6| Bioelectrochemical Systems

Lernziele:

Verstehen, wie bioelektrochemische Systeme funktionieren.

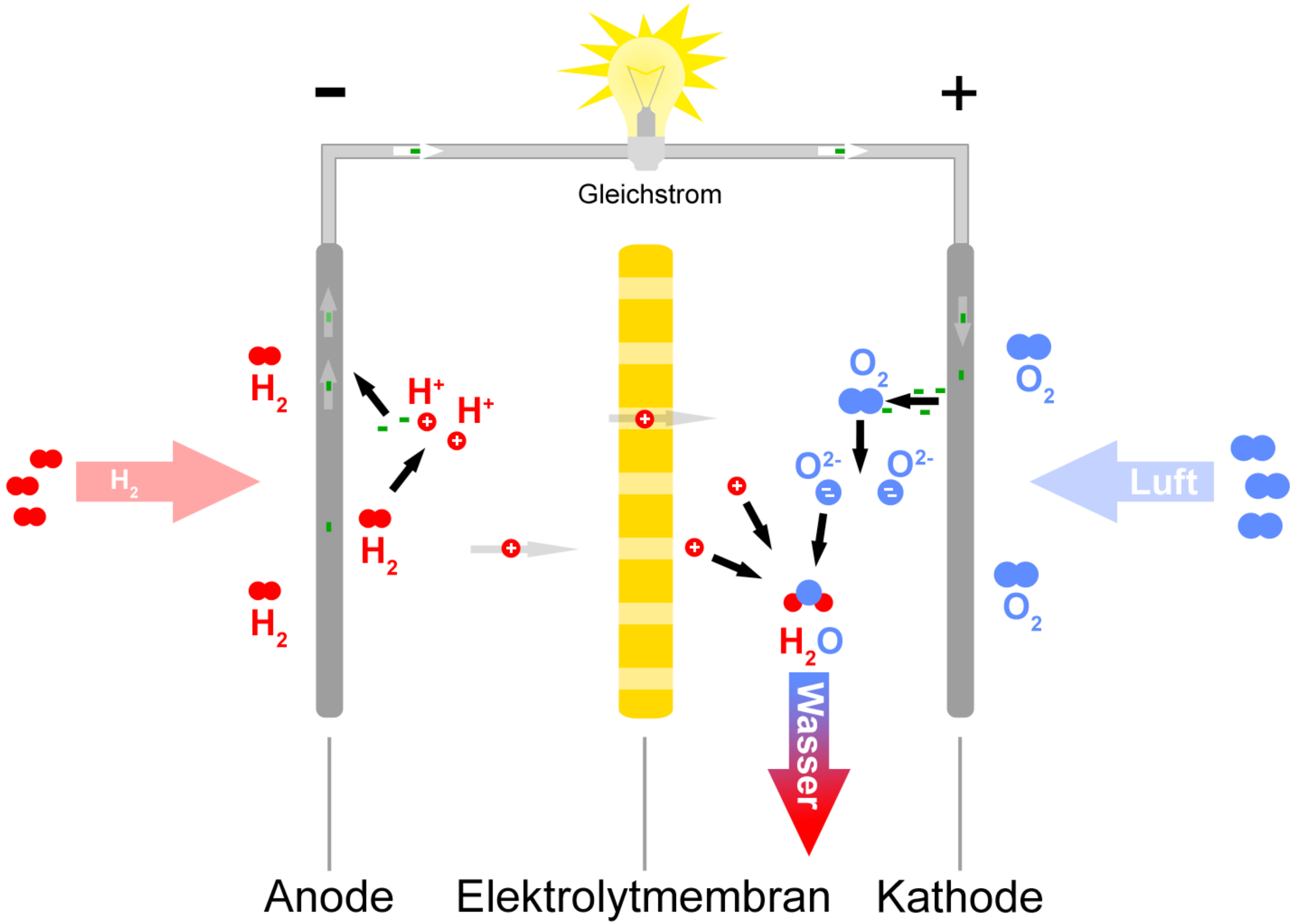
Die wichtigsten Einflussgrößen kennenlernen.

Möglichkeiten kennenlernen.

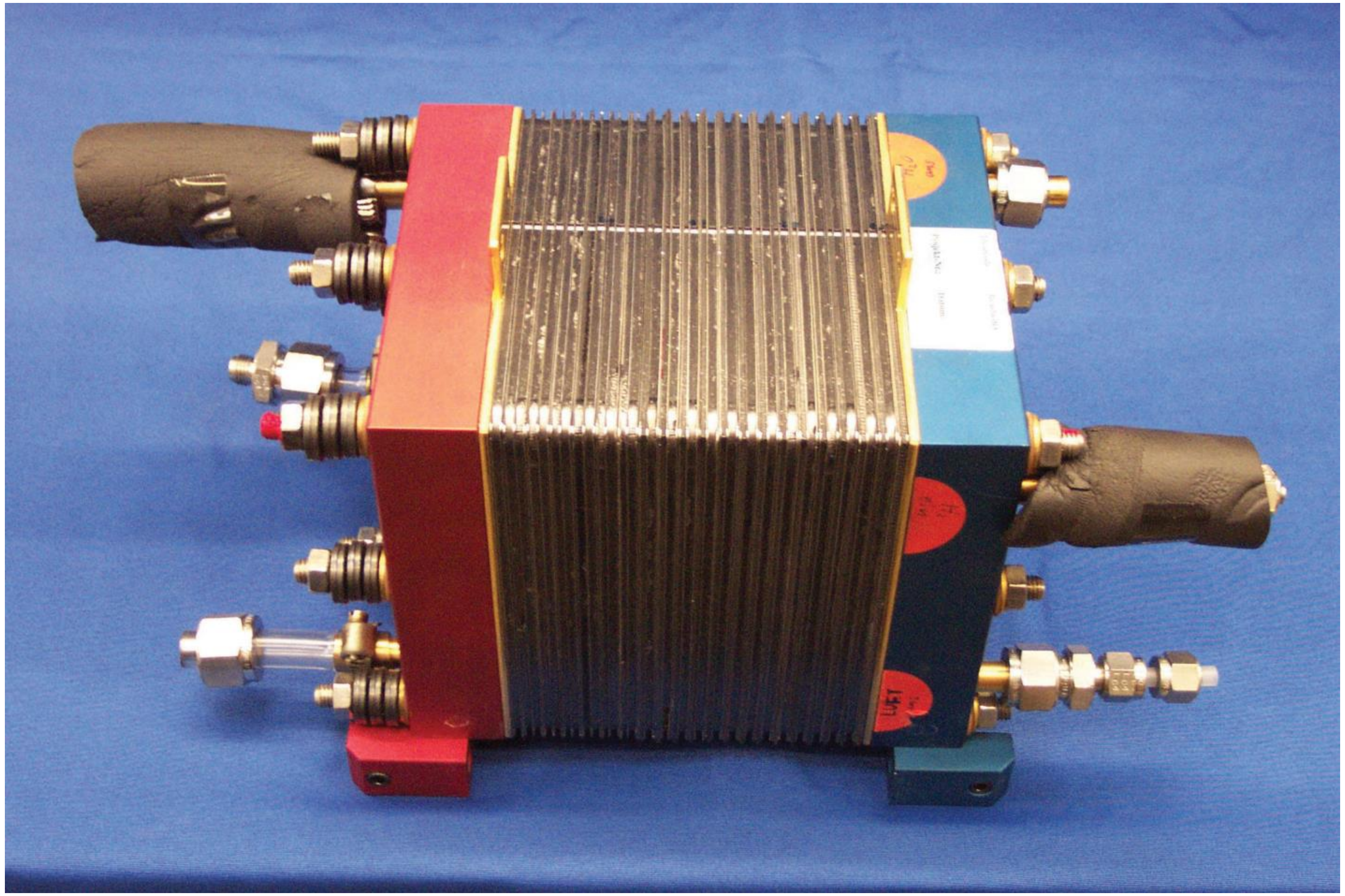
Geschichte der Brennstoffzelle

- **1838** Christian Schönbein: zwei Platindrähte in Salzsäure mit je Wasserstoff oder Sauerstoff umspült → Strom = Umkehrung der Elektrolyse
- **1870** Jules Verne: „*Das Wasser ist die Kohle der Zukunft. Die Energie von morgen ist Wasser, das durch elektrischen Strom zerlegt worden ist. Die so zerlegten Elemente des Wassers, Wasserstoff und Sauerstoff, werden auf unabsehbare Zeit hinaus die Energieversorgung der Erde sichern*."
- **1866**: Werner von Siemens → elektrischer Generator
- **1911**: Beobachtung der Stromerzeugung durch Bakterien (M. C. Potter)
- Ausrufen den Wasserstoffzeitalters in (seit) den **1950ern**
- Steigendes Interesse an mikrobiellen Brennstoffzellen seit den **1990ern**

Wie funktioniert eine herkömmliche Brennstoffzelle?

