# MICROBIAL ELECTROCHEMICAL AND FUEL CELLS

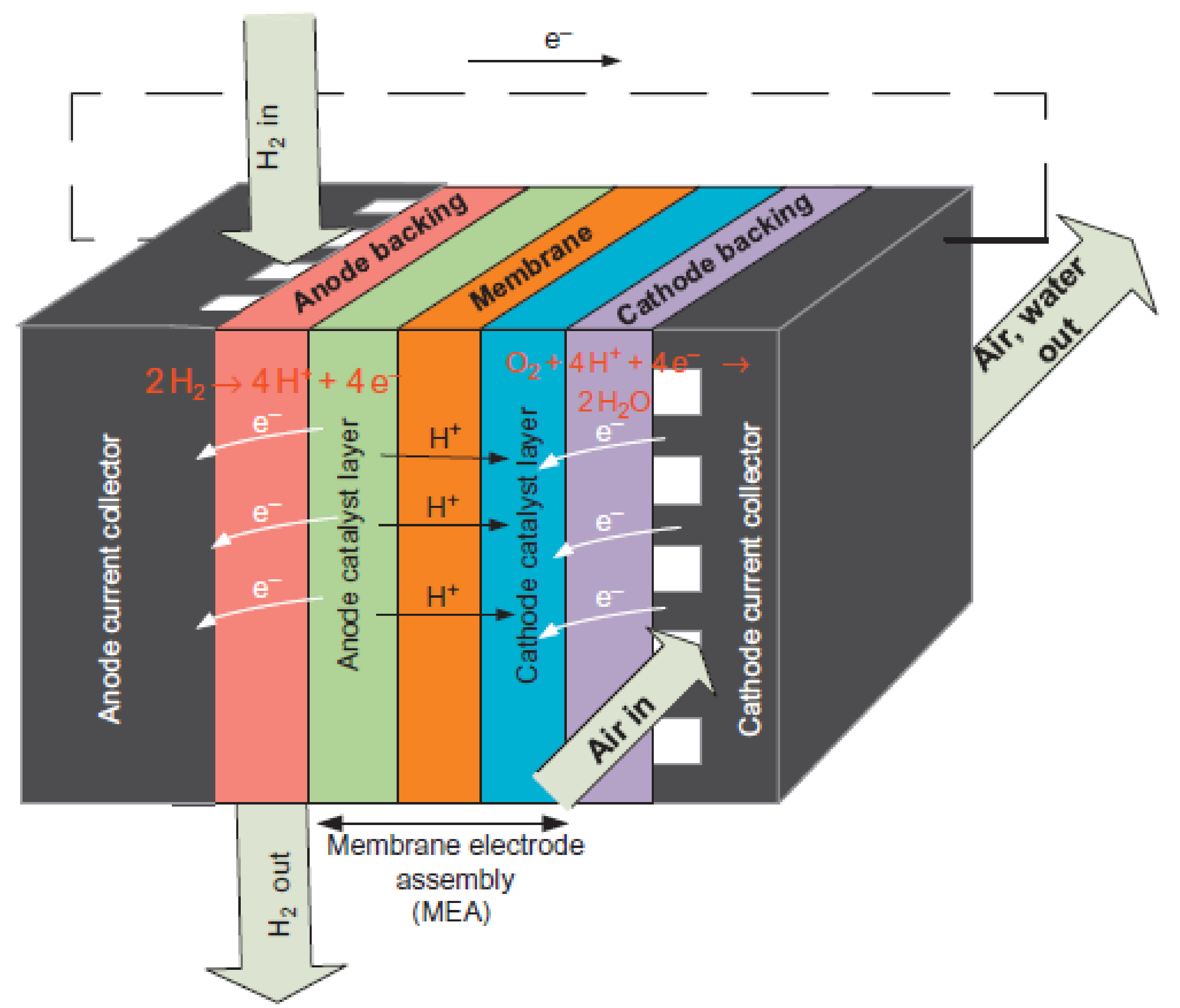
CEE 597T

Electrochemical Water and Wastewater Treatment

# Fuel Cells

- FCs are electrochemical devices that convert the intrinsic chemical energy in fuels into electrical energy directly.

In a FC, fuel is fed continuously to the anode (negative electrode) and an oxidant (often oxygen in air) is fed continuously to the cathode (positive electrode). The electrochemical reactions take place at the electrodes to produce an electric current through an electrolyte, while driving a complementary electric current that performs work on the load.



- At the anode of the FC, hydrogen gas ionizes, releasing electrons and creating H+ ion (protons), thereby releasing energy

$2H_2 \rightarrow 4H^+ + 4e^-$

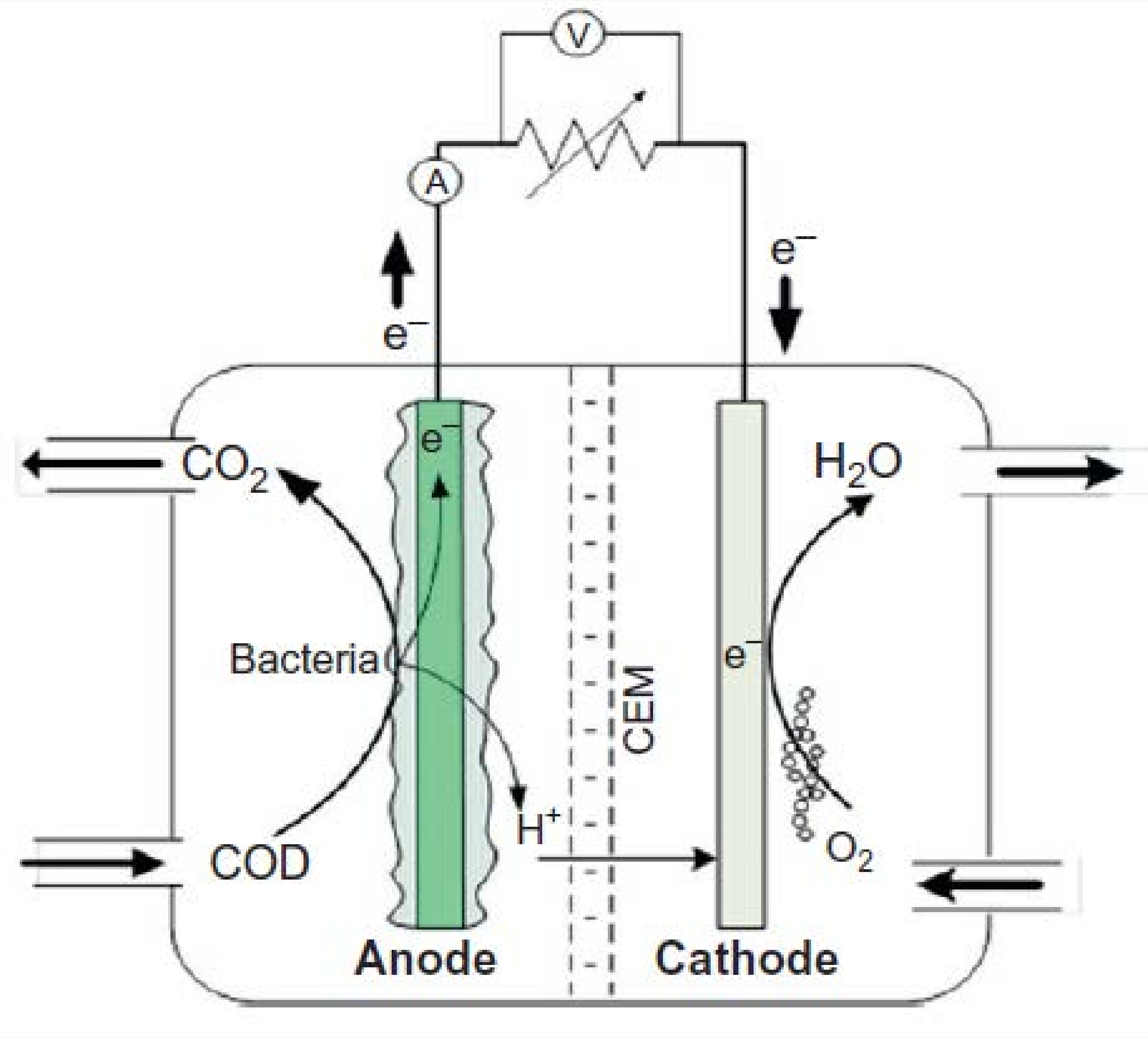
- At the cathode oxygen reacts with protons and electrons taken from the anode to form water

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

- The electrons (negative charge) flow from anode to cathode in the external circuit and the $H^+$ ions pass through the electrolyte.
- *Importantly! the electrolyte should only allow proton transfer (or other ions in the case of other FC types) and not electron transfer (i.e., the electrolyte should be an electronic insulator). Otherwise the electrons would not pass around the external circuit and thus they would "short circuit" the cell and the function of the FC would be lost.*

# Biological FCs

- Biological FCs work in a similar way to chemical FCs with a supply of fuel to the anode and a supply of oxidant to the cathode.
- Biological FCs convert the chemical energy of carbohydrates, such as sugars and alcohols, directly into electric energy.
- At the anode, a fuel (e.g., glucose) is oxidized (assuming an acidic electrolyte) according to the reaction
- $C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 24H^+ + 24e^-$ $E_o = 0.014V$
- At the cathode, oxidant is reduced by the presence of a catalyst (or enzyme) specific to the oxidant (e.g., oxygen):
- $6O_2 + 24H^+ + 24e^- \rightarrow 12H_2O$ $E_o = 1.23V$


V
A
e⁻
e⁻
e⁻
CO2
H2O
Bacteria
e⁻
CEM
H⁺
COD
O2
Anode
Cathode

- The resultant electrochemical reaction creates a current as electrons and protons are produced from the oxidation of the fuel. The theoretical cell potentials for such reactions are similar to those of conventional FCs.
- The distinguishing feature, central to a biological FC, is the *use of the living organism* itself.
- In general a BioFCs functions in one of two ways, using biocatalysts, enzymes, or even whole cells.

1. The biocatalyst generates the fuel substrate for the electrochemical cell by a biocatalytic transformation or metabolic process. Thus the biocatalyst does not take part directly in electron transfer.

2. The biocatalyst participates in the electron transfer chain between the fuel and the anode.

- When enzymes are employed to achieve electrode activity, we have the so-called enzymatic biofuel cell;
- when microorganisms are responsible for the bioelectrocatalysis, we have the microbial fuel cell (MFC).
- Through the use of clean and renewable catalysts, MFCs provide a means to obtain renewable and sustainable energy and to treat wastewater, which is generally employed as the carbon source for the electrochemical system.

# Types of biological FCs

- In general, *microorganisms* can be used in *four ways* for producing electrical energy:

(i) To produce electrochemically active substances through fermentation or metabolism. The fuels are produced in separate reactors and pumped to the anode of a conventional FC, to generate electrical energy. In this configuration, the microbial bioreactor is kept separated from the FC; the system is not truly a BioFC.

(ii) The microbiological fermentation process proceeds directly in the anodic compartment of the FC.

(iii) The electron transfer mediators shuttle electrons between the microbial biocatalytic system and the electrode. The mediators accept electrons from the biological electron transport chain of the microorganisms and supply them to the anode of the biological FC.

(iv) Metal-reducing bacterium, having cytochromes in the outer membrane that are able to directly communicate electrically with the electrode surface and create a mediatorless biological FC.

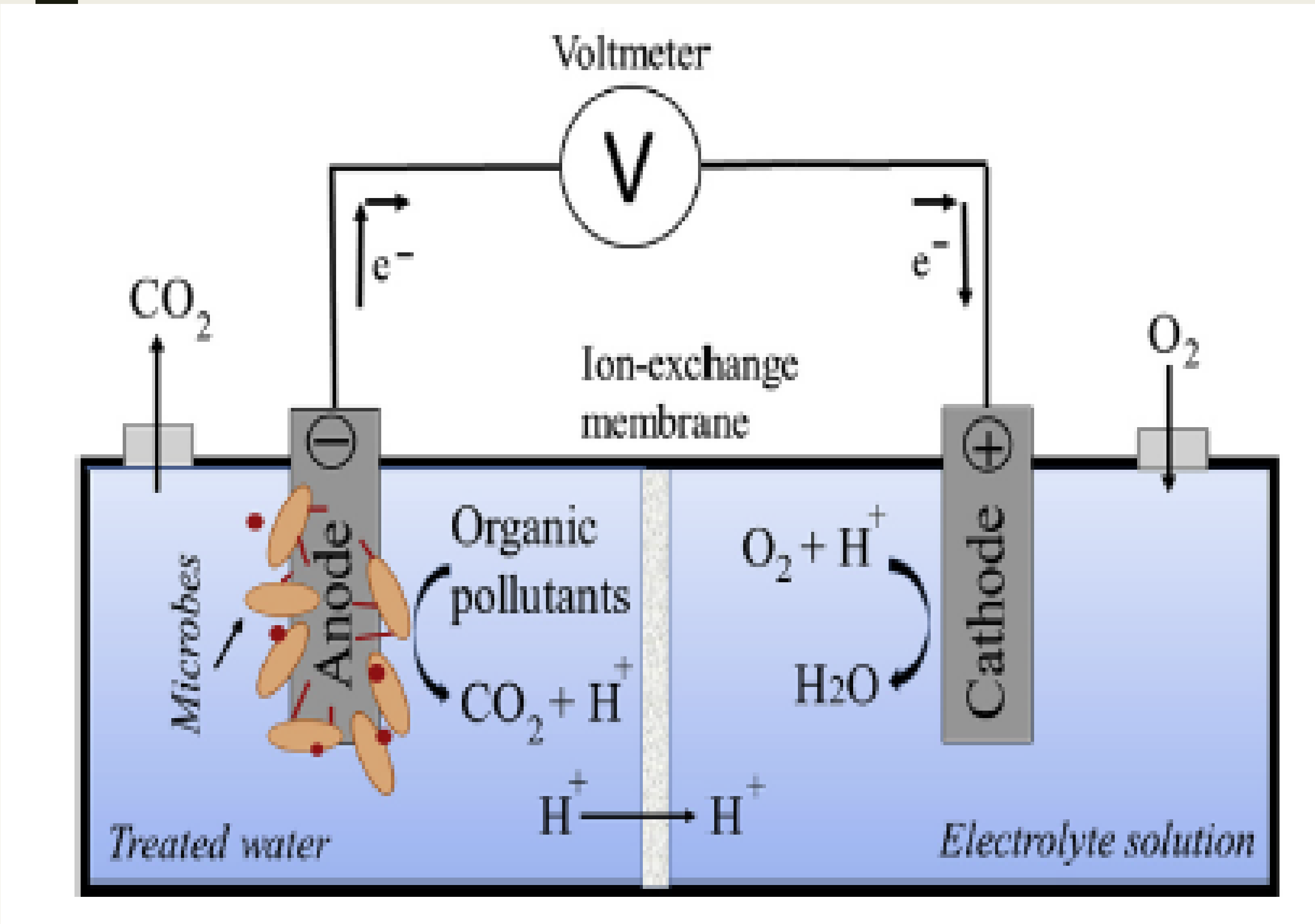
There are two basic types of biological FCs; namely,

- microbial fuel cells (MFCs) and
- Enzymatic FCs.

- Electron mediators (relays) are used for the electrical connection of the biocatalyst and the electrode.
- Several methods have thus been used to functionalize the electrode surface with layers consisting of redox enzymes, electrocatalysts, and biocatalysts that promote electrochemical transformation at the electrode interface.

# Microbial fuel cell (MFC)

- Microbial fuel cell (MFC) is a part of microbial electrochemical Technologies where cathode and anode combined with microorganisms serve for different purposes.
- MFC is an emerging biotechnological device that converts the chemical energy of organic matter into electricity by means of microorganisms.
- Similar to fuel cells MFC is theoretically highly efficient device able to produce electrical energy.
- However, in contrast to the fuel cell running on hydrogen or methanol, MFC can use wastewater simultaneously treating it and producing electric power.
- MFC is based on the metabolism of the bacteria and its ability to reduce redox active compounds.
- MFC is the only technology allowing generation of electricity directly from the solid and liquid organic wastes.
- Bacteria play the role of  biocatalysts.

