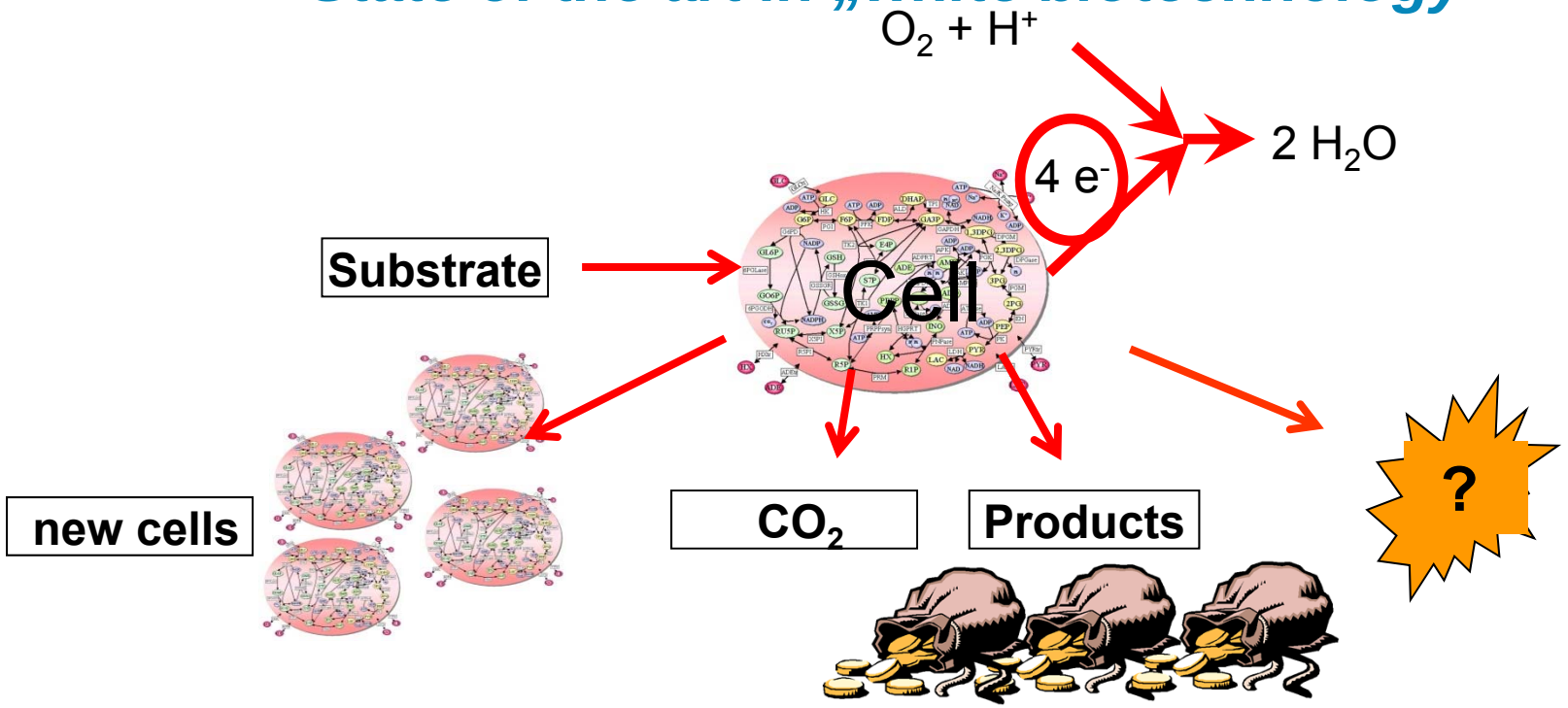
Nachhaltige Energieerzeugung mittels Biotechnologie

Stand (15.12.2014)

Thomas Maskow
Department Umweltmikrobiologie
Thomas.maskow@ufz.de

HELMHOLTZ
ZENTRUM FÜR
UMWELTFORSCHUNG
UFZ

State of the art in „white biotechnology“



Substrate S **Biomass X** **Product P**

$$Y_{S/X}\ \mathbf{C_{S1}H_{S2}O_{S3}} + Y_{N/X}\ \mathbf{NH_4^+} + Y_{O/X}\ \mathbf{O_2} \longrightarrow Y_{CO2/X}\ \mathbf{CO_2} + \mathbf{C_{X1}H_{X2}O_{X3}N_{X4}} + Y_{P/X}\ \mathbf{C_{P1}H_{P2}O_{P3}N_{P1}}$$

$(CH_{1.84}O_{0.53}N_{0.23})$

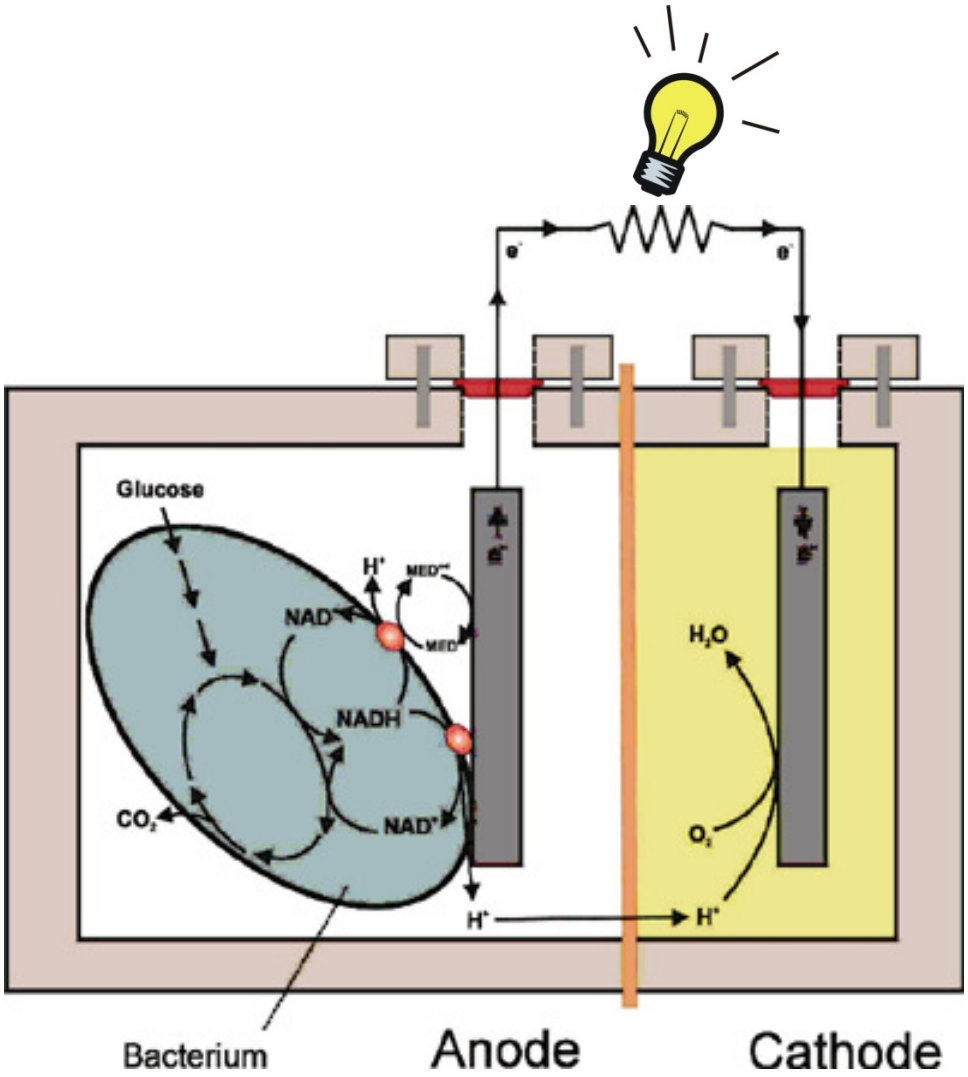
Why waste of energy?

Microbial fuel cells (Electrons not to oxygen to electrode)

- General Principles
- History
- The energy metabolisms of microorganisms
- The most important bottleneck of MFC
- Factors limiting the electrical energy generation
- Microbial electrolyses cells (MEC)
- Other bulk chemicals using (MFC/BES) ?
- Pro and con of MFC, MEC or BES

HELMHOLTZ ZENTRUM FÜR UMWELTFORSCHUNG UFZ

General principle of microbial fuel cell



$C_6H_{12}O_6 + 6\ H_20$ ->

$6\ CO_2 + 24\ H^+ + 24\ e^-$

$O_2 + 4\ H^+ + 4\ e^-$ ->

$2\ H_2O$

Brief history of microbial fuel cell

1911	M.C. Potter (University of Durham): Electricity from *E. coli*
1931	Barnet: MFC connected in series -> 35 volts but just 0.2 mA
1963	DelDuca et al.: used hydrogen (from fermentation of glucose by *Clostridium butyricum*) as the reactant for a „normal fuel cell“; Problem: unreliable due to unstable H_2 production, indirect MFC
1976	Suzuki: Solved the problem with unstable H_2 production
1976	Suzuki et al.: Current design concept of an MFC
Seventies	Suzuki et al.: Some basics of function of MFC revealed
Seventies	MJ Allen, H. Peter Bennetto (King‘s College London): MFC -> generation of electricity for third world countries.
May 2007	University of Queensland, Australia; prototype MFC; The prototype (10 L) converts the brewery waste water into CO_2, clean water, and electricity. 660 gallon waste water -> 2 kilowatts; Negligible amount of power but clean water

The energy metabolism of microorganims

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6H_2O + 6CO_2 \quad \Delta G^{\ominus\prime} = -2895\ kJ\ mol^{-1}$$

$$C_6H_{12}O_6 \rightarrow C_3H_7COOH + 2CO_2 + 2H_2 \quad \Delta G^{\ominus\prime} = -225\ kJ\ mol^{-1}$$

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 2CO_2 + 4H_2 \quad \Delta G^{\ominus\prime} = -206\ kJ\ mol^{-1}$$

$$\Delta G^{\Theta'} = n\ x\ F\ \left[E^{\Theta'}(donor) - E^{\Theta'}(acceptor)\right]$$

$$\Delta G^{\Theta'} = 24\ x\ 96485.3\ As\ mol^{-1}\ (-0.43 - 0.82)V$$

$$\Delta G^{\Theta'} = -2894.55\ kJ\ mol^{-1}$$

$$\Delta G^{\Theta'} = 24\ x\ 96485.3\ As\ mol^{-1}\ (-0.43 - 0.51)V$$

$$\Delta G^{\Theta'} = -2176.70\ kJ\ mol^{-1}$$

Redox couple	$E^{\ominus\prime a}$/V
CO_2/Glucose	−0.43[23]
CO_2/Formate	−0.43[23]
$2H^+/H_2$	−0.42[23]
CO_2/Acetate	−0.28[23]
CO_2/CH_4	−0.24[23]
SO_4^{2-}/HS^-	−0.22[23]
Pyrovate/lactate	−0.19[23]
Fumarate/succinate	+0.33[23]
NO_3^-/NO_2^-	+0.43[23]
MnO_2/Mn^{2+}	+0.60[24]
Fe^{3+}/Fe^{2+}	+0.77[23]
$1/2O_2/H_2O$	+0.82[23]
$1/2O_2/H_2O$	+0.51[25,26b]

[a] Standard potential, measured at pH 7. [b] Effective (irreversible) potential, determined in MFC experiments (pH 7).

Due to:

- **Side reaction at the cathode**

  (impurities in the electrolyte and at the electrode surface)

- **Mixed potentials are formed**

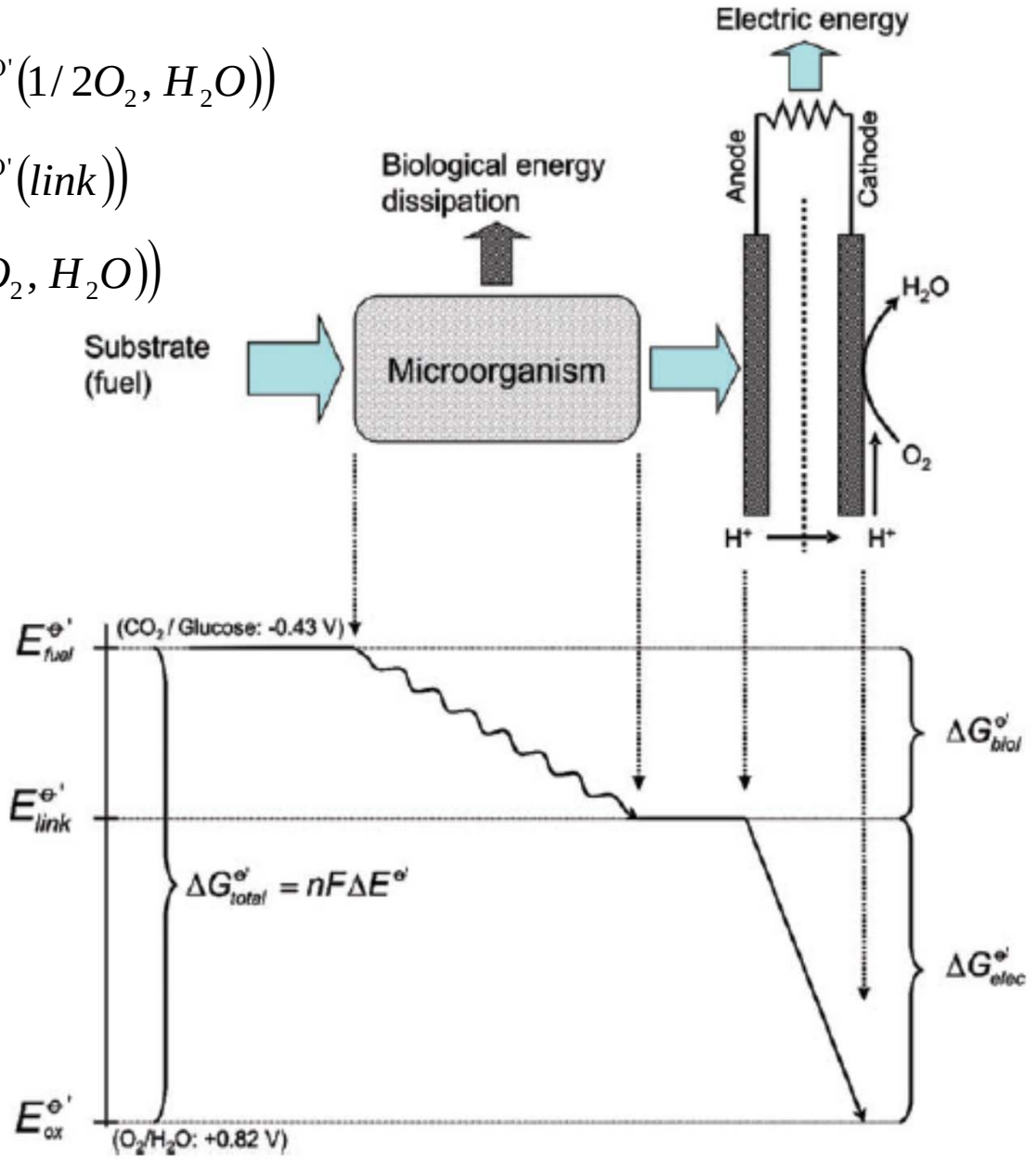
$$\Delta G^{\Theta'}_{elec.} = \Delta G^{\Theta'}_{total} - \Delta G^{\Theta'}_{biol.}$$

$$\Delta G^{\Theta'}_{total} = n\,F\left(E^{\Theta'}\left(glu\cos e, CO_2\right) - E^{\Theta'}\left(1/2O_2, H_2O\right)\right)$$

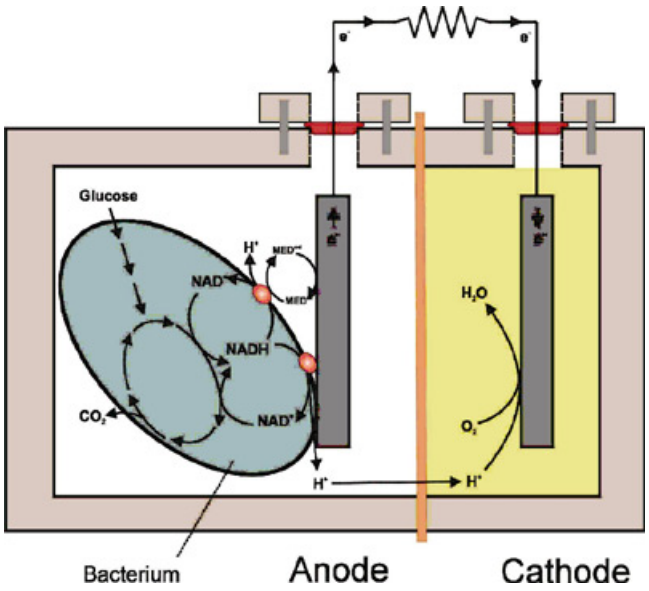
$$\Delta G^{\Theta'}_{biol} = n\,F\left(E^{\Theta'}\left(glu\cos e, CO_2\right) - E^{\Theta'}\left(link\right)\right)$$

$$\Delta G^{\Theta'}_{elec.} = n\,F\left(E^{\Theta'}\left(link\right) - E^{\Theta'}_{effective}\left(1/2O_2, H_2O\right)\right)$$

- A part of the energy is „wasted“ to biomass !!!
- $E^{\Theta'}$ (link) determines the electrical energy available!!!

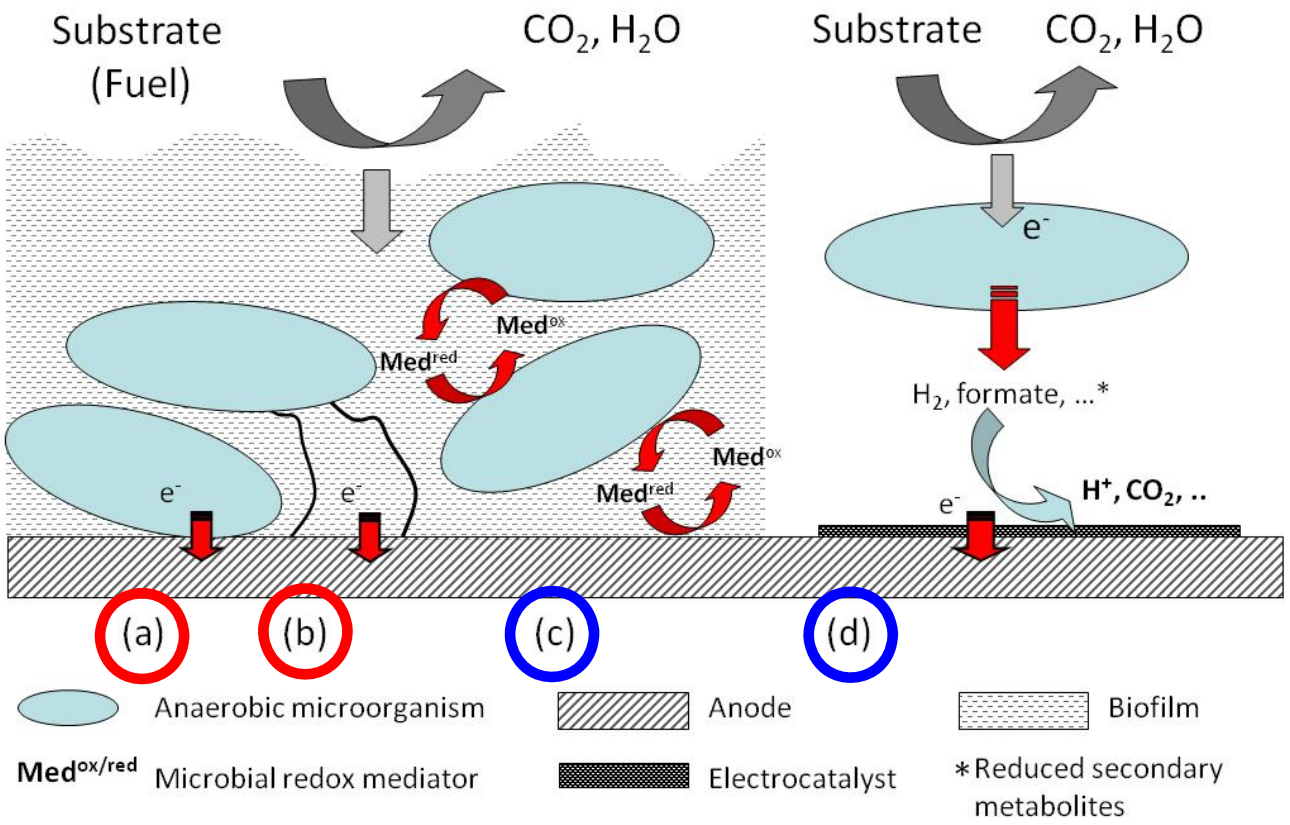


The most important bottleneck of MFC ???