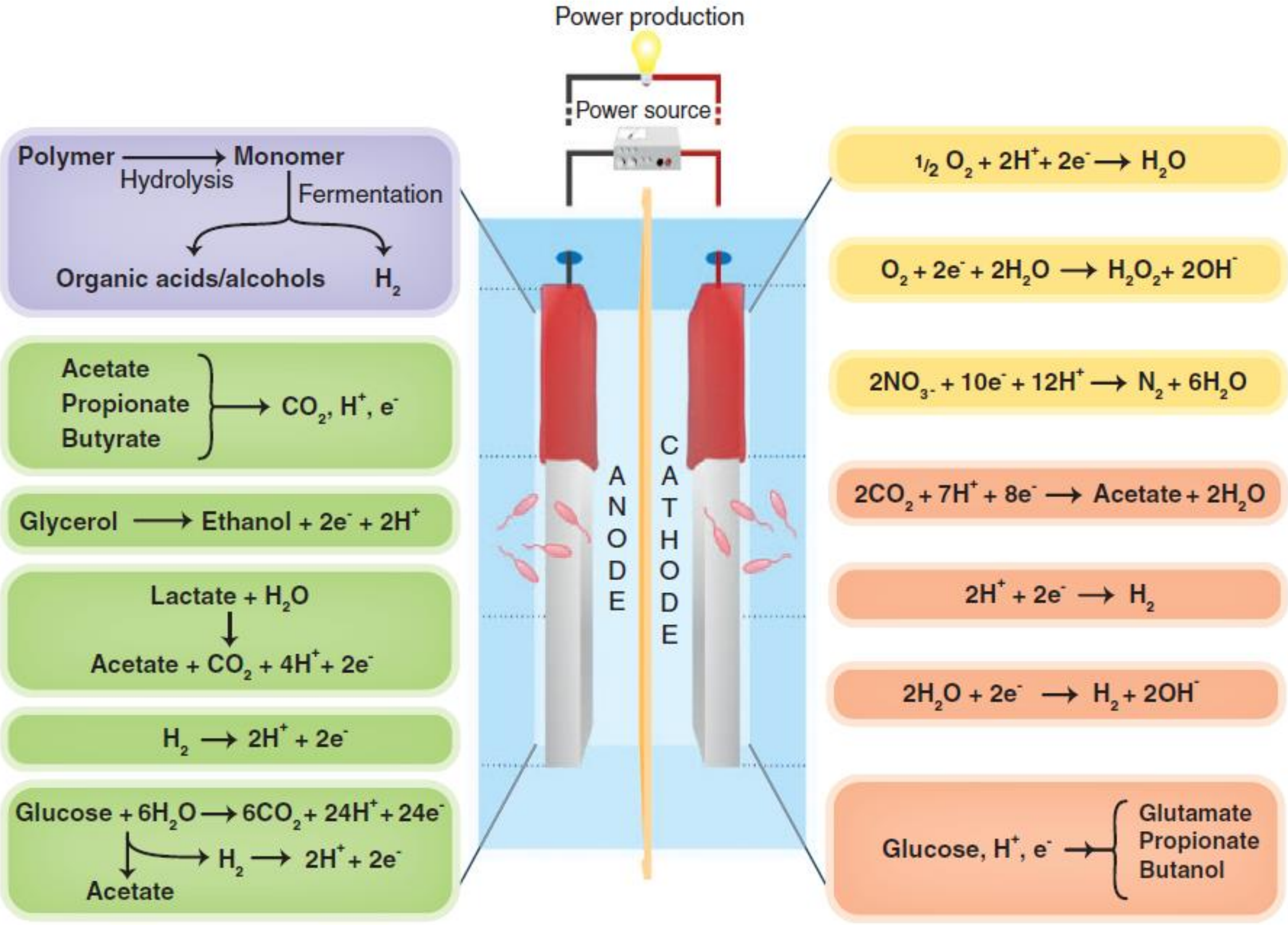


Eine echte Brennstoffzelle



[www.mvv-energie.de]

Prozesse im Bioelektrochemischen Systems



Purple indicates reactions that do not directly result in current generation; green, reactions that can produce current; yellow, reactions that can occur spontaneously or can be accelerated by adding additional power; orange, power addition is required. The stoichiometry of the reactions is principally theoretical because many conversions lead to side products as well as biomass formation.

[Logan and Rabaey 2012 *Science*]

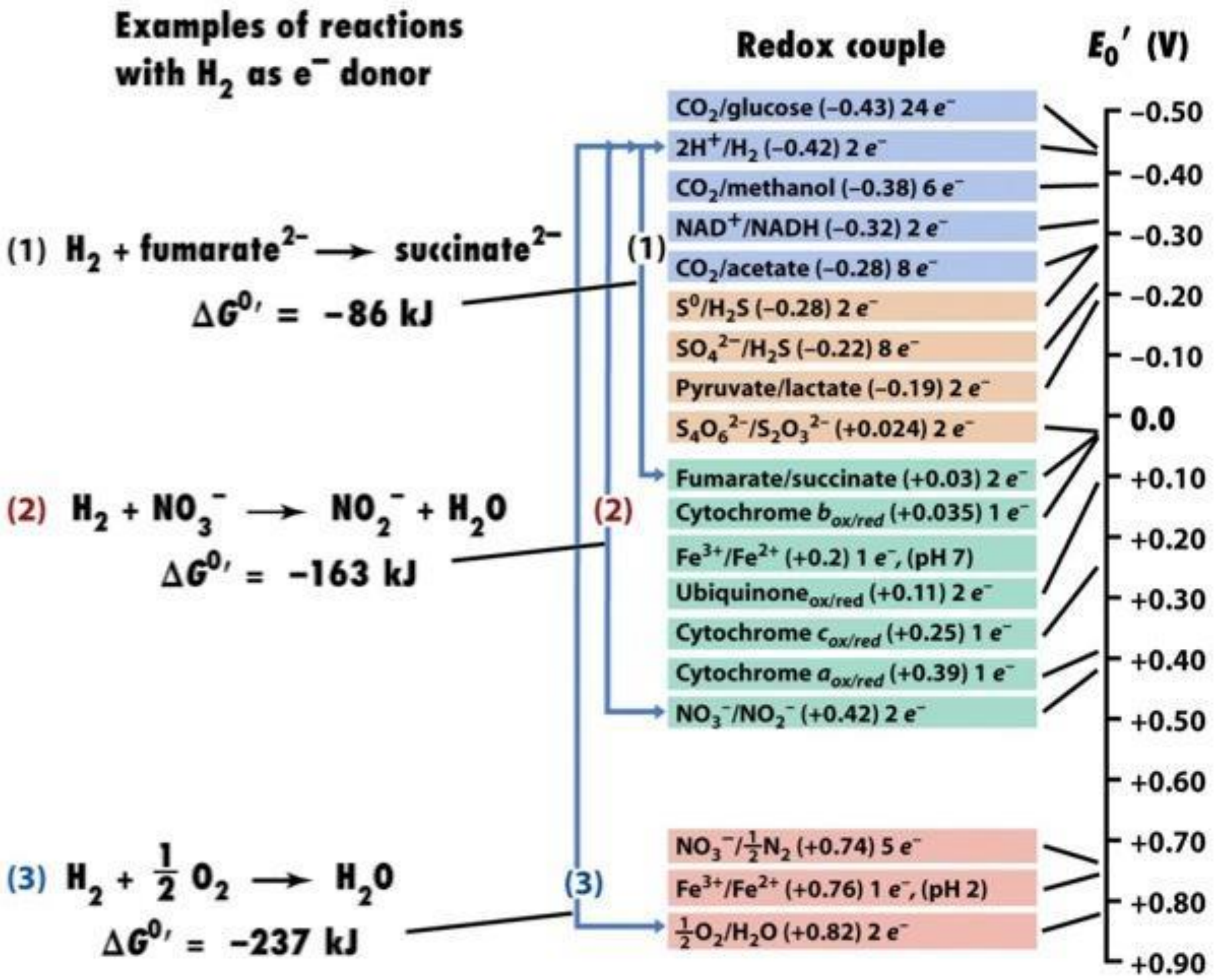
Definitionen:

- Bioelectrochemical System (BES):
  - An electrochemical system in which electrochemically active microorganisms catalyse the anode and/or cathode reaction
  - Most common systems: Microbial Fuel Cell and Microbial Electrolysis Cell

- Microbial Fuel Cell (MFC):
  - Bioelectrochemical system that is capable of converting the chemical energy of dissolved organic materials directly into electrical energy

- Microbial Electrolysis Cell (MEC):
  - Bioelectrochemical system that is capable of generating a product (e.g. hydrogen) from dissolved organic materials and that drives the reactions with an electrical energy input

Wichtige Redoxpotentiale



[Brock – Microbiology]

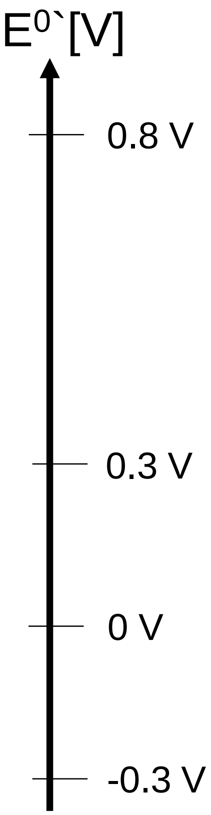
Ein Beispiel...

Anode

$E^{0`}[\text{Acetate}] = -0.3\ V$

Kathode

$E^{0`}[O_2] = +0.8\ V$



Maximales Zellpotential

$E'_{emf} = E'_{Cat} – E'_{An}$

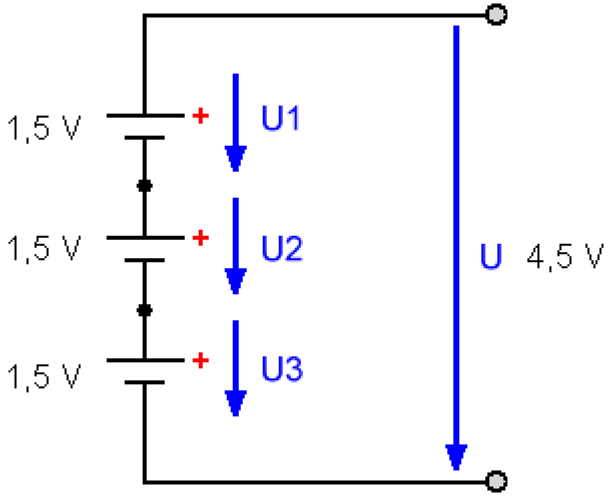
$E'_{emf} = 0.8\ V – (-0.3\ V)$

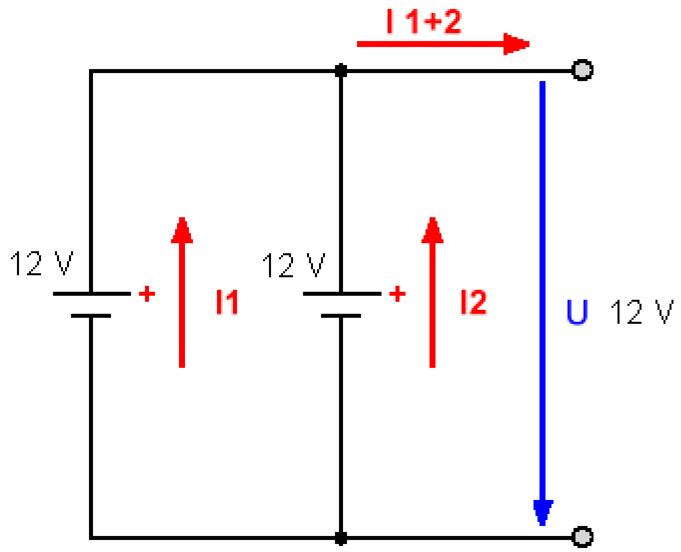
$E'_{emf} = 1.1\ V$

→ Spannung kann durch Serienschaltung erhöht werden.

emf = electron motive force

Kurzer Ausflug in die Elektrophysik





- Reihenschaltung
  - Spannung addiert sich
  - Strom bleibt konstant

- Parallelschaltung
  - Spannung bleibt gleich
  - Strom addiert sich

Energiedichte

- In MFC (microbial fuel cell) kleiner als in CFC (chemical fuel cell) weil:
  - Hoher interner Widerstand
  - Lösungsbedingungen lebender Organismen (Elektrolyt-Konzentration niedrig, pH, etc.)
  - Niedrigere Temperatur (Diffusion)
  - Substrat Verfügbarkeit
  - Biofilmkinetik

	Reaktion	**Power density**
Konventionelle Batterien	Zn/MnO_2 Li-ion	$30\ kW\ m^{-3}$ $90\ kW\ m^{-3}$
CFC (chemical fuel cells)	e.g. H_2/O_2	$140\ kW\ m^{-3}$
Anaerobic digestion	COD* to kW_{el} and kW_{heat}	$4\ kW\ m^{-3}$
BES anode	COD* to kW_{el}	$0.1\ kW\ m^{-3}$

COD = chemical oxygen demand

[Arends and Verstraete 2012 *Microbial Biotechnology*]

Vergleich HFC - MFC

- Die Redoxhalbreaktionen müssen getrennt werden für Anode und Kathode

- HFC hat Ionenaustauschmembran für Trennung Anode – Kathode
- HFC braucht kein Lösungsmittel

- MFC braucht nicht notwendigermaßen eine Membran (Membran erhöht Widerstand → aber Trennung der Reaktionen!)
- Höhere Leitfähigkeit des Mediums (Salzgehalt > Biologische Toleranz)
  → geringerer Widerstand
- Ladungsausgleich hauptsächlich durch Gegenionen (Natrium, Kalium)
  → pH Gradient!