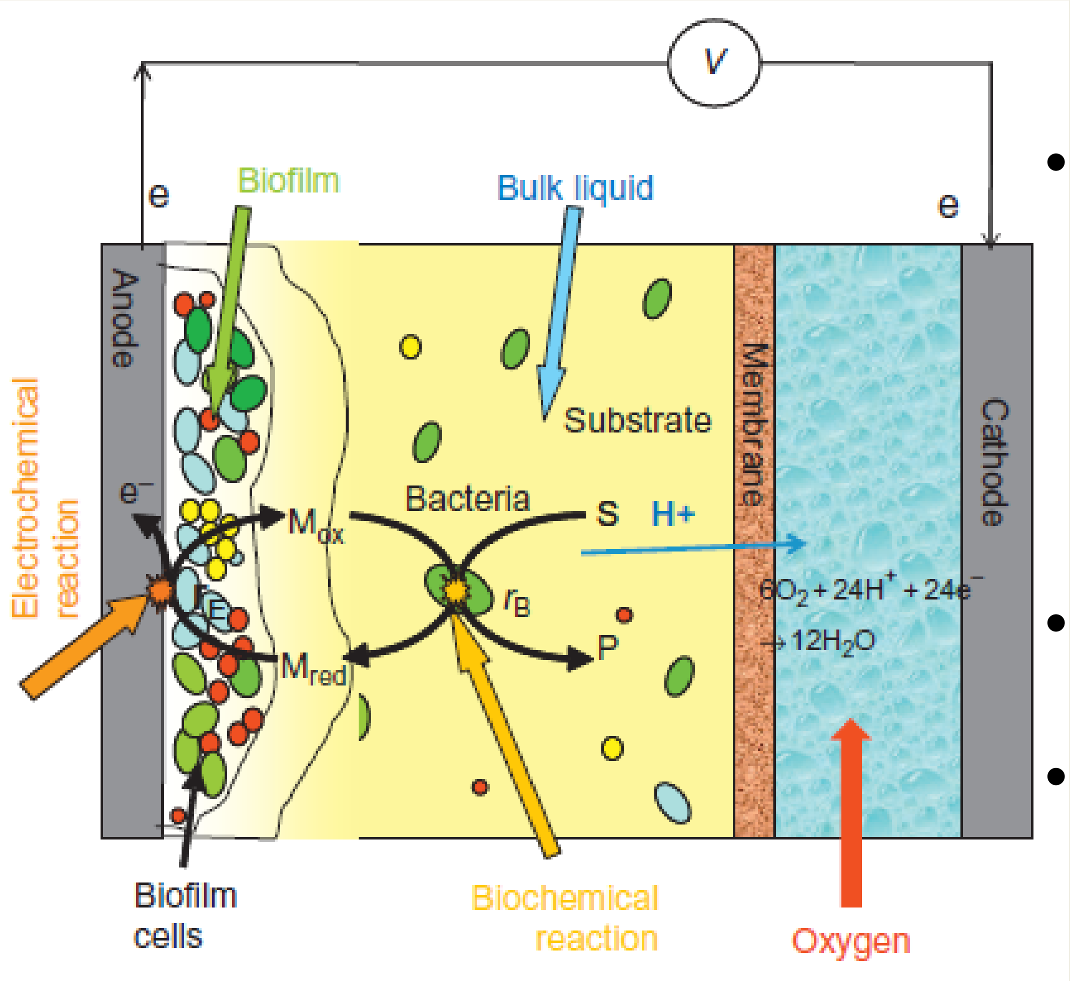


- Conventional MFC consists of three basic parts such as an anodic and cathodic compartments and an ion-exchange membrane separating them, allowing hydrogen protons to pass only in one direction from the anodic to the cathodic compartment.
- Anode is a negative electrode and cathode is the positive electrode in MFC.
- Carbon electrodes are commonly used as the anode, and catalytic materials are used for the cathode to provide better reduction of oxygen to water.

- Microorganisms that produce electricity are placed into the anodic compartment, wherein anaerobic conditions are maintained.
- The cathode is kept under aerobic conditions, which is provided by oxygen bubbling through the cathodic compartment or keeping the compartment and cathode exposed to the air.
- Microorganisms attached to the surface of anodic compartment (biofilm) receive a carbon source of energy (nutrients) in the form of wastewater, for example, that is necessary for them to grow and sustain life.
- Because bacteria are isolated in electrode compartment, the only way for them to survive is to process the organic substrate, which is fed for them and perform anaerobic respiration through the electrode.
- The principle of MFE operation is the detachment of electrons from the nutrient by microorganisms and electron transfer to the anode.
- Anode is connected with the cathode by a wire/electric circuit. Because of the difference of redox potentials, electrons start to move toward the cathode, where oxygen reduction occurs to form water.
- Electrons moving from the negative electrode to the positive generate the electric current produced by MFC.
- When electrons are detached from the nutrient, hydrogen protons are formed in the anodic compartment. The generated hydrogen ions pass from the anodic compartment through the ion-exchange membrane into the cathodic one where they are combined with oxygen to form water.

Microbes in the anode chamber oxidize fuel (electron donor) generating electrons and protons.

- The generation of current is due to the microorganisms, which transfer electrons from a reduced electron donor to an electron acceptor at a higher electrochemical potential.
- Anode-respiring bacteria, which have accumulated as an anode biofilm, carry out an oxidation (half-cell) reaction of organic matter, producing protons (one proton for every electron) and thus an electrical current from biomass.
- Carbon dioxide may eventually be obtained as an oxidation product.
- Electrons and protons are consumed in the cathode chamber, reducing oxygen to water and generating electricity.



## *Anode microbial behavior*

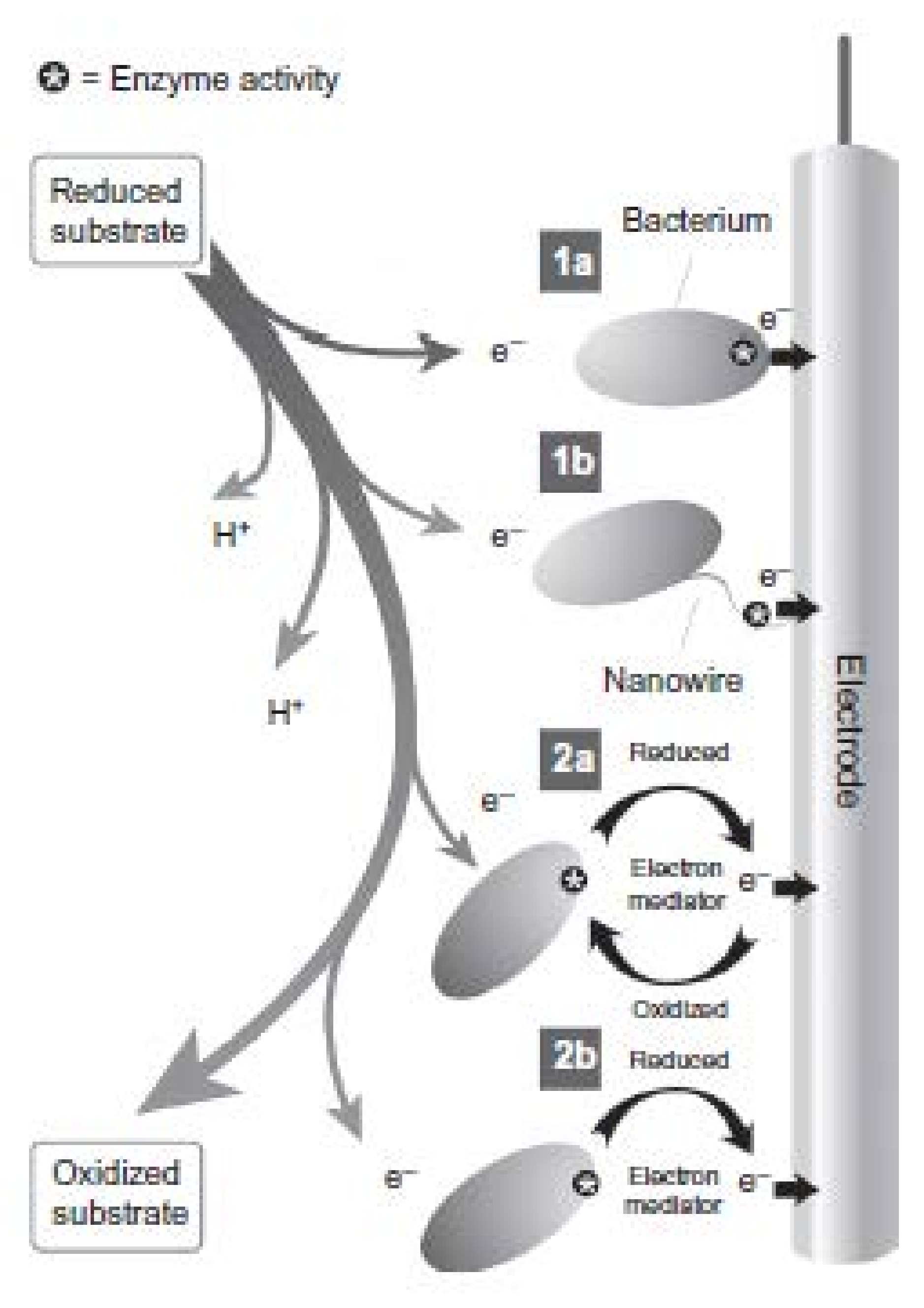
- The MFC is reliant upon the organism’s own generation of electrons from the electron transport chain.
- The electron transport chain involves the cell wall of a microorganism, where there exist proteins responsible for energy generation.
- In the case of aerobic respiration, the core reaction is oxidation of an energy-rich compound, such as glucose, to allow the reduction of nicotinamide adenine dinucleotide (NAD+) to NADH by the electrons donated from the glucose. In turn NADH is oxidized and its electrons are transferred to adenosine triphosphate (ATP).
- However the cells can be connected (wired) to the electrode surface using low molecular weight redox species, called mediators. The mediators assist the shuttling of electrons between the intracellular bacterial space and electrode.
- A variety of organic compounds have been used as mediators for electron transfer between bacteria and electrodes, including thionine and organic dyes.

- In general for good MFC power output, electrodes should be designed to facilitate good electrical contact between a biocatalytic system and an anode. The mediators can be coupled to the microorganisms in three ways:
- (i) diffusion mediator shuttling between the microbial suspension and the anode surface,
- (ii) diffusion mediator shuttling between the anode and microbial cells covalently linked to the electrode. The microbial cells can be covalently linked to the electrode surface having – COOH groups, through amino groups of the microbial membrane resulting in the formation of amide bond. Organic reagents such as carbodiimide and acetyl chloride can be used to link the microbial cells to the surface, and
- (iii) mediator adsorbed on the microbial cells providing electron transport from the cells to the anode.

# MFC bacteria

- The behavior of microorganisms in MFCs can involve several complex processes.
- This complexity will in particular be most apparent in the use of mixed microbial communities that would be present in most waste streams.
- Which species and how they populate the anode in MFCs will have a great bearing on both waste treatment (COD/BOD removal) as well as power generation.
- In addition to microorganisms that can transfer electrons to the anode, the presence of other organisms may influence the MFC performance, both positively and negatively.
- Mixed species may result in faster feed substrate removal without generation of power.

- One mechanism proposed describes direct electron transfer, in which some outer membrane-bound proteins, such as cytochrome, play the role of transferring electrons to the electrode.
- Another mechanism concerns the use of external or bacteria-produced mediators while another concerns bacteria-forming “nanowires” contacting the electrode, through which electrons transfer.



Schematic overview of the two EET mechanisms for th
use of a solid-state electron acceptor. Reversing all arrows represents electron uptake from a solid-state electron donor.

1a) A microorganism can perform EET by directly contacting the electrode with redox proteins or other electron transfer molecules.

(1b) Variation on 1a whereby conductive nanowires enable electron transfer over micrometerlong distances
The latter mechanism has not yet been observed for electron uptake reactions.

(2a) A microorganism can use an electron shuttle for th
transport of electrons to/from the cell. Microbial-secreted molecules, as well as added artificial compounds, can act as electron shuttle.

(2b) Variation on 2a where electrons are transferred by primarymetabolites such as $H_2$.

## *Terminology available in literature to describe microorganisms interacting with electrodes*

- Electrochemically active bacteria (EAB)/ electroactive bacteria (EAB)

Microorganisms able to donate electrons to or accept electrons from an electrode via a direct contact mechanism or self-secreted mediators.

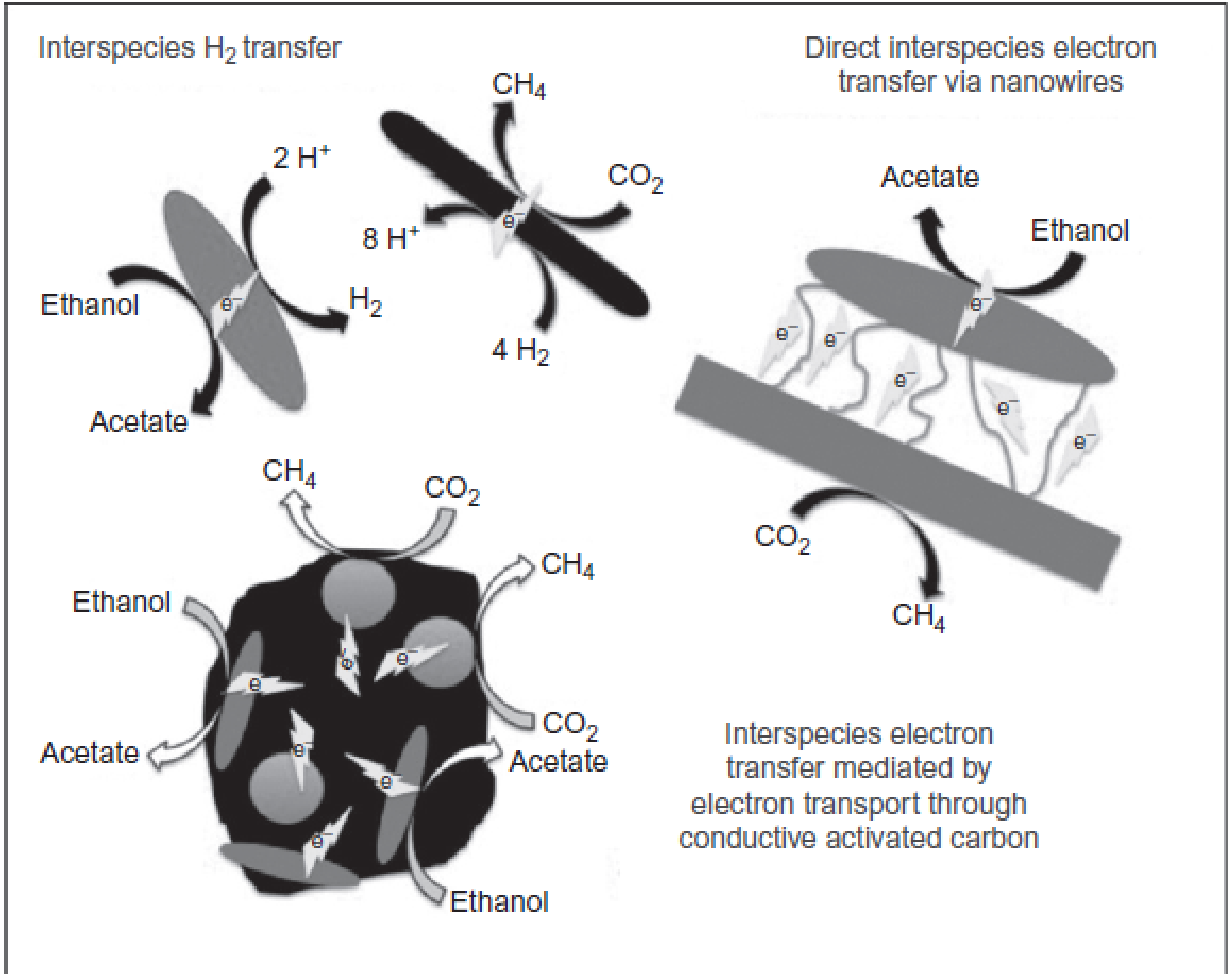
- **Electron donating microorganisms**

*Anode-reducing bacteria (ARB):* Microorganisms able to donate electrons to an anode

*Anode-respiring bacteria (ARB):*Microorganisms able to conserve energy by respiration with an anode as electron acceptor

- **Electron accepting microorganisms**

*Cathode oxidizing bacteria:* Microorganisms able to draw electrons from a cathode



Three modes of electron transfer between microorganisms.
(1) Via a soluble component such as $H_2$ or formate;
(2) direct contact; or
(3) mediated electron transfer through a conductive abiotic carrier material.