Transport of the electrons to the anode ?

HELMHOLTZ ZENTRUM FÜR UMWELTFORSCHUNG UFZ



A number of hypotheses have been proposed which explain how an efficient electron transfer from the microbial cells to the fuel cell anode can be achieved:

Direct electron transfer (DET): a, b

Mediated electron transfer (MET): c, d

Direct electron transfer (DET):

Physical contact between microorganism and anode material is necessary.

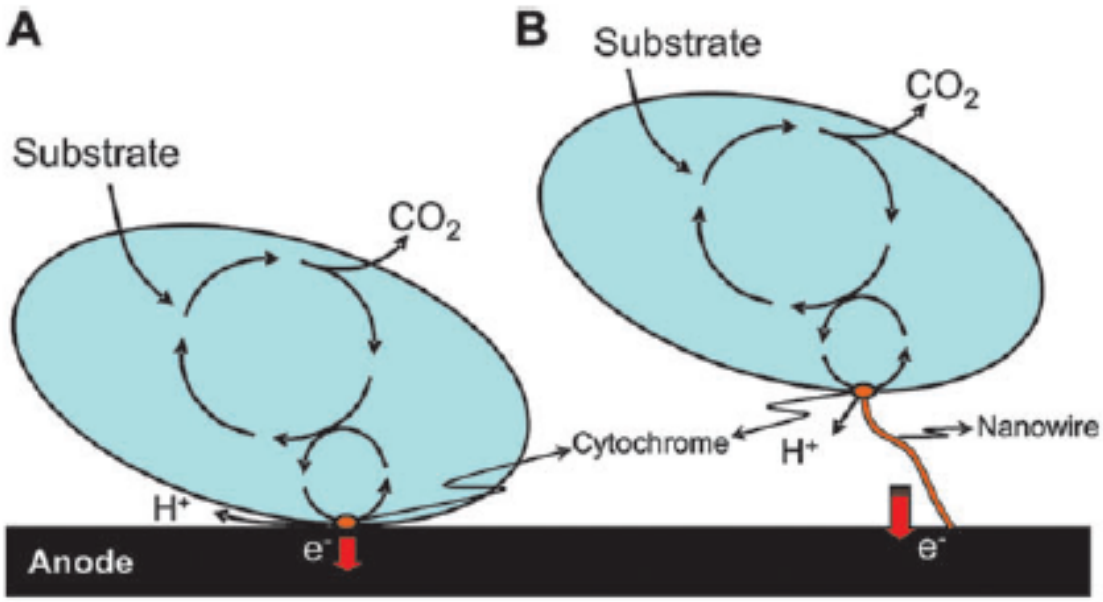


Fig. 3 Illustration of the DET *via* (A) membrane bound cytochromes, (B) electronically conducting nanowires.

The link are cytochromes

HELMHOLTZ ZENTRUM FÜR UMWELTFORSCHUNG UFZ

Direct electron transfer (DET):

Physical contact between microorganism and anode material **is necessary.**

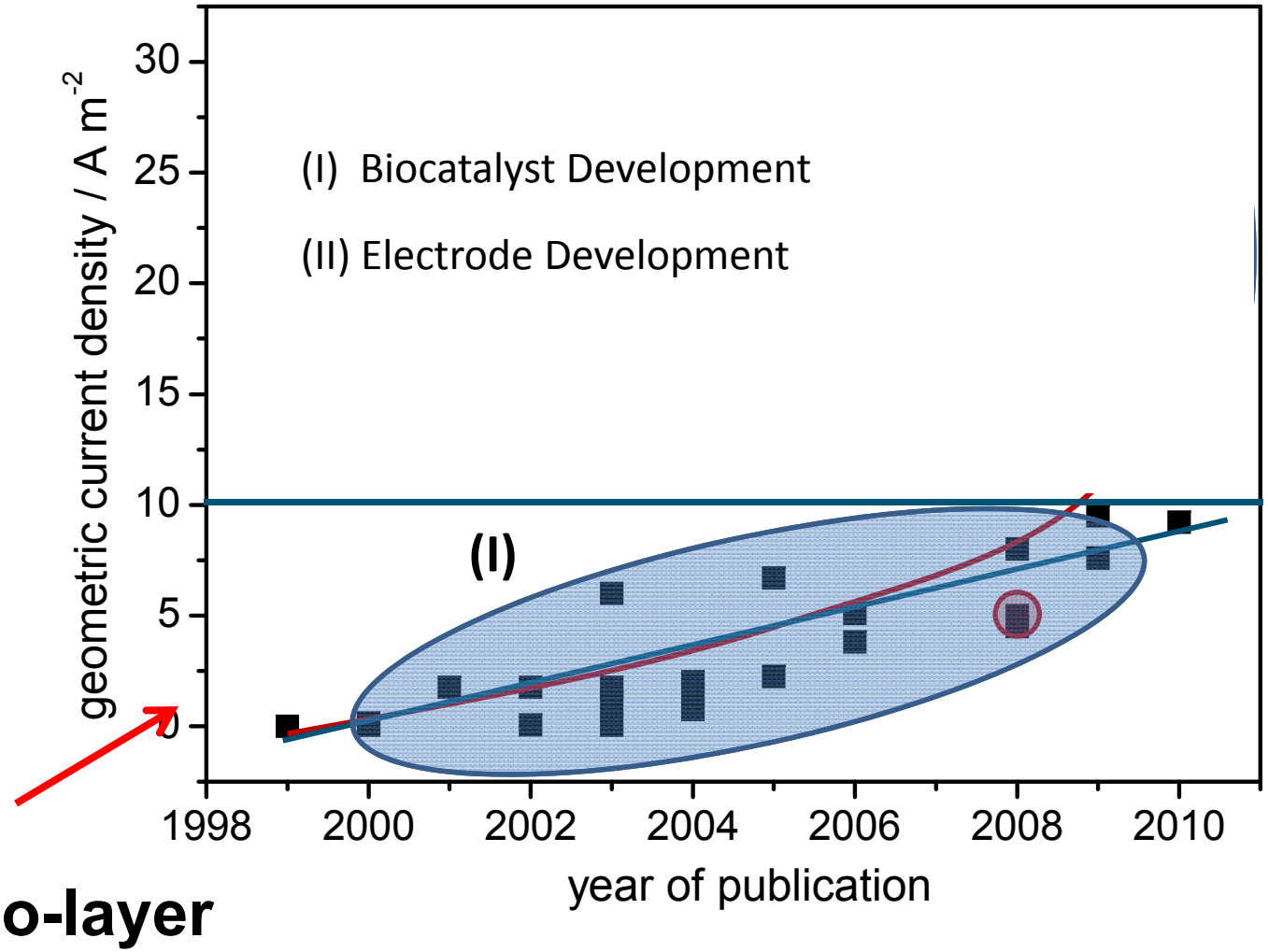
(a) Direct electron transfer via membrane bound cytochromes.

- Most straightforward electron transfer mechanism (the whole bacterial cell is adherent to the anode)
- Ascribed to a number of microorganisms (e.g. *Geobacter, Rhodoferax)*
- Direct cell contact to the fuel cell anode confines the number of electro-chemically active cells to a **mono-layer** and thus severely limits the **maximum current densities (to e.g., 3 µA cm^{-2})**

(b) Electron transfer via microbial nanowires:

- Recently found (2005)
- Ascribed to the *Geobacteraceae* and species of the *Shewanella* family
- Electron transfer via a conductive "pili"; work over several microbial layers.
- Increase the **achievable current** density by **one order of magnitude**

Recent progress of BES anode current densities ….



Mono-layer

nature Vol 435|23 June 2005|doi:10.1038/nature03661

LETTERS

Extracellular electron transfer via microbial nanowires

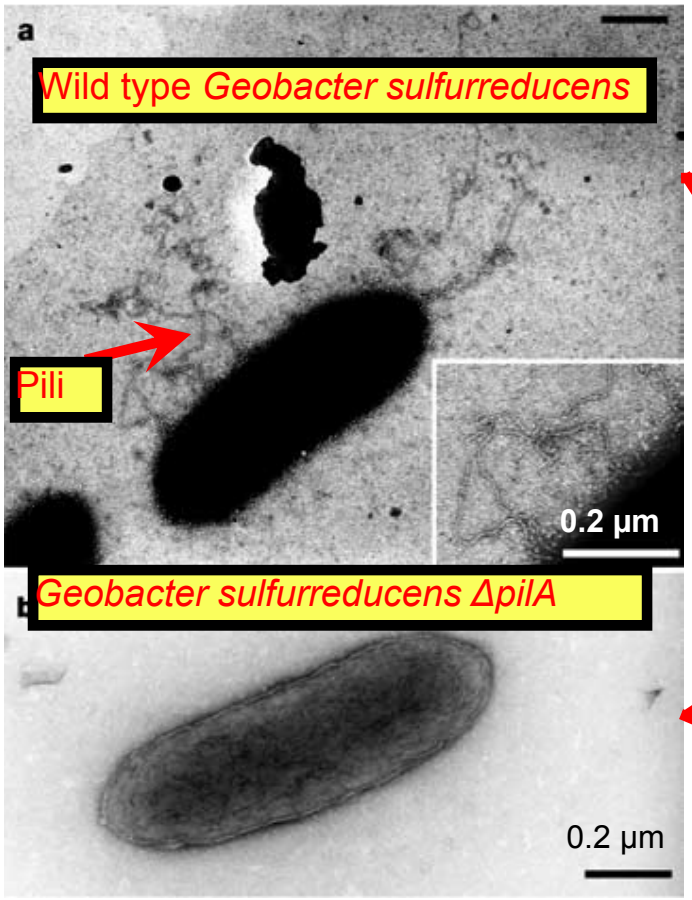
Gemma Reguera[1], Kevin D. McCarthy[2]*, Teena Mehta[1]*, Julie S. Nicoll[1], Mark T. Tuominen[2] & Derek R. Lovley[1]

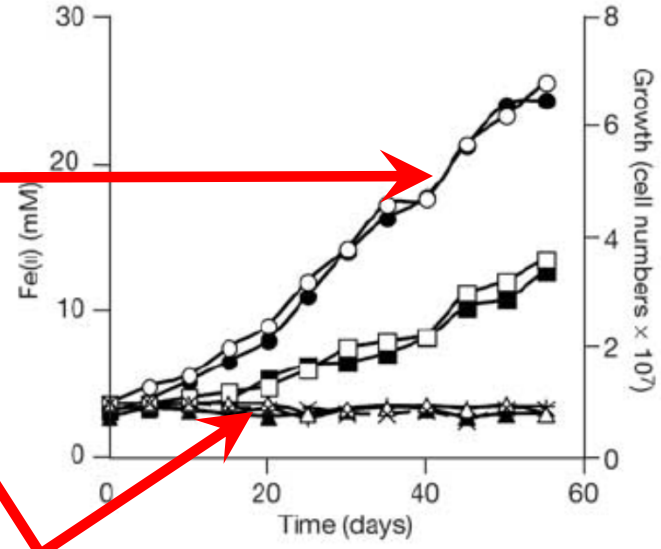
Microbes that can transfer electrons to extracellular electron acceptors, such as Fe(III) oxides, are important in organic matter degradation and nutrient cycling in soils and sediments[1,2]. Previous investigations on electron transfer to Fe(III) have focused on the role of outer-membrane *c*-type cytochromes[1,3]. However, some Fe(III) reducers lack *c*-cytochromes[4]. *Geobacter* species, which are the predominant Fe(III) reducers in many environments[1], must directly contact Fe(III) oxides to reduce them[5], and produce monolateral pili[6] that were proposed[1,2], on the basis of the role of pili in other organisms[7,8], to aid in establishing contact with the Fe(III) oxides. Here we report that a pilus-deficient mutant of *Geobacter sulfurreducens* could not reduce Fe(III) oxides but could attach to them. Conducting-probe atomic force microscopy revealed that the pili were highly conductive. These results indicate that the pili of *G. sulfurreducens* might serve as biological nanowires, transferring electrons from the cell surface to the surface of Fe(III) oxides. Electron transfer through pili indicates possibilities for other unique cell-surface and cell–cell interactions, and for bioengineering of novel conductive materials.

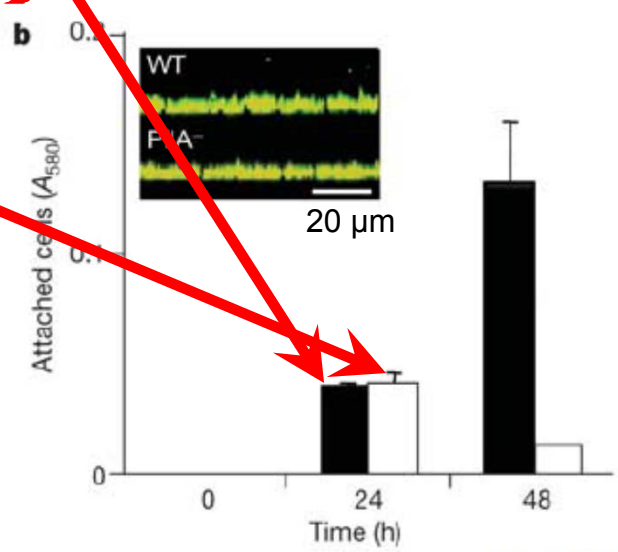
(Fig. 1a) but not on soluble Fe(III) (Fig. 1b), and the pili were localized to one side of the cell. The formation of pili could also be induced during growth on the alternative electron acceptor fumarate if the cells were grown at the suboptimal temperature of 25 °C (Fig. 2a), indicating that pilin production in *G. sulfurreducens* might be growth-regulated as it is in other bacteria[11].

The genome sequence of *G. sulfurreducens* contained two open reading frames (ORFs), GSU1496 and GSU1776, predicted to code for pilin domain proteins with the conserved amino-terminal amino acid characteristics of type IV pilins[12]. Phylogenetic analyses placed the protein encoded by ORF GSU1776 among bacterial pseudopilins of type II secretion systems, and subsequent studies have confirmed the role of this gene, termed *gspG*, in protein secretion to the outer membrane[13]. The protein encoded by ORF GSU1496 formed an independent line of descent along with pilin subunits of other members of the *Geobacteraceae* such as *Geobacter metallireducens* and *Pelobacter propionicus* (Fig. 1c). The predicted length of these *Geobacter* pilin proteins was considerably shorter than other bacterial pilins (see Supplementary Fig. S1) and was restricted to the highly conserved N-terminal domain of bacterial type IV$_1$ pilins, which

$Fe^{3+} + e^{-} \rightarrow Fe^{2+}$







Transmission electrone microscopy analysis

HELMHOLTZ ZENTRUM FÜR UMWELTFORSCHUNG UFZ

Table 2 Formal potentials measured for DET of different bacterial species

Bacterial strain	E'/V^a
Shewanella putrefaciens IR-1	0.01 [40]
Shewanella putrefaciens MR-1	−0.02 [40]
Shewanella putrefaciens SR-1	−0.01 [40]
Aeromonas hydrophila PA 3	0 [45]
Clostridium sp. EG 3	0 [46]

[a] Determined as mid-peak potential in cyclic voltammetry; pH 7.

Table 3 Theoretical energy efficiency of DET

Linking species	E'/V	$\Delta G'_{elec,\ n=1}/kJ\ mol^{-1}$	$\Delta G'_{elec,\ n=1}/\Delta G'_{total,\ n=1}$ (%)	n	$\Delta G'_{elec}/kJ\ mol^{-1}$	$\Delta G'_{elec}/\Delta G'_{total}$ (%)
Outer membrane cytochrome	0	−49.2	54.2	24[a]	−1181.0[a]	54.2

[a] Theoretical (maximum) number of electrons derivable from a full oxidation of glucose.

$$\Delta G^{\Theta'}_{elec} = n\ x\ F\ \left[E^{\Theta'}(link) - E^{\Theta'}(0.5O_2 / H_2O)\right]$$

$$\Delta G^{\Theta'}_{elec} = 24\ x\ 96485.3\ A\,s\,mol^{-1}\ (\pm 0 - 0.51)V$$

$$\Delta G^{\Theta'}_{elec} = -1181\ kJ\ mol^{-1}$$

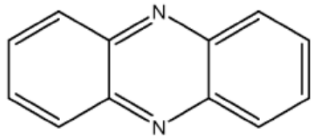
A maximum of 54 % of the energy can be got

Mediated electron transfer (MET):

Physical contact between microorganism and anode material is necessary.

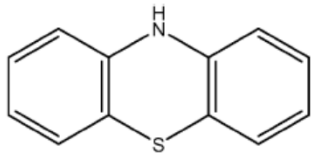
(a) MET via exogenous (artificial) redox mediators

- current densities (3 – 30 µA cm^{-2}) → (10 -100 µA cm^{-2})
- regular addition of sometimes harmful substances



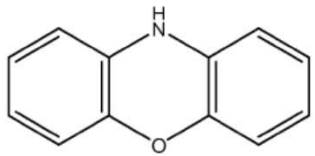
Phenazines

Neutral Red	−0.32
Safranine	−0.29
Phenazine ethosulfate	0.06



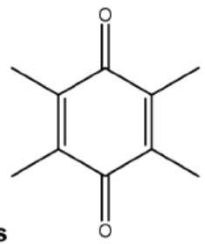
Phenothiazines

New Methylene Blue	−0.02
Toluidine Blue O	0.03
Thionine	0.06
Phenothiazinone	0.13



Phenoxazines

Resorufin	−0.05
Gallocyanine	0.02



Quinones

2-Hydroxy-1,4-naphthoquinone	−0.14
Anthraquinone-2,6-disulfonate	−0.18

Redoxpotential in $E^{\Theta'}/V$

HELMHOLTZ ZENTRUM FÜR UMWELTFORSCHUNG UFZ

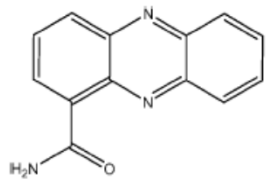
Mediated electron transfer (MET):

Physical contact between microorganism and anode material is necessary.