Schematische Übersicht eines BES

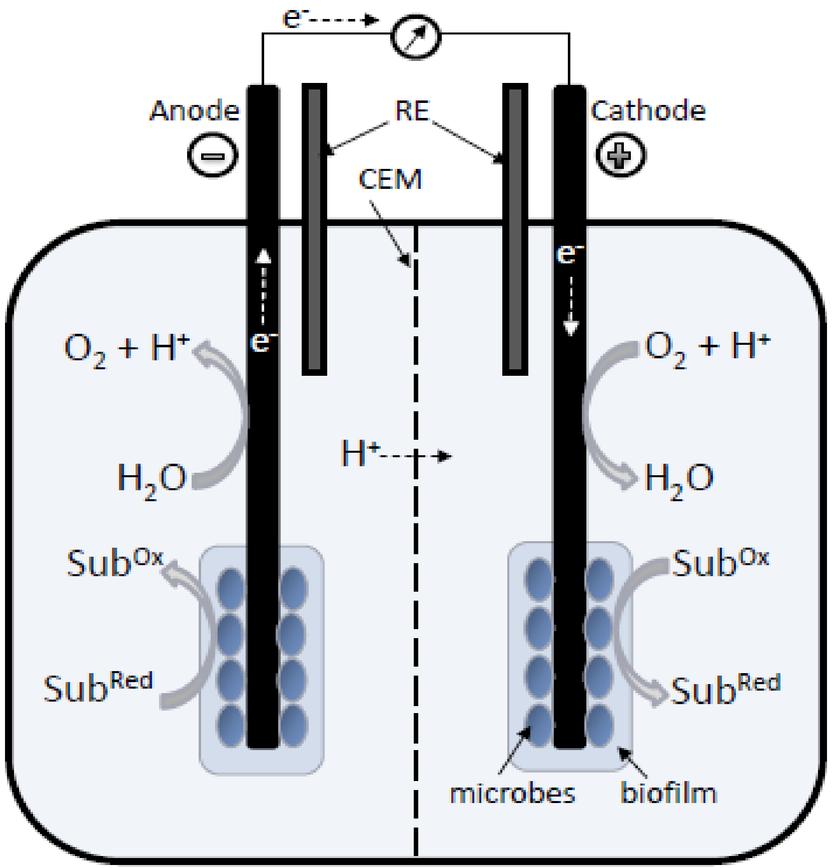
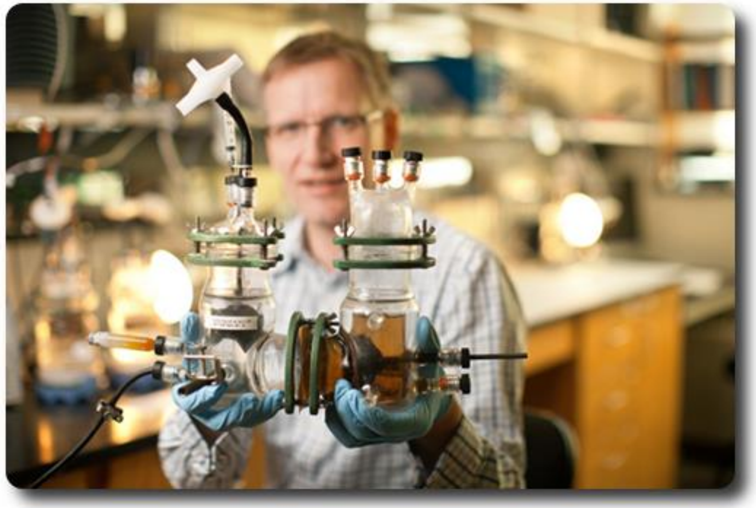


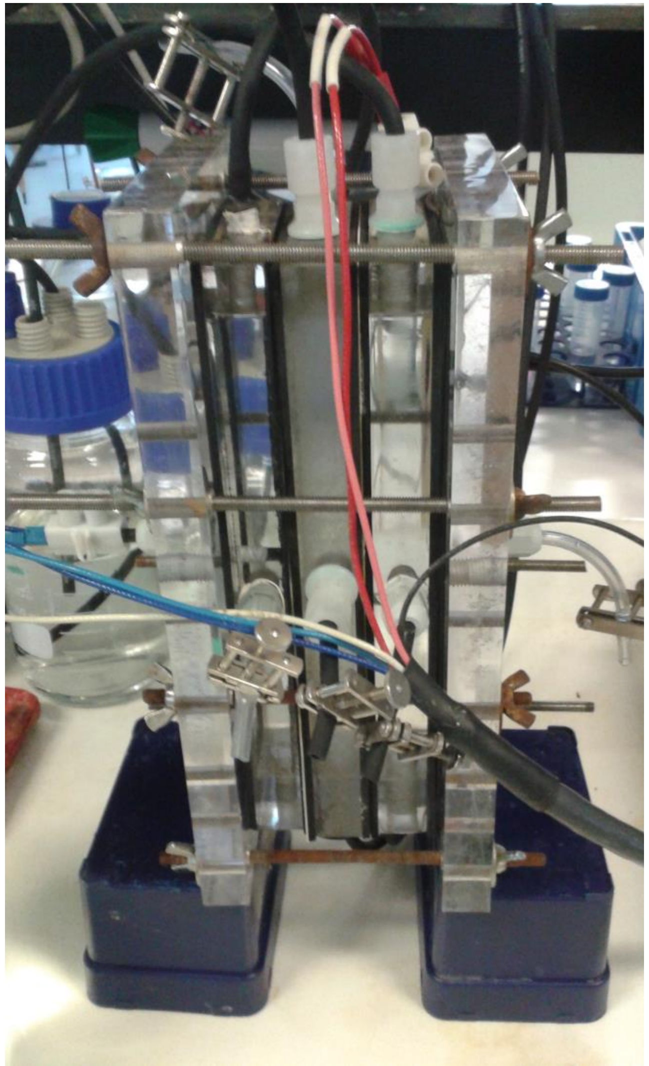
Figure 1 | Schematic overview of a bioelectrochemical system. Substrates (Sub) are oxidised or reduced by microorganisms living in biofilms. Abiotic reactions (e.g. oxidation/reduction of water) also take place. RE = reference electrode. CEM = cation exchange membrane.