# Parameters Influencing Microbial Fuel Cell Efficiency

- *The choice of microorganisms*: Many biological species have limitations in terms of consumption of different organic substrate and sensitivity to oxygen and other compounds.
- For example, Geobacteraceae can utilize only acetate, ethanol, and fatty acids, thus limiting the application area of MFC using this biological species.
- Partially, the problem can be solved by inhabiting anode with different species at the same time. Mixed culture of microorganisms provides higher power recovery, higher resistance against process disturbances, higher rates of substrate consumption, and smaller substrate specificity.
- Common composition of mixed cultures in wastewater and sludge from wastewater plants includes species such as Geobacteraceae, Proteobacteria, Clostridia, Bacteroides, Desulfuromonas, Alcaligenes faecalis, Enterococcus faecium, Pseudomonas aeruginosa, and Aeromonas.
- The increased temperature of MFC operation can enhance the mass transport in the cell. Moreover, elevated temperatures reduce the solubility of oxygen, thus keeping anaerobic conditions in anodic chamber, and prevent the contamination of cell with mesophilic microorganisms.

- *The distance between electrodes:*
- Too close placement of electrodes in undivided MFCs (membrane free MFCs) leads to power reduction due to interruption of bacteria activity by oxygen generated at the cathode.
- In such cells, a cloth separator for example could reduce the effect of oxygen crossover.
- Electrodes should not be placed at a distance where oxygen interaction with anode is minimum, however not far beyond that point, because resistance of solution will rise too high and decrease power production efficiency.

- Acidity of solution has a direct impact on the performance of microorganisms.
- The best conditions for microbial growth are in the range of neutral pH.
- However, slightly alkaline conditions are also acceptable and even can improve pollutant degradation and power generation due to the presence of free OH ions, which improve the conductivity of solution.
- High salinity of wastewater also contributes to the greater removal efficiencies for the same reason.

## Anode Materials

- Aside from other factors affecting the MFC performance, the anode material is a deciding factor for overall performance of MFCs because its

- composition,
- morphology, and
- surface properties

directly affect

- microbial attachment,
- electron transfer, and
- substrate oxidation.

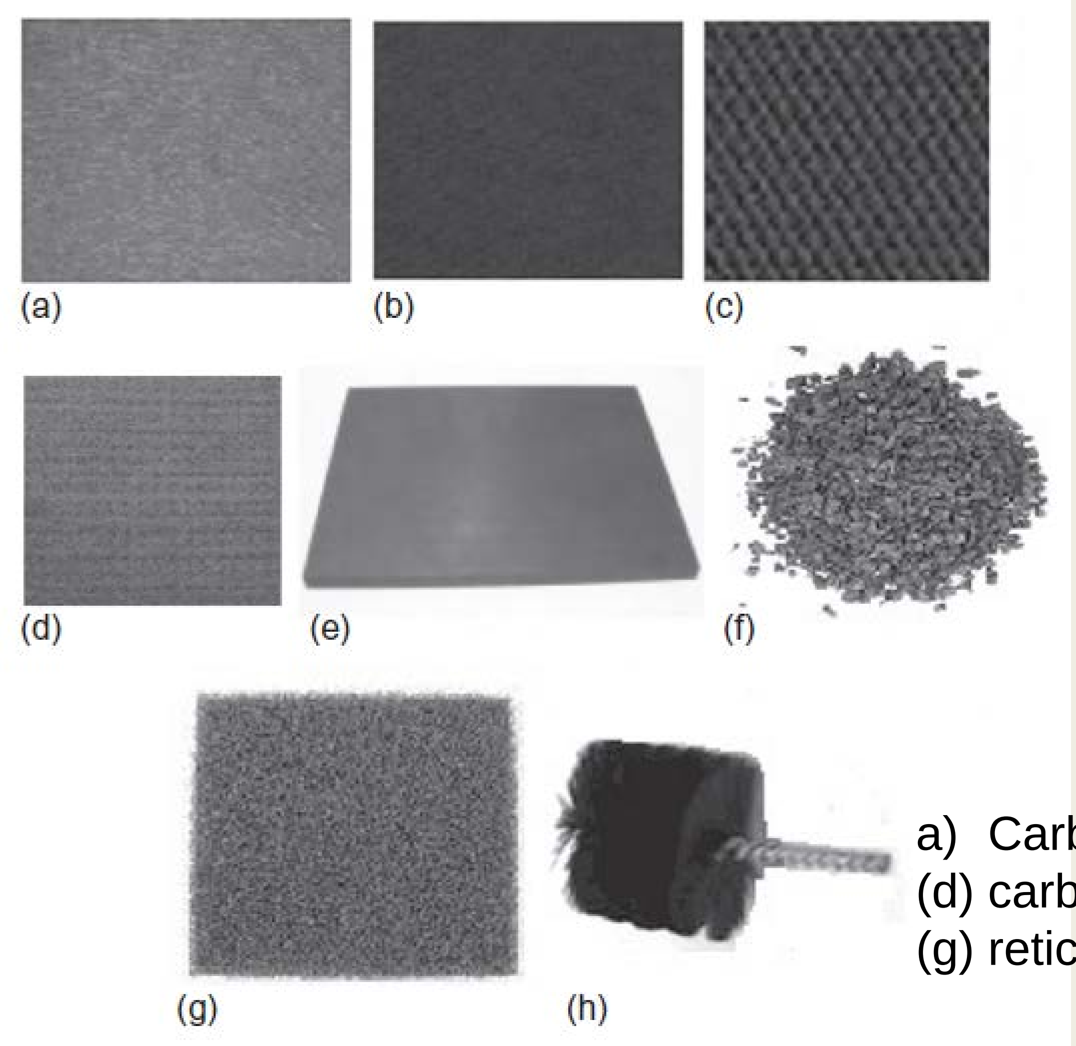
Ideal anode materials require *high electrical conductivity*, *enhanced biocompatibility*, *high chemical and physical stabilities of electrodes*, and *low-cost materials*.

- Material of electrode plays an important role in efficiency of the process.
- For example anodes with higher specific surface area, i.e., surface area per volume of the electrode, such as graphite brush, carbon felt, and foam provides more stable power generation comparing to flat electrodes.
- Moreover, electrodes with high specific surface area are less prone to fouling.
- This can be explained by the fact that oxygen is consumed by bacteria on the surface of such electrodes and bacteria, which are located inside thick electrodes and stay in anaerobic conditions, thus processing more organic matter and transferring electrons.
- Cathode materials should have low overpotential toward oxygen reduction to water and have surface area significantly greater than surface area of anodes.

- In the anode compartment of MFC,
  - microorganisms adhere to the anode,
  - generate electrons by substrate oxidation, and
  - then transfer the electrons to anode.
- The surface characteristics of the anode directly affect the microbial adhesion and therefore the electrical performance of MFC.
- ***Increased specific surface area and more positive charge on electrode surface, which interact with negatively charge bacteria, aided the microbial adhesion and electron transfer on the anode surface.***
- Thus, anode modification is an effective strategy for enhanced characteristics of the electrode.

# Carbon materials

- The traditional materials used for MFCs include carbon—paper, mesh, felt, cloth foam; graphite—rod, granules, sheets, brush; and reticulated vitreous carbon (RVC)

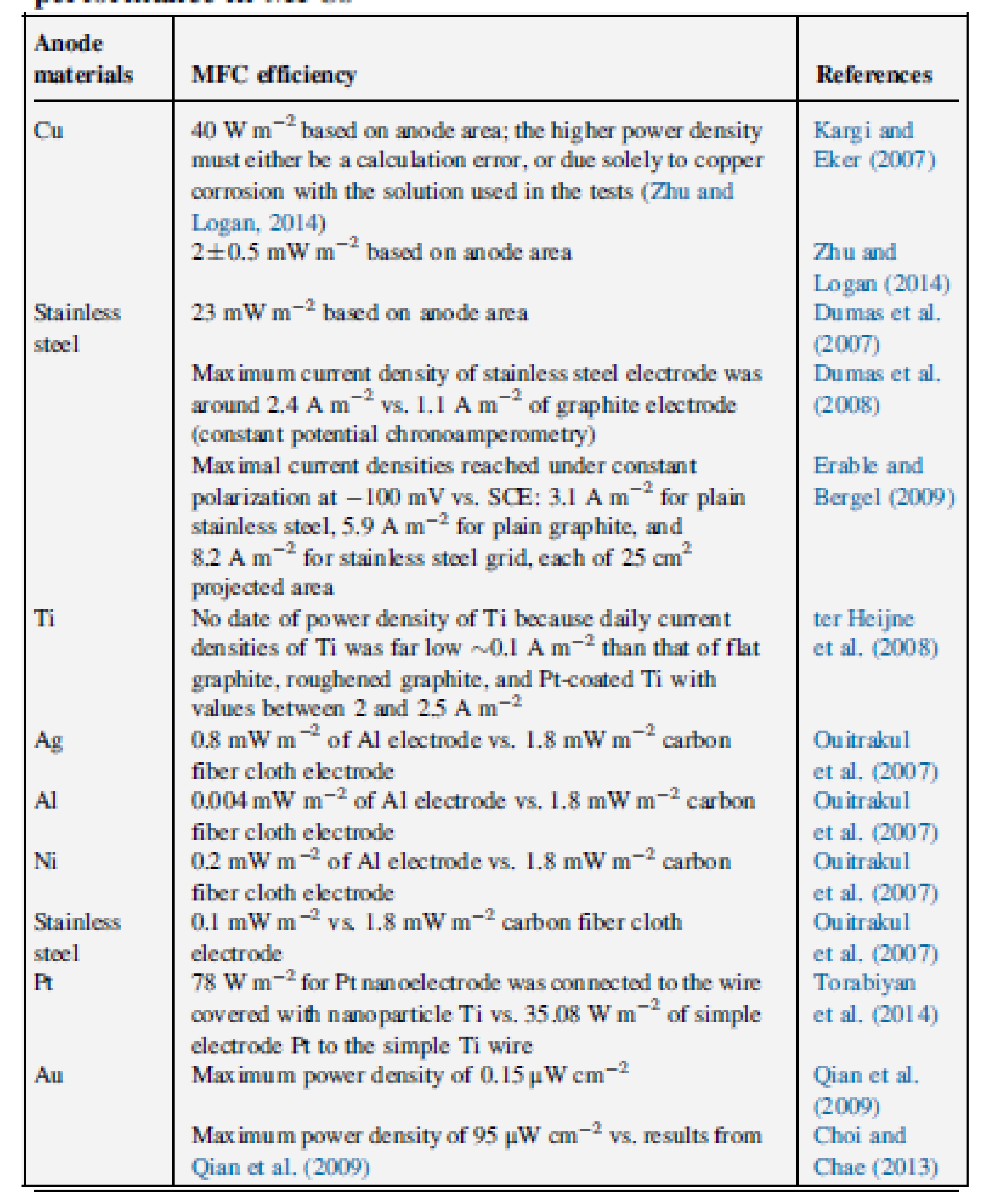


a) Carbon paper, (b) carbon cloth, (c) carbon mesh,
(d) carbon felt, (e) graphite plate, (f) granular graphite,
(g) reticulated vitrified carbon, and (h) carbon brush.

- One of the main limitations of using traditional carbon materials as MFC anodes is related to the electrocatalytic activity for the electrode microbial reactions, because the pores or spaces became clogged with the biofilm and lose efficiency.
- Furthermore, in some cases, the low specific area, lack of durability, brittleness, and high cost of carbonaceous materials inhibit the application of these electrodes in large-scale MFCs.

# *Metal materials*

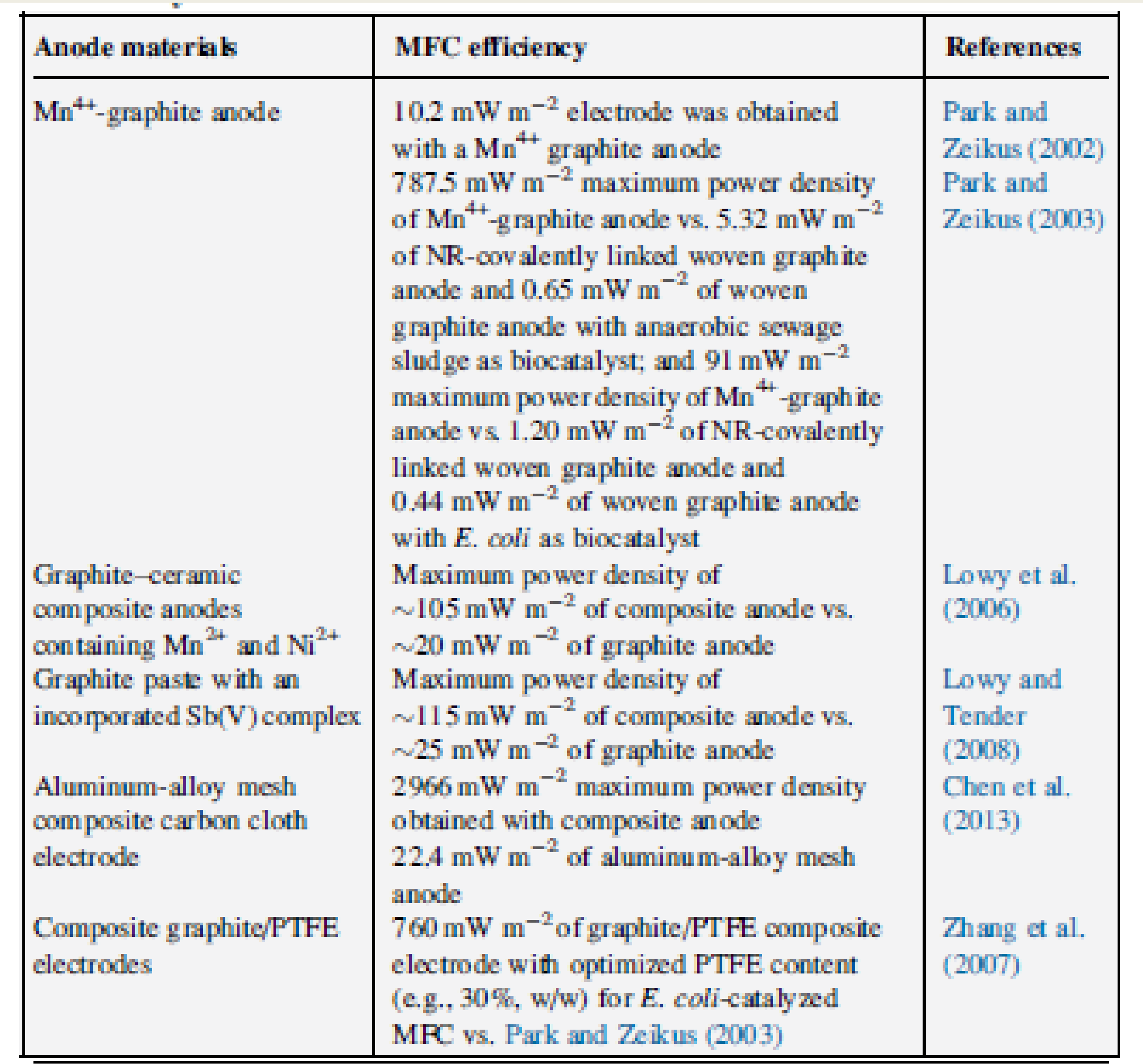
- Several metal materials have been used as MFC anode due to the higher conductivity of metal materials over carbon materials.
- The noncorrosive requirement of MFC anode limited the choice of metal materials used for MFC applications.
- **Stainless steel and titanium** are common metals proposed as potential anode materials in several studies. Several studies investigated stainless steel as MFC anode, because of the better mechanical properties expected for long-time operation and scale-up applications compared with carbon electrode
- However**, copper** was investigated as anode for MFC. MFCs with Cu anodes showed that copper is an unsuitable anode material, due to corrosion and its toxicity to microorganisms, even if it initially showed high current generation comparable to that of carbon electrode.
- Noble metals as electrode materials in MFC reduce the internal resistance of the cell, but the high cost and week adhesion of bacteria prevent their wide-scale integration in MFC