(b) MET via secondary metabolites

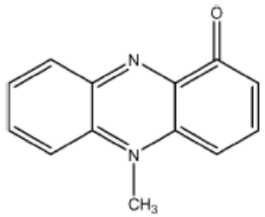
- current densities (10 -100 µA cm^{-2})
- no addition of redox mediators required
- the efficiency of current generation higher due to higher redox potential in comparison to cytochromes

Phenazine-1-carboxamide



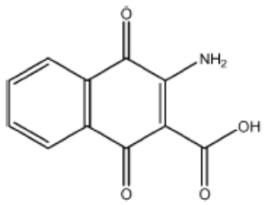
−0.115

Pyocyanine (phenazine)



−0.03

2-Amino-3-carboxy-1,4-naphthoquinone (ACNQ)



−0.071

Redoxpotential in

$E^{\Theta'}/V$

HELMHOLTZ ZENTRUM FÜR UMWELTFORSCHUNG UFZ

Linking species	E'/V	$\Delta G'_{elec,\ n=1}$/kJ mol^{-1}	$\Delta G'_{elec,\ n=1}/\Delta G'_{total,\ n=1}$ (%)	n	$\Delta G'_{elec}$/kJ mol^{-1}	$\Delta G'_{elec}/\Delta G'_{total}$ (%)
Phenazine-1-carboxamide	−0.115	−60.3	66.5	24[a]	−1447	66.5
Pyocyanine	−0.03	−52.1	57.4	24[a]	−1250	57.4
ACNQ	−0.07	−55.9	61.7	24[a]	−1343	61.7

[a] Theoretical (maximum) number of electrons derivable from a full oxidation of glucose.

$$\Delta G^{\Theta'}_{elec} = n\ x\ F\ \left[E^{\Theta'}(link) - E^{\Theta'}(0.5O_2 / H_2O)\right]$$

$$\Delta G^{\Theta'}_{elec} = 24\ x\ 96485.3\ As\ mol^{-1}\ (-0.11 - 0.51)V$$

$$\Delta G^{\Theta'}_{elec} = -1447\ kJ\ mol^{-1}$$

66 % energy efficiency possible

Weaknesses:

- potential loss of mediators -> decreasing in n and thus coulombic and energetic efficiency
- Synthesis and replacement of this components energetically expensive

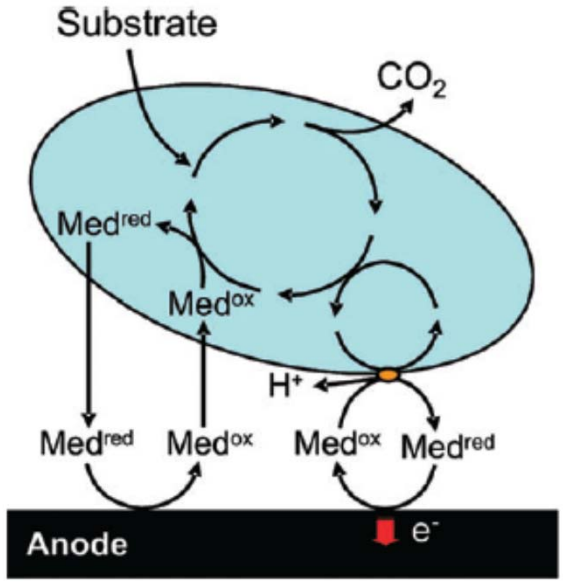


Fig. 4 Simplified, schematic illustration of MET *via* microbial secondary metabolites. Two possible redox mechanisms have been proposed: shuttling *via* outer cell membrane cytochromes and *via* periplasmatic or cytoplasmatic redox couples.

Mediated electron transfer (MET):

Physical contact between microorganism and anode material is necessary.

(c) MET via primary metabolites

- Any terminal electron acceptor applicable if:

  + redox potential sufficiently negative to that of oxygen,

  + water soluble in oxydized and reduzed form,

  + reversibly oxidizable

via anaerobic respiration

$$SO_4^{2-} + 8H^+ + 8e^- \underset{\text{Anode}}{\overset{\text{Bacteria}}{\rightleftharpoons}} S^{2-} + 4H_2O$$

$\Delta E^{\Theta'} = -220\ mV$ $\Delta G^{\Theta'}_{elec,\,n=1} = -70.4\ kJ\ mol^{-1}$ $\Delta G^{\Theta'}_{elec} = -1690\ kJ\ mol^{-1}$

Maxium energy efficiency = 77.6 %

HELMHOLTZ ZENTRUM FÜR UMWELTFORSCHUNG UFZ

via fermentation

$$C_6H_{12}O_6 + 2\,H_2O \rightarrow 2\,CH_3COOH + 2\,CO_2 + 4\,H_2$$

$$\Delta G^{\Theta'}_{elec} = n\ x\ F\ \left[E^{\Theta'}(link) - E^{\Theta'}(0.5O_2 / H_2O)\right]$$

$$\Delta G^{\Theta'}_{elec} = 8\ x\ 96485.3\ As\,mol^{-1}\ (-0.42 - 0.51)V$$

$$\Delta G^{\Theta'}_{elec} = -718\ kJ\ mol^{-1}$$

Maximum energy efficiency = 33 %

- **Perfect negative potential**
- **But low because only 8 electrons ($4H_2$) are formed**

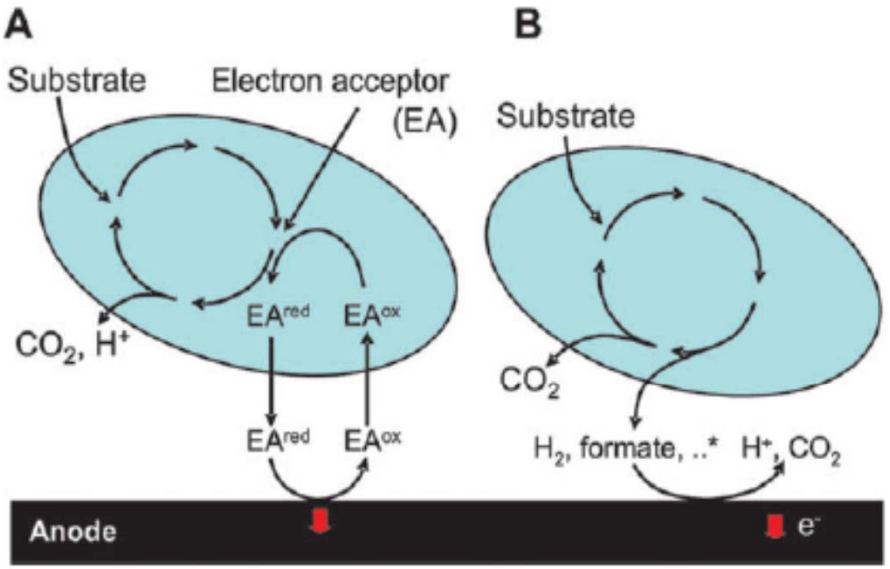


Fig. 5 Simplified, schematic illustration of MET *via* microbial primary metabolites (A) *via* reduced terminal electron acceptors (use of anaerobic respiration), (B) *via* oxidation of reduced fermentation products.

What is the best electron transfer ?

DET:

- High coulombic efficiencies
- Low current and power densities
- Requires extremely large anodic surfaces
- The involved microorganisms (e.g. *Geobacter*) call for low molecular substances (i.e. acetate, butyrate etc.)

MET:

- High current and power densities
- High diversity of exploitable microorganisms
- Big variety of utilizable substances
- low coulombic efficiency due to formation of electrochemically inactive side products

Physical factors limiting the electrical energy generation

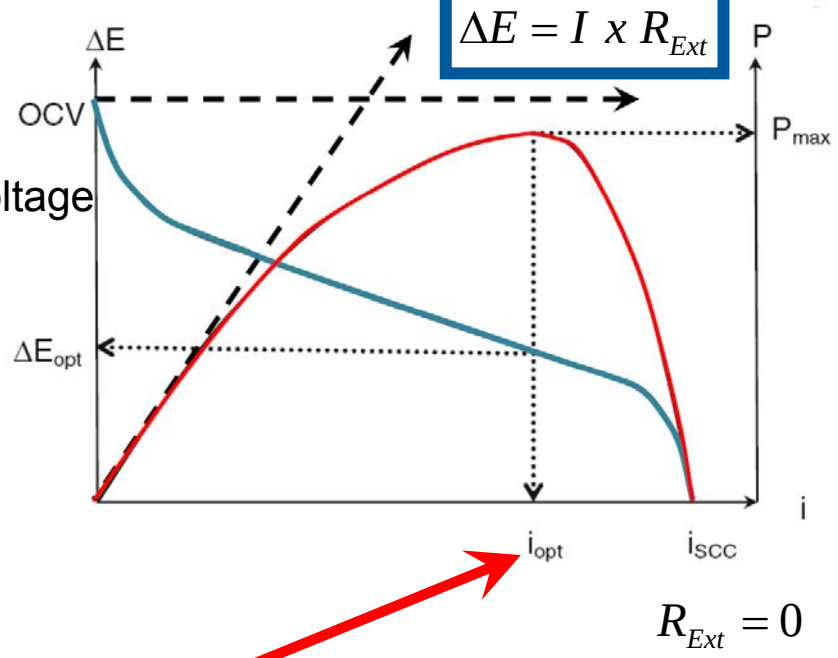
1. Electrical parameters

$$P = I \; x \; \Delta E$$

$$\Delta E = I \; x \; R_{Ext}$$

$R_{Ext} = \infty$

Open **c**ircuit **v**oltage



Voltage

Power (E x I)

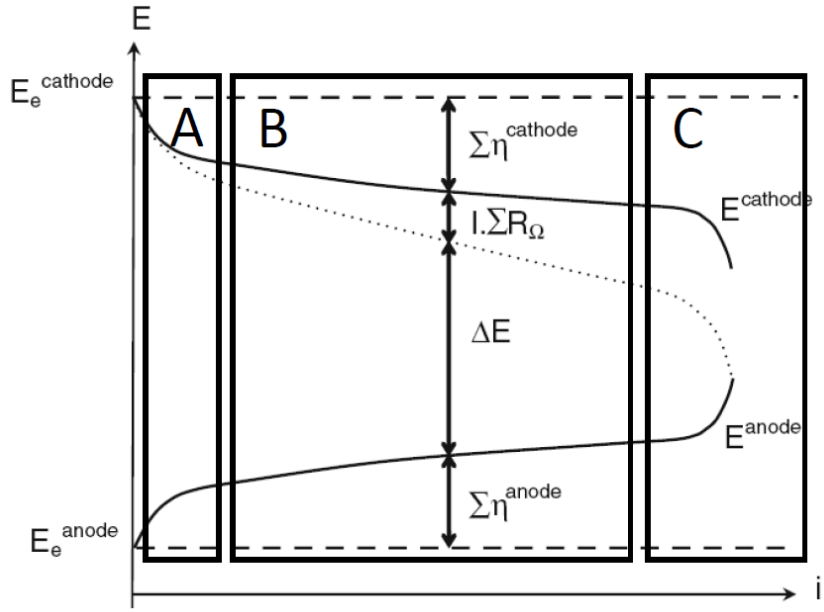
$R_{Ext} = 0$

Short **c**ircuit **c**onditions

Optimum

External load matches internal resistance

HELMHOLTZ ZENTRUM FÜR UMWELTFORSCHUNG UFZ



Cathodic ($E^{cathode}$) and anodic (E^{anode}) polarization curve. ΔE – cell voltage; $1.\Sigma R_\Omega$ ohmic losses

A - Activitation loss

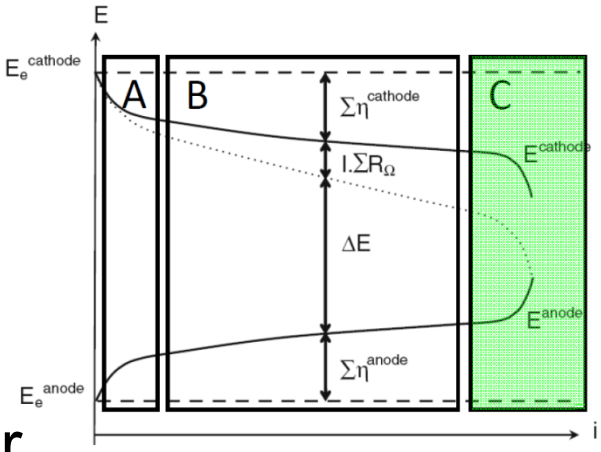
B - Ohmic loss E = R x I

C - Mass transfer loss

HELMHOLTZ ZENTRUM FÜR UMWELTFORSCHUNG UFZ

Mass transfer loss:

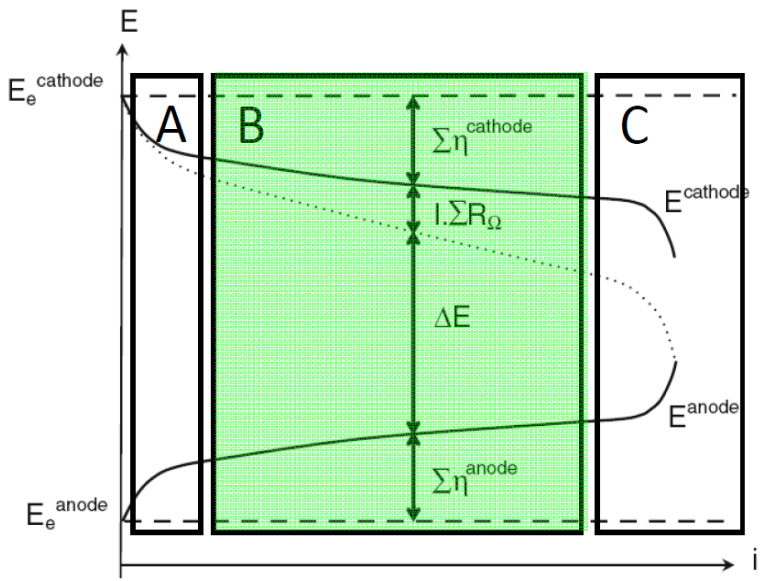
- Substrate rate to the anodic biofilm limits the rate of current generation
- Oxygen rate to the cathode surface limits the rate of current generation
- Prevention of accumulation of waste products (e.g. oxidized intermediates or protons)
- Proton accumulation leads to pH-gradient affecting the MFC performance



HELMHOLTZ ZENTRUM FÜR UMWELTFORSCHUNG UFZ

Ohmic loss

- Resistance of the electrode material
- High conductivity of the material
- Short travel distances for the electrode
- Conductivity, buffer capacity, minimal distance between electrodes are of uttermost importance

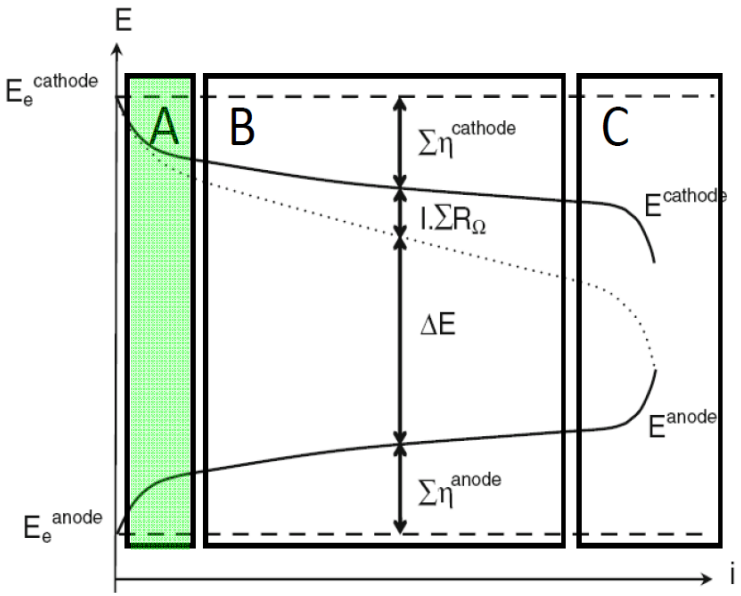


Activation loss

Energy barrier:
to start electron transfer to the anode
or cathode

Low activation losses by:

- Increasing electrode surface
- Increasing the operating temperature
- Establishment of an enriched biofilm on the electrode
- Bacteria can optimize their electron transferring strategies



Electron quenching reactions and energy efficiency

- Loss of electrons due to alternative reactions (e.g. Methanogenesis, respiration (if oxygen intrudes))
- Loss by formation of anodophilic biomass such losses measured as coulombic efficiency (CE)

Coulombic efficiency (CE):

Electrons recovered/ available electrons

Potential efficiency (PE):

actual voltage (ΔE)/OCV

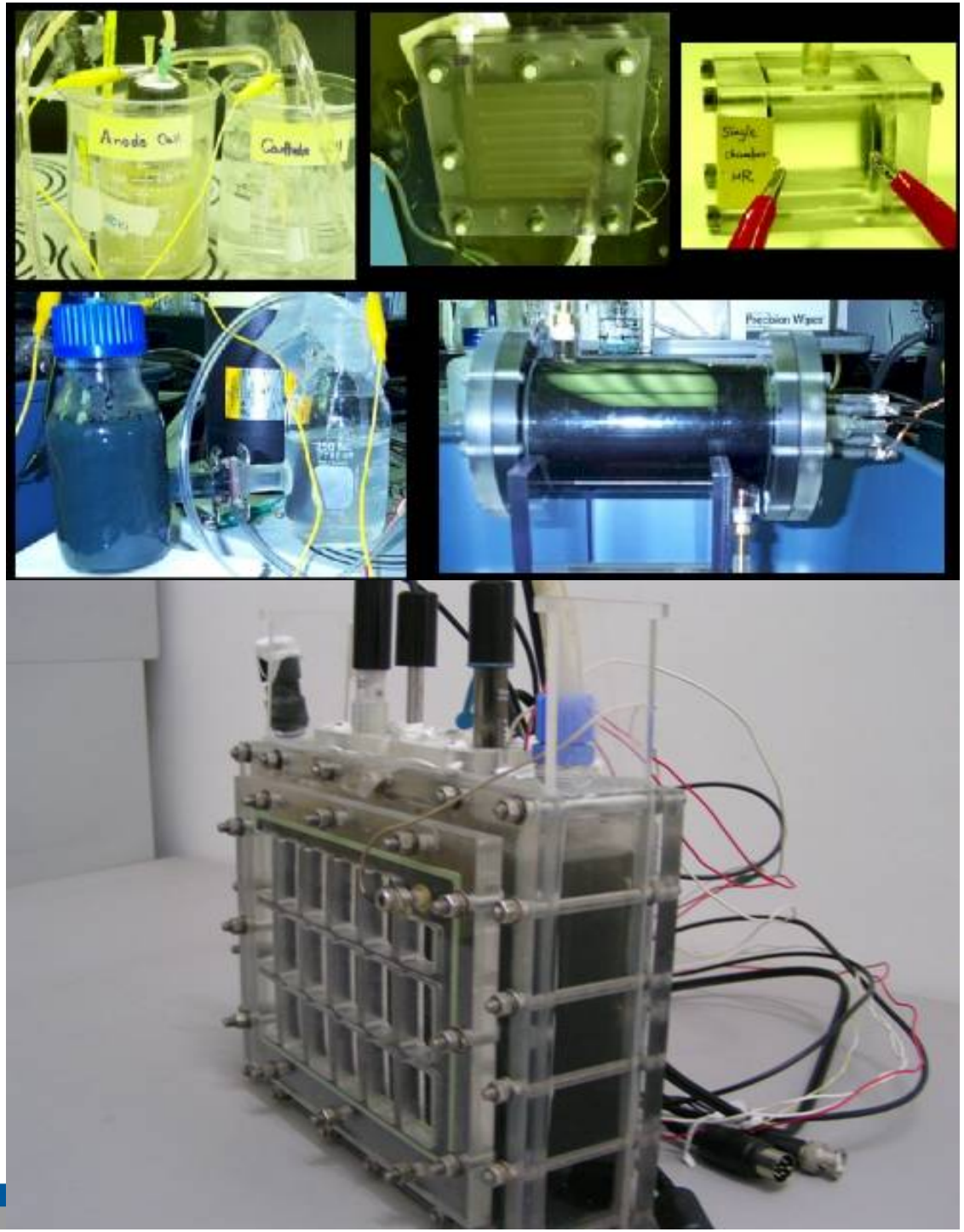
Energy conversion efficiency (ECE):