Mögliche Reaktoraufbauten

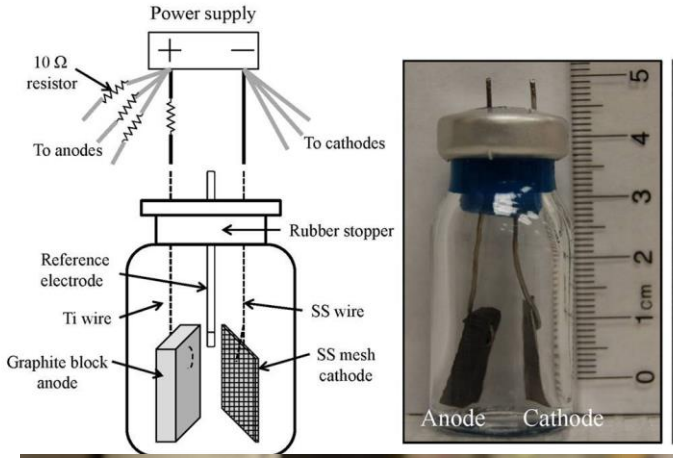


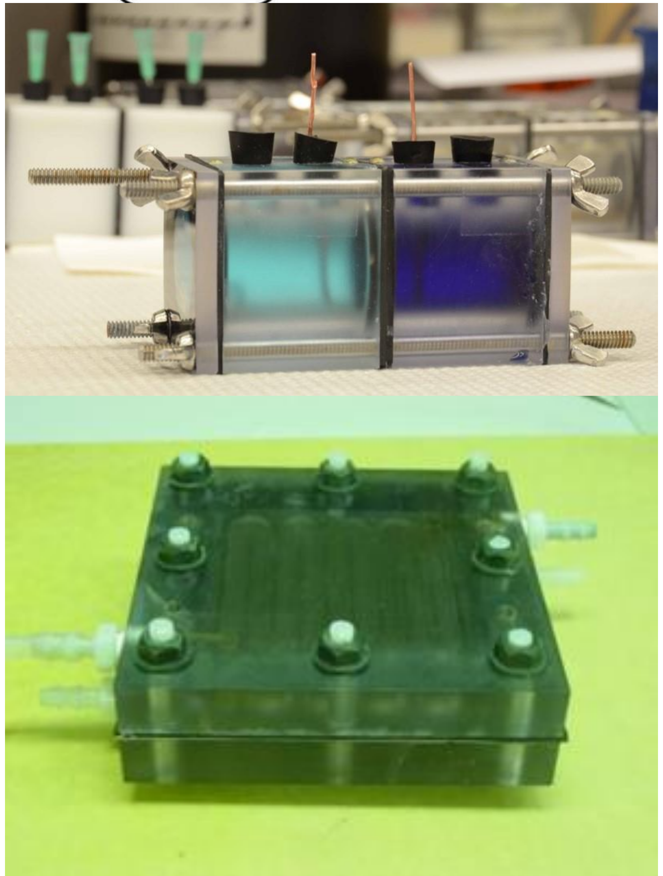
Prof. PhD Lars Angenent

Prof. Dr. Miriam Rosenbaum



Prof. Dr. ir. Korneel Rabaey





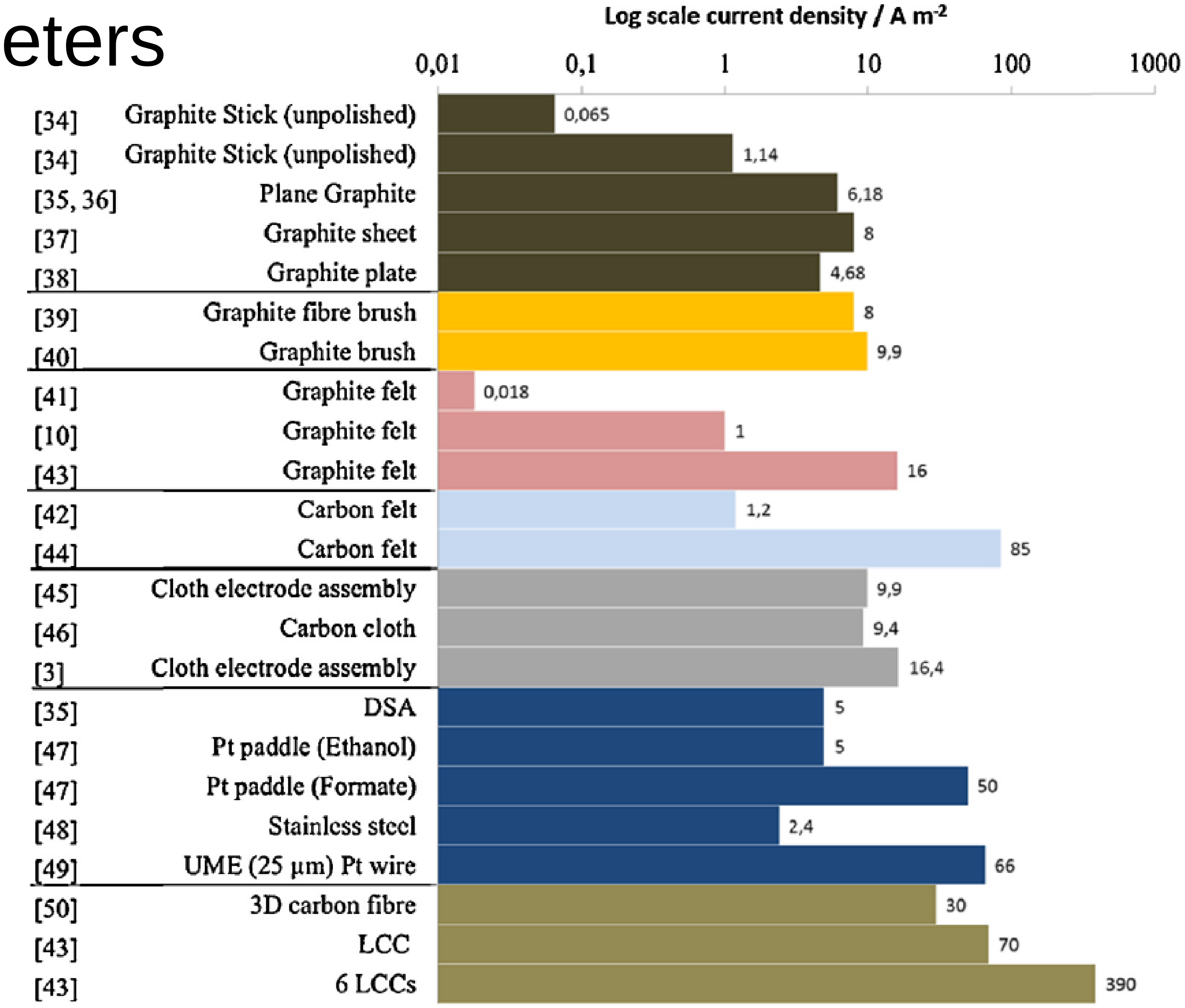
Prof. PhD Bruce Logan

Performance parameters

Electrode materials

- Roughness
- Surface area
- Biocompatibility
- Conductivity
- Resistance to corrosion
- Mechanical strength

BES architecture



[Sharma et al. 2014 *Electrochim Acta*]

Performance parameters

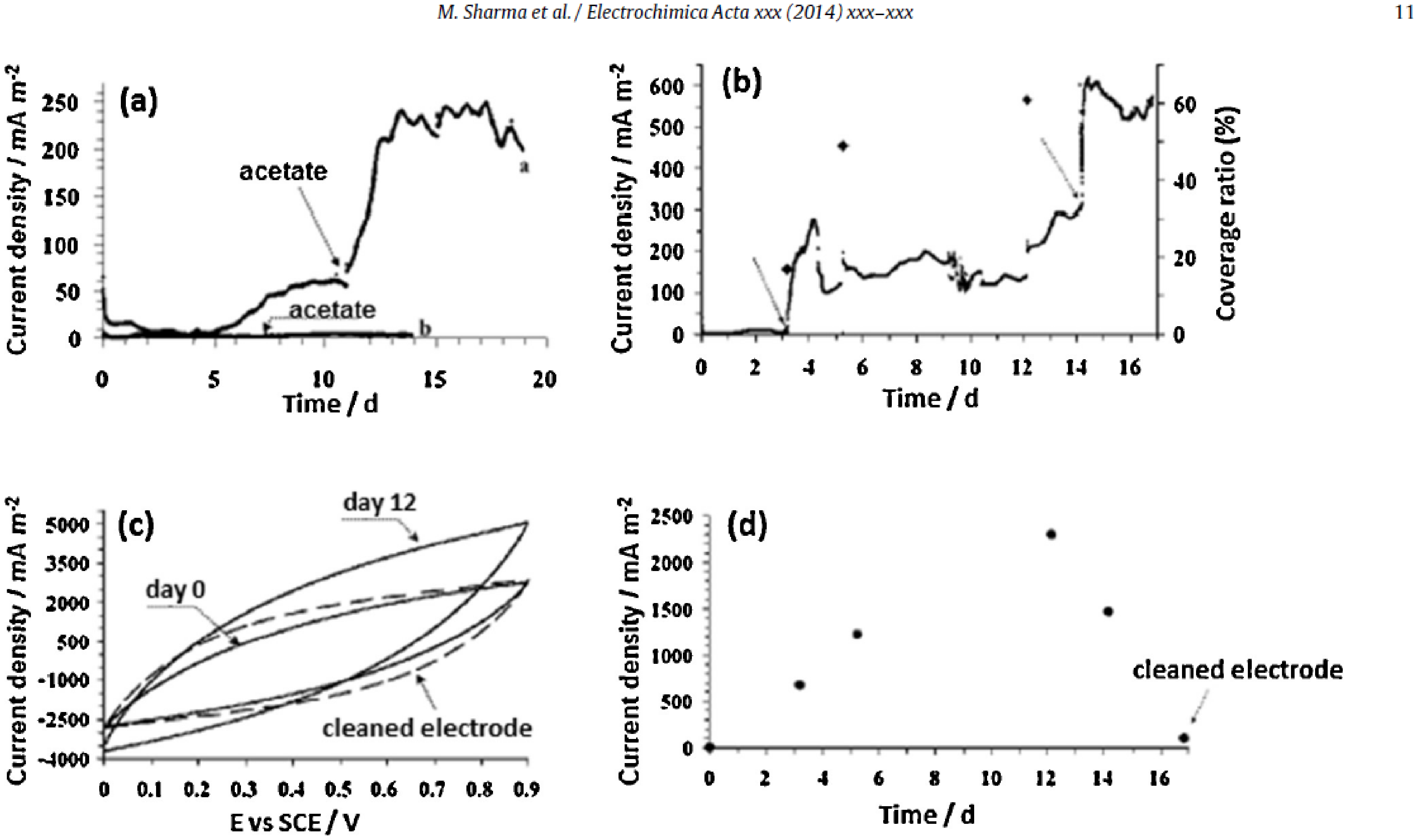
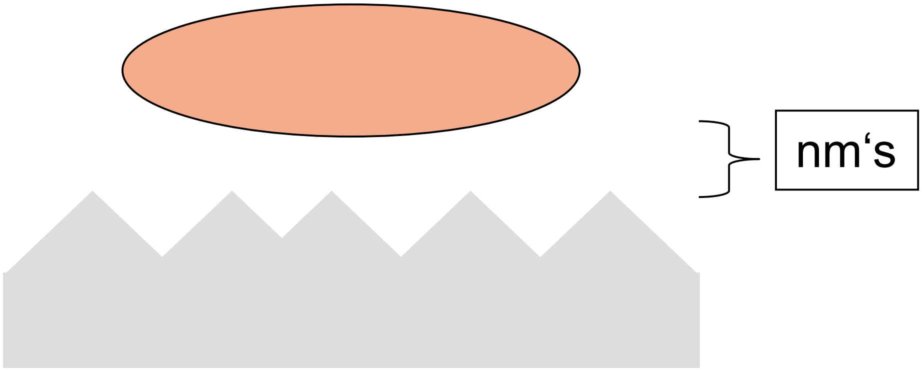
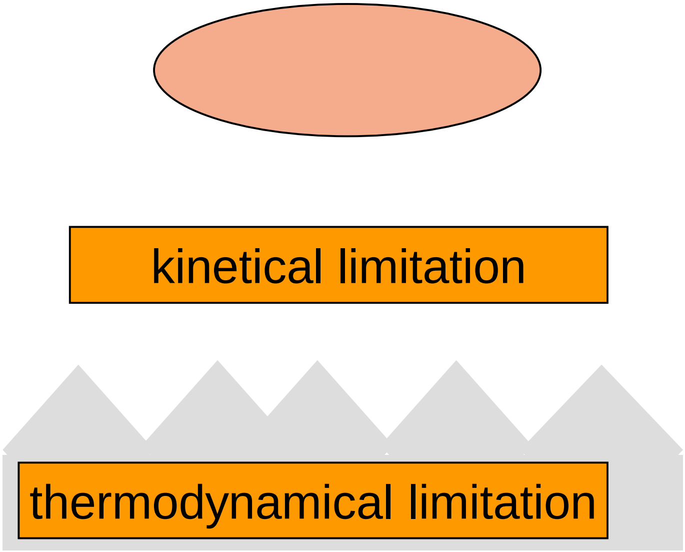


Fig. 4. Current densities (by PSA) achieved by addition of sodium acetate in EABs enriched from garden compost (a,b). (c) The corresponding cyclic voltammetry values taken at regular time intervals, along with a final CV of cleaned electrode (d) [107]. PSA, projected surface area; EABs, electroactive biofilms; CV, cyclic voltammetry

Wie kommen Elektronen auf die Elektrode?