| Anode materials | MFC efficiency | References |
|---|---|---|
| Cu | 40 W $m^{-2}$ based on anode area; the higher power density must either be a calculation error, or due solely to copper corrosion with the solution used in the tests (Zhu and Logan, 2014) | Kargi and Eker (2007) |
| | 2±0.5 mW $m^{-2}$ based on anode area | Zhu and Logan (2014) |
| Stainless steel | 23 mW $m^{-2}$ based on anode area | Dumas et al. (2007) |
| | Maximum current density of stainless steel electrode was around 2.4 A $m^{-2}$ vs. 1.1 A $m^{-2}$ of graphite electrode (constant potential chronoamperometry) | Dumas et al. (2008) |
| | Maximal current densities reached under constant polarization at −100 mV vs. SCE: 3.1 A $m^{-2}$ for plain stainless steel, 5.9 A $m^{-2}$ for plain graphite, and 8.2 A $m^{-2}$ for stainless steel grid, each of 25 $cm^2$ projected area | Erable and Bergel (2009) |
| Ti | No date of power density of Ti because daily current densities of Ti was far low ~0.1 A $m^{-2}$ than that of flat graphite, roughened graphite, and Pt-coated Ti with values between 2 and 2.5 A $m^{-2}$ | ter Heijne et al. (2008) |
| Ag | 0.8 mW $m^{-2}$ of Al electrode vs. 1.8 mW $m^{-2}$ carbon fiber cloth electrode | Ouitrakul et al. (2007) |
| Al | 0.004 mW $m^{-2}$ of Al electrode vs. 1.8 mW $m^{-2}$ carbon fiber cloth electrode | Ouitrakul et al. (2007) |
| Ni | 0.2 mW $m^{-2}$ of Al electrode vs. 1.8 mW $m^{-2}$ carbon fiber cloth electrode | Ouitrakul et al. (2007) |
| Stainless steel | 0.1 mW $m^{-2}$ vs. 1.8 mW $m^{-2}$ carbon fiber cloth electrode | Ouitrakul et al. (2007) |
| Pt | 78 W $m^{-2}$ for Pt nanoelectrode was connected to the wire covered with nanoparticle Ti vs. 35.08 W $m^{-2}$ of simple electrode Pt to the simple Ti wire | Torabiyan et al. (2014) |
| Au | Maximum power density of 0.15 μW $cm^{-2}$ | Qian et al. (2009) |
| | Maximum power density of 95 μW $cm^{-2}$ vs. results from Qian et al. (2009) | Choi and Chae (2013) |

Metal materials applied as anode MFC and their performance in MFCs

# Composite materials

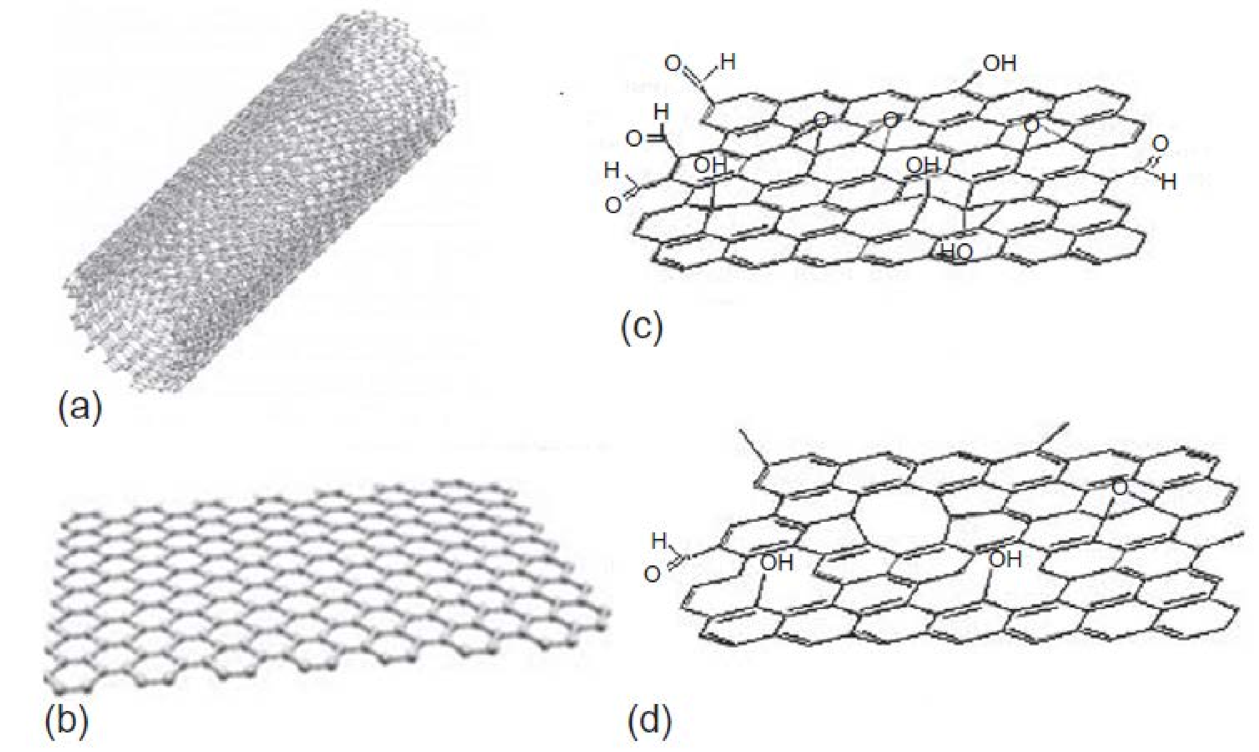


| Anode materials | MFC efficiency | References |
|---|---|---|
| $Mn^{4+}$-graphite anode | 10.2 mW $m^{-2}$ electrode was obtained with a $Mn^{4+}$ graphite anode<br>787.5 mW $m^{-2}$ maximum power density of $Mn^{4+}$-graphite anode vs. 5.32 mW $m^{-2}$ of NR-covalently linked woven graphite anode and 0.65 mW $m^{-2}$ of woven graphite anode with anaerobic sewage sludge as biocatalyst; and 91 mW $m^{-2}$ maximum power density of $Mn^{4+}$-graphite anode vs. 1.20 mW $m^{-2}$ of NR-covalently linked woven graphite anode and 0.44 mW $m^{-2}$ of woven graphite anode with *E. coli* as biocatalyst | Park and Zeikus (2002)<br>Park and Zeikus (2003) |
| Graphite–ceramic composite anodes containing $Mn^{2+}$ and $Ni^{2+}$ | Maximum power density of ~105 mW $m^{-2}$ of composite anode vs. ~20 mW $m^{-2}$ of graphite anode | Lowy et al. (2006) |
| Graphite paste with an incorporated Sb(V) complex | Maximum power density of ~115 mW $m^{-2}$ of composite anode vs. ~25 mW $m^{-2}$ of graphite anode | Lowy and Tender (2008) |
| Aluminum-alloy mesh composite carbon cloth electrode | 2966 mW $m^{-2}$ maximum power density obtained with composite anode<br>22.4 mW $m^{-2}$ of aluminum-alloy mesh anode | Chen et al. (2013) |
| Composite graphite/PTFE electrodes | 760 mW $m^{-2}$ of graphite/PTFE composite electrode with optimized PTFE content (e.g., 30%, w/w) for *E. coli*-catalyzed MFC vs. Park and Zeikus (2003) | Zhang et al. (2007) |

Composite materials applied as anode MFC and their efficiency as MFC anode

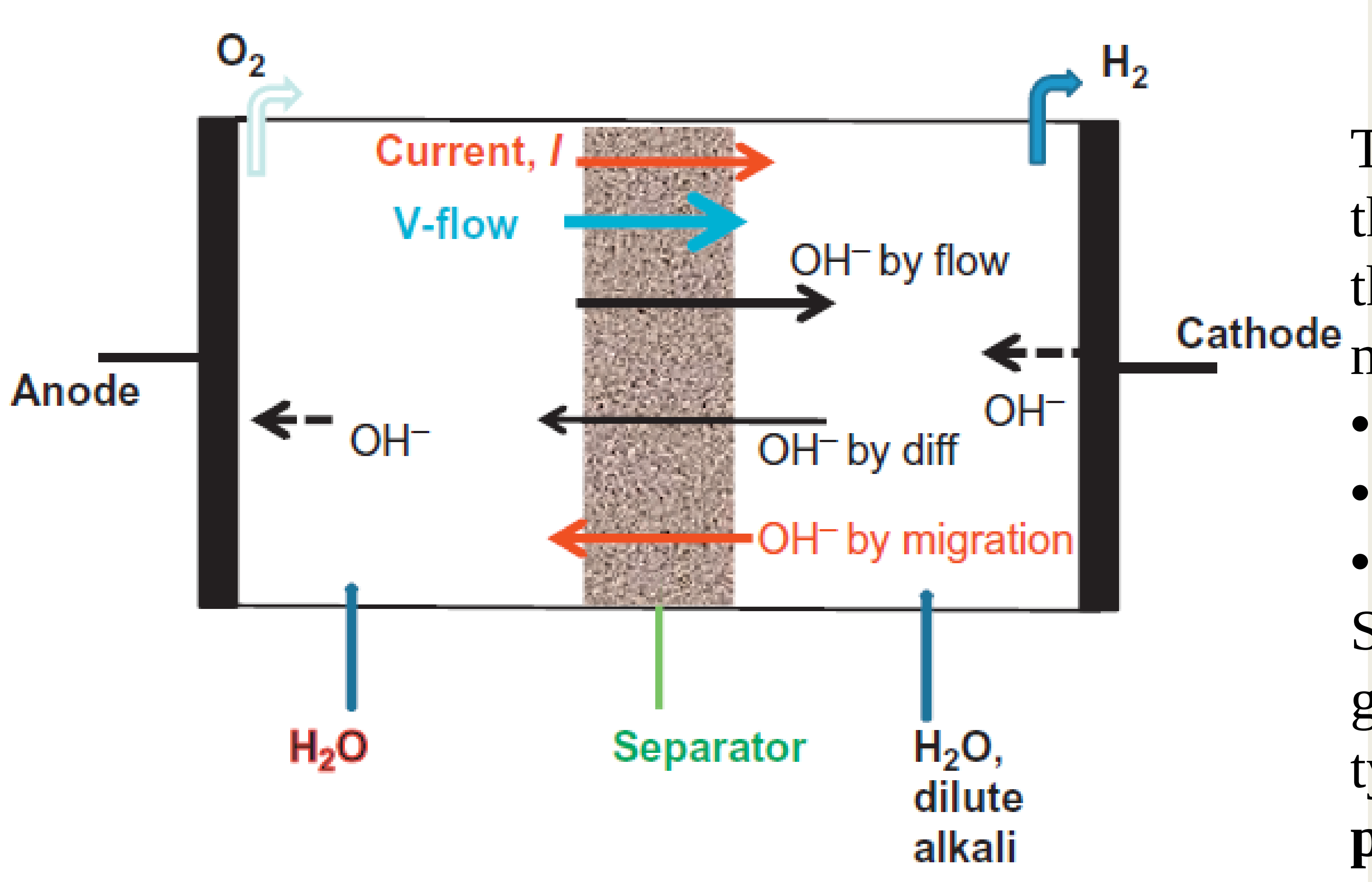
# *Three-dimensional macroporous-based anode*

- Three-dimensional architectures of anode with structured porosity combined with high surface area allow internal colonization through a large pore volume inside the electrode.
- Most of the studies show that the general design of novel 3D macroporous-based anode involve two steps:
- the development of macroporous 3D scaffold followed by
- its modification with conductive materials (micro- or nanoporous structure) responsible for the strong interaction with the microbial biofilm



Structures of carbon nanostructures. (a) Carbon nanotubes (CNTs); (b) graphene (G); (c) graphene oxide (GO); and (d) reduced graphene oxide (rGO).

# Membranes and separators for microbial fuel cells



The three important parameters that determine
the behavior of the separator material are

- the pore size,
- the porosity, and
- the ion Exchange capability.

Separators used in cells are generally classified into two types,
**permeable and semipermeable**.

# *Separators used in cells are generally classified into two types,*

- permeable and semipermeable.

(1) Permeable separators permit the bulk flow of liquid through their structure and are thus nonselective regarding transport of ions or neutral molecules. In electrochemical processes these are frequently referred to as diaphragms.

(2) Semipermeable separators permit the selective passage of certain species by virtue of molecular size or charge. In electrochemical processes these are termed “membranes” and separation is based on the charge carried by the molecule.

- The simplest of separators are the porous separators, which prevent the mixing of for example, gaseous products (and solid particles) by the appropriate size of the pores in the structure, typically in the range of 1–50 μm.

# *Semipermeable membranes: ion-exchange membranes*

- The main properties required of ion-exchange membranes for them to be successful in technical processes are

1. low electrical resistance, to minimize the membrane internal resistance (IR) losses,

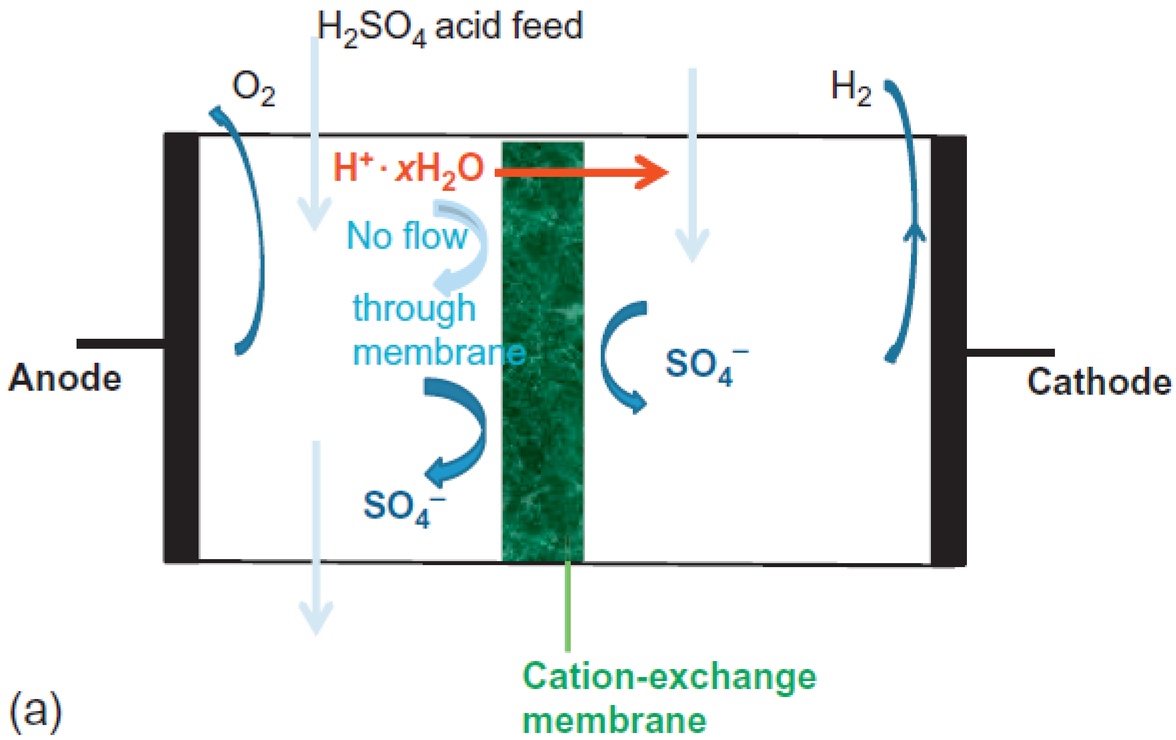
2. high permselectivity; that is, it should be highly permeable for an ion of one charge, but should be highly impermeable to coions, and to nonionised molecules and solvents,