CE x PE

HELMHOLTZ ZENTRUM FÜR UMWELTFORSCHUNG UFZ

Hong Liu

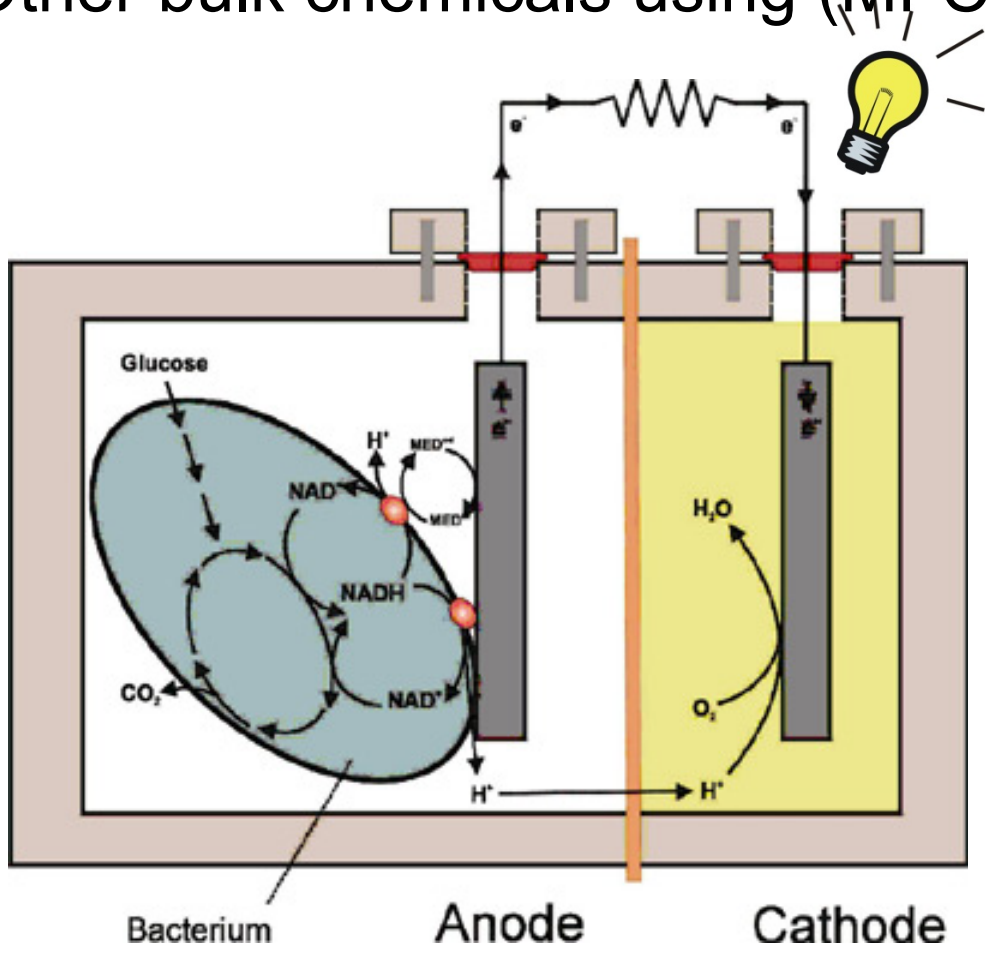
Bruce Logan



Other bulk chemicals using (MFC/BES) ?

HELMHOLTZ
ZENTRUM FÜR
UMWELTFORSCHUNG
UFZ

Other bulk chemicals using (MFC/BES) ?



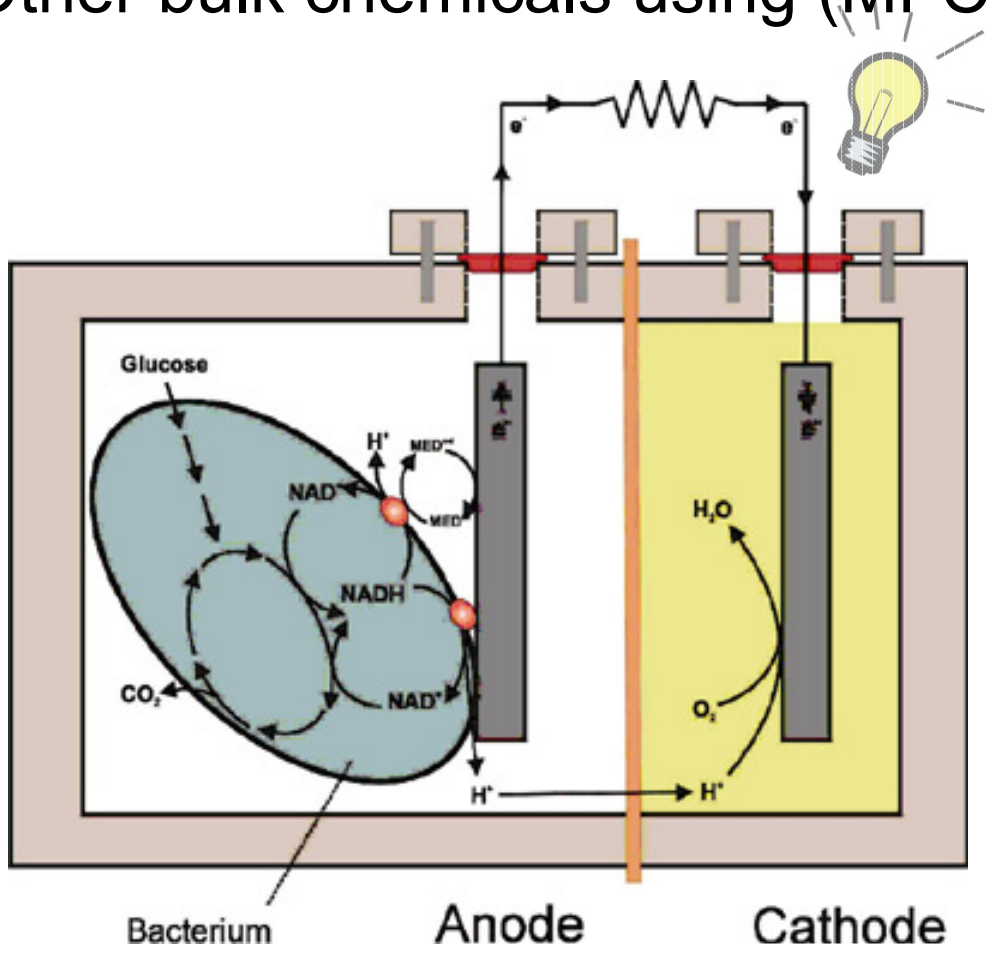
$C_6H_{12}O_6 + 6\ H_20 \rightarrow$

$6\ CO_2 + 24\ H^+ + 24\ e^-$

$O_2 + 4\ H^+ + 4\ e^- \rightarrow 2\ H_2O$ (1 157 mV)

HELMHOLTZ ZENTRUM FÜR UMWELTFORSCHUNG UFZ

Other bulk chemicals using (MFC/BES) ?



$C_6H_{12}O_6 + 6\ H_20 \rightarrow$

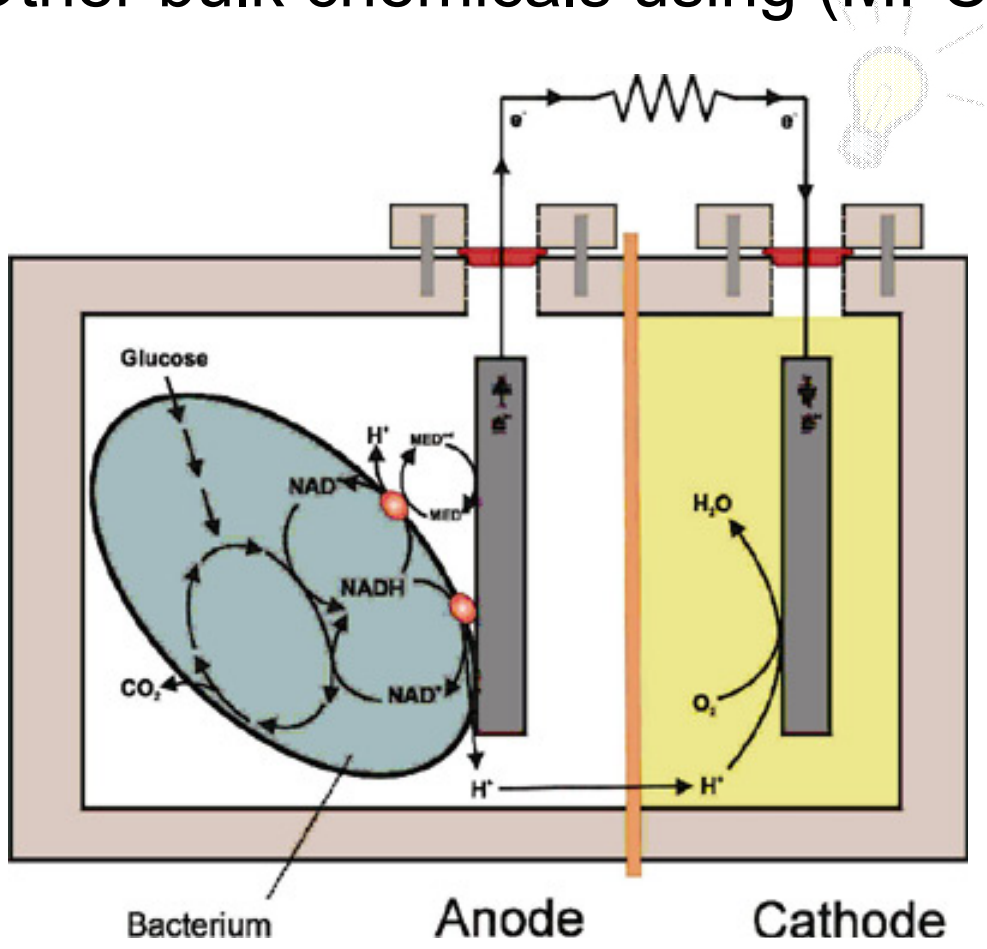
$6\ CO_2 + 24\ H^+ + 24\ e^-$

$O_2 + 4\ H^+ + 4\ e^- \rightarrow 2\ H_2O$ (1 157 mV)

$O_2 + 2\ H^+ + 2\ e^- \rightarrow H_2O_2$ (623 mV)

HELMHOLTZ ZENTRUM FÜR UMWELTFORSCHUNG UFZ

Other bulk chemicals using (MFC/BES) ?



$C_6H_{12}O_6 + 6\ H_20 \rightarrow$

$6\ CO_2 + 24\ H^+ + 24\ e^-$

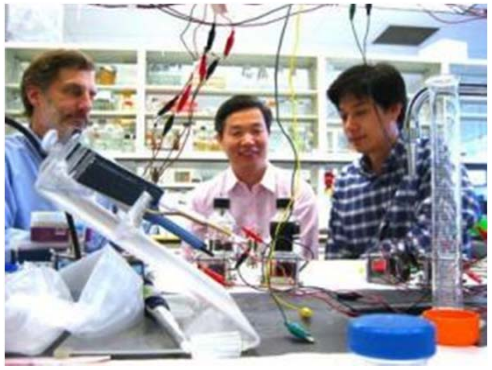
$O_2 + 4\ H^+ + 4\ e^- \rightarrow 2\ H_2O$ (1 157 mV)

$O_2 + 2\ H^+ + 2\ e^- \rightarrow H_2O_2$ (623 mV)

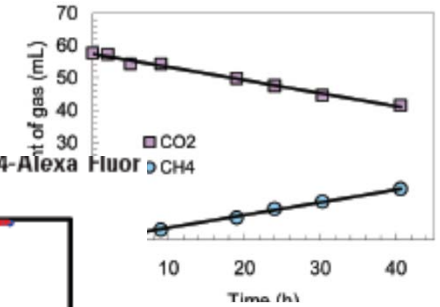
$CO_2 + 8\ H^+ + 8\ e^- \rightarrow 2\ H_2O + CH_4$ (98 mV)

UMWELTFORSCHUNG
UFZ

Methan production unsing BES (bioelectrochemical systems)



Bruce E. Logan, Shaoan Ch *rmation and loss of carbon*
Xing with a microbial cell tha *set potential of -1.0 V (100*
directly from elect



using the *Methanobacterium*-specific probe MB1174-Alexa Fluor

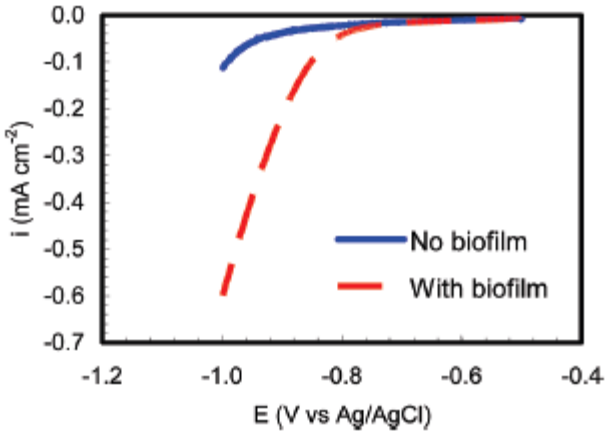
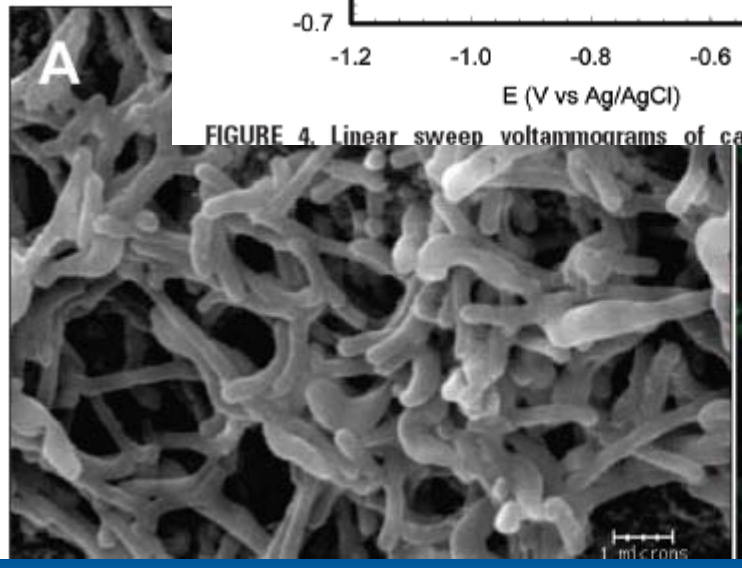
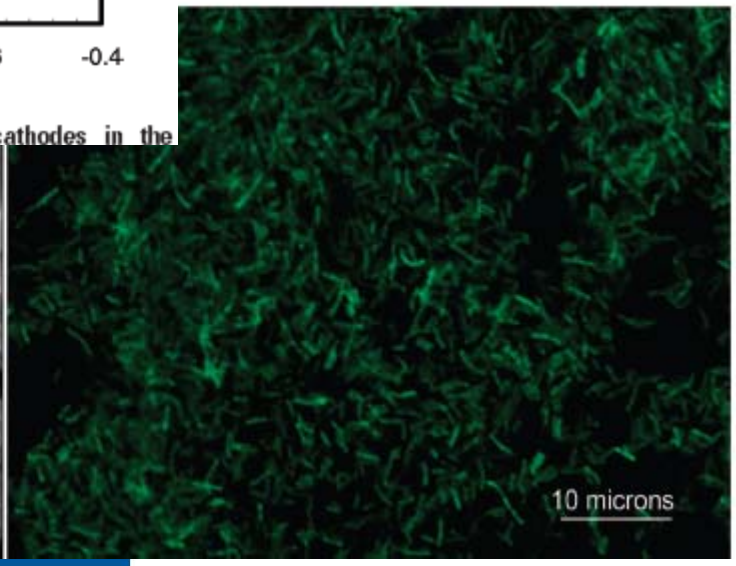
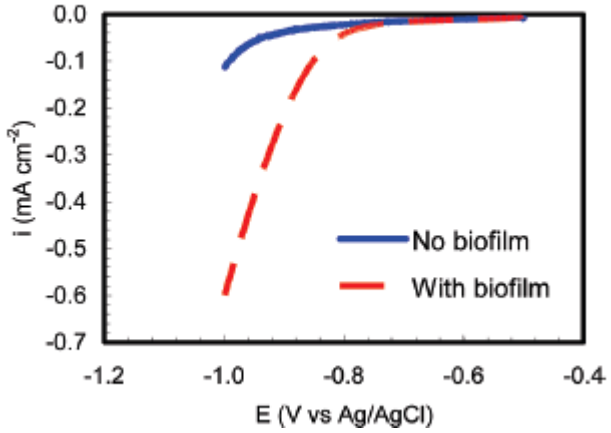


