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Microbial Fuel Cells
Overview and First Simple Experiments

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1 Introduction

The idea is just amazing: electrical energy generation without complex conversion processes just from the “environment” by microorganisms. This would be wonderful – not only in the present times of energy prize increases and a looming energy deficit. And indeed: it is possibly – though: just partly and often to a very limited extent and under certain special conditions.

In fact, the idea might be old. Even already in 1912 [POTTER, 1912] had reported on the generation of electrical energy by *E. coli* decomposing organic compounds. However the first more technical implementation and document is a US patent [SISLER, 1969] – not even 40 years old. There, a biochemical fuel cell for electric power generation (from light energy) was described, having two chambers. The corrosion-resistant electrodes in the chambers are linked by a salt bridge. In the cathode chamber algae or other photosynthetic microorganisms should supply the oxygen for the electrode. In addition, the dead biomass from cathode chamber should be substrate for the anode chamber. The anaerobic bacteria culture for the anode chamber is derived from sea sediment and consists of sulphate reducing bacteria (e.g. *Desulfovibrio* sp.). According to the patent, hydrogen, hydrogen sulphide or other reduced organic compounds are oxidised at the anode and form hydronium ions, which are neutralised with hydroxyl ions, formed at the cathode.

Though, this publication is referring to the used cell as biochemical fuel cell, most authors are calling it microbial fuel cell (MFC). Here also this term is applied, referring to the (deliberate) use of living microorganisms – independent of the fact, whether specific species or just consortia or a certain milieu biomass is used or stimulated. Maybe the latter induces some authors to use the term biological fuel cells, to contrast to chemical fuel cells.

Power generation is just one potential application for MFC. For that a variety of substrates are applicable. Some interesting are: organic waste, sewage sludge or waste water to give power to the respective treatment plant, while digesting the residues. Though main developments are for smaller applications: e.g. for measuring the BOD (biological oxygen demand) of waste water [KIM ET AL., 2003].

Whereas engineers are just beginning to contribute to the development and application of MFC, a rather huge community of (micro-)biologists is working and publishing in the field. Thus, a lot of work is attributed to the microorganisms and their potential use in MFC (cf. [RABAEY ET AL., 2005]). In a younger publication was reported, that more than 35 bacteria strains were isolated and genetically identified, showing activity in MFC [LOGAN ET AL., 2005].

Main reason for the reluctance of technicians and engineers are obviously the low currents (just some mA) and power (some mW), which are generated by and reported for MFC (cf. [RABAEY ET AL., 2005]). Though, electrode areas of up to some 100 cm^2 are reported. Nevertheless, for such low energy densities there are surely applications with low energy demand or maybe for larger cells, giving a higher absolute power. Just this should be the driver to look for some technical aspects, besides the microbiological ones.

2 Microbial Fuel Cells

2.1 General Design

A MFC uses microorganisms and their activities to transform chemical energy directly (e.g. from organic compounds and/or indirectly from light) into electrical energy. The configuration of a typical MFC ist shown in Fig. 1. In general it has two chambers (or compartments) with electrodes: an anode, which acts as electron acceptor, and a cathode, which uses the electrons for a redox reaction. In the anodic chamber, where reducing (anaerobic) conditions are prevailing, microorganisms oxidise substrates which are inherently present or supplementally added – generating electrons and protons. In the cathodic chamber oxidising (aerobic) conditions are predominating. The electrodes give a different potential, which could be derived by an external resistance or circuit. The two chambers are typically separated, either by an ion (i.e. cation) exchange membrane or by a salt bridge (cf. Fig. 2 – left side).

However, also one-chamber cells exist, where the two parts are not physically separated, but by the placement of the electrodes in a distance of several 10 cm in different layers of a water body (cf. Fig. 2 – right side).

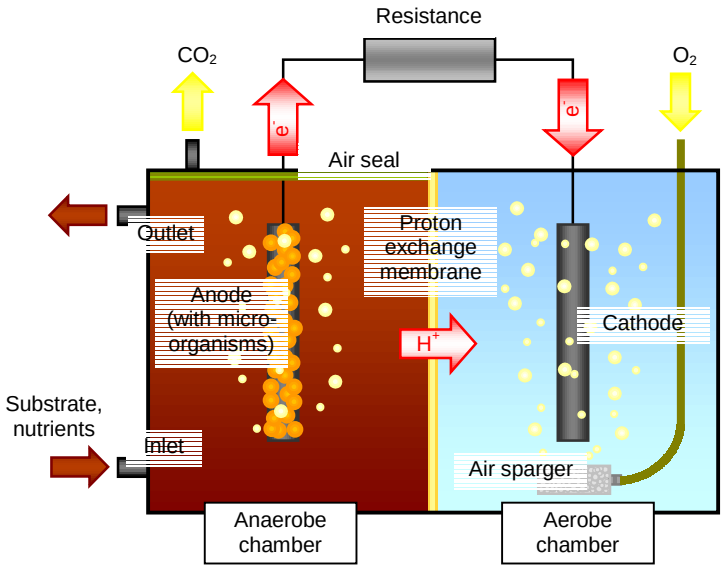

Fig. 1: Configuration of a typical MFC (main components and material flows)