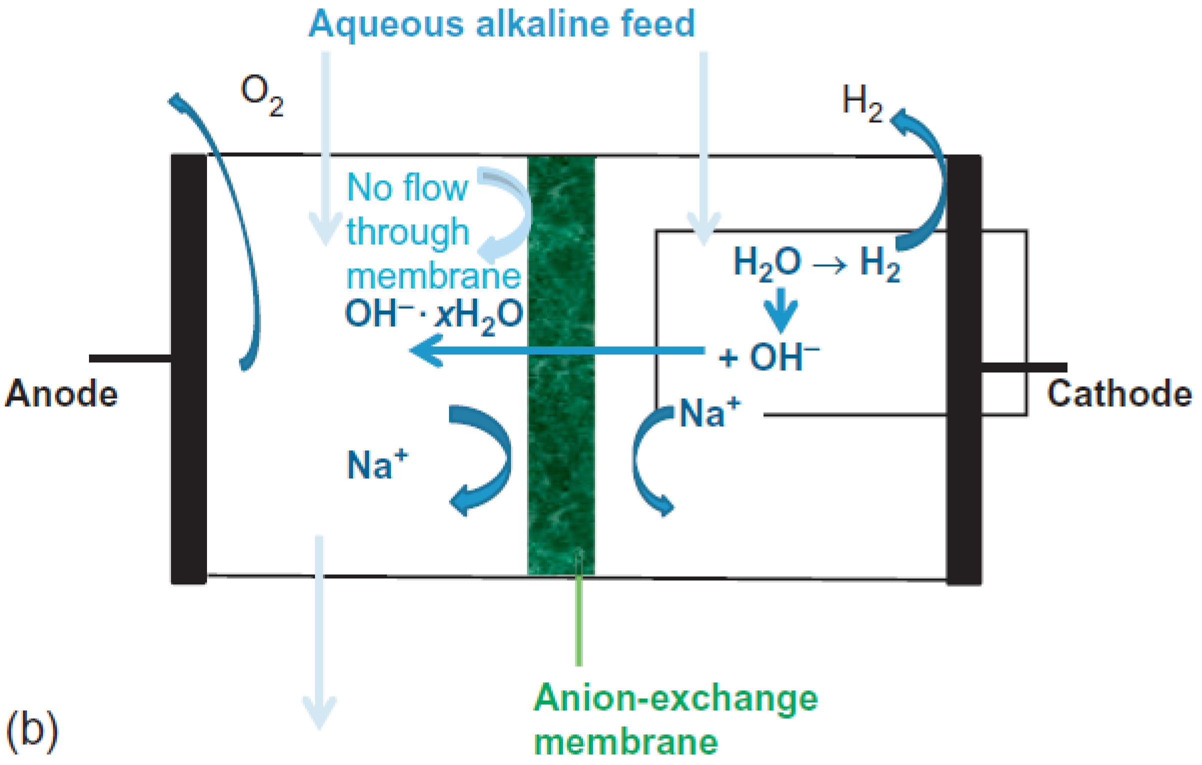
3. good mechanical and dimensional stability,

4. good chemical stability, over a wide pH range and in the presence of oxidizing agents,

5. good operating characteristics; that is, it should be capable of operation over a wide range of current densities and under varying conditions of temperature, current density, pH, etc.

- The properties of ion-exchange membranes are determined by two parameters; that is, the basic polymer matrix and the type and concentration of the fixed ionic group.
- The electric properties and the selectivity of ion-exchange membranes are determined mainly by the type and the concentration of the fixed ionic charges in the polymer matrix.
- There are a series of different cationic and anionic groups that can be introduced into a basic polymer matrix





- Cation-exchange membranes (CEMs), that is, those selectively permeable to cations, are made from strong or weak acids in a polymeric sheet, and AEMs are similarly made of strong or weak bases.

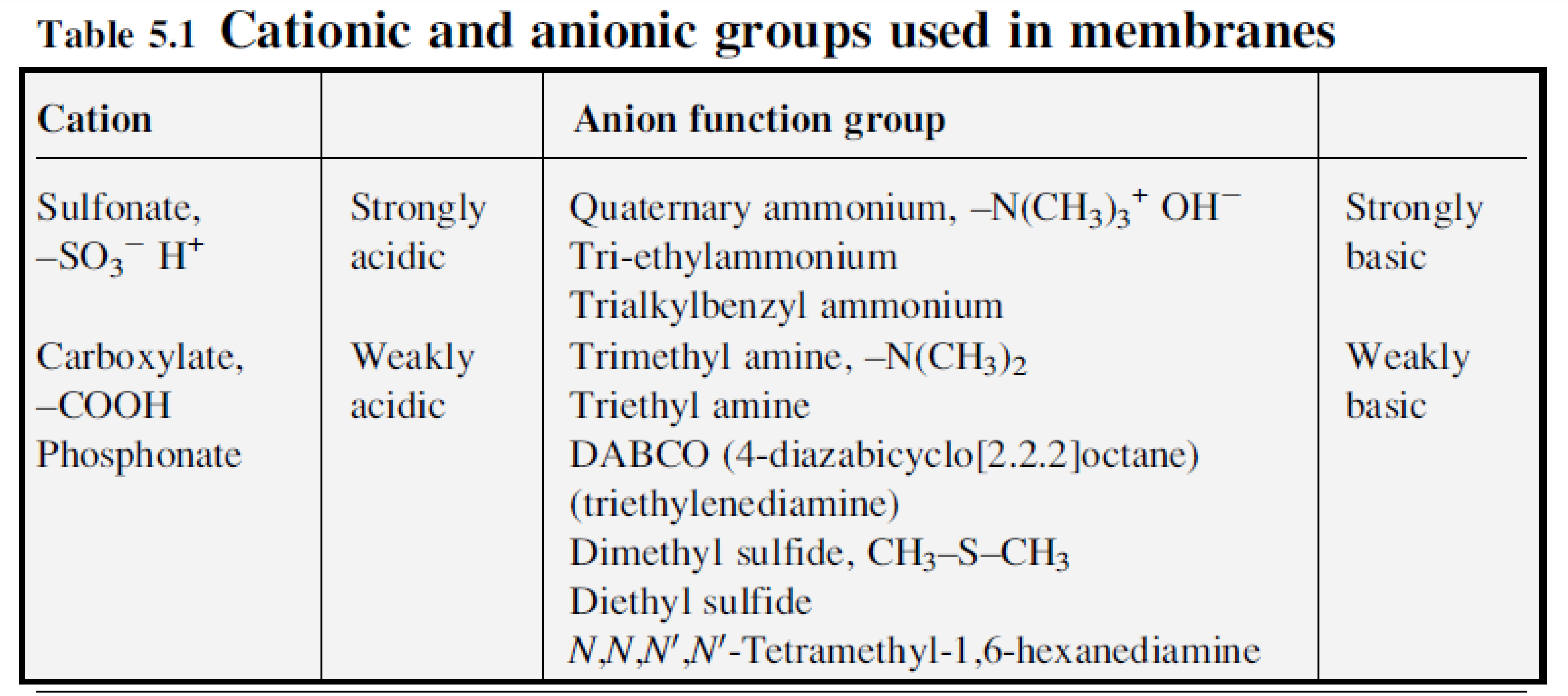
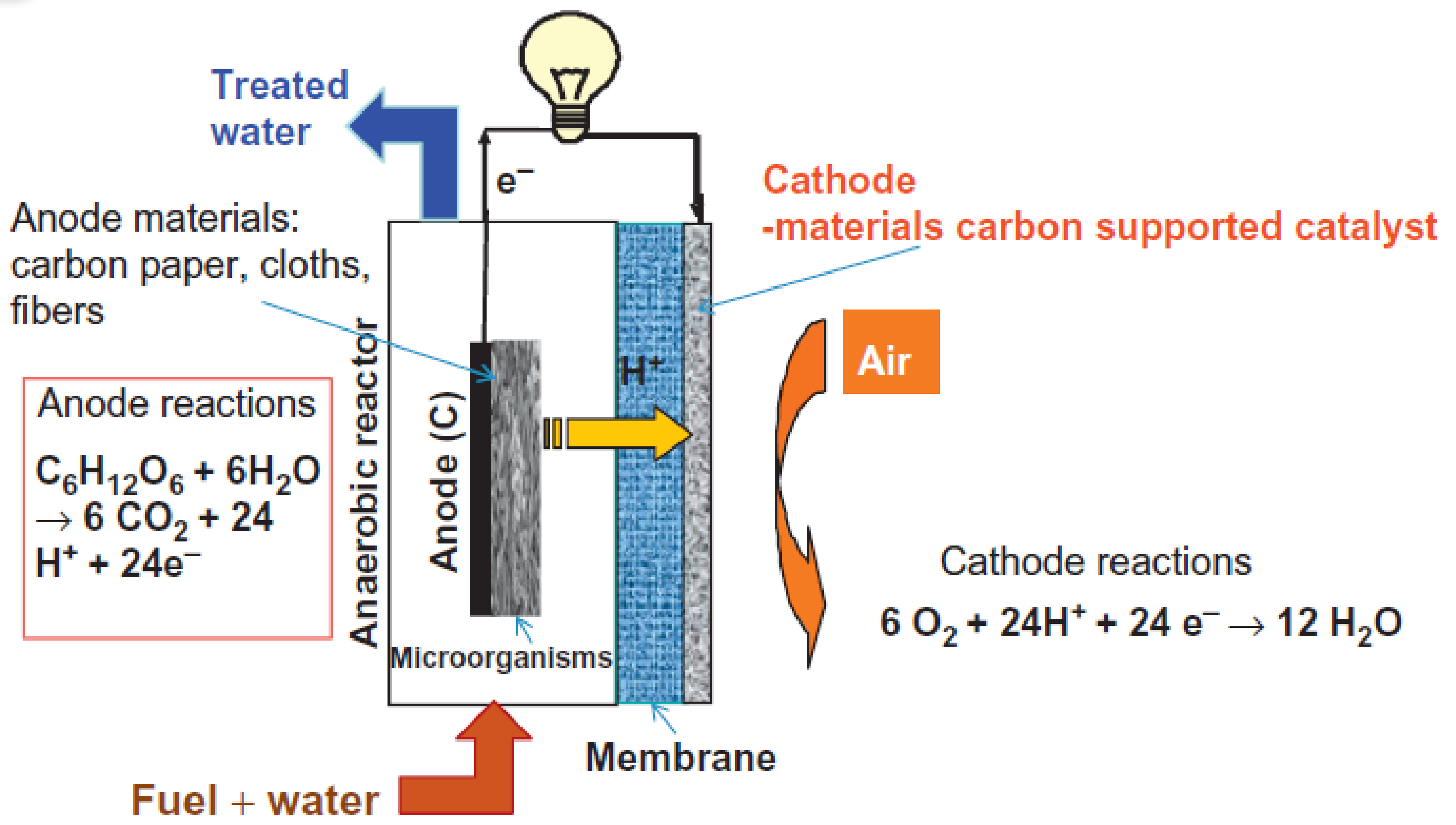


**Table 5.1** Cationic and anionic groups used in membranes

| Cation | | Anion function group | |
|---|---|---|---|
| Sulfonate, $-SO_3^- H^+$ | Strongly acidic | Quaternary ammonium, $-N(CH_3)_3^+ OH^-$<br>Tri-ethylammonium<br>Trialkylbenzyl ammonium | Strongly basic |
| Carboxylate, –COOH<br>Phosphonate | Weakly acidic | Trimethyl amine, $-N(CH_3)_2$<br>Triethyl amine<br>DABCO (4-diazabicyclo[2.2.2]octane) (triethylenediamine)<br>Dimethyl sulfide, $CH_3-S-CH_3$<br>Diethyl sulfide<br>*N,N,N′,N′*-Tetramethyl-1,6-hexanediamine | Weakly basic |

The sulfonic acid groups are strong acids, completely dissociated over nearly the entire pH range, and carboxylic acid groups are weak acids and undissociated at values of pH of 6.

AEMs mostly use the quaternary ammonium (QA) group in the polymer matrix leading to a strongly basic membrane. Tertiary, secondary, and primary amines and to a lesser extent phosphonium and sulfonium groups, are used as less strongly basic functional groups.



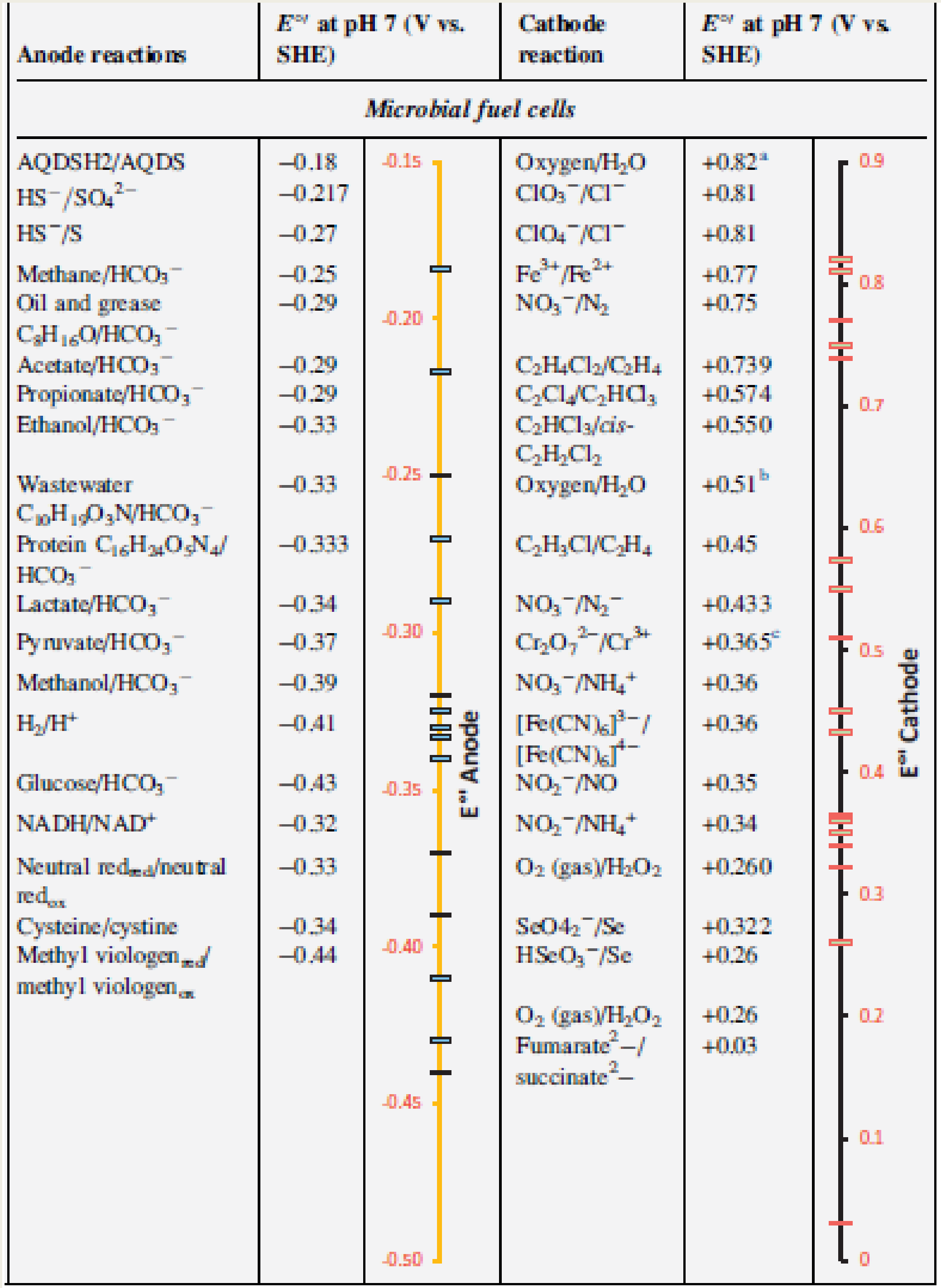
Anode reactions

$C_6H_{12}O_6 + 6H_2O \rightarrow 6\ CO_2 + 24\ H^+ + 24e^-$

Cathode reactions

$6\ O_2 + 24H^+ + 24\ e^- \rightarrow 12\ H_2O$

Membrane electrode assemblies used in microbial fuel cells.



