ASU BIODESIGN INSTITUTE
ARIZONA STATE UNIVERSITY

Center for Environmental Biotechnology

Non-photosynthetic Biohdyrogen – Overview of Options

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I will overview three ways to produce renewable bio-H_2 from biomass.

I view this as "indirect" photosynthetic bio-H_2, since the biomass ultimately came from photosynthesis.

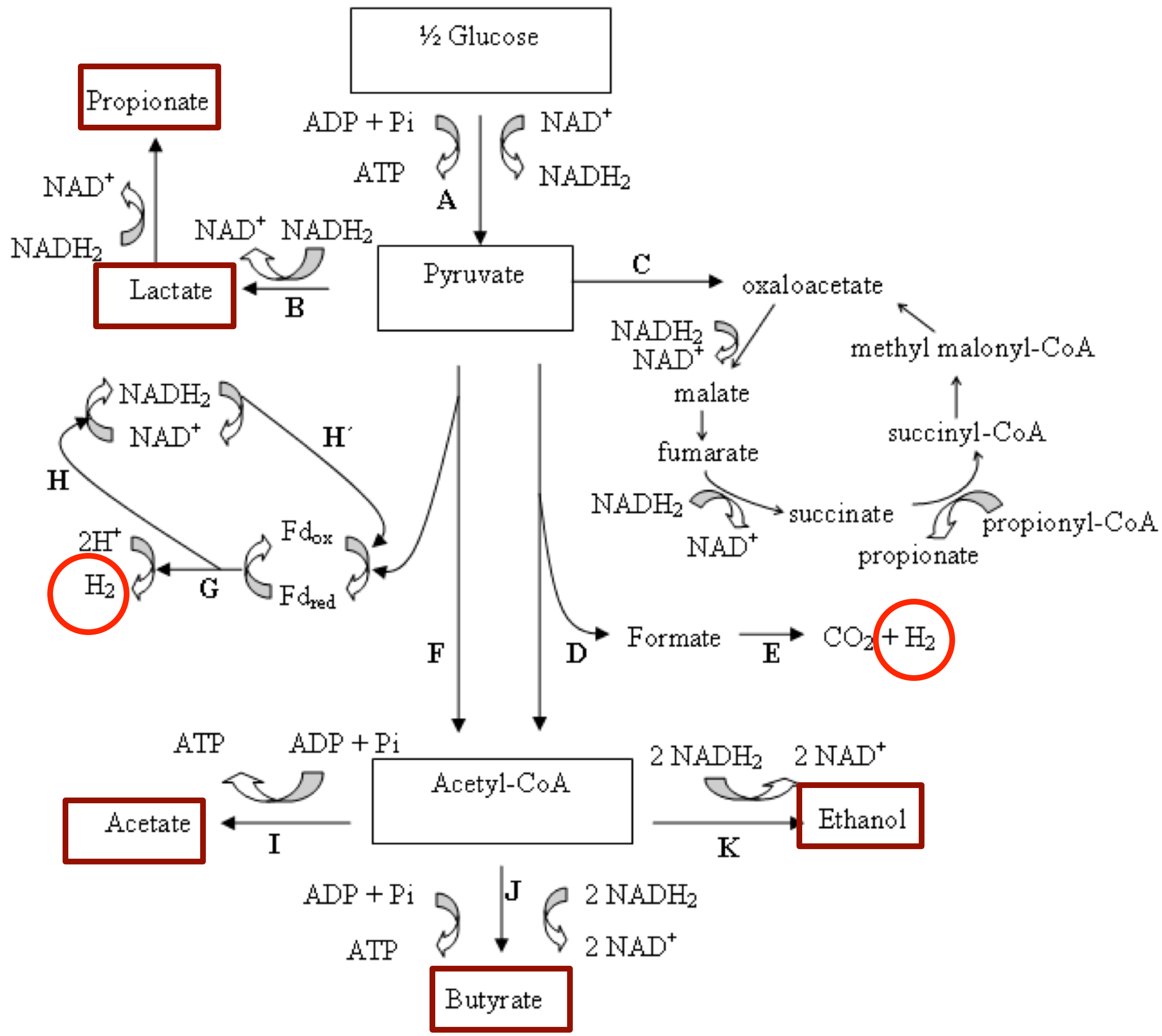
1 Fermentation

- Sometimes called “dark fermentation”
- Has a very long history
  - Technology is mature, at least for fermenting sugars
  - Advantages and disadvantages are well established

Metabolic steps in mixed-acid glucose fermentation. Fd: ferredoxin, Fd_{ox}: oxidized form of ferredoxin, Fd_{red}: reduced form of ferredoxin. $NADH_2$: NADH + H^+.