FIGURE 4. Linear sweep voltammograms of cathodes in the

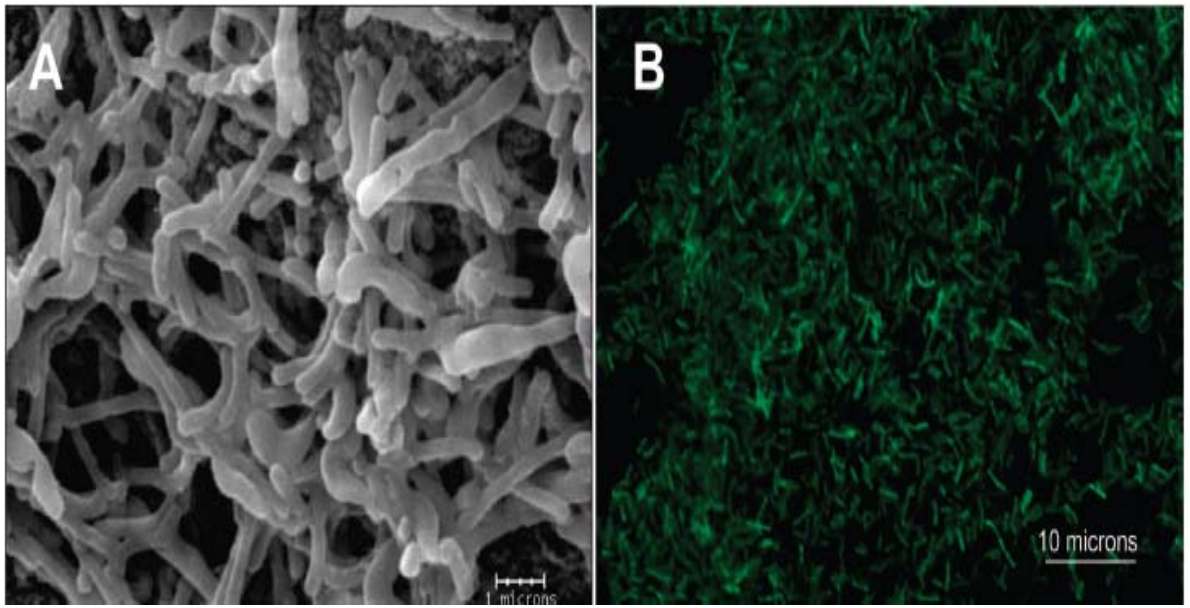




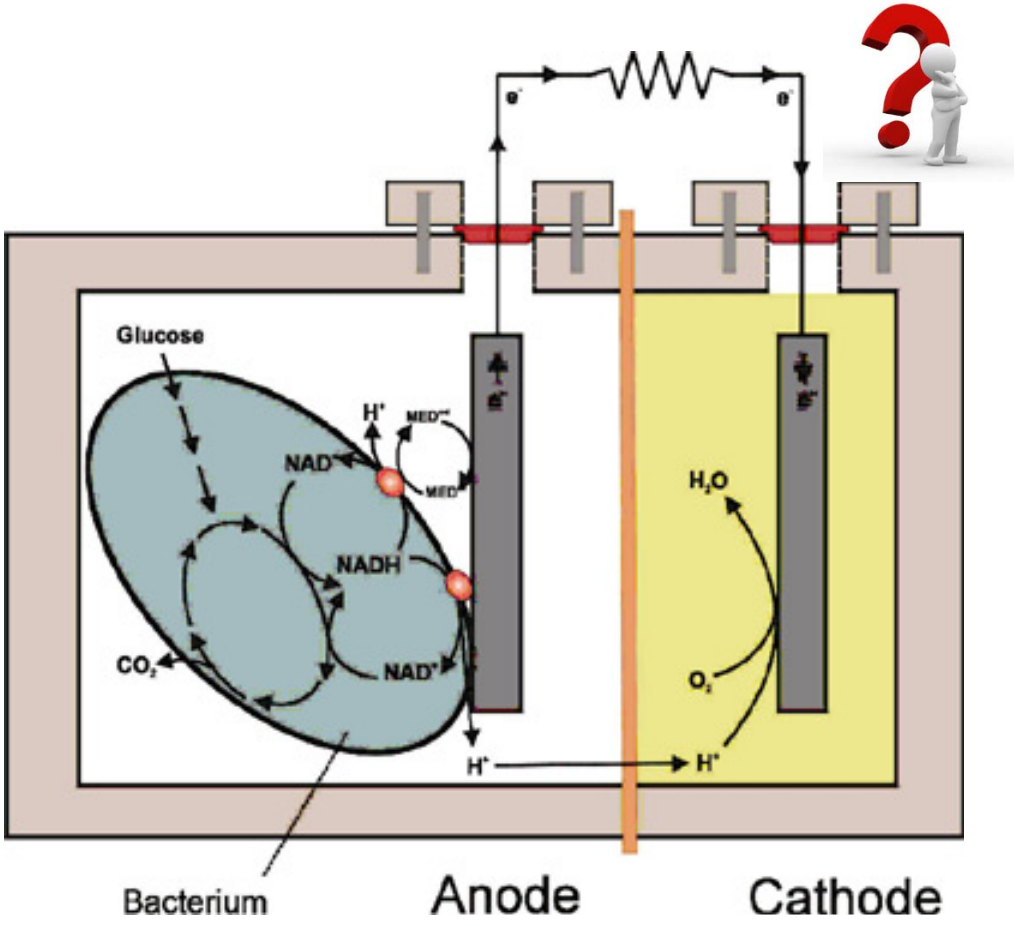
Methan production unsing BES (bioelectrochemical systems)



According to the expectations, the processes happens in biofilms.



Other bulk chemicals using (M?C) ?

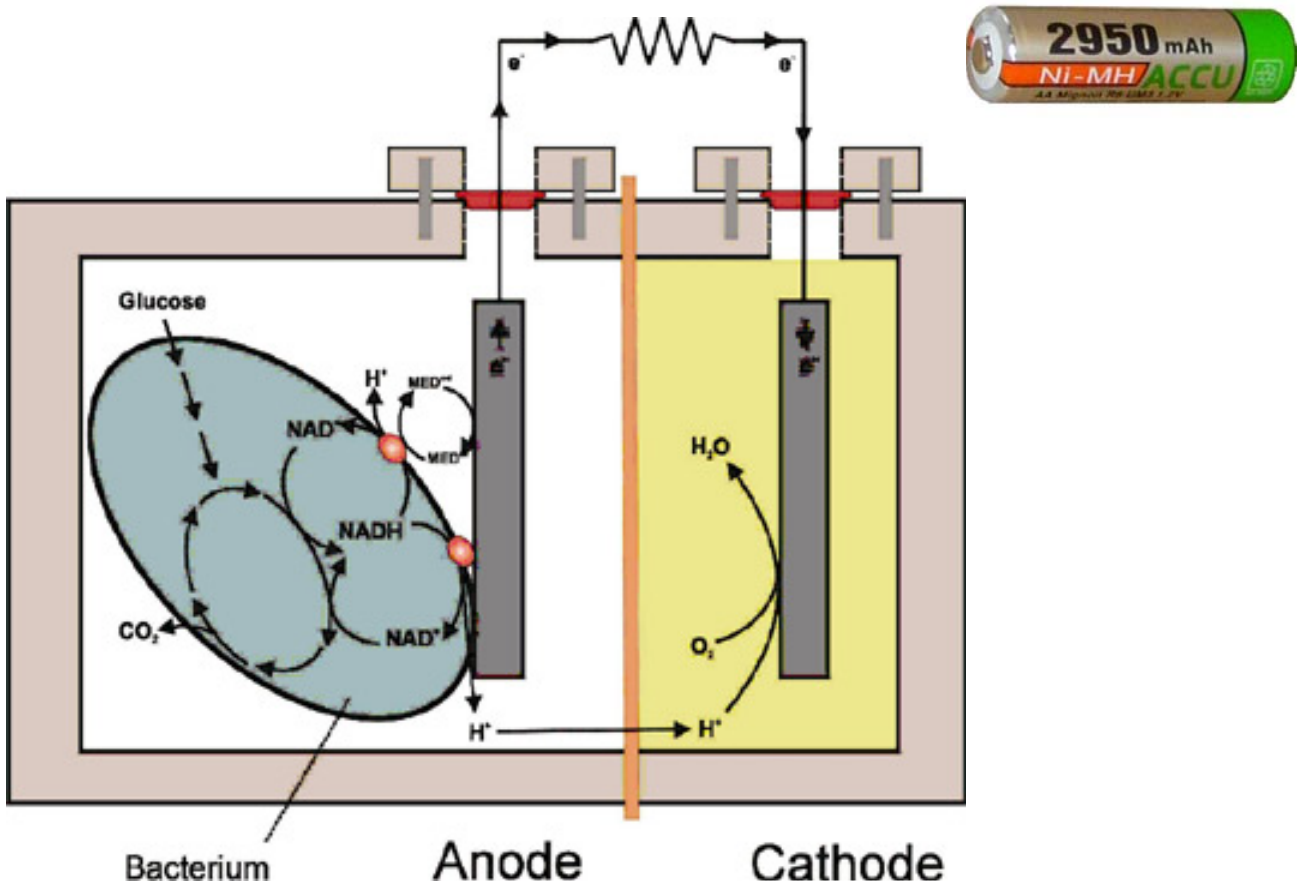


$C_6H_{12}O_6 + 6\ H_20 \rightarrow$

$6\ CO_2 + 24\ H^+ + 24\ e^-$

$O_2 + 4\ H^+ + 4\ e^- \rightarrow 2\ H_2O$	(1 157 mV)
$O_2 + 2\ H^+ + 2\ e^- \rightarrow H_2O_2$	(623 mV)
$CO_2 + 8\ H^+ + 8\ e^- \rightarrow 2\ H_2O + CH_4$	(98 mV)
$2\ H^+ + 2\ e^- \rightarrow H_2$	(- 76 mV)

Other bulk chemicals using (M?C) ?



$C_6H_{12}O_6 + 6\ H_20 \rightarrow$

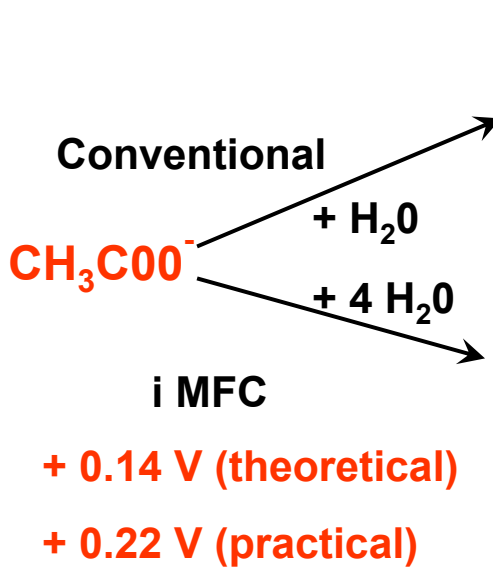
$6\ CO_2 + 24\ H^+ + 24\ e^-$

$O_2 + 4\ H^+ + 4\ e^- \rightarrow 2\ H_2O$	(1 157 mV)
$O_2 + 2\ H^+ + 2\ e^- \rightarrow H_2O_2$	(623 mV)
$CO_2 + 8\ H^+ + 8\ e^- \rightarrow 2\ H_2O + CH_4$	(98 mV)
$2\ H^+ + 2\ e^- \rightarrow H_2$	(- 76 mV)

Hydrogenproduction using microbial catalysis

HELMHOLTZ
ZENTRUM FÜR
UMWELTFORSCHUNG
UFZ

Basic Idea:



-890 kJ mol^{-1}

$CH_4 + HCO_3^-$

ΔG^o = -28.5 kJ mol^{-1}

-55,6 kJ g^{-1}

4 x -286 kJ mol^{-1} = -1144 kJ mol^{-1}

4 H_2 + 2 HCO_3^- + H^+

ΔG^o = 104 kJ mol^{-1}

-143 kJ g^{-1}

Thermodynamically impossible

but

$$\Delta G = n F \Delta E$$

- 28 % more energy gained
- H_2 wears more energy

HELMHOLTZ ZENTRUM FÜR UMWELTFORSCHUNG UFZ

Inverse MFC (i-MFC), Electrohydrogenesis, Biocatalysed Electrolysis, Microbial Electrolysis Cell (MEC)

- **Electrohydrogenesis or biocatalyzed electrolysis** is the name given to a process for generating hydrogen gas from organic matter being decomposed by bacteria.

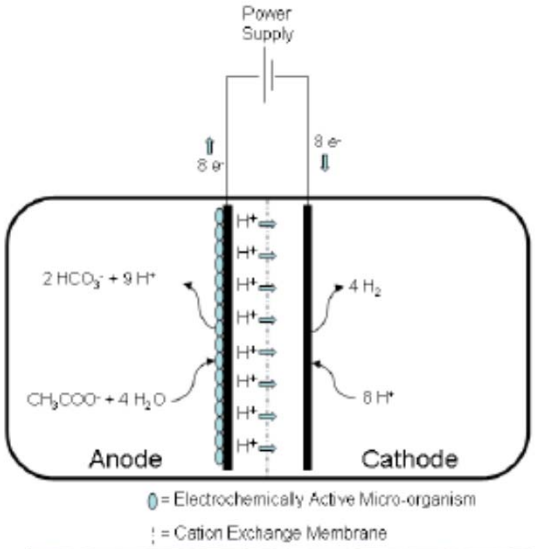
- This process uses a modified fuell cell, 0.2 - 0.8 V of electricity is used,

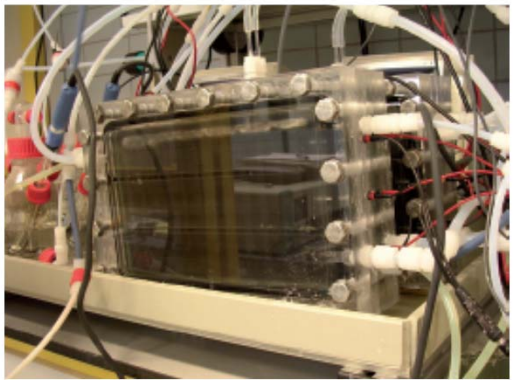
- Energy efficiency of 288%

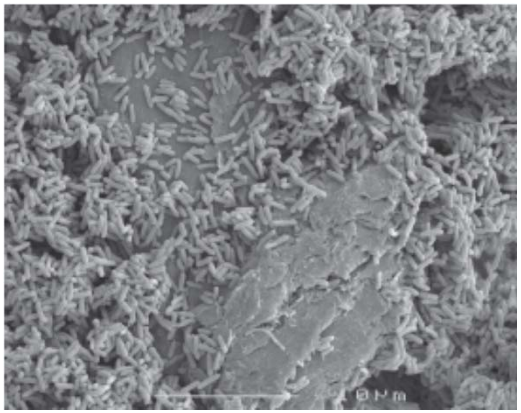
HELMHOLTZ ZENTRUM FÜR UMWELTFORSCHUNG UFZ