| **Anode reactions** | **$E^{\circ\prime}$ at pH 7 (V vs. SHE)** | **Cathode reaction** | **$E^{\circ\prime}$ at pH 7 (V vs SHE)** |
|---|---|---|---|
| ***Microbial fuel cells*** | | | |
| AQDSH2/AQDS | –0.18 | Oxygen/$H_2O$ | +0.82[a] |
| $HS^-/SO_4^{2-}$ | –0.217 | $ClO_3^-/Cl^-$ | +0.81 |
| $HS^-/S$ | –0.27 | $ClO_4^-/Cl^-$ | +0.81 |
| Methane/$HCO_3^-$ | –0.25 | $Fe^{3+}/Fe^{2+}$ | +0.77 |
| Oil and grease | –0.29 | $NO_3^-/N_2$ | +0.75 |
| $C_8H_{16}O/HCO_3^-$ | | | |
| Acetate/$HCO_3^-$ | –0.29 | $C_2H_4Cl_2/C_2H_4$ | +0.739 |
| Propionate/$HCO_3^-$ | –0.29 | $C_2Cl_4/C_2HCl_3$ | +0.574 |
| Ethanol/$HCO_3^-$ | –0.33 | $C_2HCl_3$/*cis*-$C_2H_2Cl_2$ | +0.550 |
| Wastewater $C_{10}H_{19}O_3N/HCO_3^-$ | –0.33 | Oxygen/$H_2O$ | +0.51[b] |
| Protein $C_{16}H_{24}O_5N_4/HCO_3^-$ | –0.333 | $C_2H_3Cl/C_2H_4$ | +0.45 |
| Lactate/$HCO_3^-$ | –0.34 | $NO_3^-/N_2^-$ | +0.433 |
| Pyruvate/$HCO_3^-$ | –0.37 | $Cr_2O_7^{2-}/Cr^{3+}$ | +0.365[c] |
| Methanol/$HCO_3^-$ | –0.39 | $NO_3^-/NH_4^+$ | +0.36 |
| $H_2/H^+$ | –0.41 | $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ | +0.36 |
| Glucose/$HCO_3^-$ | –0.43 | $NO_2^-/NO$ | +0.35 |
| NADH/$NAD^+$ | –0.32 | $NO_2^-/NH_4^+$ | +0.34 |
| Neutral $red_{red}$/neutral $red_{ox}$ | –0.33 | $O_2$ (gas)/$H_2O_2$ | +0.260 |
| Cysteine/cystine | –0.34 | $SeO4_2^-/Se$ | +0.322 |
| Methyl $viologen_{red}$/methyl $viologen_{ox}$ | –0.44 | $HSeO_3^-/Se$ | +0.26 |
| | | $O_2$ (gas)/$H_2O_2$ | +0.26 |
| | | $Fumarate^{2}$–/$succinate^{2}$– | +0.03 |

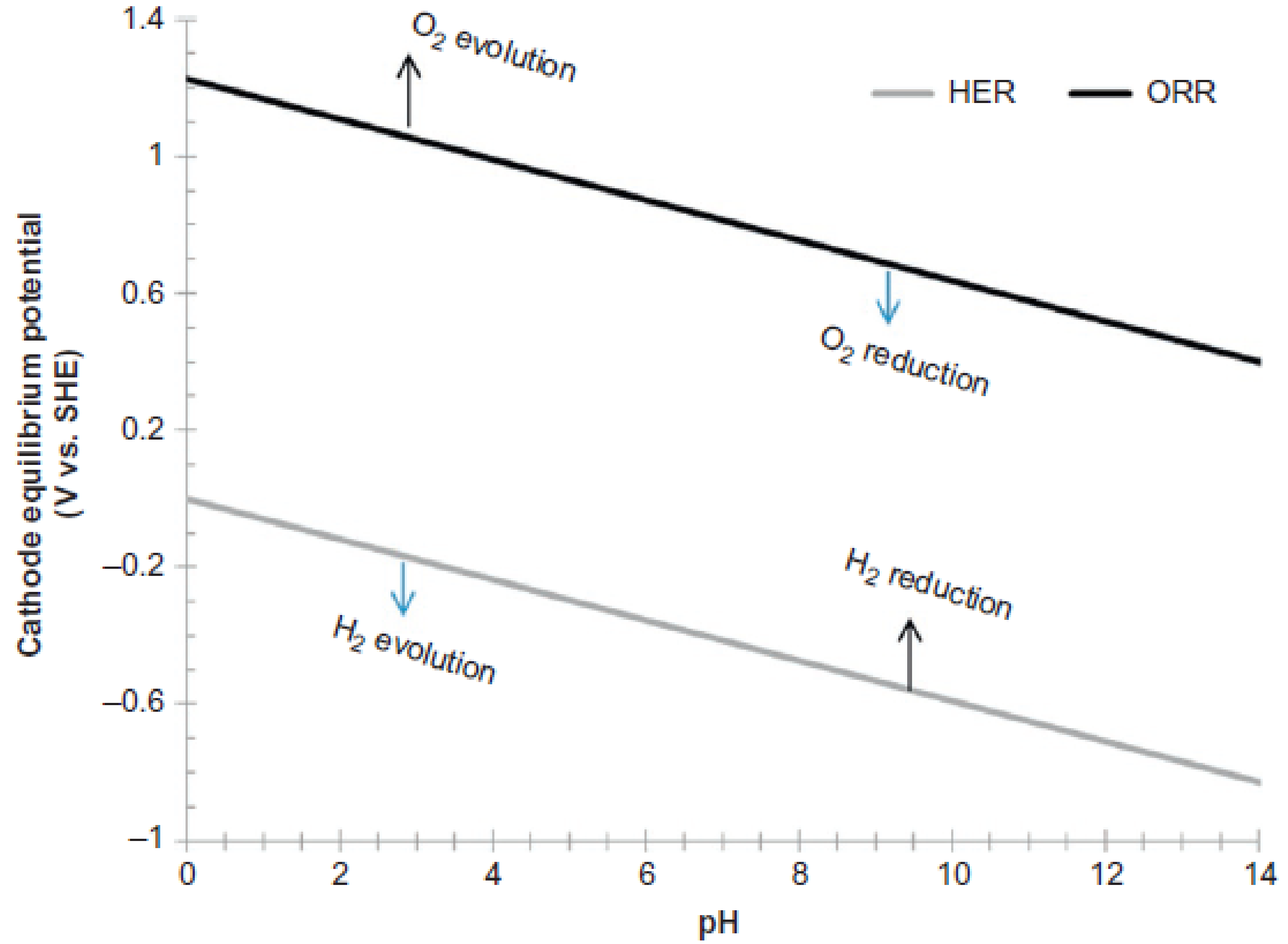


**Figure 6.2** Cathode equilibrium potential of ORR and HER as a function of pH from Nernst equation.

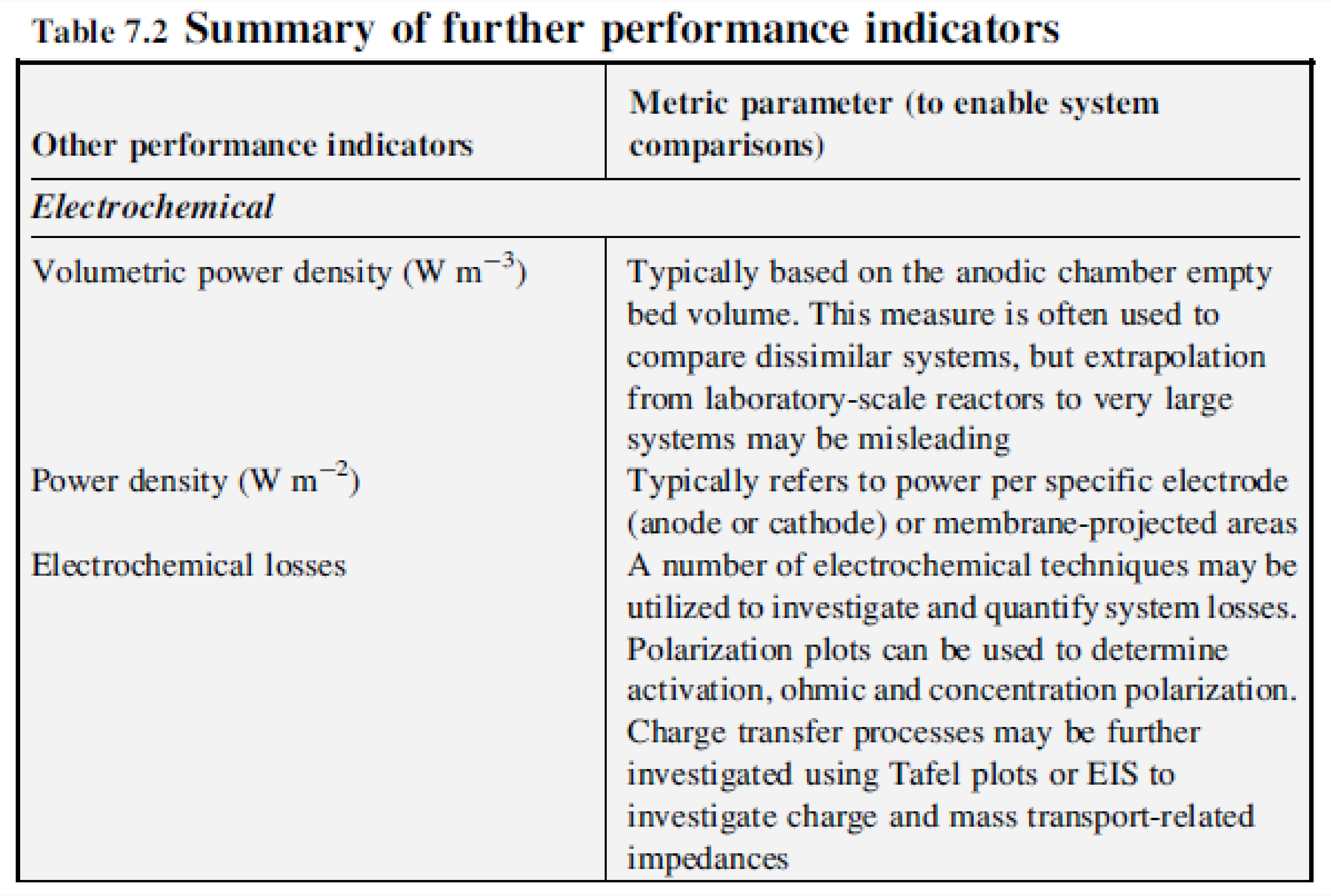
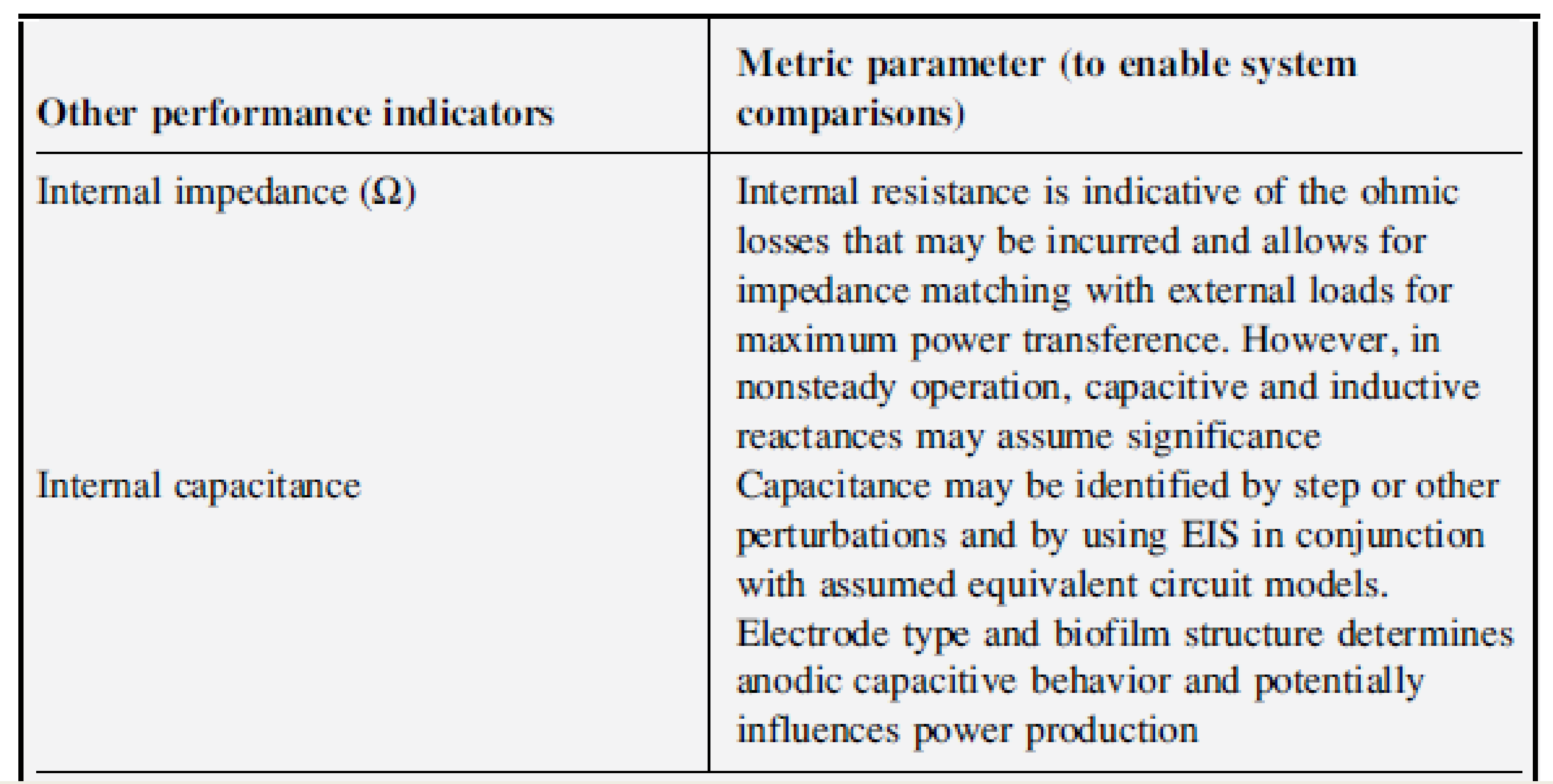
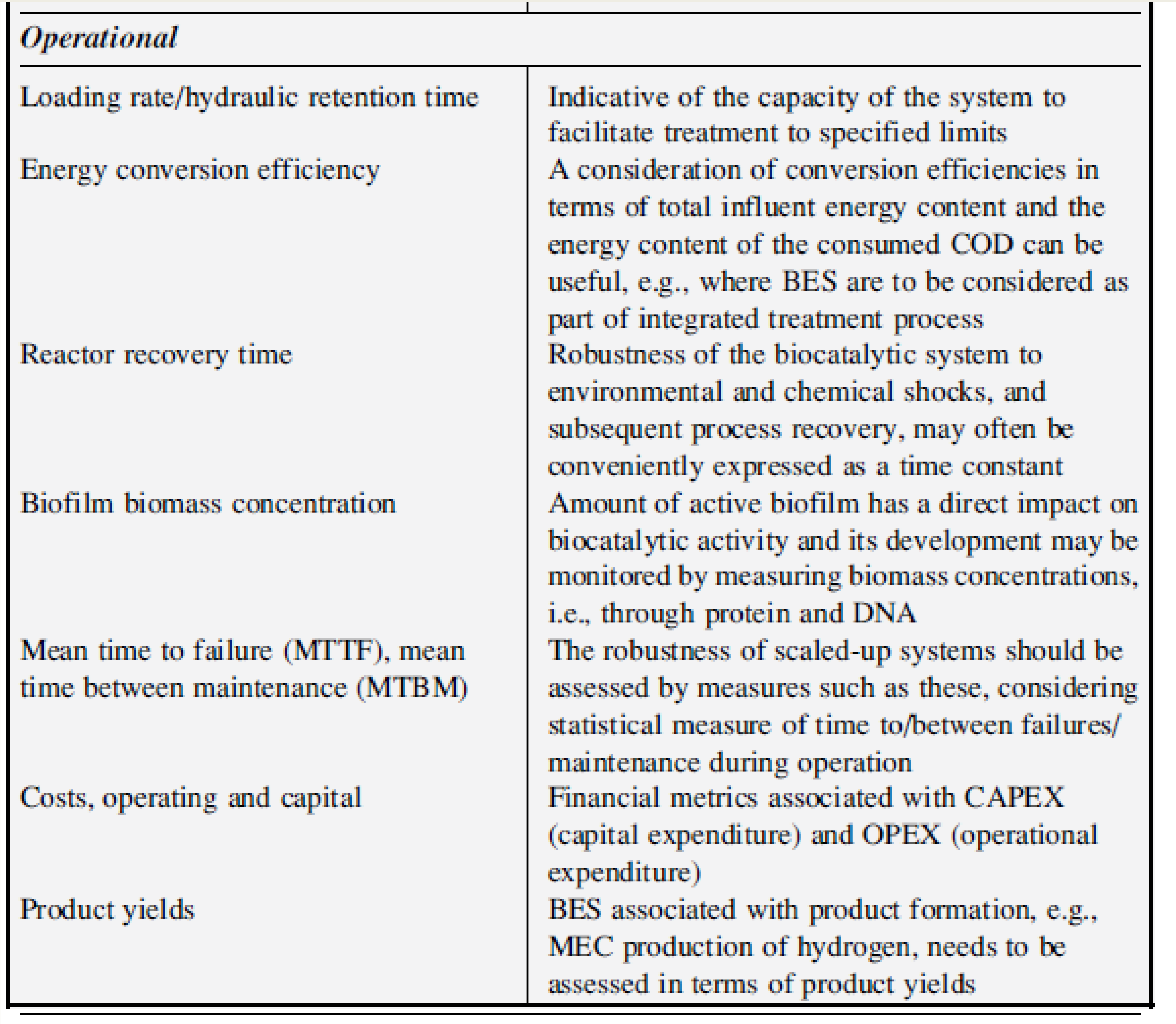