H_2 is produced only from oxidations of Fd_{red} (main source) and formate.

All electron equivalents that go to acetate, ethanol, butyrate, lactate, or propionate are lost for bio-H_2.

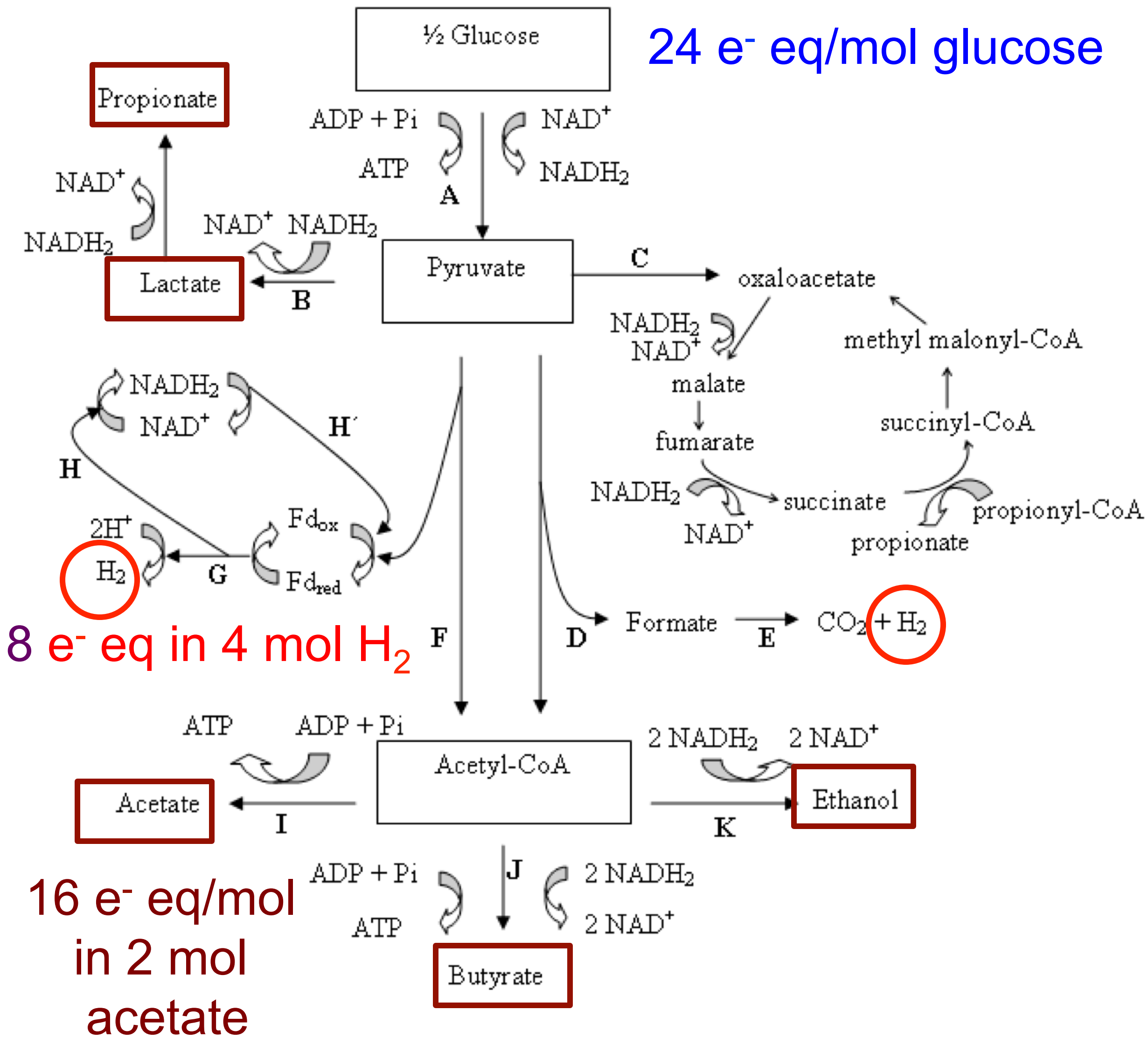


The need to balance $NADH_2$ among oxidation and reduction reactions means that the mix of products contains mostly non-H_2 sinks.