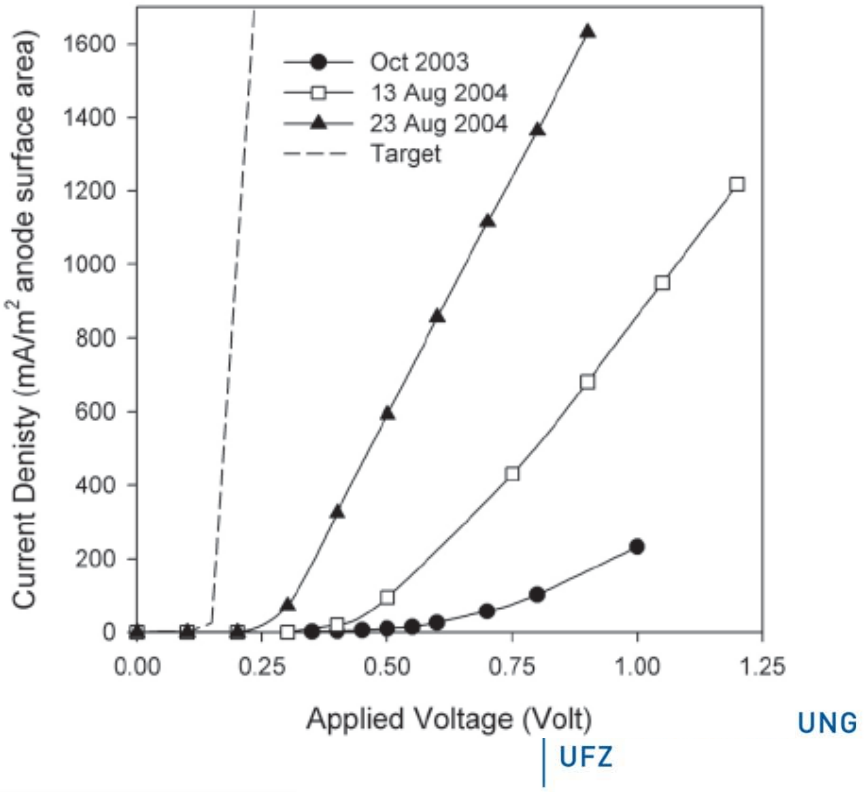
2004

René Rozendal





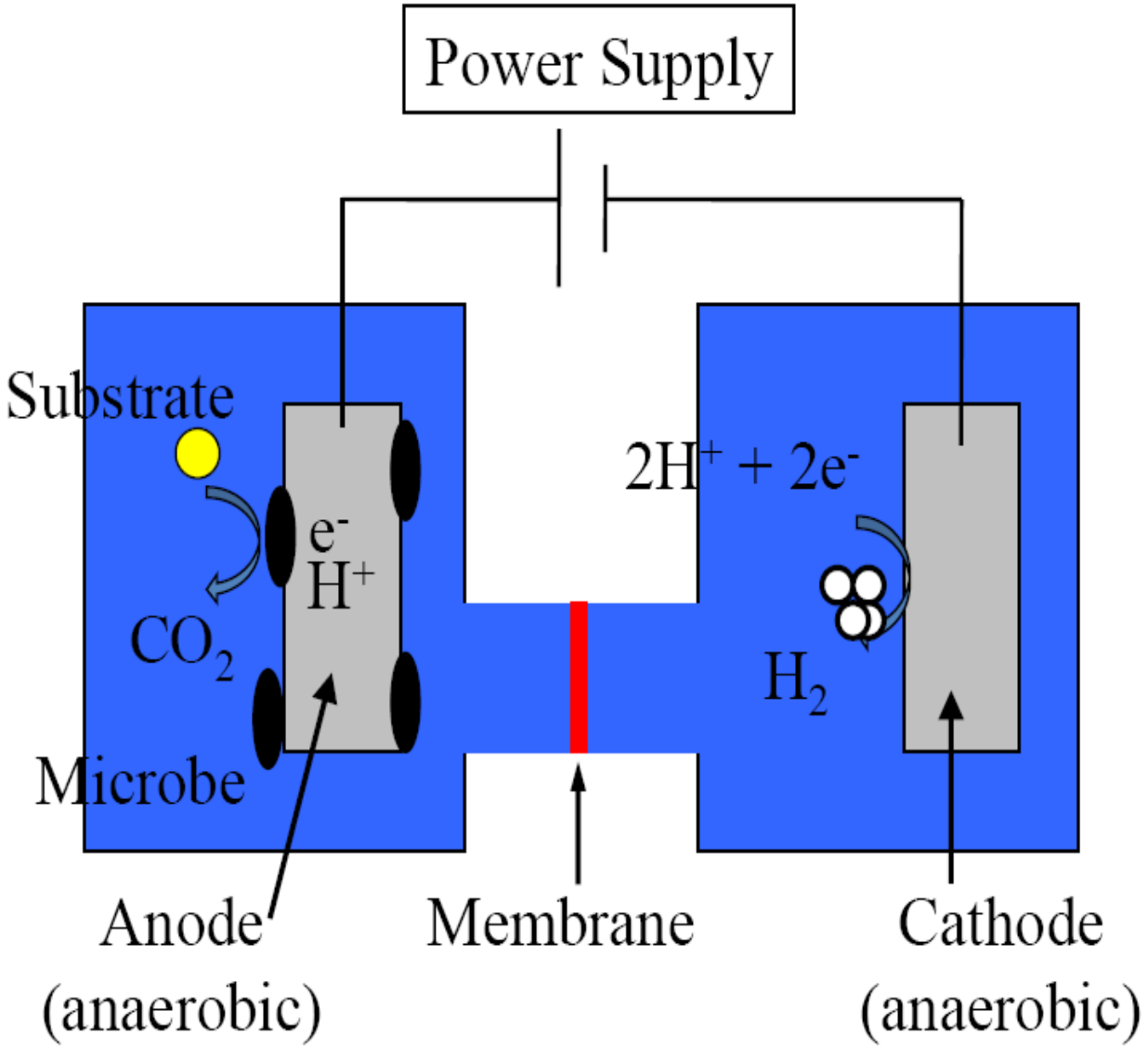




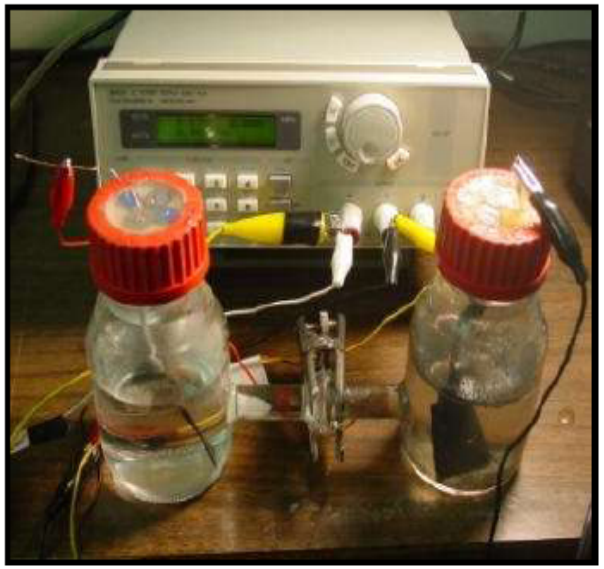
UNG

UFZ

Microbial electrolysis cells (MECs) produce hydrogen from organic matter

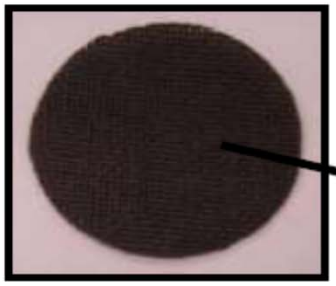


Two-chamber MEC

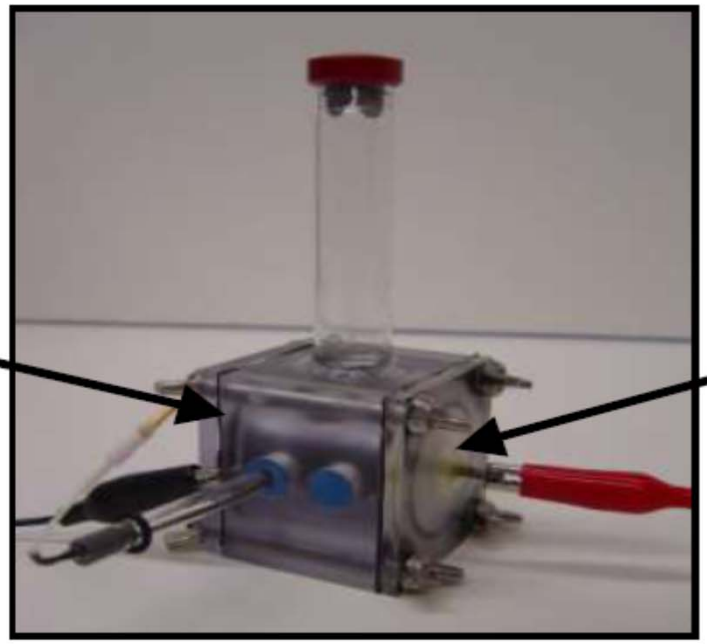


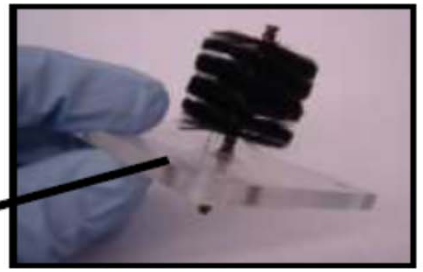
Is the membrane really needed?

A single-chamber MEC was tested without a membrane



Carbon cloth with Pt catalyst



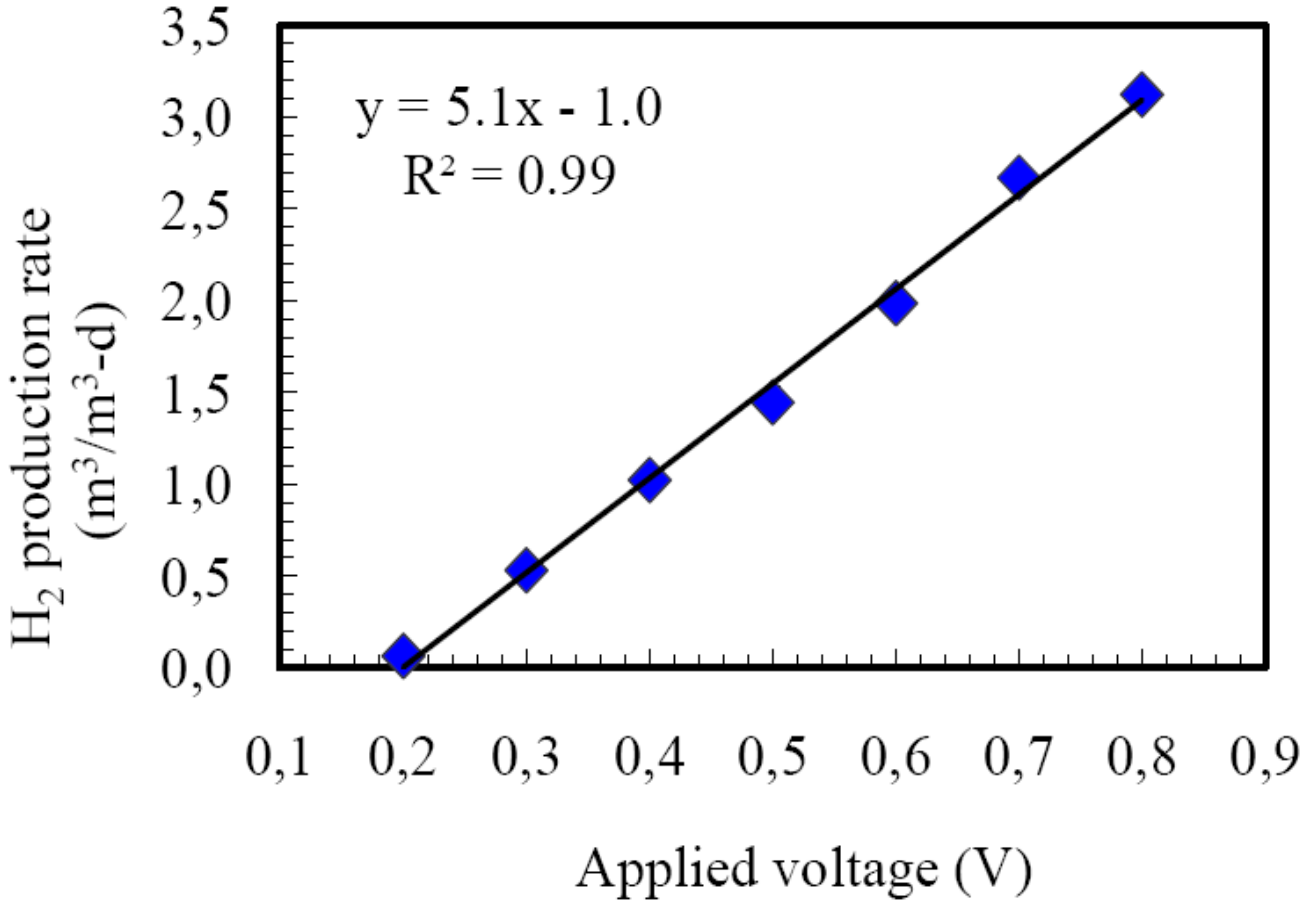


Graphite fiber brush anode

Substrate:	1 g/L sodium acetate
Inoculum:	MFC acclimated culture
Buffer:	50 mM phosphate buffer
Operation:	Fed-batch

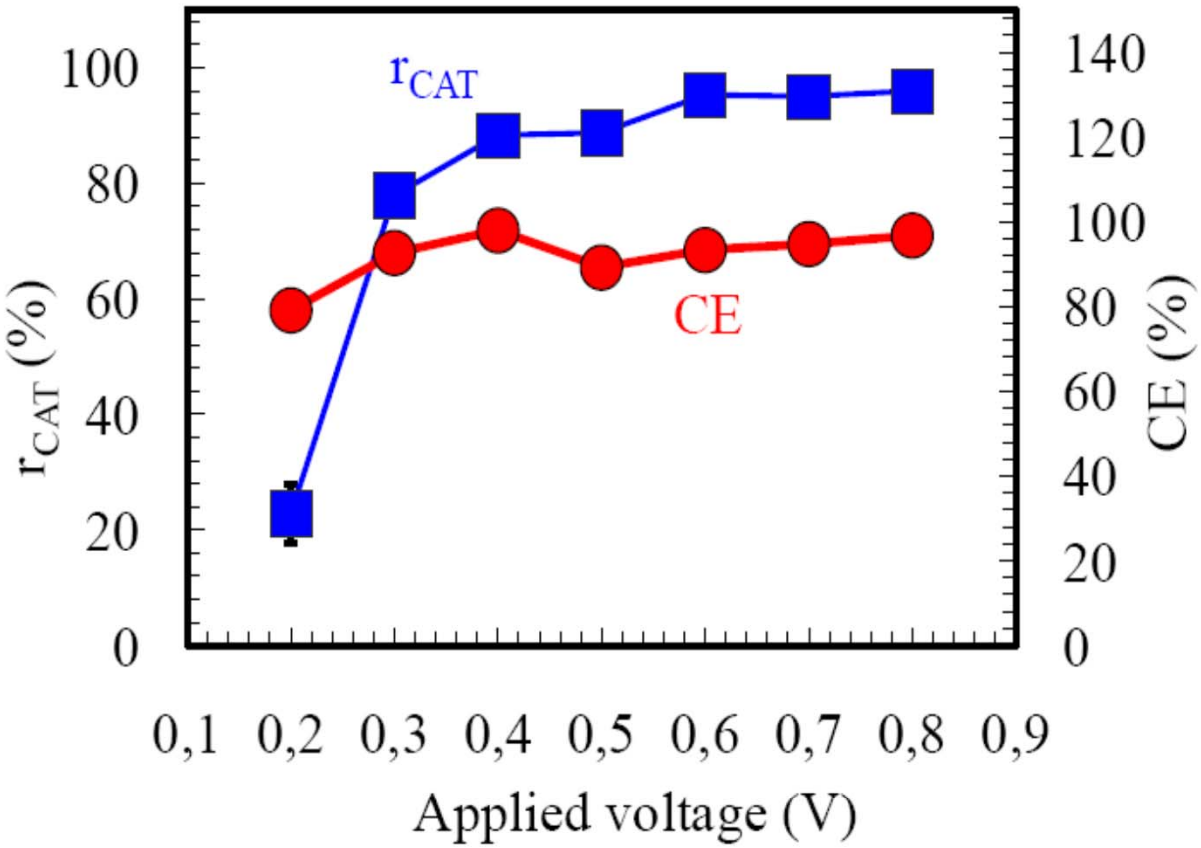
Call, D. and B.E. Logan. *Environ. Sci. Technol*. 42(9). 2008.

The hydrogen production rate was dependent on the applied voltage



The maximum production rate was over 3 m^3-H_2/m^3-d

Electrons from the substrate were efficiently captured as current and used to produce H_2



r_{CAT} range = 78 – 96%

CE range = 79 – 98%

(For E_{ap} = 0.3 – 0.8 V)

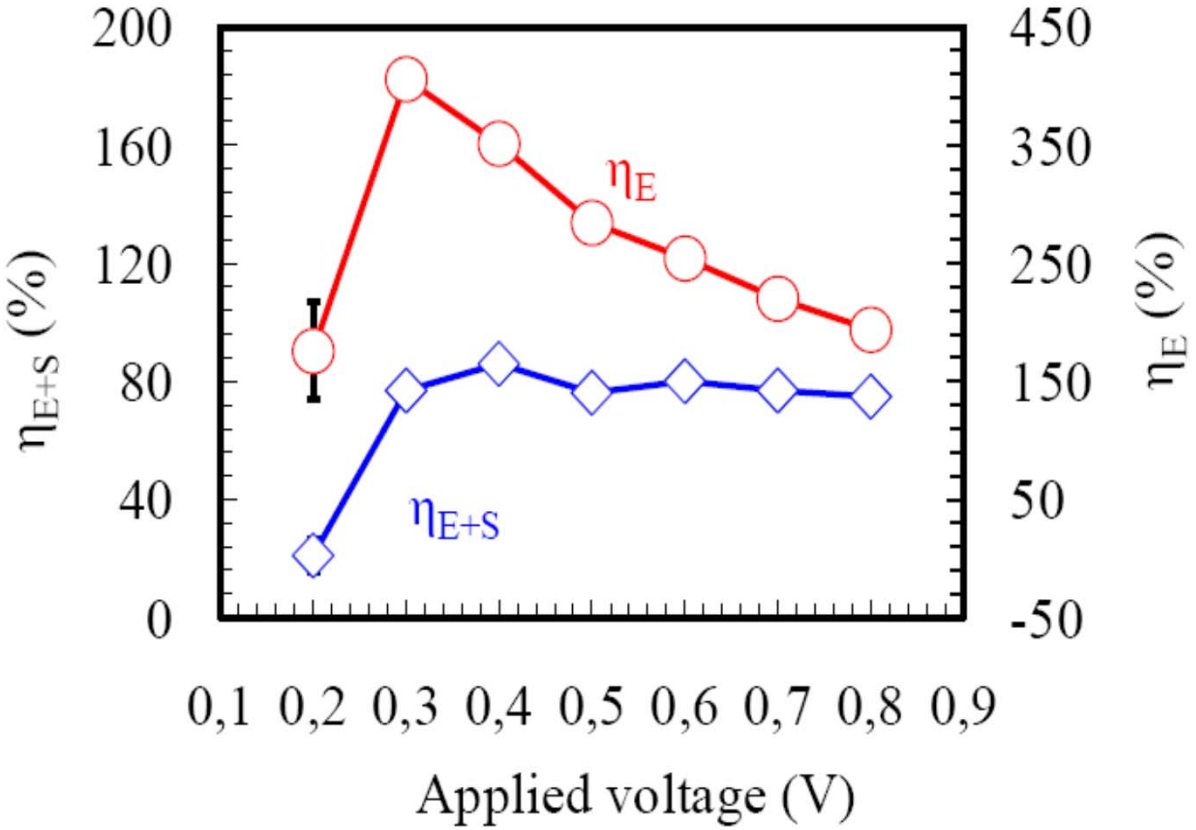
r_{CAT} (cathodic hydrogen recovery)

$$\frac{\text{moles } H_2 \text{ recovered}}{\text{moles } H_2 \text{ expected}}$$

CE (coulombic efficiency)

$$\frac{\text{moles } e^- \text{ recorded}}{\text{moles } e^- \text{ expected}}$$

Energy recoveries were based on electrical energy and substrate energy inputs



η_E
max = 405 %
(E_{ap} = 0.3 V)

η_{E+S}
max = 86 %
Average = 78 %
(For E_{ap} = 0.3 – 0.8 V)

η_E (electrical energy efficiency) = $\frac{\text{energy of } H_2 \text{ produced}}{\text{electrical energy input}}$

η_{E+S} (overall energy efficiency) = $\frac{\text{energy of } H_2 \text{ produced}}{\text{electrical energy input + substrate energy}}$

How does this MEC compare to traditional water electrolyzers?

Water electrolyzer vs. MEC

Technology	Energy efficiency (%)	Energy demand (kWh/m^3-H_2)	Cost ($/kg-$H_2$)	Comments
Water electrolyzer	56 - 73%	5.6	3.80	source (5)
MEC	350%	0.9	0.62	E_{ap} = 0.4 V

Department of Energy (DOE) target for hydrogen[6]

$2.00 - $3.00 / kg-$H_2$

Summary

Biocatalysed electrolysis: <1.0 kWh/Nm^3 H_2;
Water electrolysis: >4.5 kWh/Nm^3 H_2

Realistic target: > 10 Nm^3 H_2/m^3 of reactor volume/day ΔE = 0.3 - 0.4 Volt.

Hydrogen production efficiencies: >90%

HELMHOLTZ
ZENTRUM FÜR
UMWELTFORSCHUNG
UFZ

Other sources of biohydrogen

- Why is hydrogen important?
- Fermentative hydrogen production
- Hydrogen from sunlight

HELMHOLTZ
ZENTRUM FÜR
UMWELTFORSCHUNG
UFZ

Why is hydrogen important and environmentally friendly?

- Hydrogen can be produced domestically, cleanly and cost-effectively from a variety of resources (**sunlight, biomass and water**)
- Hydrogen (other as bioethanol or methane) combusted simply to water; **No green house effect**
- Hydrogen can be efficiently converted into electricity using fuel cells (efficiency approx. **50 %;** Otto engine approx. **20%**)
- Energy density (J/g) **>** traditional fuel sources
- But energy density (J/m^3) **<** traditional fuel sources
- **No NOx emission** in burning hydrogen

HELMHOLTZ ZENTRUM FÜR UMWELTFORSCHUNG UFZ

Fermentative hydrogen production?