Table 7.2 **Summary of further performance indicators**

| **Other performance indicators** | **Metric parameter (to enable system comparisons)** |
|---|---|
| *Electrochemical* | |
| Volumetric power density (W $m^{-3}$) | Typically based on the anodic chamber empty bed volume. This measure is often used to compare dissimilar systems, but extrapolation from laboratory-scale reactors to very large systems may be misleading |
| Power density (W $m^{-2}$) | Typically refers to power per specific electrode (anode or cathode) or membrane-projected areas |
| Electrochemical losses | A number of electrochemical techniques may be utilized to investigate and quantify system losses. Polarization plots can be used to determine activation, ohmic and concentration polarization. Charge transfer processes may be further investigated using Tafel plots or EIS to investigate charge and mass transport-related impedances |



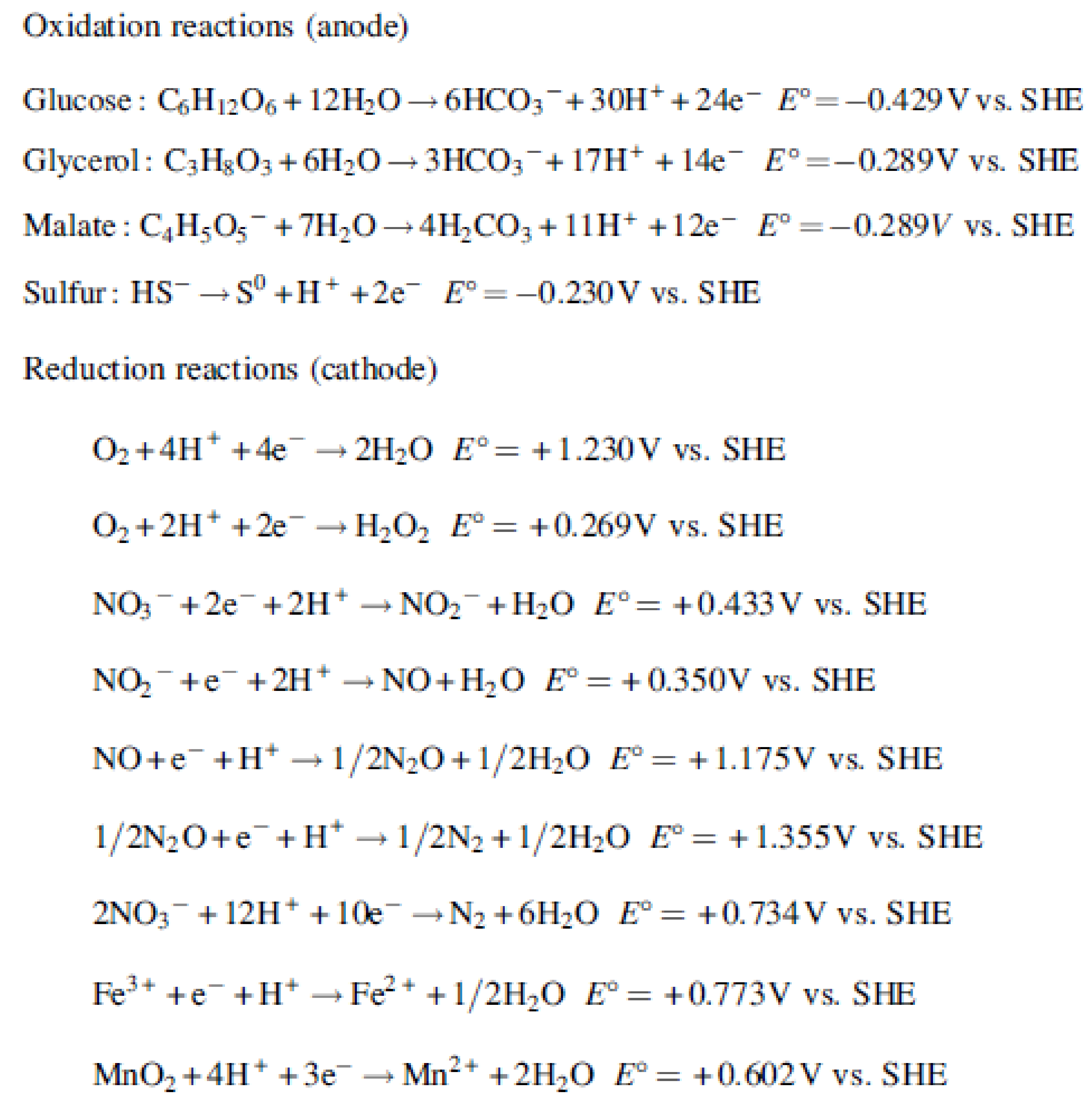
| Other performance indicators | Metric parameter (to enable system comparisons) |
|---|---|
| Internal impedance (Ω) | Internal resistance is indicative of the ohmic losses that may be incurred and allows for impedance matching with external loads for maximum power transference. However, in nonsteady operation, capacitive and inductive reactances may assume significance |
| Internal capacitance | Capacitance may be identified by step or other perturbations and by using EIS in conjunction with assumed equivalent circuit models. Electrode type and biofilm structure determines anodic capacitive behavior and potentially influences power production |



| | |
|---|---|
| *Operational* | |
| Loading rate/hydraulic retention time | Indicative of the capacity of the system to facilitate treatment to specified limits |
| Energy conversion efficiency | A consideration of conversion efficiencies in terms of total influent energy content and the energy content of the consumed COD can be useful, e.g., where BES are to be considered as part of integrated treatment process |
| Reactor recovery time | Robustness of the biocatalytic system to environmental and chemical shocks, and subsequent process recovery, may often be conveniently expressed as a time constant |
| Biofilm biomass concentration | Amount of active biofilm has a direct impact on biocatalytic activity and its development may be monitored by measuring biomass concentrations, i.e., through protein and DNA |
| Mean time to failure (MTTF), mean time between maintenance (MTBM) | The robustness of scaled-up systems should be assessed by measures such as these, considering statistical measure of time to/between failures/maintenance during operation |
| Costs, operating and capital | Financial metrics associated with CAPEX (capital expenditure) and OPEX (operational expenditure) |
| Product yields | BES associated with product formation, e.g., MEC production of hydrogen, needs to be assessed in terms of product yields |

# Applications of microbial electrochemical and fuel cells

- Wastewater treatment



Oxidation reactions (anode)

Glucose : $C_6H_{12}O_6 + 12H_2O \rightarrow 6HCO_3^- + 30H^+ + 24e^-$ $E° = -0.429$ V vs. SHE

Glycerol : $C_3H_8O_3 + 6H_2O \rightarrow 3HCO_3^- + 17H^+ + 14e^-$ $E° = -0.289$V vs. SHE

Malate : $C_4H_5O_5^- + 7H_2O \rightarrow 4H_2CO_3 + 11H^+ + 12e^-$ $E° = -0.289V$ vs. SHE

Sulfur : $HS^- \rightarrow S^0 + H^+ + 2e^-$ $E° = -0.230$ V vs. SHE

Reduction reactions (cathode)

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ $E° = +1.230$ V vs. SHE

$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$ $E° = +0.269$V vs. SHE

$NO_3^- + 2e^- + 2H^+ \rightarrow NO_2^- + H_2O$ $E° = +0.433$ V vs. SHE

$NO_2^- + e^- + 2H^+ \rightarrow NO + H_2O$ $E° = +0.350$V vs. SHE

$NO + e^- + H^+ \rightarrow 1/2N_2O + 1/2H_2O$ $E° = +1.175$V vs. SHE

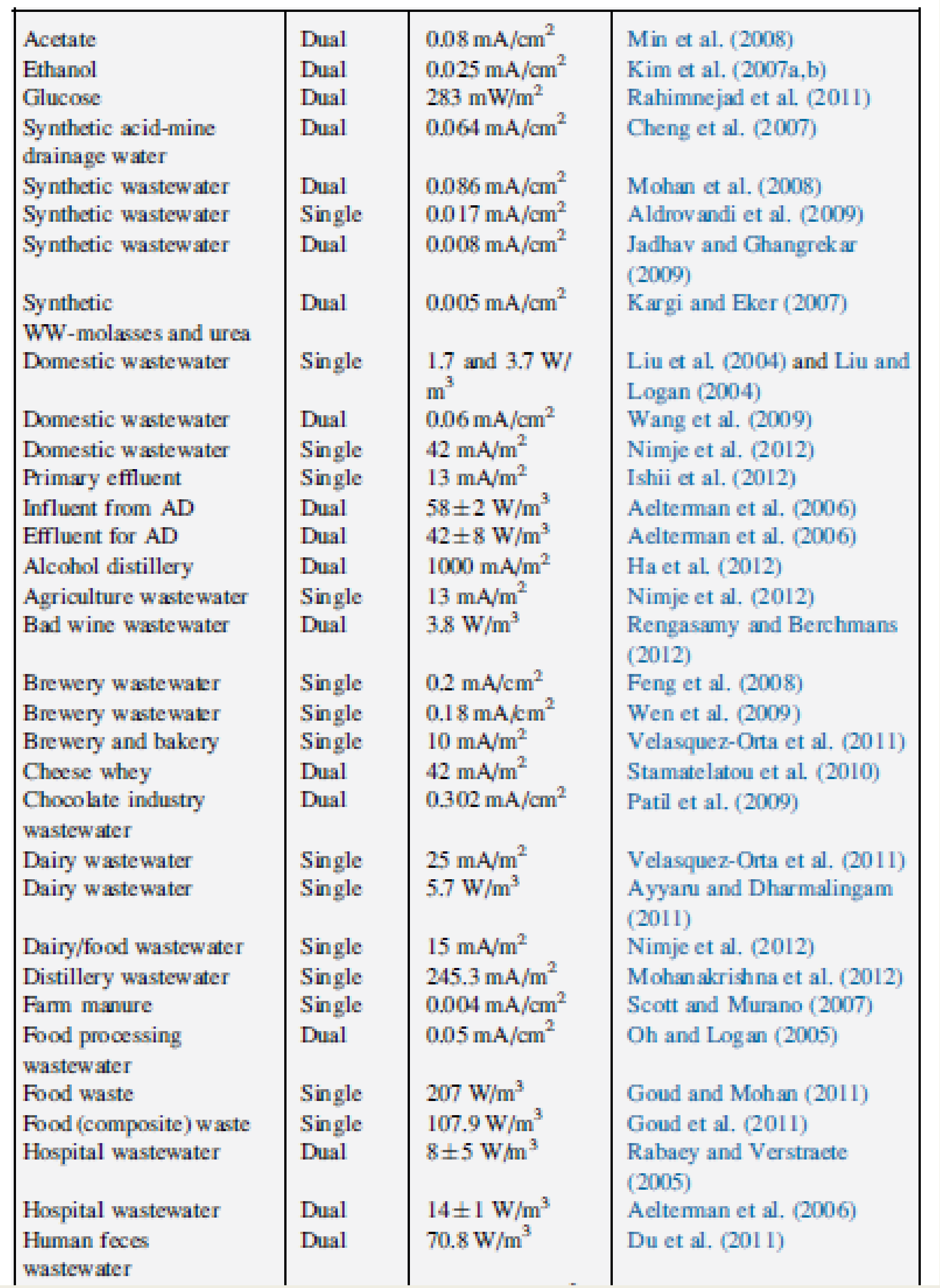
$1/2N_2O + e^- + H^+ \rightarrow 1/2N_2 + 1/2H_2O$ $E° = +1.355$V vs. SHE

$2NO_3^- + 12H^+ + 10e^- \rightarrow N_2 + 6H_2O$ $E° = +0.734$ V vs. SHE

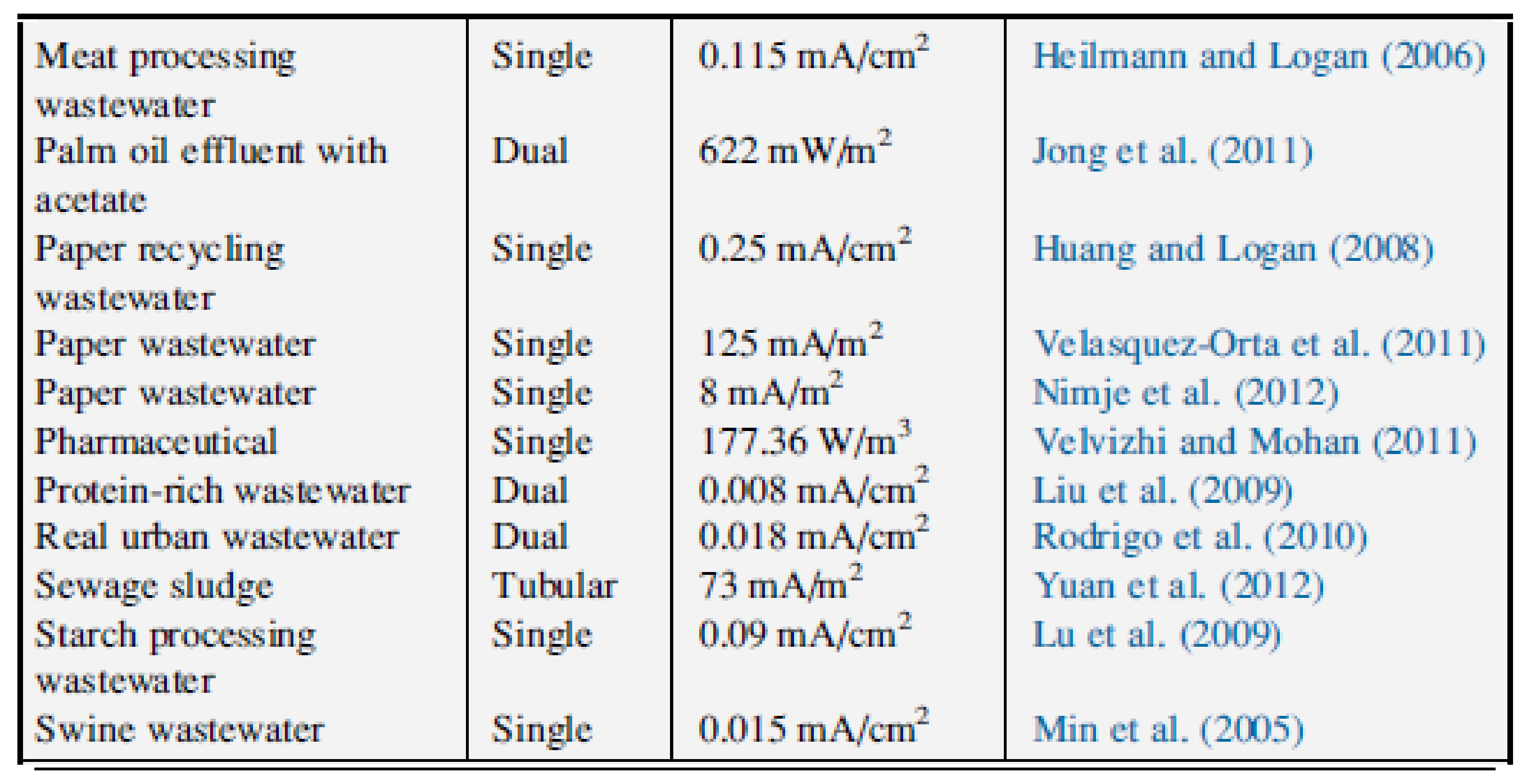
$Fe^{3+} + e^- + H^+ \rightarrow Fe^{2+} + 1/2H_2O$ $E° = +0.773$V vs. SHE