The maximum H_2 yield is 4 molH_2/mol glucose:

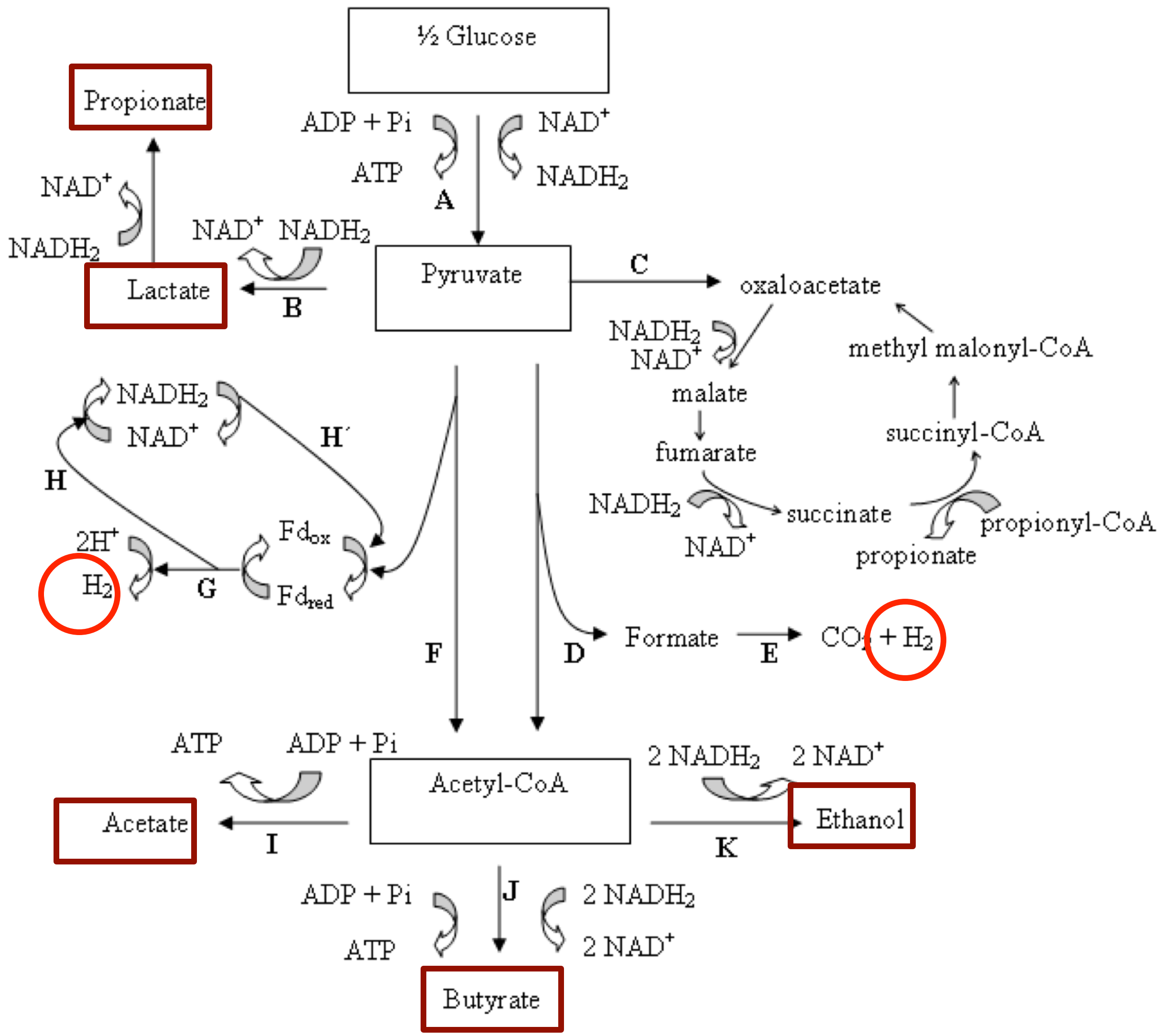
$$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 4H_2 + 2CO_2$$

17% of donor electrons ending up in H_2 (2 mol H_2/mol glucose) is accepted as the practical maximum H_2 yield. Actual H_2 conversions often are less.



Clostridium species usually are the dominant H_2-producers in acetate/ butyrate fermentation, while *Ethanoligenens* species are abundant H_2 producers in acetate/ ethanol fermentation.