Direct electron transfer requires less than 14 Angström



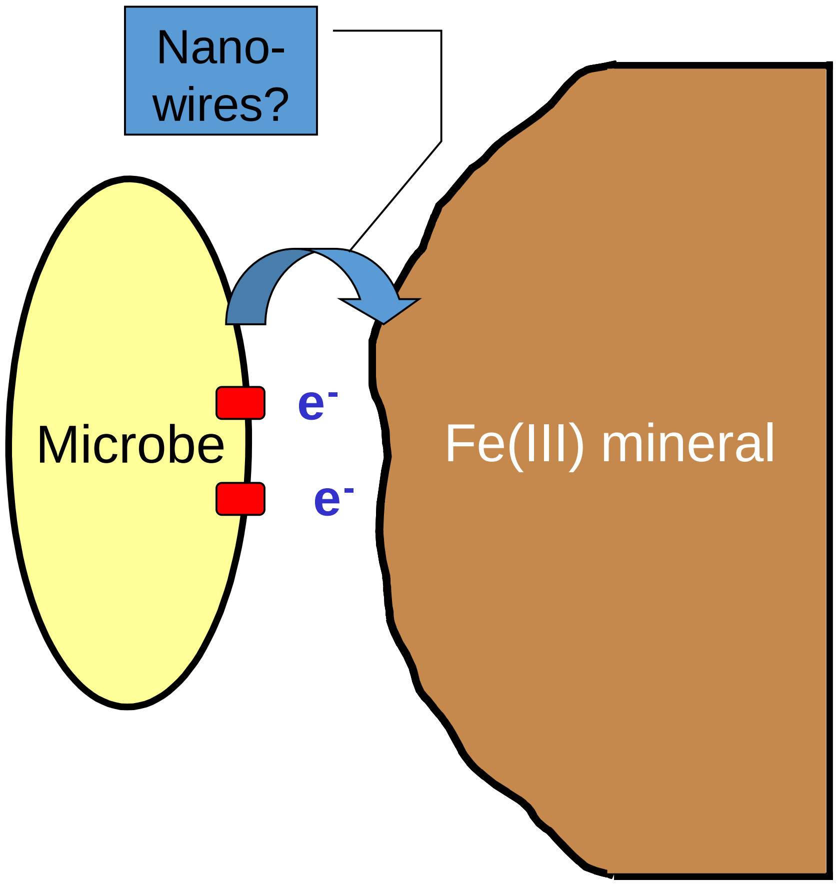
iron reducing bacteria in contaminant degradation face two limitations:

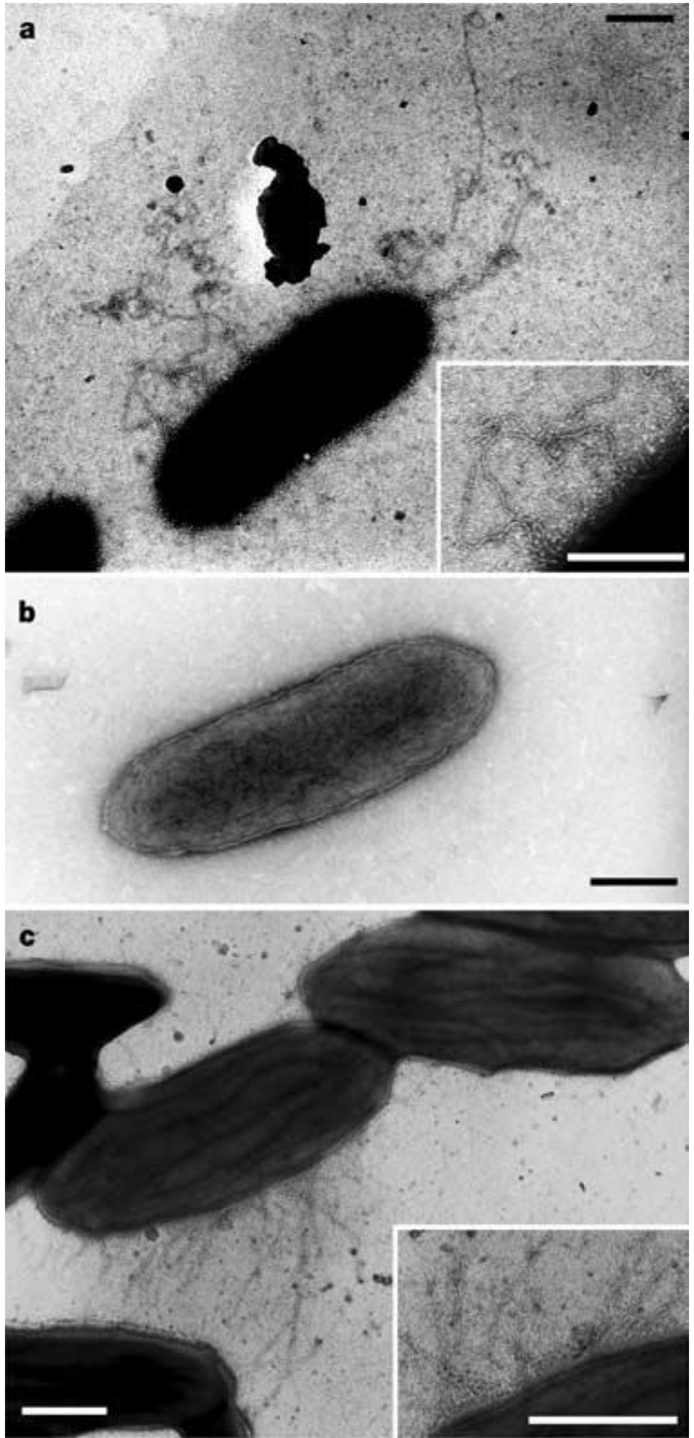
e-acceptor availability

e-acceptor potential

How do the microbes transfer their electrons to the insoluble iron(III) ?

1) Direct contact between bacterial cell and mineral surface





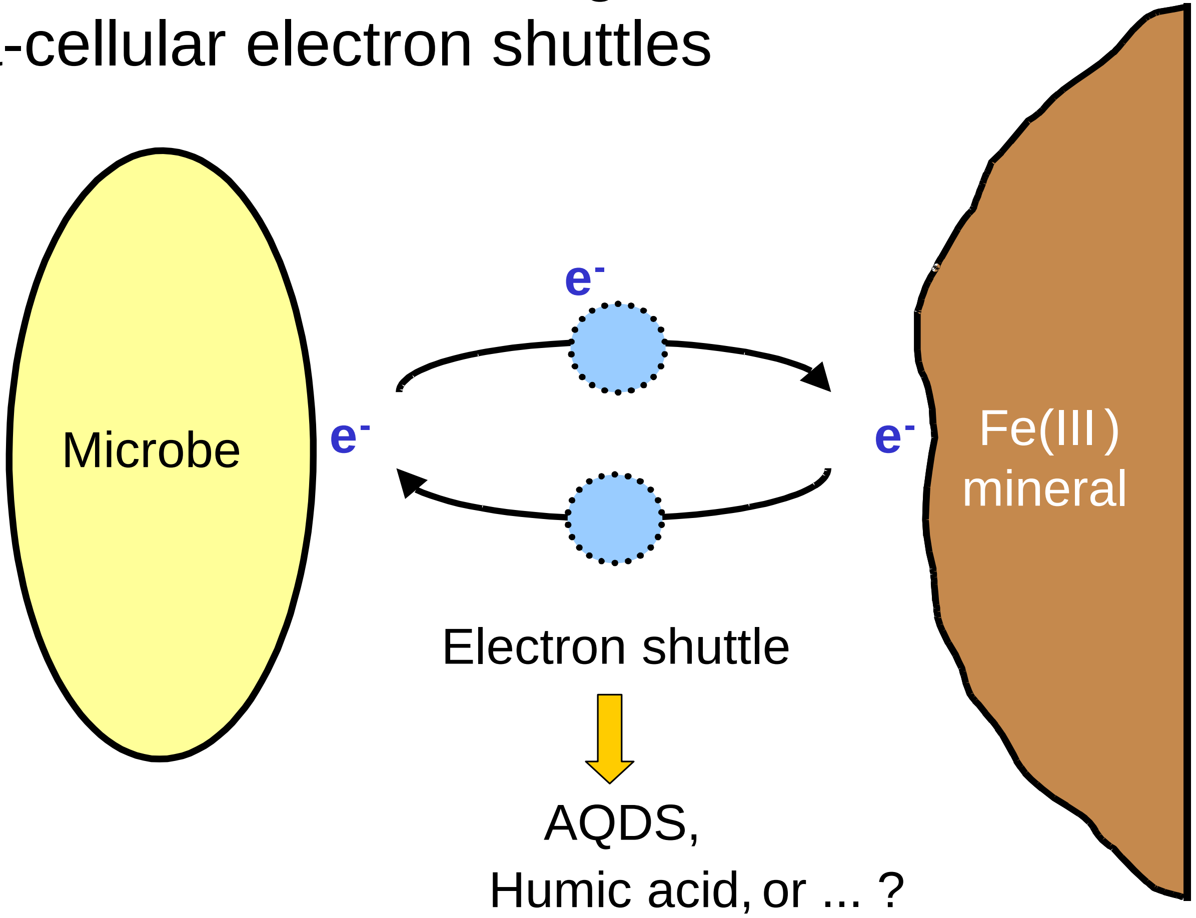
Nanowires? → sehr umstritten

Figure 2 | Transmission electron microscopy analyses. Shown are cells of a wild-type strain (a), a pilA-deficient mutant strain (b) and a complemented mutant strain (c) of *G. sulfurreducens*. Cells were grown in medium with acetate and fumarate at 25 °C to induce the formation of pili, then negatively stained. Insets in a and c show details of pili produced by the wild-type and complemented mutant strains, respectively. Scale bars, 0.2 mm.

[Reguera et al. 2005 *Nature*]

How do microbes transfer electrons to insoluble iron(III) ?

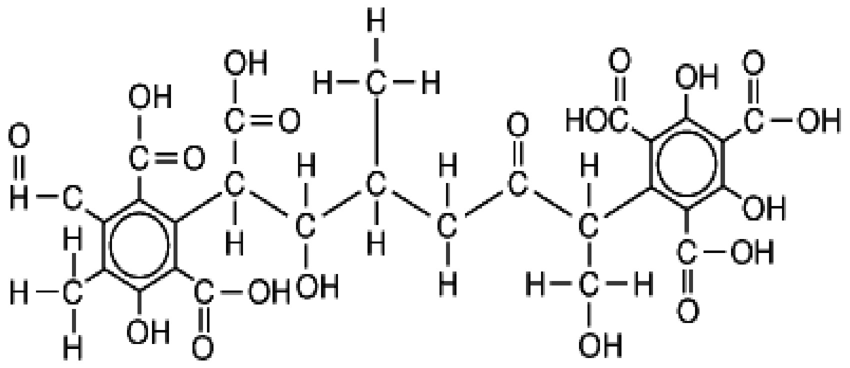
2) Humic acids and analogous substances can work as extra-cellular electron shuttles



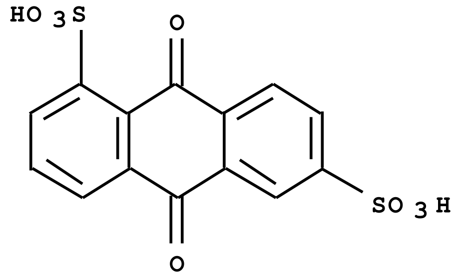
How do the microbes transfer their electrons to the insoluble iron(III) ?

