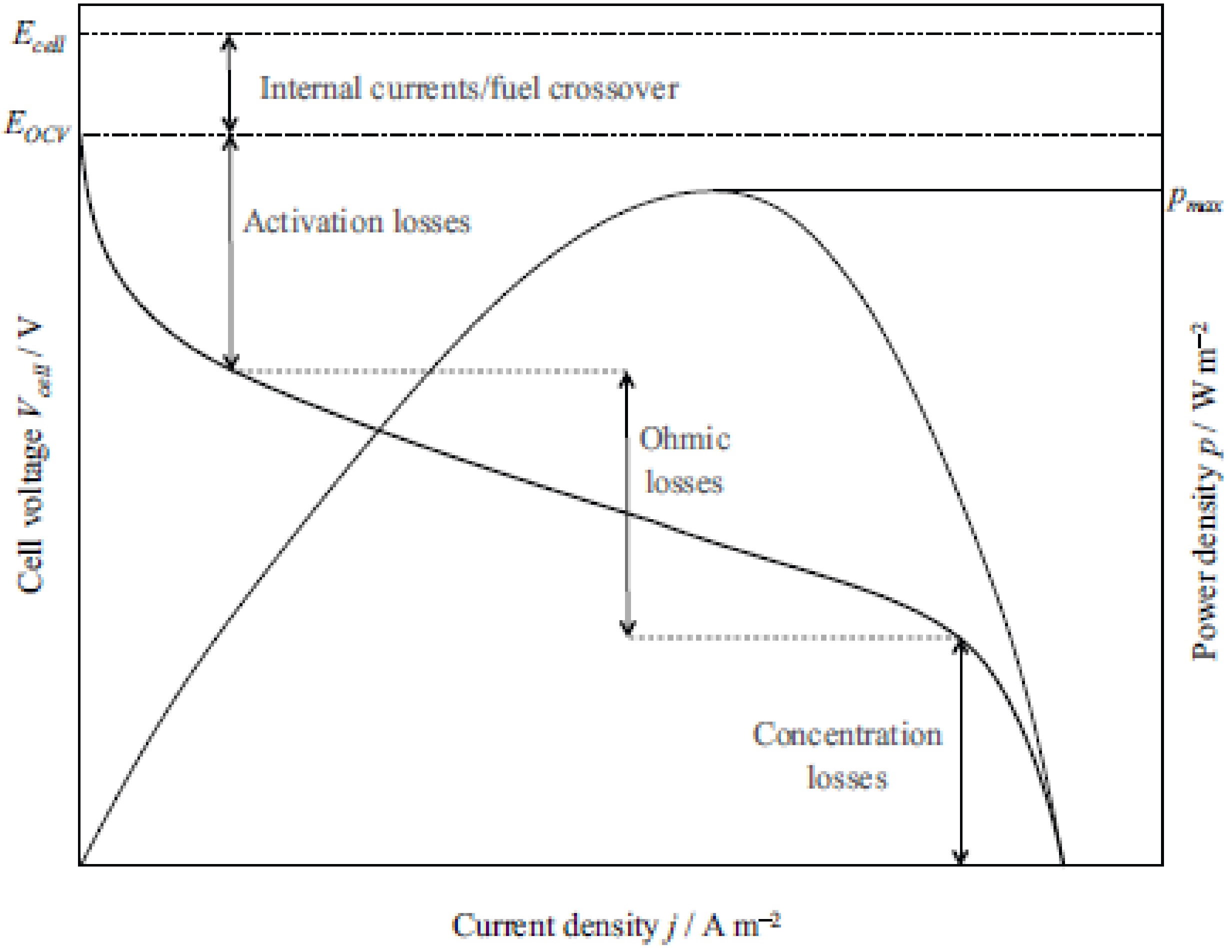
Challenges in BFC

1. Low power density
2. Short life of enzymatic BFCs
3. Potential loss in BFCs



How to measure a BFC?