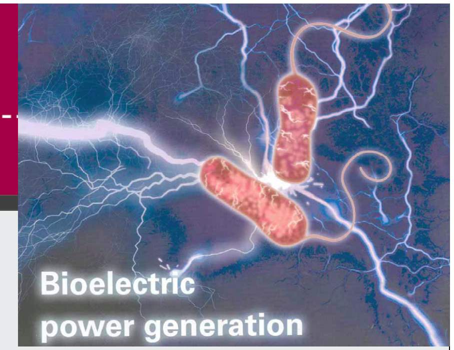
pH 5-6 generally results in acetate/butyrate formation and pH 4.5 in acetate/ ethanol.



- Advantages of Fermentative BioH_2:
  - Mature, at least for sugars
  - High volumetric rates (up to 8 L H_2/L-h)
  - Simple bioreactor configuration
  - More complex biomass can be fermented
- Disadvantages of Fermentative BioH_2:
  - Low H_2 yield
  - Not pure H_2 in the evolved gas
  - High BOD liquid effluent
  - It needs a follow up step……………..

2 Microbial Electrolysis Cells (MECs)

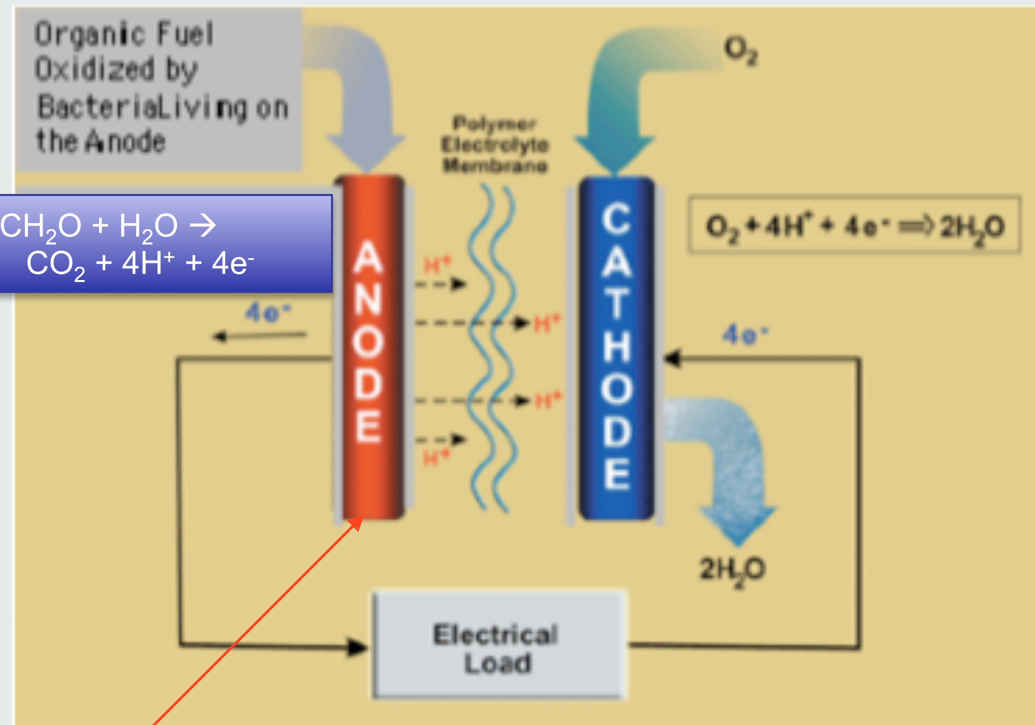
- Within the platform of Microbial Electrochemical Cells (MXCs), also sometimes called BioElectrochemical Systems (BES).
- The microbial fuel Cell (MFC) is the most well-known variation and a good place to begin to understand the platform.