Proposed mechanisms

- Humic acids and analogous substances work as extra-cellular electron shuttles



Humic acid detail



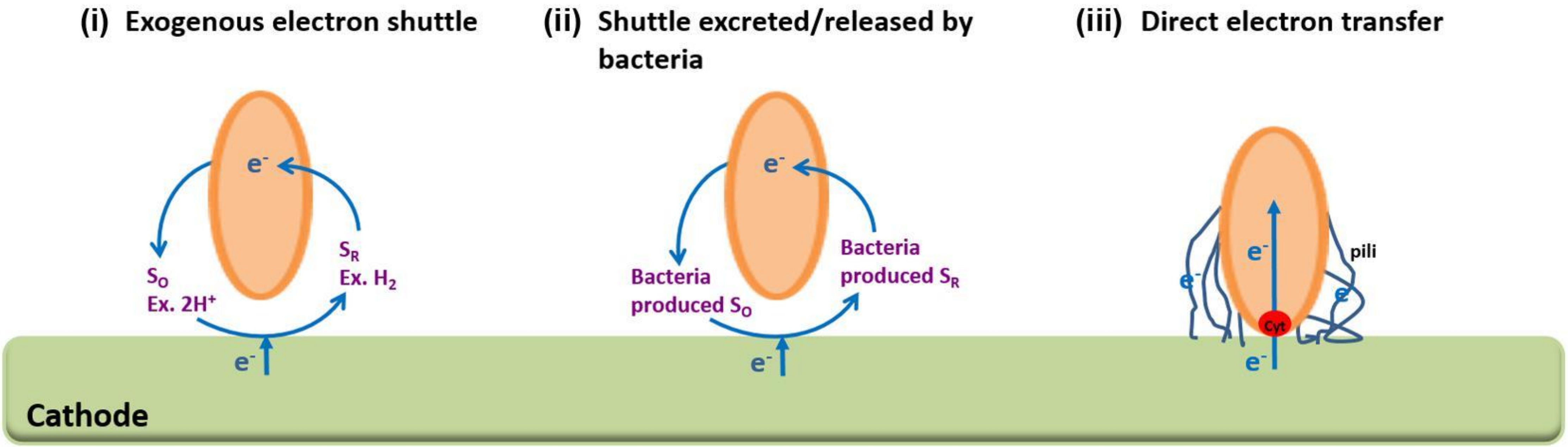
AQDS

Produktion von Elektronenüberträgern?

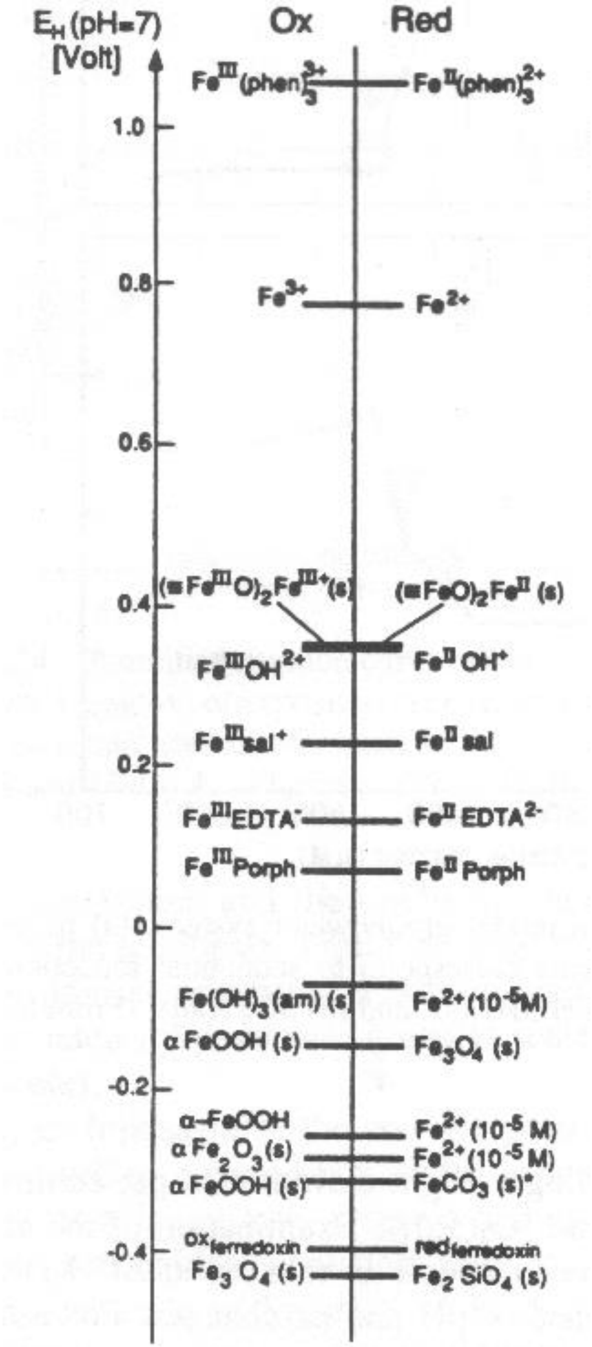
Elektronenshuttle	Organismus	Referenz
Riboflavin	*Shewanella oneidenis*	Von Canstein et al. 2008 *Appl. Environ. Microbiol.*
Phenanzine, Pyocyanin	*Pseudomonas aeruginosa*	Rabaey et al. 2005 *Environ. Sci. Technol.*
?	*Geothrix fermentans*	Mehta-Kolte & Bond 2012 *Appl. Microbiol. Biotechnol.*
Pyocyanin	e.g. *Enterococcus faecium, Lactobacillus amylovorans, Brevibacillus …*	Pham et al. 2008 *Appl. Microbiol. Biotechnol.*

Demonstration that mediators produced by one organisms can also be used by other bacteria

Verschiedene Möglichkeiten der Elektronenübertragung



[Tremblay and Zhang 2015 *Front. Microbiol*.]



Redoxpotentiale von Eisenverbindungen und Mineralen

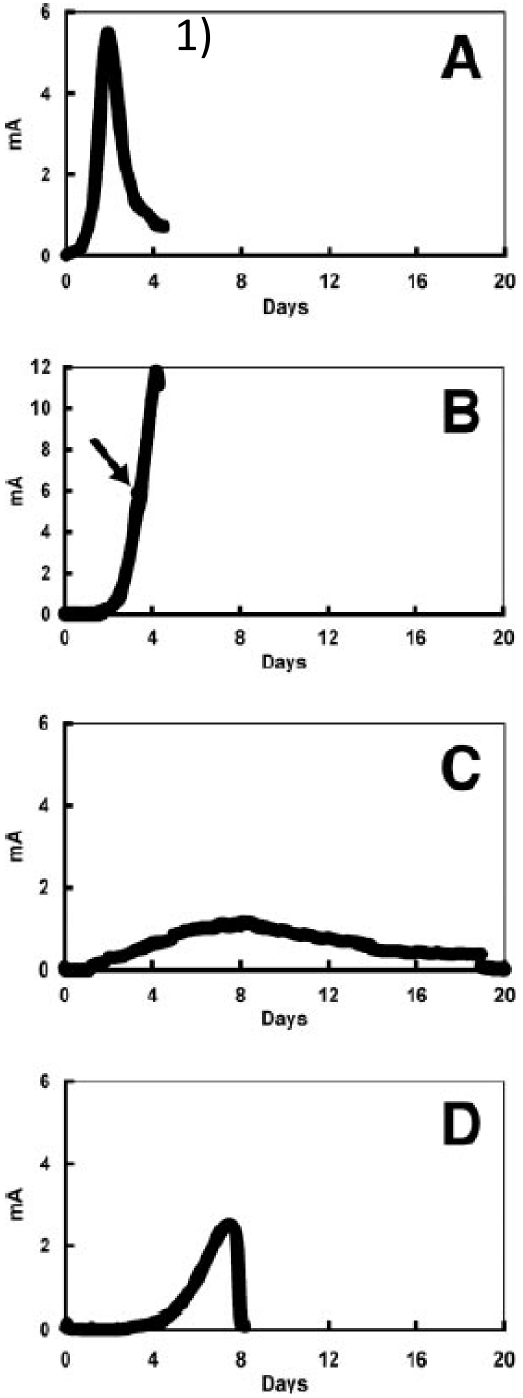
- Die Redoxpotentiale der verschiedenen Eisenmineralien unterscheiden sich sehr stark.
- Vor allem Eisenkomplexe können extreme Bandbreiten abdecken.
- In der Natur ist Eisen immer mit Huminstoffen belegt und eventuell komplexiert.
- Wie können Mikroorganismen mit diesen starken Unterschieden umgehen?

Beispiel von direktem Elektronenaustausch bei *Geobacter*?

- Bei komplexen Substraten (Abwasser) meist *Geobacteraceae* angereichert
- Begrenztes Substratspektrum → Syntrophe Interaktionen
- Komplexe Biofilme → bessere Stromproduktion als Reinkulturen

Stromproduktion hängt von Biofilmen ab

1)



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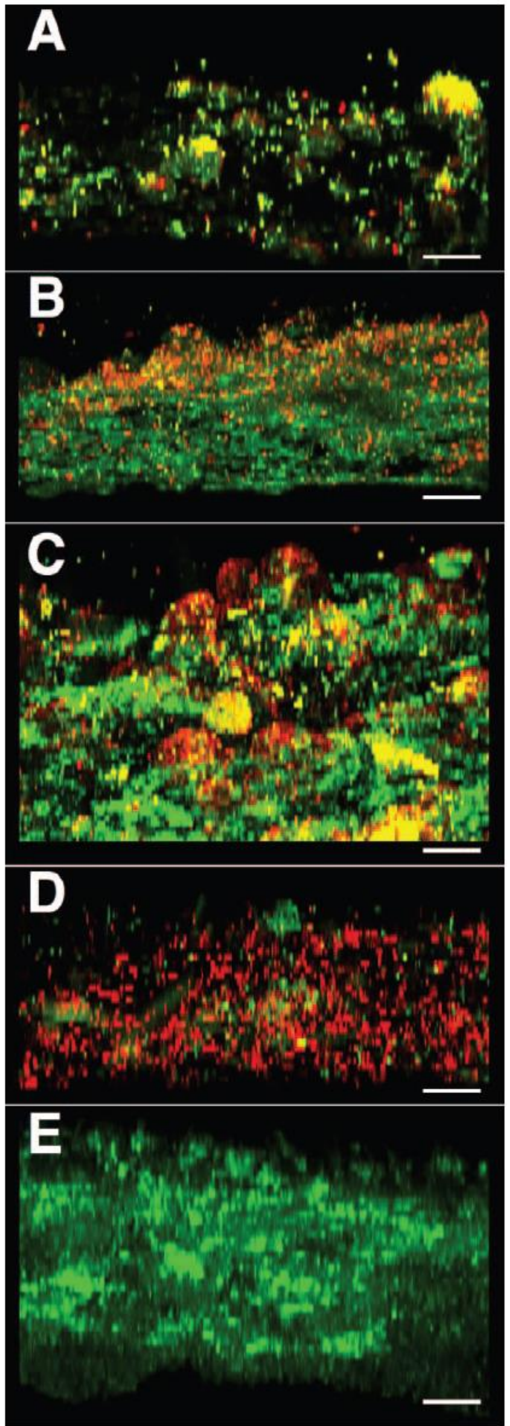