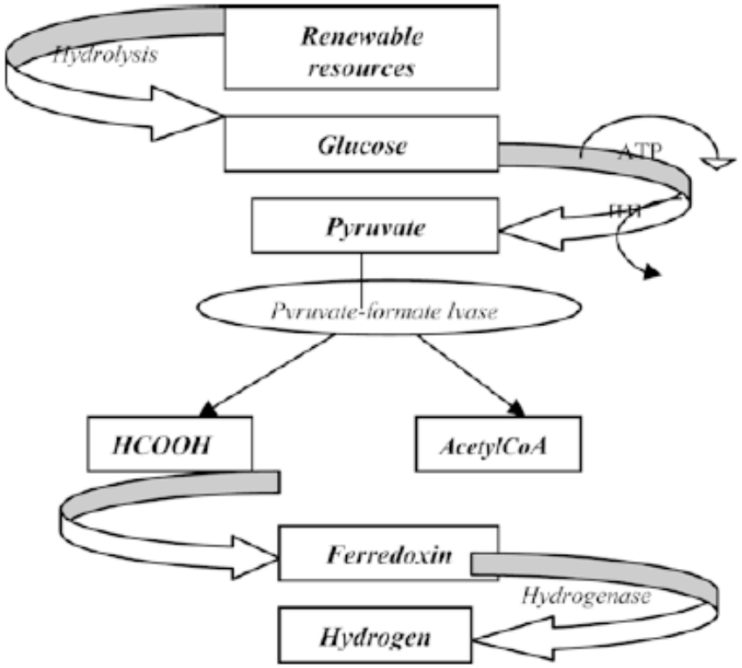
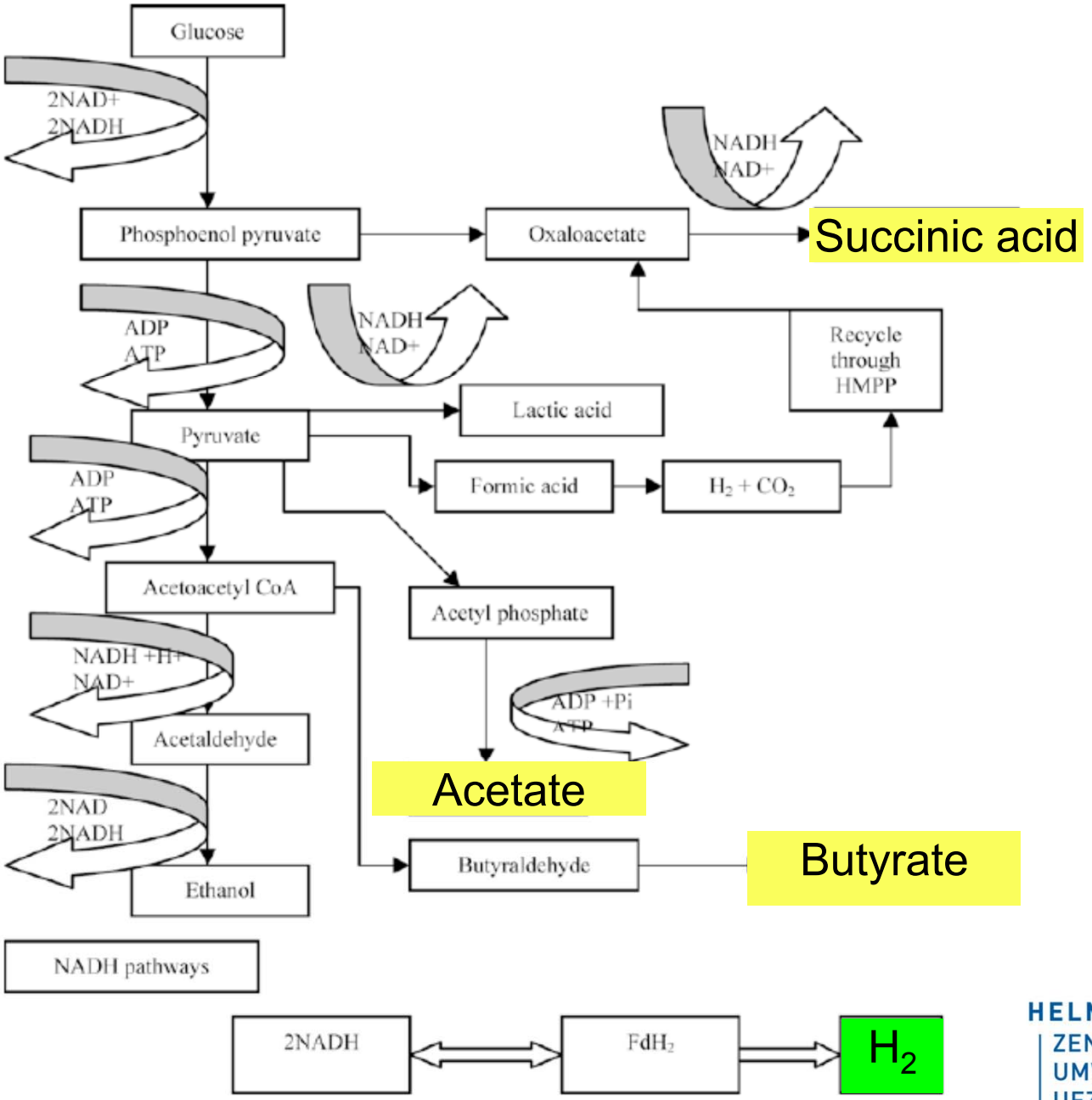


Fig. 1 A schematic pathway for conversion of renewables to hydrogen via fermentation

$$2\,\mathrm{Fd(red)} \rightarrow 2\,\mathrm{Fd(ox)} + \mathrm{H_2}$$

HELMHOLTZ ZENTRUM FÜR UMWELTFORSCHUNG UFZ



HELMHOLTZ
ZENTRUM FÜR
UMWELTFORSCHUNG
UFZ

Fermentative hydrogen production?

Chemical maximum:	**$Glucose + 6H_2O \rightarrow 6CO_2 + 12H_2$**
Biological maximum:	**$Glucose + 2H_2O \rightarrow 2Acetate + 2CO_2 + 4H_2$**
Biological minimum:	**$Glucose \rightarrow Butyrate + 2CO_2 + 2H_2$**

4 mol H2 per mol Glucose too low to be economically viable **!!!**

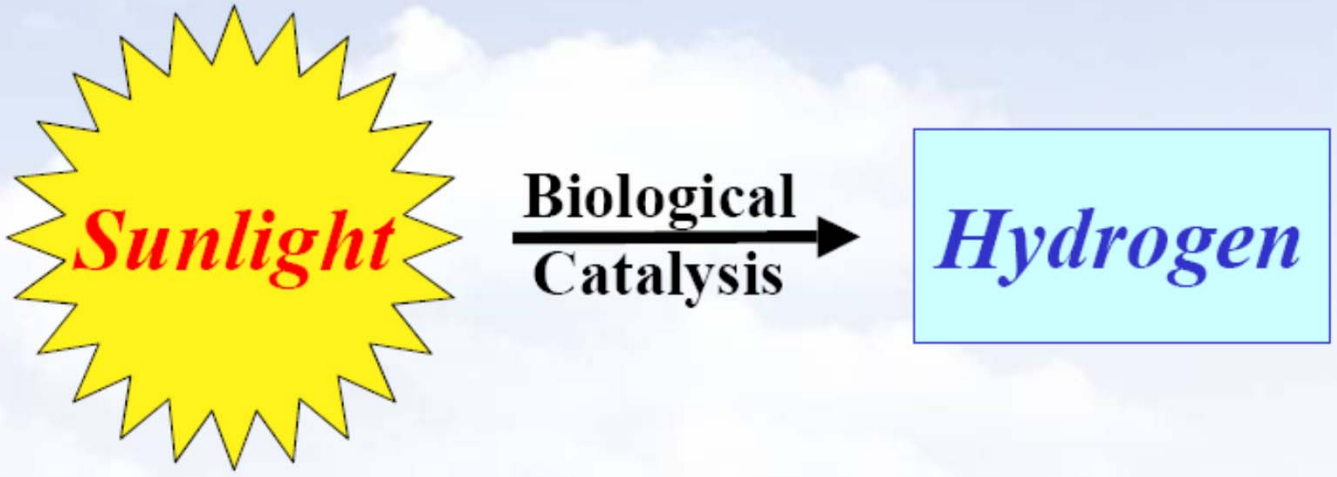
Real yields between:

0.52 (1998) from molasses using *Enterobacter aerogens*

3.8 (2001) from glucose using *Enterobacter cloacae* DM11

HELMHOLTZ ZENTRUM FÜR UMWELTFORSCHUNG UFZ

Hydrogen from sunlight?



Hydrogen biotechnology seeks to convert and store the energy of Sunlight as renewable Hydrogen.

Biological catalysts for the generation of H_2 are found in microorganisms such as unicellular green algae, cyanobacteria, photosynthetic bacteria, and in some forms of dark fermentative bacteria.

Short history

1939 - German researcher (Hans Gaffron, University of Chicago), that algae can switch between producing oxygen and hydrogen.

1997 - Anastasios Melis - deprivation of sulfur will cause the switch; the enzyme, hydrogenase, responsible for the reaction.

2006 - Researchers from the University of Bielefeld + University of Quensland have genetically qualified the green alga *Chlamydomas reinhardtii* to produce large amounts of hydrogen. 5 x more as the wild type; energy efficiency: 1.6 - 2.0 %

2007 - Discovered: if copper is added to block oxygen generation -> algae will switch to the production of hydrogen

2007 - Anastasios Melis achieved 15 % energy conversion efficiency by truncation of Chl antenna size.

2008 - Anastasios Melis achieved 25 % efficiency out of a theoretical maximum of 30%.

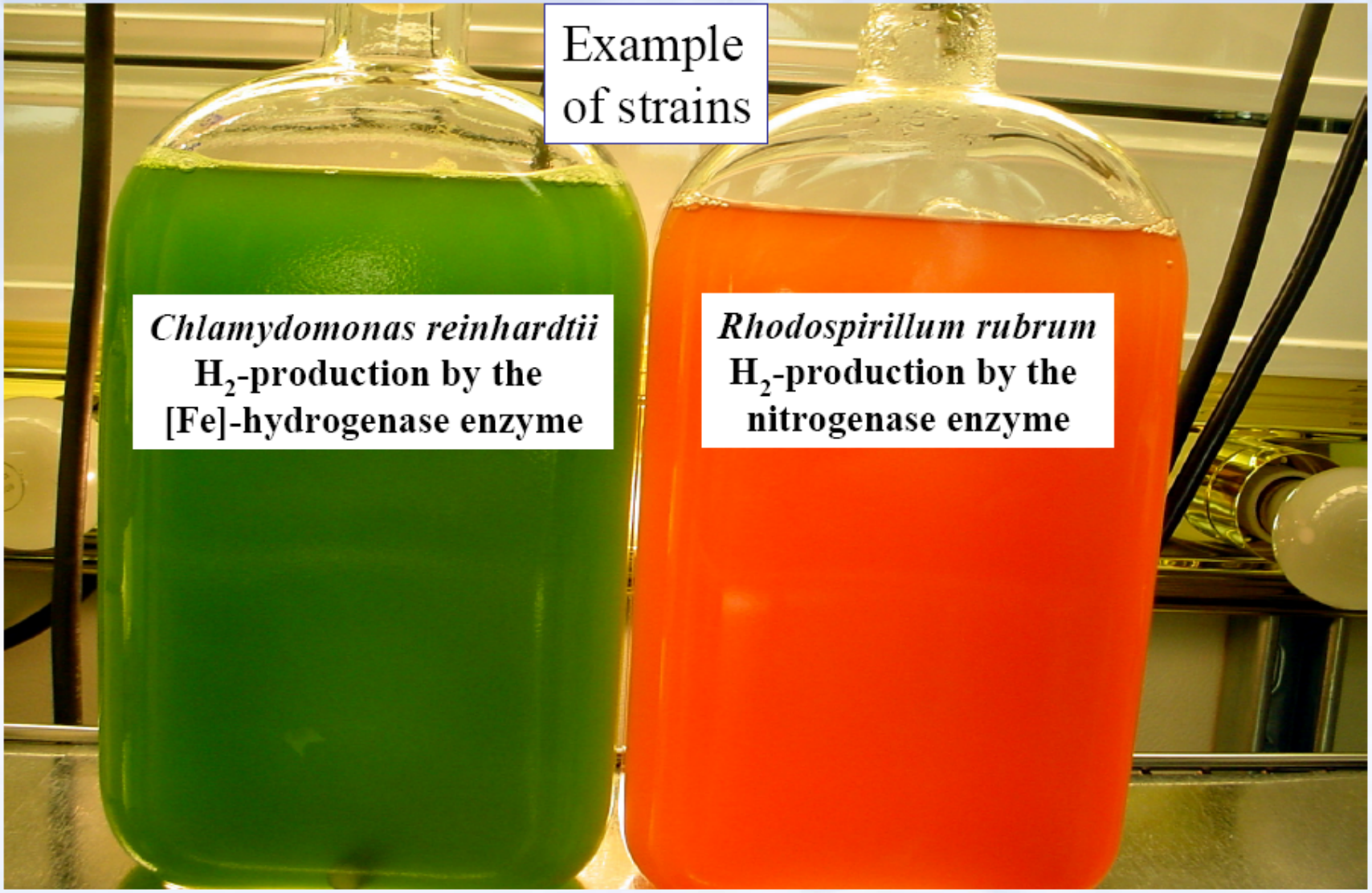
HELMHOLTZ ZENTRUM FÜR UMWELTFORSCHUNG UFZ

Prospects for Photobiological Generation of Renewable Hydrogen

- Average solar insolation in the US : 4.2 kWh m^{-2} d^{-1}
- Photosynthetic solar conversion efficiency : 0.42 kWh m^{-2} d^{-1}
- To displace all of the gasoline consumed in the United States, an area of 5,500 square miles would be needed, which is equivalent to 0.15% of the land area of the U.S.

Sunlight as a source of energy is Clean and Unlimited. But it is also diffuse, averaging 4.2 kWh per square meter per day in the US. Assuming a 10% solar conversion efficiency to hydrogen, it was estimated that about 5,500 square miles of surface area would be needed for the harvesting and conversion of the enough sunlight to displace all of the gasoline consumed in the United States.

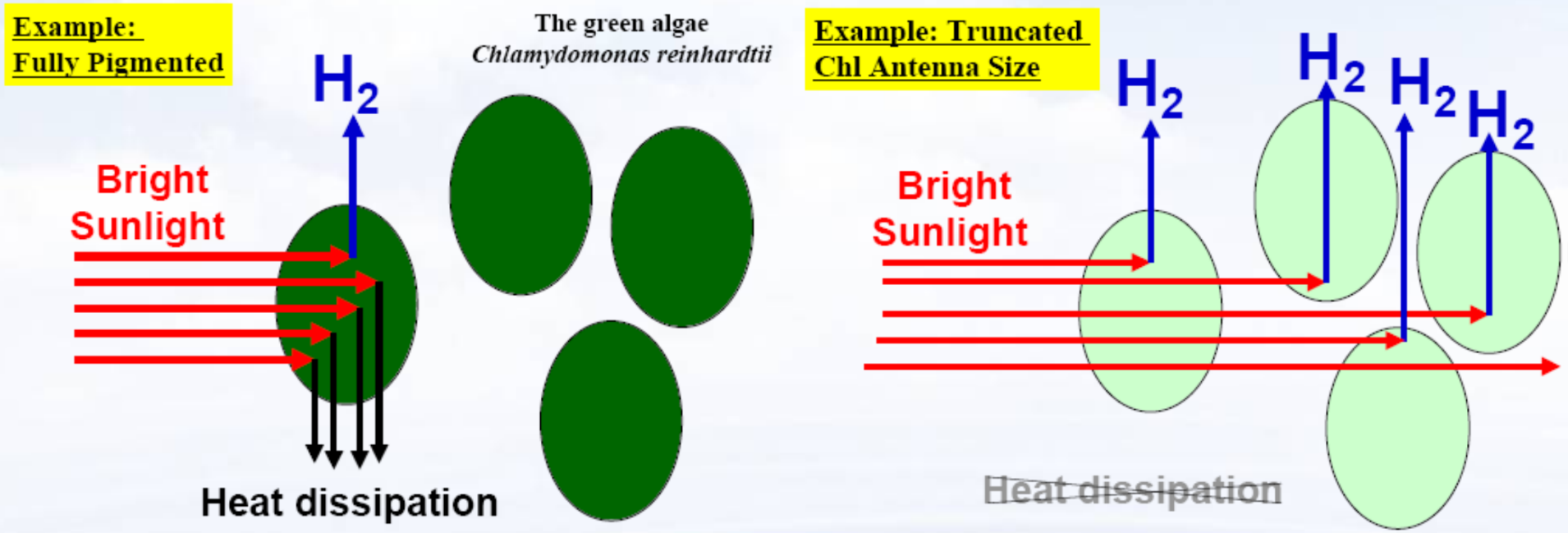
Example of strains



H_2-producing green algae **H_2-producing photosynthetic bacteria**

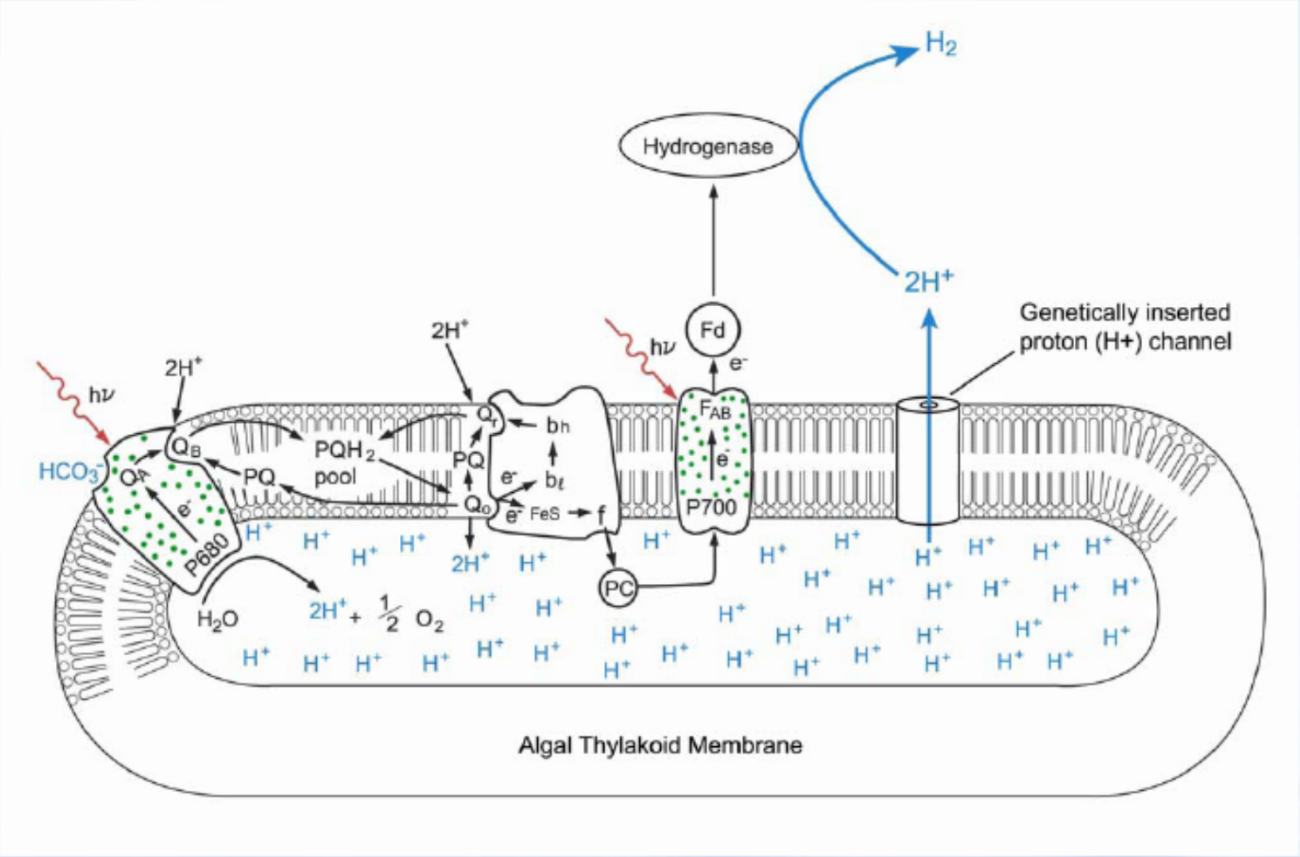
Green algae and photosynthetic bacteria could operate with a solar energy conversion efficiency to H_2 as high as ~10% and ~6%, respectively, provided that specific barriers are overcome.