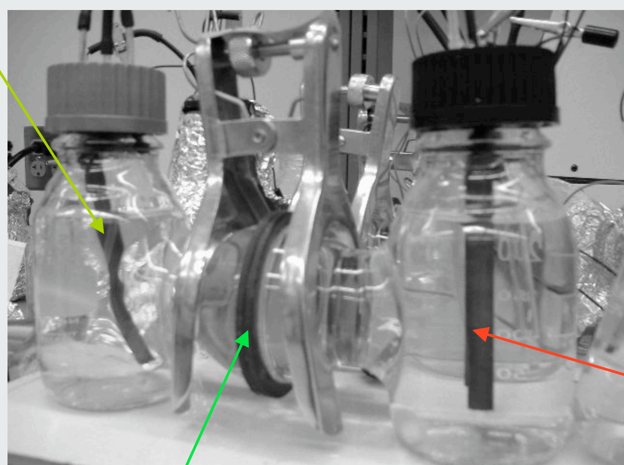
MFC illustrated

The goal is to harvest the electrical power: P = IV

$CH_2O + H_2O \rightarrow CO_2 + 4H^+ + 4e^-$



Cathode



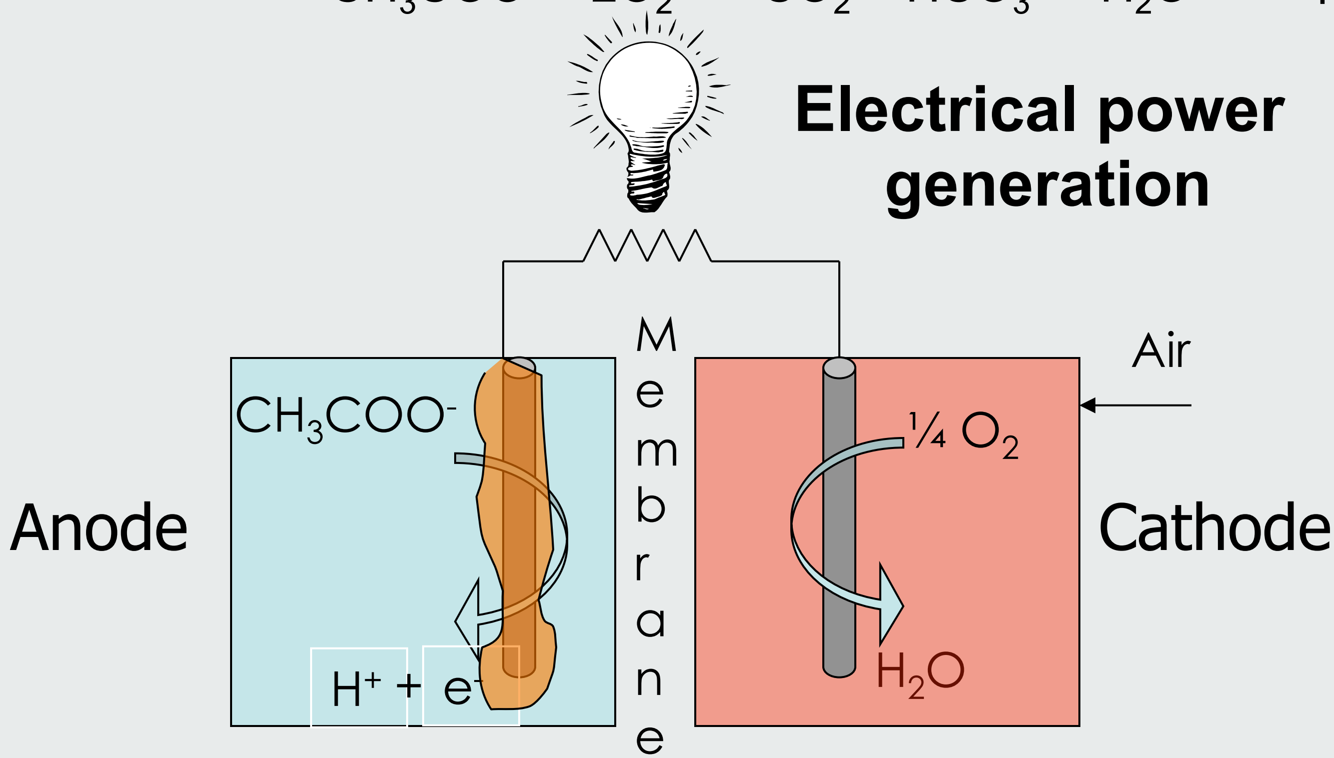
PEM

Anode, usually a graphite rod, paper, or mesh
With a biofilm of anode-respiring bacteria (ARB)

e^- donor half reaction: $CH_3COO^- + 3\ H_2O \rightarrow CO_2 + HCO_3^- + 8H^+ + 8e^-$ - 0.29 V