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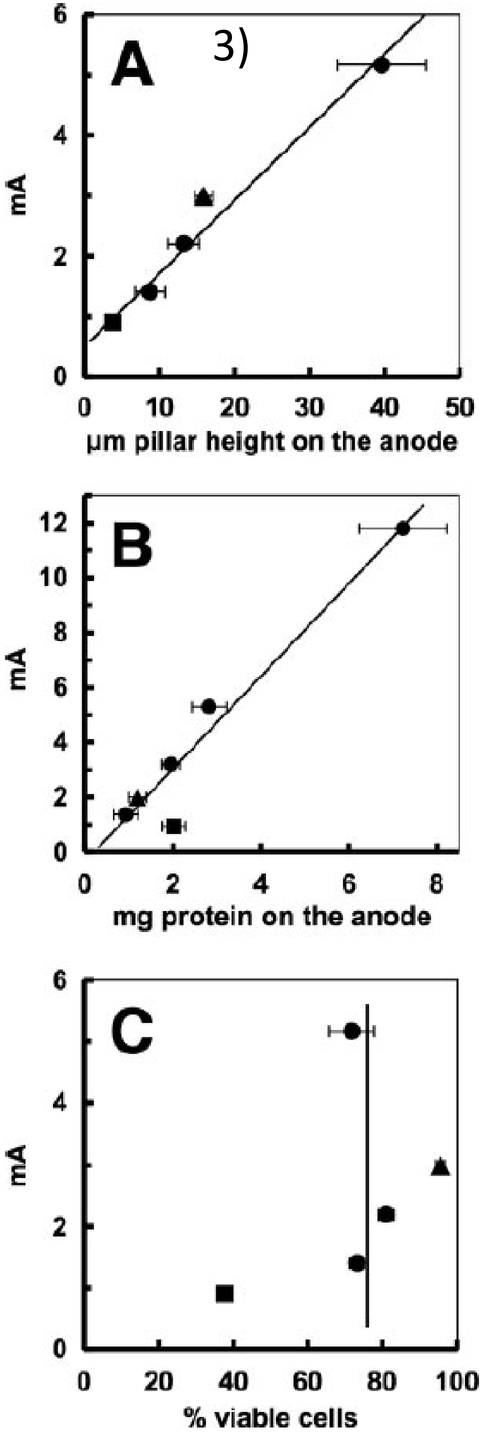


FIG. 1. Current in *G. sulfurreducens* fuel cells. (A and B) Current with wild-type cells growing on a one-time batch feed of acetate (A) or when the system was switched to continuous flowthrough mode at the point indicated by the arrow (B). Note the difference in scale on the *y* axis. (C and D) Current with a pilin-deficient mutant (C) and a strain with the capacity for pilin production restored (D) in batch systems. The data are representative time courses for multiple replicates for each treatment.

FIG. 2. Confocal scanning laser microscopy of *G. sulfurreducens* on anode surfaces. (A to C) Wild-type biofilms producing 1.4 mA (A), 2.2 mA (B), and 5.2 mA (C). (D and E) Biofilms of a pilin-deficient mutant (D) and the genetically complemented mutant strain (E) when current production was nearing maximum (ca. 1 mA and 3 mA, respectively). Live cells are green, while dead cells are red. The images are three-dimensional side-view images at a 45° angle reconstructed from the fluorescence patterns of a series of two-dimensional optical sections collected by CSLM. Bars, 20 µm.

FIG. 3. Pillar height (A), biomass (B), and cell viability (C) of *G. sulfurreducens* anode biofilms at different rates of current production. ●, wild-type cells; ■, pilin-deficient mutant; ▲, genetically complemented mutant strain. The pilin-deficient mutant produced equivalent amounts of power whether it was in batch or flowthrough mode. The error bars for pillar heights indicate standard deviations for all pillars from at least five fields (140 by 140 μm^2). The lines are the regression lines calculated for the wild-type anode biofilms.

[Reguera et al. 2006 *Appl. Environ. Microbiol.*]

100 years of microbial electricity production: three concepts for the future

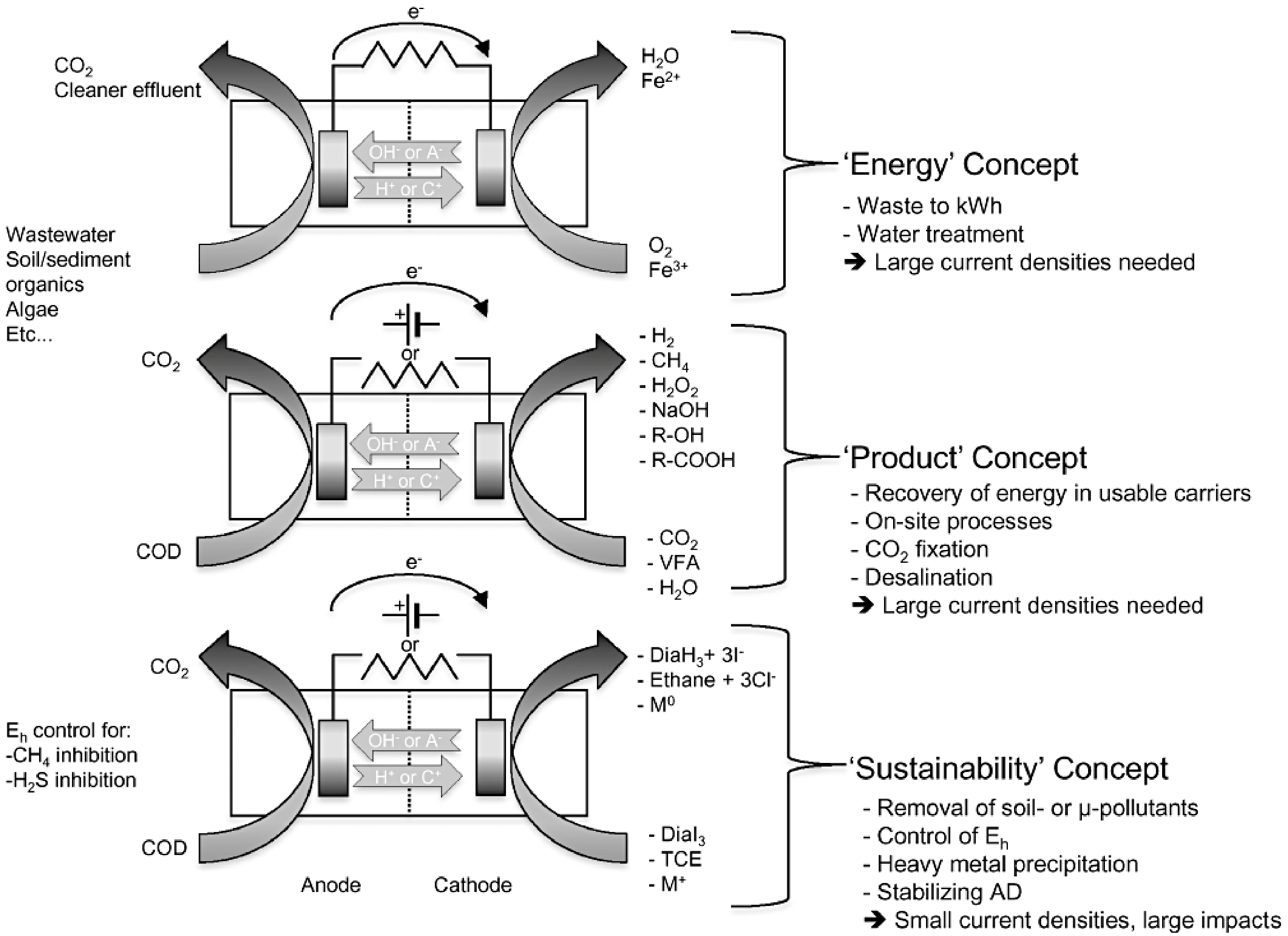


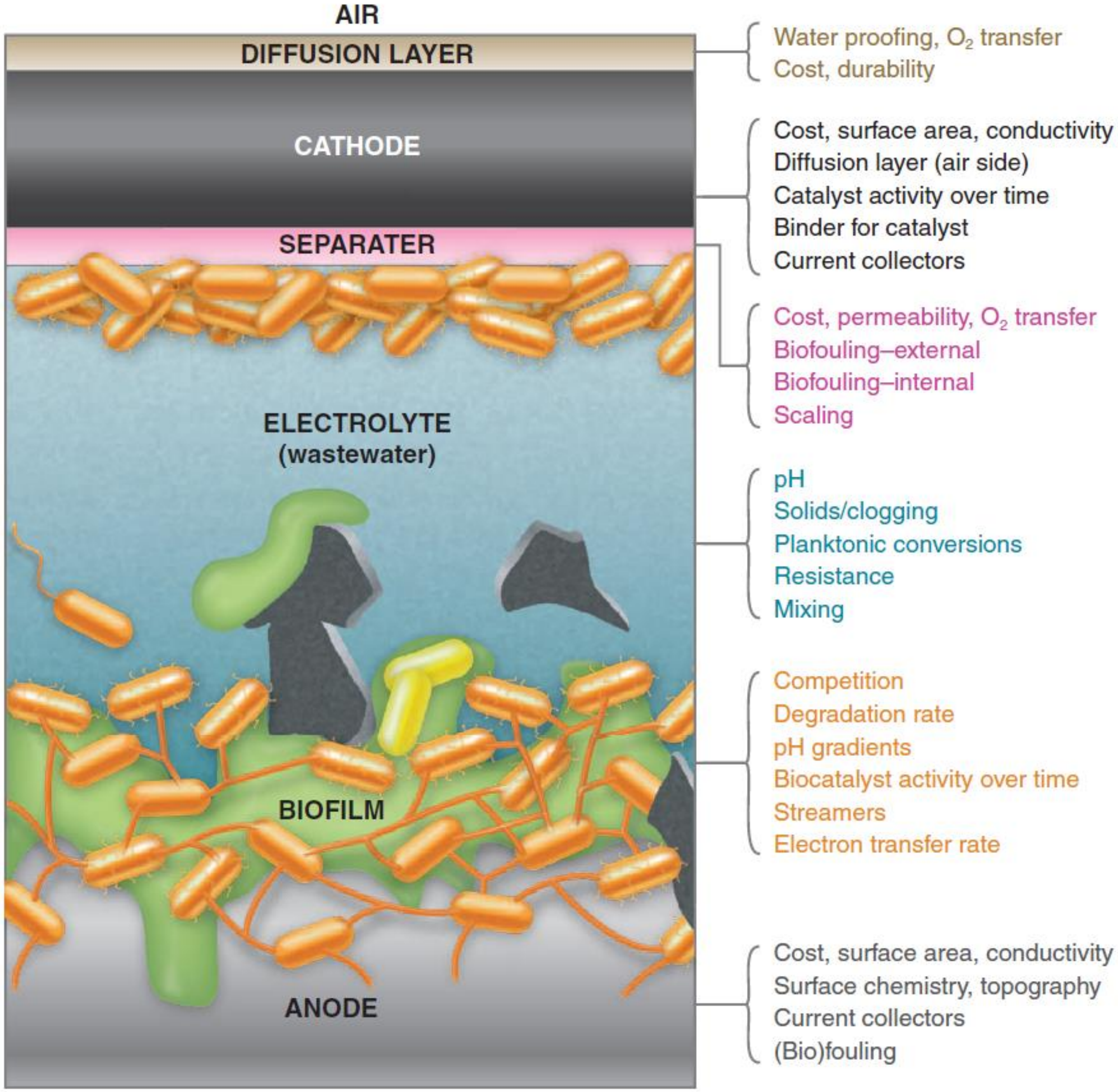
Figure 1. Three concepts for positioning a BES. A^- = anion. C^+ = cation. M^+ = oxidized metal. M^0 = zero valent metal. $DiaI_3$ = diatrizoate, medical contrast medium. $DiaH_3$ = de-iodated medical contrast medium. TCE= tri-chloroethylene.