$MnO_2 + 4H^+ + 3e^- \rightarrow Mn^{2+} + 2H_2O$ $E° = +0.602$ V vs. SHE

# Energy recovery from various wastewater substrates in MFCs

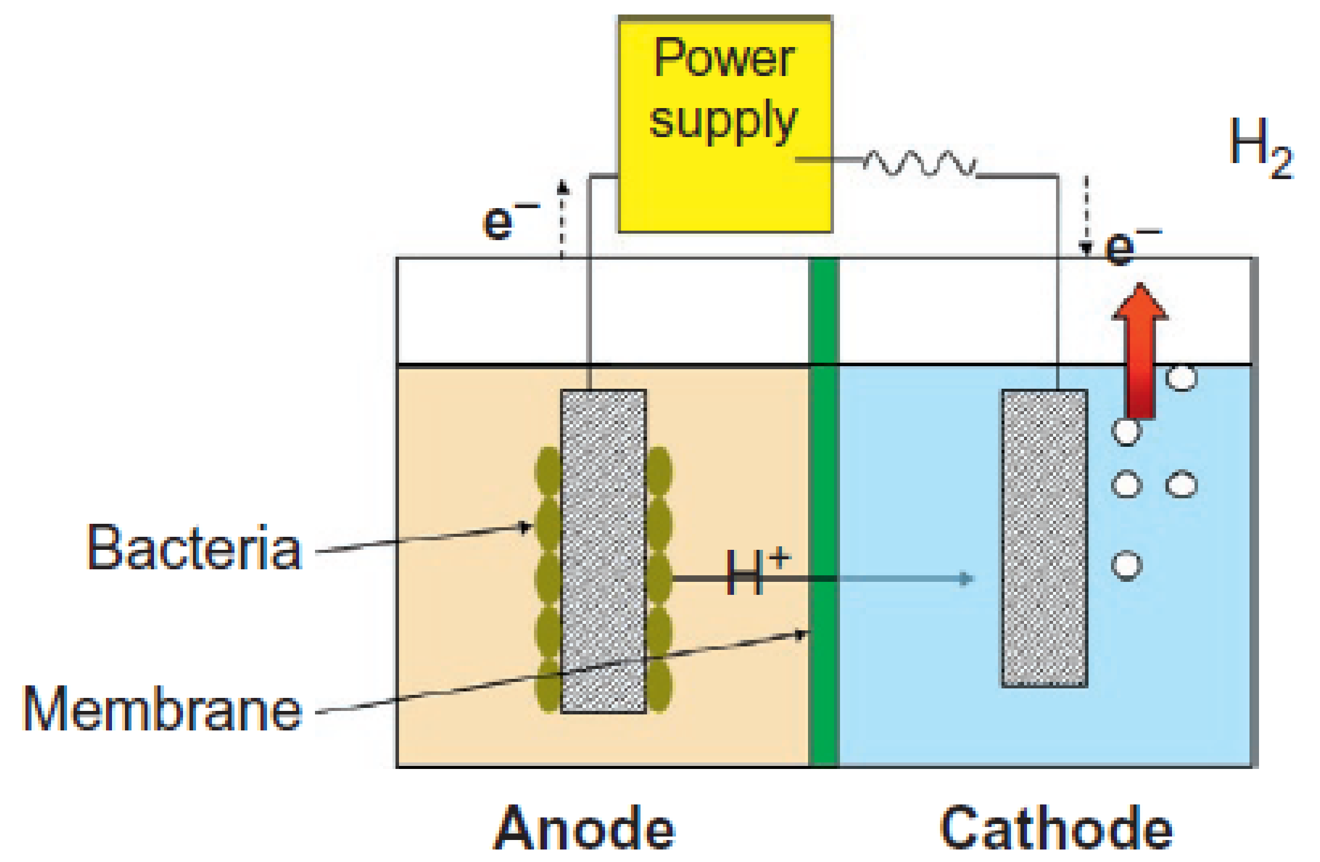


| | | | |
|---|---|---|---|
| Acetate | Dual | 0.08 mA/cm$^2$ | Min et al. (2008) |
| Ethanol | Dual | 0.025 mA/cm$^2$ | Kim et al. (2007a,b) |
| Glucose | Dual | 283 mW/m$^2$ | Rahimnejad et al. (2011) |
| Synthetic acid-mine drainage water | Dual | 0.064 mA/cm$^2$ | Cheng et al. (2007) |
| Synthetic wastewater | Dual | 0.086 mA/cm$^2$ | Mohan et al. (2008) |
| Synthetic wastewater | Single | 0.017 mA/cm$^2$ | Aldrovandi et al. (2009) |
| Synthetic wastewater | Dual | 0.008 mA/cm$^2$ | Jadhav and Ghangrekar (2009) |
| Synthetic WW-molasses and urea | Dual | 0.005 mA/cm$^2$ | Kargi and Eker (2007) |
| Domestic wastewater | Single | 1.7 and 3.7 W/m$^3$ | Liu et al. (2004) and Liu and Logan (2004) |
| Domestic wastewater | Dual | 0.06 mA/cm$^2$ | Wang et al. (2009) |
| Domestic wastewater | Single | 42 mA/m$^2$ | Nimje et al. (2012) |
| Primary effluent | Single | 13 mA/m$^2$ | Ishii et al. (2012) |
| Influent from AD | Dual | 58 ± 2 W/m$^3$ | Aelterman et al. (2006) |
| Effluent for AD | Dual | 42 ± 8 W/m$^3$ | Aelterman et al. (2006) |
| Alcohol distillery | Dual | 1000 mA/m$^2$ | Ha et al. (2012) |
| Agriculture wastewater | Single | 13 mA/m$^2$ | Nimje et al. (2012) |
| Bad wine wastewater | Dual | 3.8 W/m$^3$ | Rengasamy and Berchmans (2012) |
| Brewery wastewater | Single | 0.2 mA/cm$^2$ | Feng et al. (2008) |
| Brewery wastewater | Single | 0.18 mA/cm$^2$ | Wen et al. (2009) |
| Brewery and bakery | Single | 10 mA/m$^2$ | Velasquez-Orta et al. (2011) |
| Cheese whey | Dual | 42 mA/m$^2$ | Stamatelatou et al. (2010) |
| Chocolate industry wastewater | Dual | 0.302 mA/cm$^2$ | Patil et al. (2009) |
| Dairy wastewater | Single | 25 mA/m$^2$ | Velasquez-Orta et al. (2011) |
| Dairy wastewater | Single | 5.7 W/m$^3$ | Ayyaru and Dharmalingam (2011) |
| Dairy/food wastewater | Single | 15 mA/m$^2$ | Nimje et al. (2012) |
| Distillery wastewater | Single | 245.3 mA/m$^2$ | Mohanakrishna et al. (2012) |
| Farm manure | Single | 0.004 mA/cm$^2$ | Scott and Murano (2007) |
| Food processing wastewater | Dual | 0.05 mA/cm$^2$ | Oh and Logan (2005) |
| Food waste | Single | 207 W/m$^3$ | Goud and Mohan (2011) |
| Food (composite) waste | Single | 107.9 W/m$^3$ | Goud et al. (2011) |
| Hospital wastewater | Dual | 8 ± 5 W/m$^3$ | Rabaey and Verstraete (2005) |
| Hospital wastewater | Dual | 14 ± 1 W/m$^3$ | Aelterman et al. (2006) |
| Human feces wastewater | Dual | 70.8 W/m$^3$ | Du et al. (2011) |



| | | | |
|---|---|---|---|
| Meat processing wastewater | Single | 0.115 mA/cm$^2$ | Heilmann and Logan (2006) |
| Palm oil effluent with acetate | Dual | 622 mW/m$^2$ | Jong et al. (2011) |
| Paper recycling wastewater | Single | 0.25 mA/cm$^2$ | Huang and Logan (2008) |
| Paper wastewater | Single | 125 mA/m$^2$ | Velasquez-Orta et al. (2011) |
| Paper wastewater | Single | 8 mA/m$^2$ | Nimje et al. (2012) |
| Pharmaceutical | Single | 177.36 W/m$^3$ | Velvizhi and Mohan (2011) |
| Protein-rich wastewater | Dual | 0.008 mA/cm$^2$ | Liu et al. (2009) |
| Real urban wastewater | Dual | 0.018 mA/cm$^2$ | Rodrigo et al. (2010) |
| Sewage sludge | Tubular | 73 mA/m$^2$ | Yuan et al. (2012) |
| Starch processing wastewater | Single | 0.09 mA/cm$^2$ | Lu et al. (2009) |
| Swine wastewater | Single | 0.015 mA/cm$^2$ | Min et al. (2005) |

# Microbial electrolysis cells (MEC) for hydrogen production



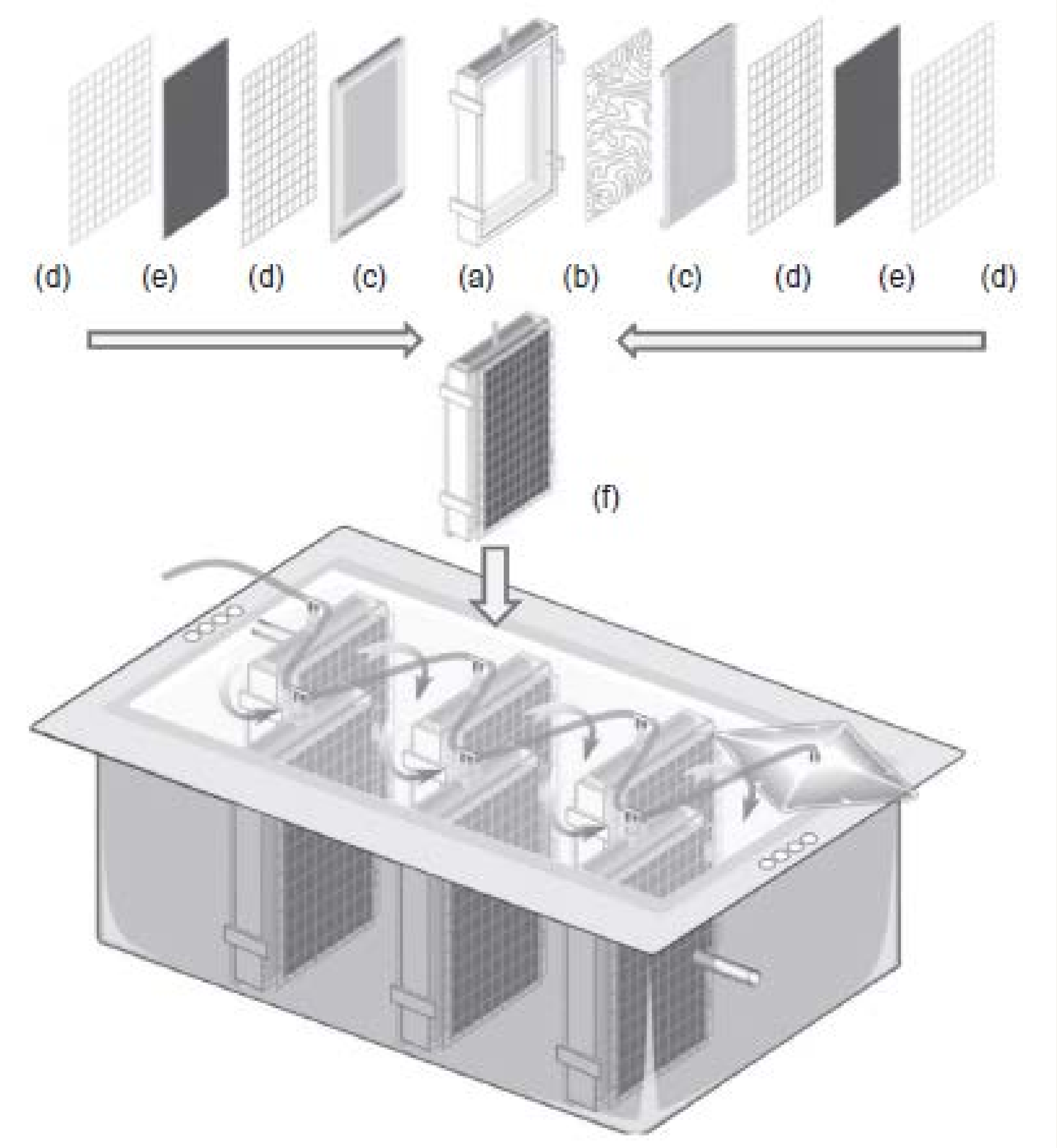
- Electrons (e) travel in a circuit from anode to cathode, supplemented by an external power supply. Protons (H+) are released by anodic bacteria and travel through a membrane to the cathode, where they are reduced to form hydrogen gas.

- The microbial electrolytic process, that is, the conversion of electrical energy into chemical energy and the simultaneous production of hydrogen, can be called electrohydrogenesis or microbial electrolysis. In other words, MEC is a reactor that produces hydrogen whereas MFC is a system that generates electricity, and both MEC and MFC consume organic matter. The cathodic reduction reaction is fueled by the protons and electrons generated in the anodic bioelectrocatalysis and by some extra electrical energy required for the occurrence of the cathodic reaction

- MECs make use of exoelectrogens (electrochemically active microorganisms) to harvest electrons (and protons) from organic matter in an anaerobic anode chamber.
- These electrons are transferred in a circuit from anode to cathode, producing an electrical current.
- In MECs, protons ($H^+$ ions) are transferred (under acidic conditions) via a membrane from the anode to an anaerobic cathode (unlike in an MFC) and therefore oxygen is not present and not reduced to form water.
- The $H^+$ ions can be used to form hydrogen at the cathode (or other useful products such as hydrogen peroxide), yet this will not occur spontaneously due to the energy required to drive the chemical reaction.

- Cathodic reaction under acidic conditions, $2H^+ + 2e \rightarrow H_2$
- Or under alkaline conditions, $2H_2O + 2e \rightarrow H_2 + 2OH$

Bottle (left) and tubular (right) laboratory-scale microbial electrolysis cells.



Schematic of a practical MEC system and the modular components:

(a) PVC outer frame,
(b) stainless steel wire wool cathode,
(c) Rhinohide membrane fixed around a PVC frame,
(d) stainless steel wire mesh current collector, and
(e) carbon felt anode.

These components fit together to form a single module (f ), and six of these go into the reactor tank where wastewater flows around them. Gas is collected through Tygon tubing into a Tedlar gas bag.

## Advantages

- MECs are fully anaerobic. With an MEC both electrodes can be fully submerged in a tank, whereas with an MFC the cathode must be exposed to air either through aeration of the associated electrolyte or by direct exposure as an air cathode.
- MECs produce higher-value products. MECs produce products that are higher in value than the electricity produced by MFCs. It has been estimated that the financial value of hydrogen produced in an MEC could range from 3 times to almost 10 times that of electricity produced in an MFC.

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