Addressing Barrier X: Low sunlight utilization efficiency due to a large chlorophyll antenna size



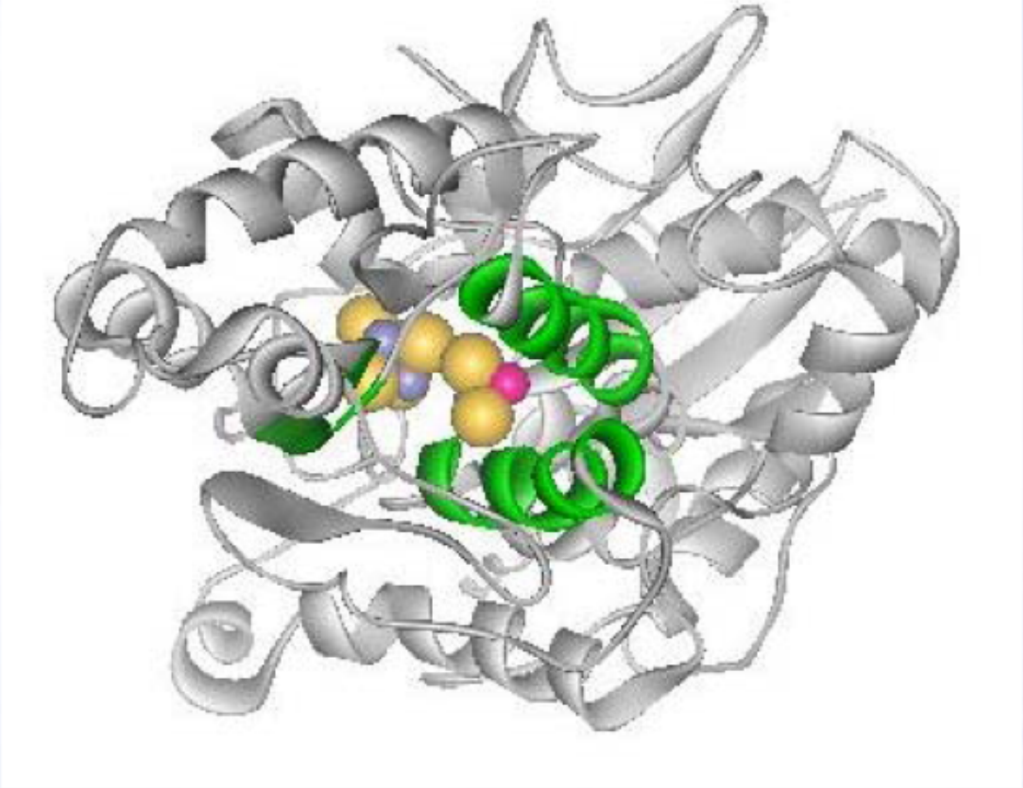
Schematic presentation of the fate of absorbed sunlight in fully pigmented (left) and truncated Chl antenna size algae (right). Fully pigmented cells at the surface of the culture over-absorb incoming sunlight (i.e., they absorb more than can be utilized by photosynthesis), and 'heat dissipate' most of it. This is alleviated by the truncated, or smaller Chl antenna size of the photosystems. The research seeks to develop green algae with a "truncated light-harvesting chlorophyll antenna", which produce more H_2 per bioreactor surface area.

Addressing Barrier Y: Slow rate of H_2 production due to non-dissipation of proton gradient across thylakoid membranes



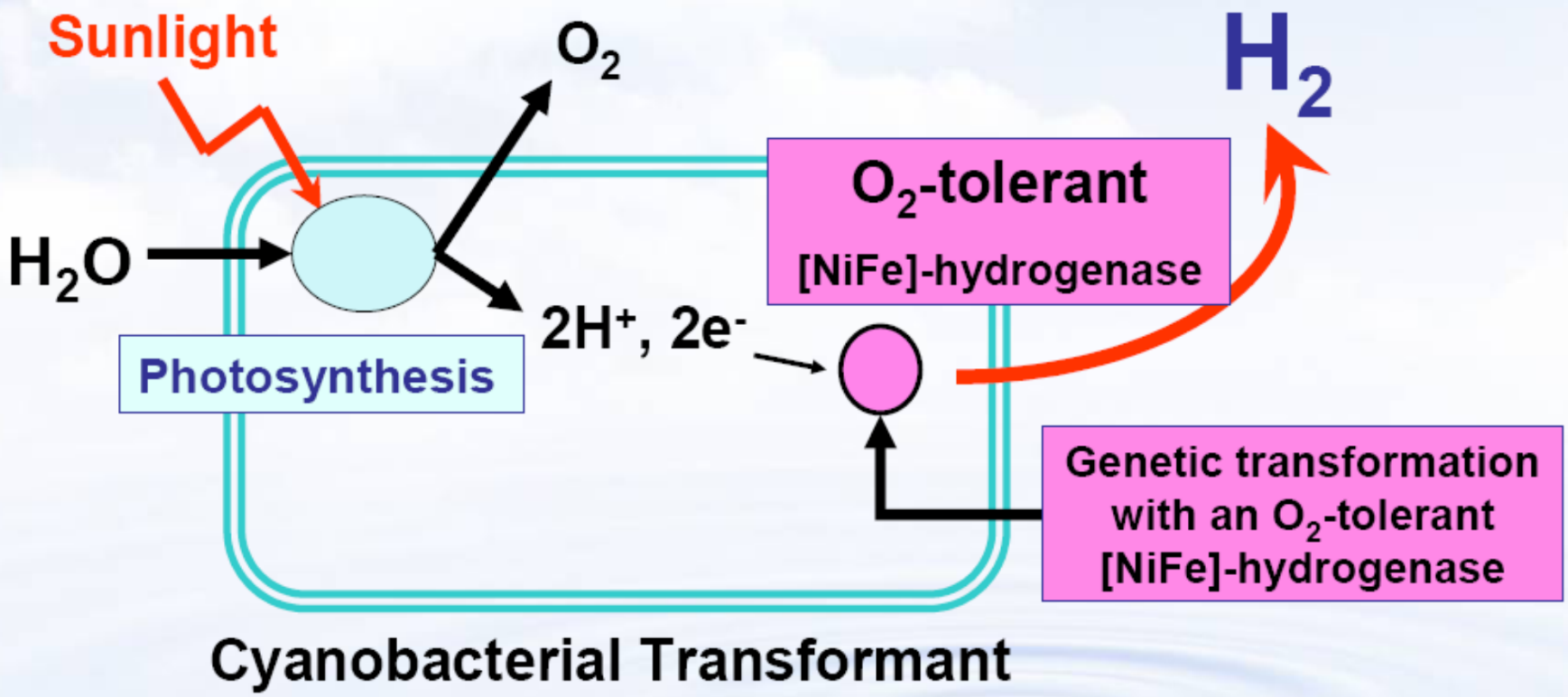
The rate of photobiological H_2 production from water is limited by proton accumulation inside the algal thylakoids. This barrier is being eliminated upon a genetic insertion of proton channels into the algal thylakoid membranes. The proper application of such proton channels across thylakoid membranes could substantially enhance photobiological H_2 production. Moreover, it would also alleviate other competitive processes, such as inhibition of H_2 production by electron flow to CO_2.

Addressing Barrier Z: (I) Discontinuity of H_2 photo-production due to co-generation of O_2, an inhibitor of the [Fe]-hydrogenase



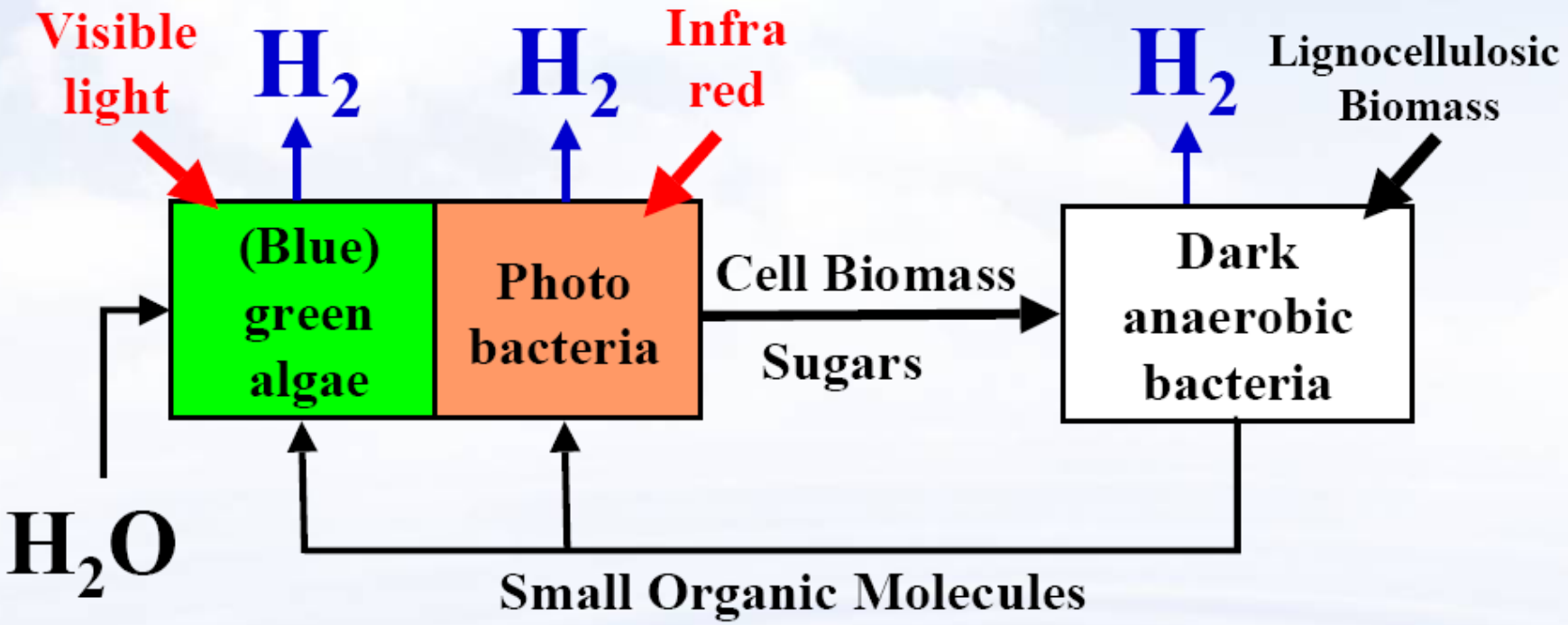
Structural model of the *Chlamydomonas reinhardtii* [Fe]-hydrogenase. The O_2-sensitive catalytic site cluster is identified by yellow, red and purple space-filled atoms. The alpha helices, shown in green, line one of two hydrophobic gas pathways, which allows gas diffusion between the active site and the surface of the protein. The viewer is looking straight down one such pathway. The research seeks to engineer the gas pathways to prevent O_2 from reaching the catalytic site, but not H_2 from diffusing out of the protein.

Addressing Barrier Z: (IV) Discontinuity of H_2 photo-production due to co-generation of O_2, an inhibitor of the [Fe]-hydrogenase



An O_2-tolerant [NiFe]-hydrogenase has been identified from the photosynthetic bacteria, *Rubrivivax gelatinosus* and *Thiocapsa roseopersicina*. This O_2-tolerant [NiFe]-hydrogenase will be genetically expressed in a cyanobacterium for continuous photo-production of H_2 and O_2 from water.

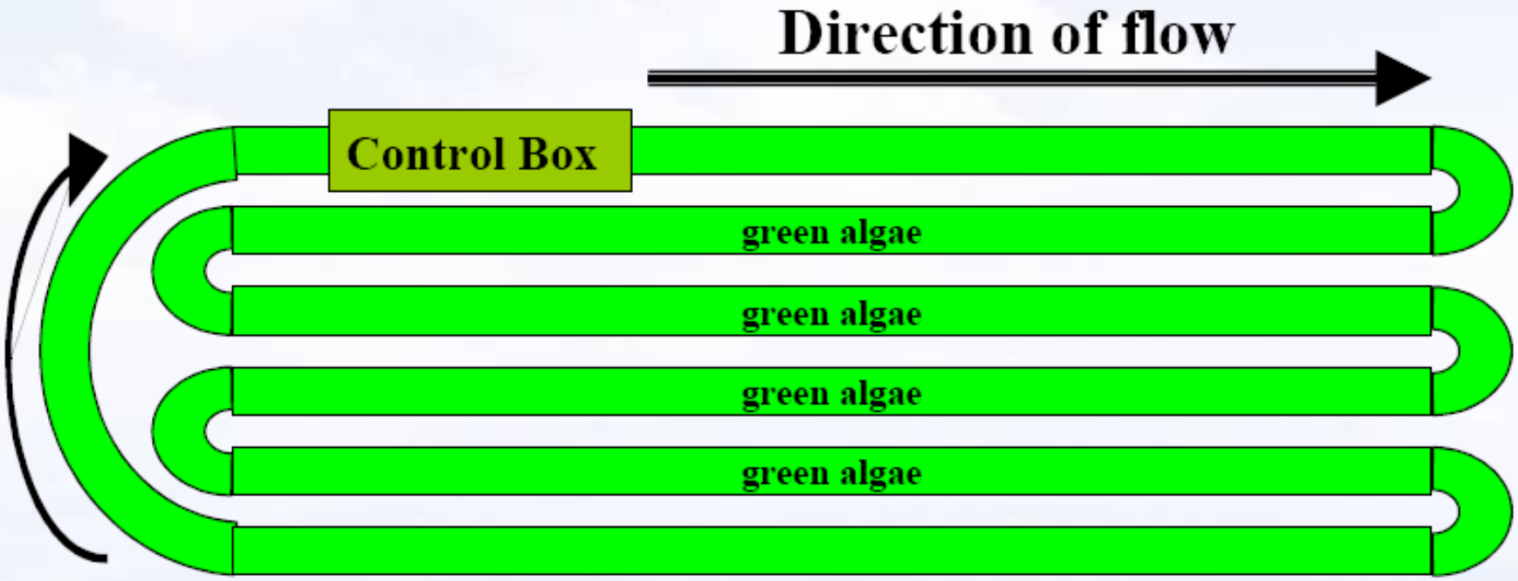
Integrated Biological H_2 Production



Illustrative Scenario: Green algae, cyanobacteria, and photosynthetic bacteria are co-cultured anaerobically in a photoreactor, and dark anaerobic bacteria in a fermentor. Feedstock for the dark anaerobic bacteria is derived from the cell biomass/sugars of the algae, cyanobacteria and photosynthetic bacteria. Additional feedstock for the dark anaerobic bacteria is derived from lignocellulosic products. The small organic molecule by-products of the dark, anaerobic, bacterial fermentation are subsequently utilized as feedstock for the algae, cyanobacteria and photosynthetic bacteria. The research seeks to implement specific aspects of this Integrated Biological H_2 Production System.

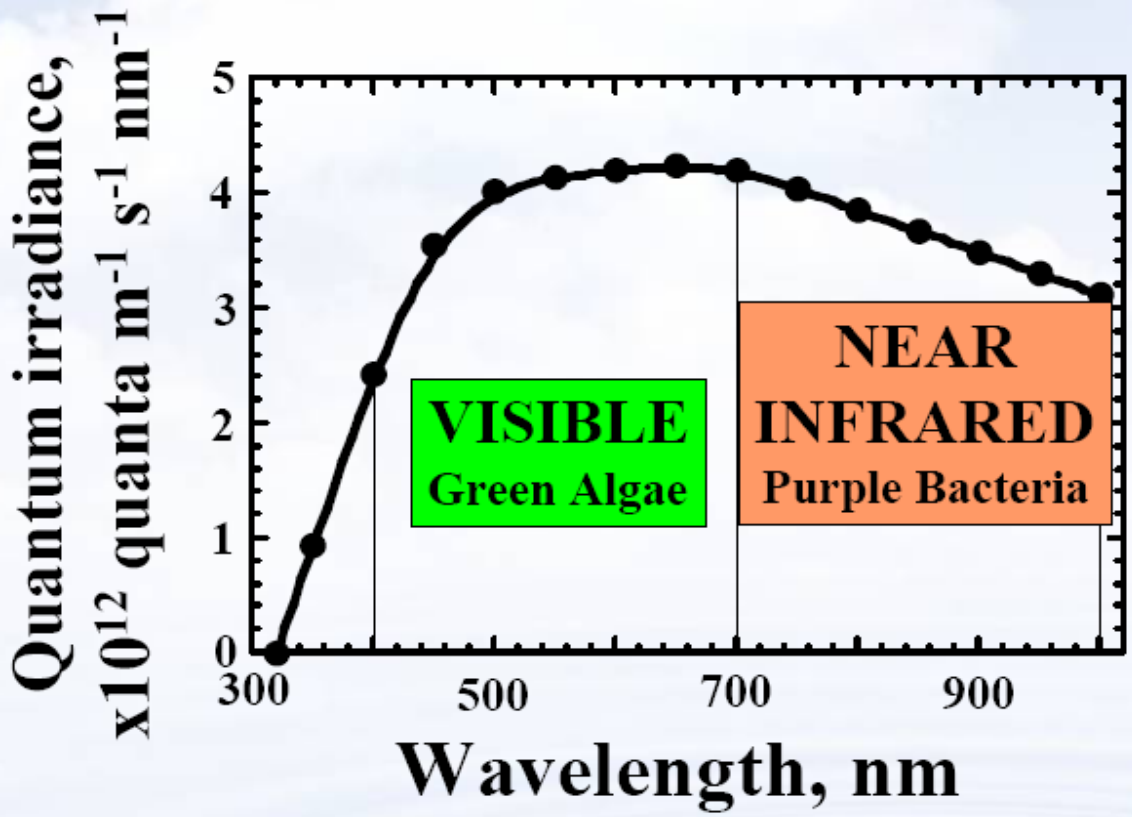
Addressing Barrier AA: Systems engineering for cost-effective photobiological H_2 production

Tubular Racetrack Photoreactor Design



Example of an enclosed, tubular racetrack, low-cost photobioreactor for photosynthetic microorganism growth, H_2-production, and H_2-gas harvesting. Depending on the optical properties of the cells (e.g. Barrier X), the tube diameter would be 6-12 inches wide. Other reactor configurations are possible, depending on climatic and local conditions.

Addressing Barrier AF: Limitation due to the high nitrogen/carbon (N/C) ratio in photosynthetic bacteria



To extend the absorption spectrum of H_2-photoproduction to the infrared region (700-900 nm), anoxygenic photosynthetic bacteria would be included to work in tandem with green algae and cyanobacteria. Hydrogen in photosynthetic bacteria, e.g. *Rhodospirillum rubrum*, is generated by the nitrogenase enzyme. This enzyme is expressed only under conditions of inorganic nitrogen limitation (low N/C ratio). To maximize H_2-production activity in photosynthetic bacteria, it is important to alleviate the positive suppression of gene expression by inorganic nitrogen in the medium. The research seeks to apply molecular engineering techniques to achieve constitutive expression of the nitrogenase enzyme under high N/C ratios in the medium.


Thanks for your Attention !
Questions ?
Source: http://img.metro.co.uk