The influence of external and internal resistances can be understood by such polarization graphs. There are three distinct regions at different current ranges:

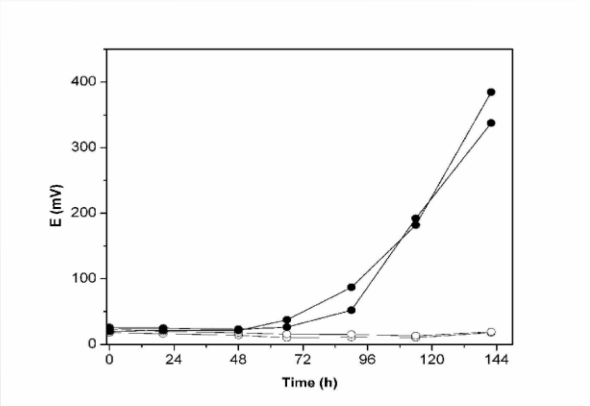


- Ohm's law: **I = V/R** **P = V I**

It is customary to express current and power by electrode area or cell volume (A/m^2-A/m^3 or W/m^2-W/m^3).

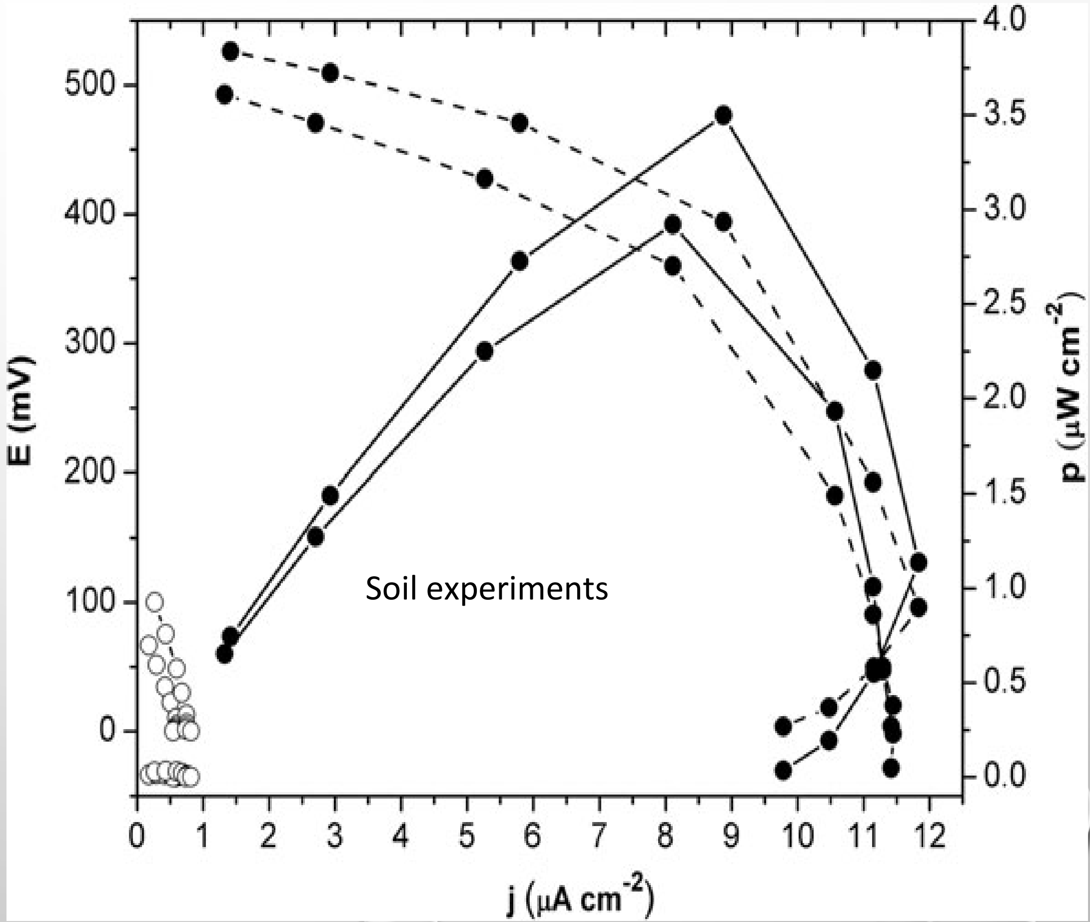
MFC application – Life searching devices for planetary exploration

Microbial fuel cells we were able to differentiate samples with or without heterotrophic life



Natrialba magadii is a prokaryotic microorganism that belongs to the domain Archaea and is a heterotrophic aerobic member of the family Halobacteriaceae. It is an extremophilic haloalkaliphilic microorganism that lives in 3.5–4.0M NaCl and pH values between 9 and 11 (optimum range)

Saccharomyces cerevisiae is a facultative anaerobic unicellular fungus which belongs to the domain Eukarya.