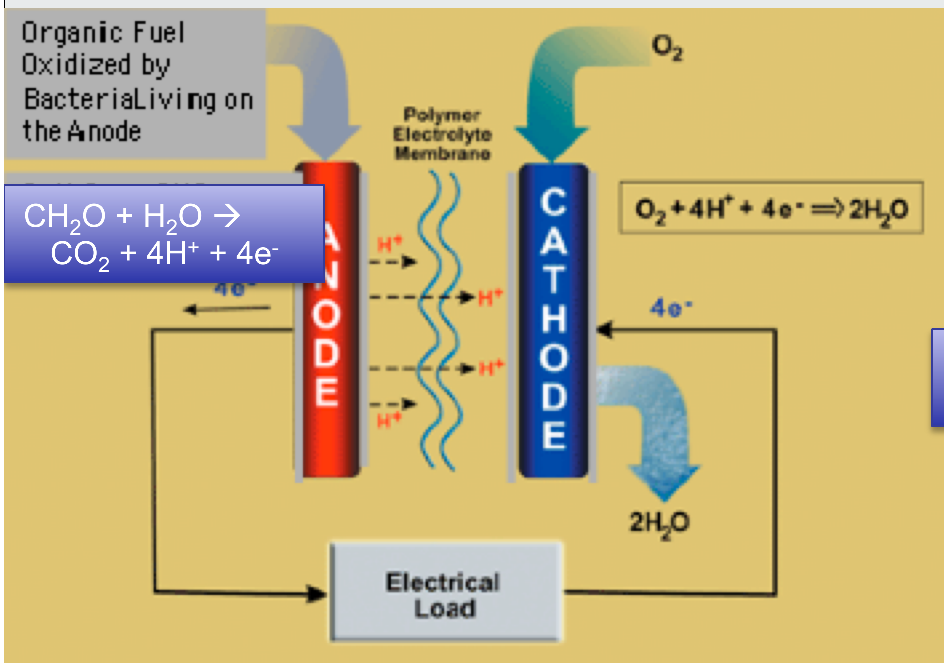
e^- acceptor half reaction: $2\ O_2 + 8H^+ + 8e^- \rightarrow 4\ H_2O$ 0.81 V

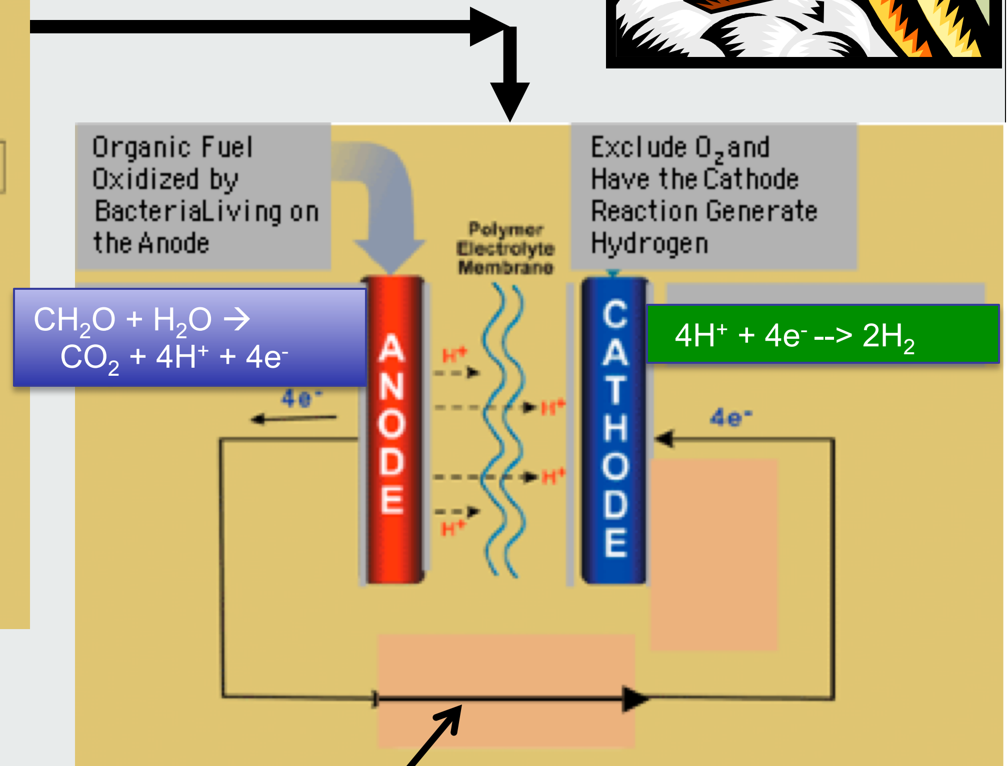
Net reaction: $CH_3COO^- + 2O_2 \rightarrow CO_2 + HCO_3^- + H_2O$ 1.10 V



The reaction potential drives all biological, chemical, and electrochemical processes in MFC => **typical recovered potentials are 0.3 - 0.6 V**

Modifying the MFC to Produce Bio-H_2





Applied Voltage

The Microbial Electrolysis Cell (MEC) opens up the possibility to convert all the energy value in biomass to H_2.