[Arends and Verstraete 2012 *Microbial Biotechnology*]

BES → future

Potential:
- Specialized waste water treatment
- Production of chemicals (acetate, hydrogen gas) from waste or cheap educts
- Other specialized applications
- Specialized electricity production

Problems →

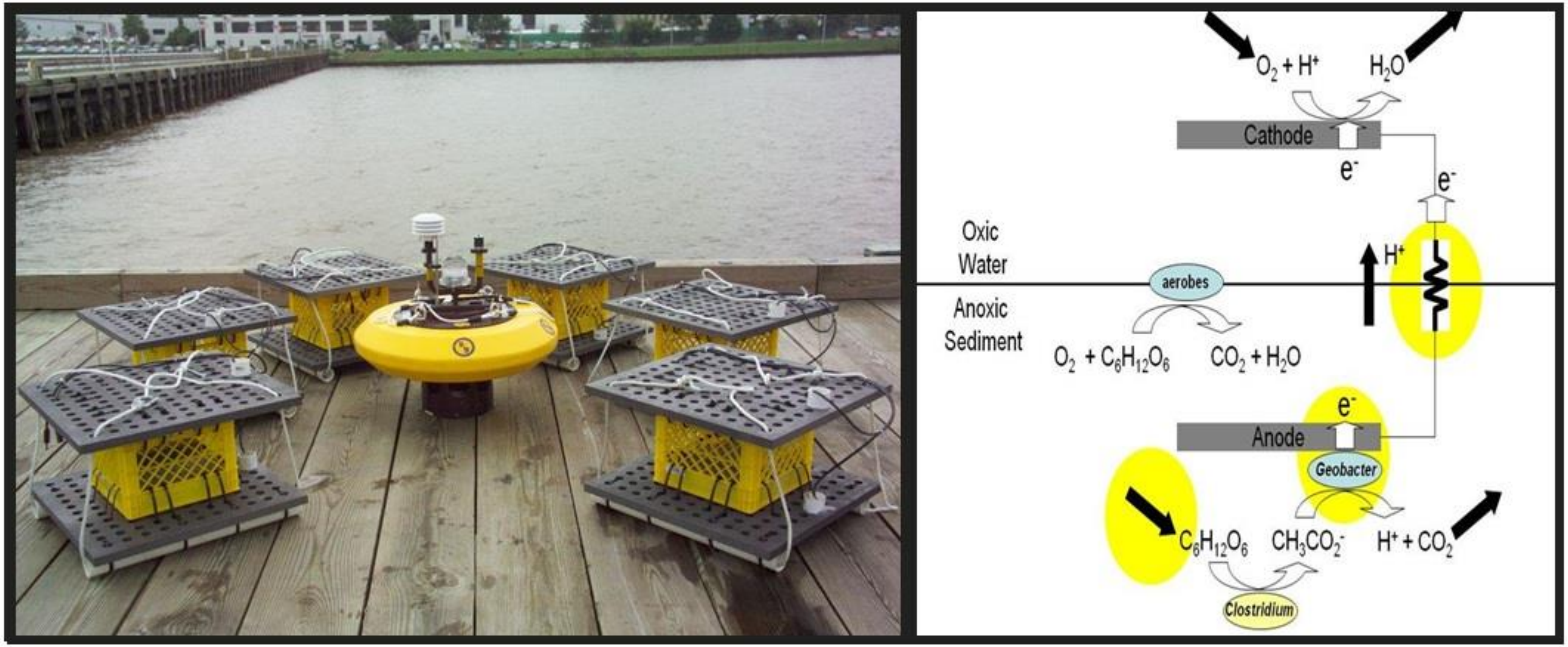


Applications:

- Energy → Bentic fuel cells
- Waste water purification
  - DOC, S^{2-}
- Fine chemical production
- Groundwater remediation

Bentic fuel cells / sediment-MFC

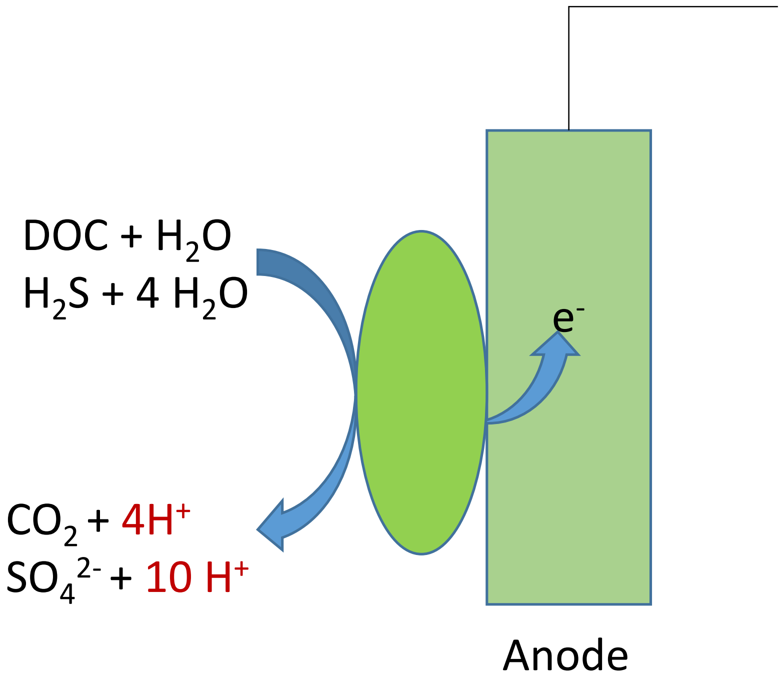
- Remote current production → scientific instruments



http://www.nrl.navy.mil/techtransfer/sites/www.nrl.navy.mil.techtransfer/files/images/benthicfuelcell.jpg

Waste water purification (DOC, H_2S)

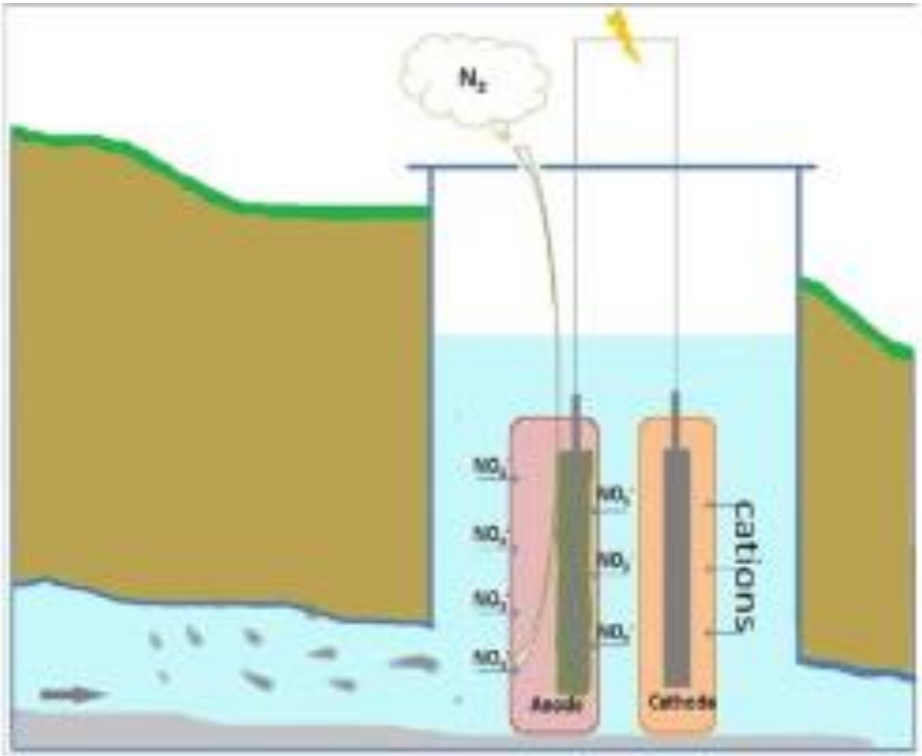
- Conventional activated sludge → -0,3 kWh m^{-3}
  - Conventional plus biogas → can be energy neutral (rare cases)
- Membrane bioreactors → - 2 kWh m^{-3}
- Anaerobic digestors → energy producing but
  - Needs concentrated waste stream (> 3 kg m^{-3})
  - Warmer temperatures (>20° C)
  - Larger reactors (z.B. Faulturm)
- BES → ??? Theoretically very high potential but:
  - Low energy recovery
  - Maximum power density: 12 W m^{-3} → 0,07 kWh m^{-3} produced over 6 h (= water residence time)
  - Energy content in domestic waster water → 2 kWh m^{-3}



Applying power to BES

- Applying power → microbial electrolysis cell (MEC)
- Hydrogen from biomass:
  - Hydrogen: $E^{0'}$ = -0,41 V
  - Acetat: $E^{0'}$ = -0,28 V
  - Needed delta = -0,14 V
  - Water splitting: → - 1,2 V
- Methane production:
  - Indirectly: hydrogen + CO_2 → methanogens
  - Directly: electrons + CO_2 → methanogens
- Cathodic production of acetate or acetoacetate by *Sporomusa oyata*.
- Ethanol from glycerol (waste product of paper industry)

Nitrate removal from groundwater driven by electricity generation and heterotrophic denitrification in a bioelectrochemical system



[Tong and He 2012 Journal of Hazardous Materials]