Abrevaya X.C., Sacco N., Mauas P.J.D., Cortón E. High Ionic Strength Microbial Fuel Cell using Salt Tolerant Archaea. Extremophiles, 2011, 15 633-642.

Abrevaya X.C., Mauas P.J.D., Cortón E. Microbial Fuel Cells Applied to the Metabolically–Based Detection of Extraterrestrial Life. Astrobiology, 2010, 10, 965-971.

Ideally, the cell voltage should be independent of the current drawn. However, in practice, this reversible cell voltage (Ecell) is not realized even under infinite load (zero current) conditions due to internal losses and fuel crossover when the cell is operated.

The cell voltage at zero current is termed OCP. As current is drawn from the fuel cell (at varying loads), the E_{cell} deviates from OCP as a result of various losses, which are known as overpotential, as depicted by the following quation

$$E_{cell} = E_{emf} - \left(\sum \eta_{act} + \sum \eta_{conc} + IR_{\Omega)} \right)$$

where ηact is the activation overpotential, ηconc is concentration overpotential, and I and R_{Ω} represent current and resistance (load), respectively. The current discharge pattern with respect to the external resistance can be illustrated by the polarization curve, which is plotted by considering the change in current density versus voltage.

Coulombic Efficiency:

The Coulombic efficiency, is defined as the ratio of total Coulombs actually transferred to the anode from the substrate, to maximum possible Coulombs if all substrate removal produced current. The total Coulombs obtained is determined by integrating the current over time, so that the Coulombic efficiency for an MFC run in fed-batch mode is evaluated over a period of time t_b, is calculated as:

$$\text{Coulombic efficiency} = \frac{\text{Coulombs transferred from substrate to anode}}{\text{Theoretical maximum coulomb produced}} \times 100\%$$

$$\epsilon_{Cb} = \frac{M \int_0^{t_b} I\, dt}{F b v_{An} \Delta COD} \qquad \epsilon_{Cb} = \frac{MI}{F b q \Delta COD}$$

Where M=32, the molecular weight of oxygen, F is Faraday's constant, b = 4 is the number of electrons exchanged per mole of oxygen, v_{An} is the volume of liquid in the anode compartment, and delta COD is the change in COD over time t_b.

The equation in right side is under steady conditions.

- **Up to 90% of the COD can be removed**
- **Columbic efficiency ~ 80% reported.**

Energy Efficiency:

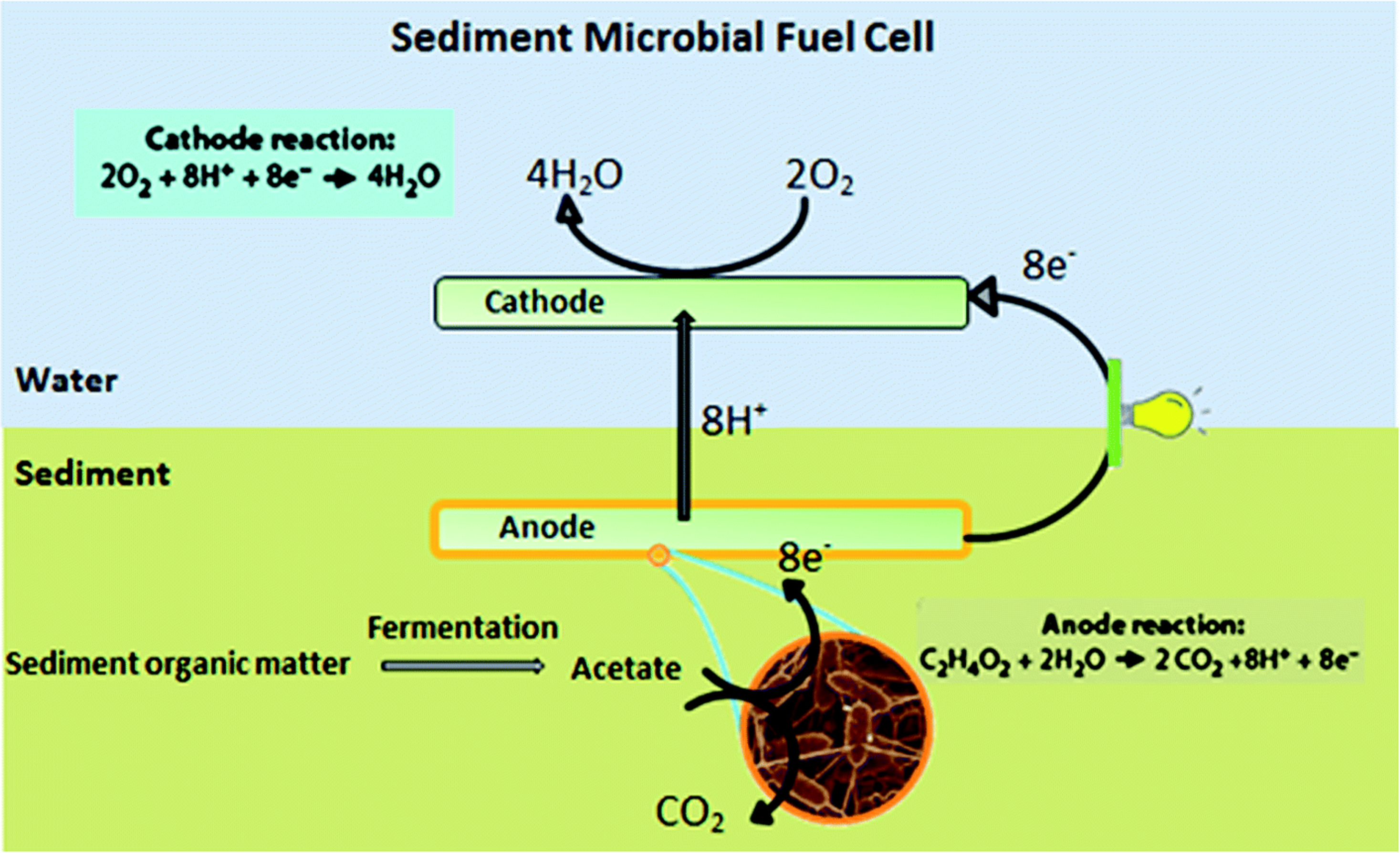
The most important factor for evaluating the performance of an MFC for making electricity, compared to more traditional techniques, is to evaluate the system in terms of the energy recovery.

The overall energetic efficiency, is calculated as the ***ratio of power produced by the cell over a time interval t to the heat of combustion of the organic substrate added in that time frame, or***

$$\epsilon_E = \frac{\int_0^t E_{cell} I dt}{\Delta H m_{added}}$$

where delta H is the heat of combustion (J mol^{-1}) and m_{added} is the amount (mol) of substrate added.

Microbial BFC integrated into water bed



Bruce Logan, PennState University

BOD sensor

➢operational > 5 years without extra maintenance, far longer in service life than BOD sensors .

OTHER APPLICATIONS OF Microbial BFC

Wastewater treatment and electricity generation

Prototype of a 200-liter MFC stack fed with domestic wastewater (Ge, et al. J. Power Sources, 2015)

660 gallon, **2 Kilowatt** MFC to clean brewery in Fosters, an Australian beer company

Emefcy Co. Ltd, Israel

- Bacteria: *Shewanella oneidensis* and *Geobacter sulfurreducens.*
- *Electrode:* carbon cloth.
- Size: ~ 1 m^3 , ~ 3 m^3 /day of wastewater depending on the amount of organic material present.
- ~ 4 watts / kg of organic material, Sludge can be cut down by 80 %.

Alcohol fuel-based BFC with 3rd generation bioelectrodes

Patent:

Goswami et al.. - ALCOHOL FUELED ENZYME BASED BIO-BATTERY CUM BIOFUEL CELL, Application No. - 201931046354 (2019).

Pranab Goswami et al. **GRAPHITE PASTE INK WITH SILK SERICIN FOR ENHANCING THE CONDUCTIVITY AND STABILITY OF ENZYME BIOELECTRODES**. Granted Patent no: 348844.