The MEC makes biohydrogen production a respiratory process!

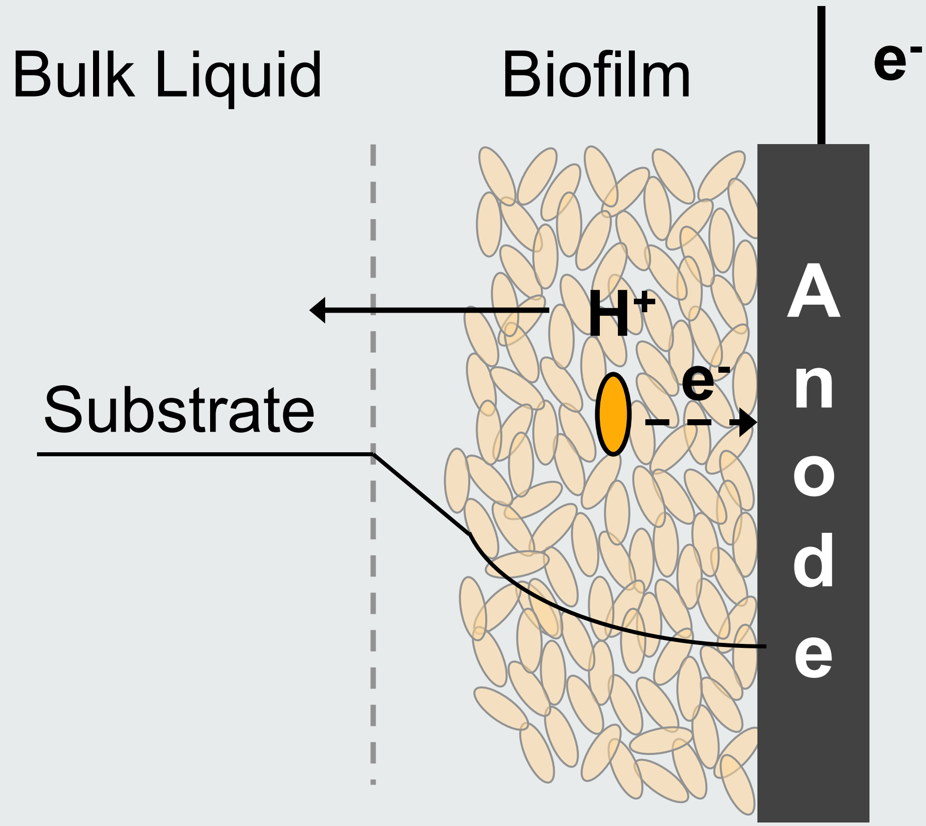
Anode Respiration

- Oxidation of an organic fuel, or electron donor: e.g.,
  - $CH_3COOH + 2H_2O \dashrightarrow 2CO_2 + 8H^+ + 8e^-$
- By anode-respiring bacteria (ARB) that
  - have the ability to transfer e^- to the solid conductive surface and conserve energy → anode respiration
  - sometimes given other names: e.g., electricigens and exo-electricigens

Processes that can limit current production

$$\text{Substrate} + H_2O \rightarrow CO_2 + 8H^+ + 8e^-$$

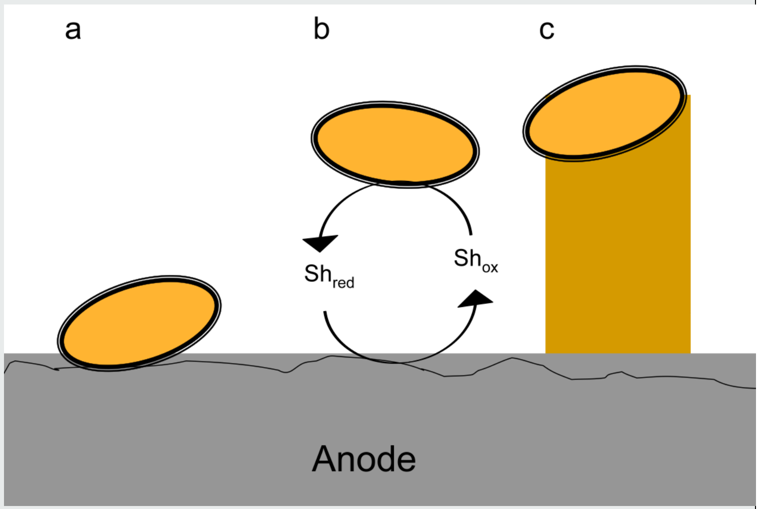
1. **Catalyst (ARB) for substrate oxidation**
2. **Substrate diffusion**
3. **e^- transport (potential driven)**
4. **H^+ transport (pH and buffering)**



Extracellular Electron Transport (EET)

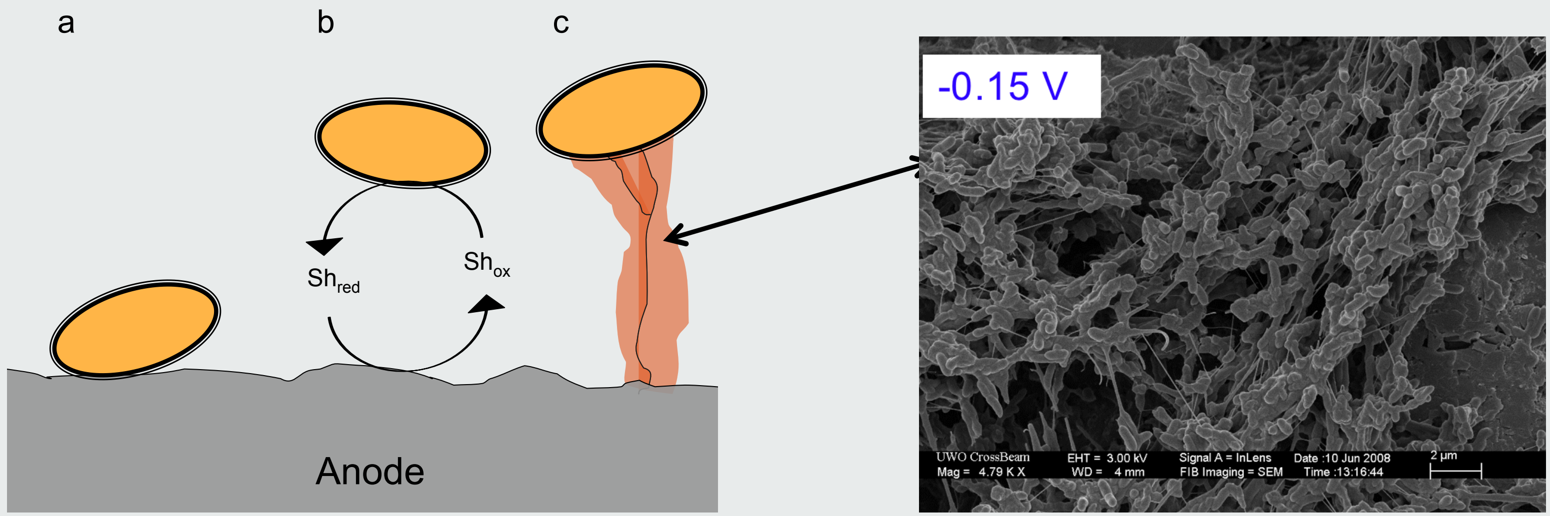
Three mechanisms are proven.

a) Direct transfer from the membrane-bound cytochromes to the anode.
b) Soluble electron shuttles.
c) Conduction through the matrix of the biofilm.



With conduction, the biofilm matrix is part of the anode: hence, the biofilm anode, a living, self-generating anode!

- Although EET can occur by three mechanisms, only conduction is fast enough to yield the observed rates of current density in modern MXCs (~ 10 A/m²). Other mechanisms are roughly 100X slower, at best.
- Good ARB produce a conductive network, perhaps using nanowires or pili.



Anode respiration with cathode reduction to H_2 provides benefits:

- Approaching 100% conversion of biomass electron equivalents to H_2 – due to respiration.
- Nearly 100% pure H_2 once water vapor is removed.
- Can produce a low-BOD effluent.

Drawbacks:

- Still "emerging"
- Applied potential creates an energy cost
- Capital costs of electrodes, membranes, controls
- Probably needs pre-fermentation to convert complex biomass organics to simple substrates that ARB use……

3 Methanogenesis Followed by Reforming

- Methanogenesis is mature and can get about the same conversion efficiency as an MEC
- Reforming CH_4 is now a mature technology and relatively inexpensive

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