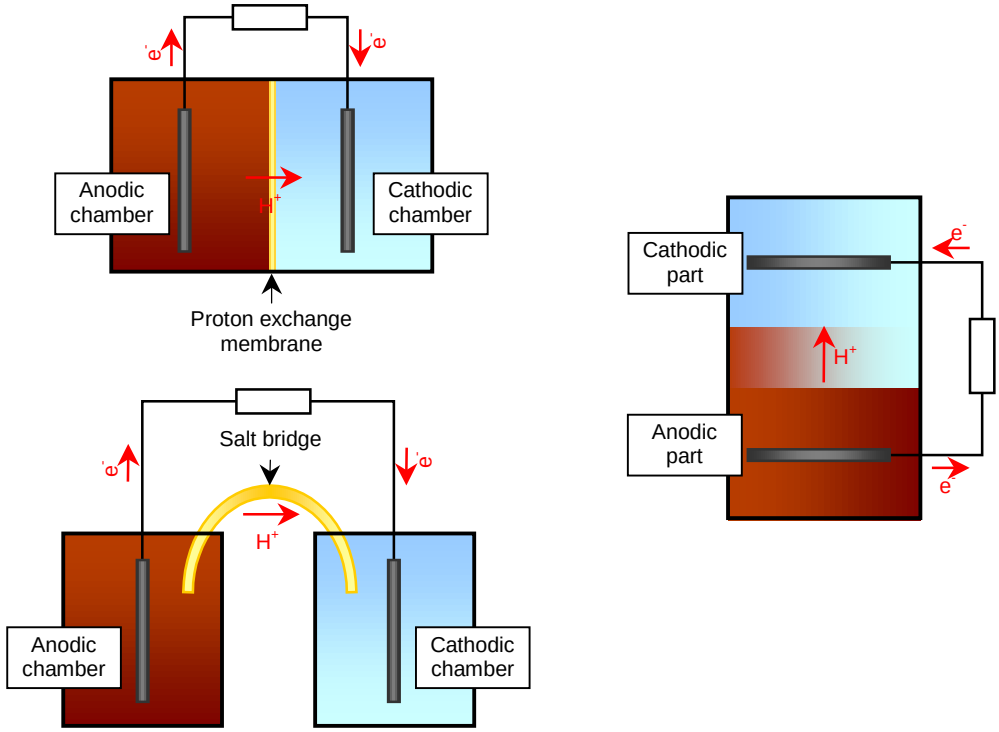

Fig. 2: Schematic views of different types of MFC (two-chamber assemblies on the left side; one-chamber assembly on the right side)

2.2 Microbial Species

There are a few microbiological systems, which are electrochemically active, i.e. they transfer the electrons directly to the anode without any mediator (i.e. electrochemical or biocatalytic support), e.g. some *Shewanella*, *Aeromonas*, *Pseudomonas* as well as *Geobacteraceae* and *Rhodoferax* species (cf. [BOND ET AL., 2002], [LOGAN ET AL., 2005] etc.). Those species have electrochemically active membrane-bound compounds, e.g. cytochrome, which can transfer electrons to materials outside the cell [RABAEY ET AL., 2005].

However, in many MFCs mediators or electron shuttles in the bulk solution are used to implement or facilitate the electron transfer. This can be natural occurring compounds, e.g. humic acids or anthraquinone, or synthetic substances including dyes and metallorganics [DU ET AL., 2007].

Tab. 1 gives an overview of different microorganisms and substrates used in MFC.

Tab. 1: Microorganisms and substrates used in MFC (according to [HOLTMANN, 2005] and [DU ET AL., 2007])

Microorganism	Substrate (energy source)
Actinobacillus succinogenes	Glucose
Aeromonas hydrophila	Acetate
Alcaligenes faecalis, Enterococcus gallinarum, Pseudomonas aeruginosa (as consortium)	Glucose
Anabaena variabilis	(Light source)
Clostridium beijerinckii	Starch, glucose, lactate, molasses
Clostridium butyricum	Starch, glucose, lactate, molasses
Desulfovibrio desulfuricans	Sucrose
Desolfuromonas acetoxidans	Acetate
Erwinia dissolven	Glucose
Escherichia coli	Glucose, sucrose
Geobacter metallireducens	Acetate, benzoate
Geobacter sulfurreducens	Acetate
Gluconobacter oxydans	Glucose
Klebsiella pneumoniae	Glucose
Lactobacillus plantarum	Glucose
Micrococcus cerificans	n-Hexadecane
Proteus mirabilis	Glucose
Proteus vulgaris	Mono- and disaccharides
Pseudomonas aeruginosa	Glucose
Rhodoferax ferrireducens	Glucose, xylose, sucrose, maltose
Saccharomyces cerevisiae	Glucose
Shewanella oneidensis	Lactate
Shewanella putrefaciens	Lactate, pyruvate, acetate, glucose
Streptococcus lactis	Glucose
Synechococcus sp.	(Light source)

2.3 Electrode Reactions

- Cathodic Reaction

The potential of the cathode is determined by those ions, which are reduced first (at the lowest potential). At the cathode, electrons are transferred, which are released at the anode. The solved oxygen is the electron acceptor.

$O_2 + 4\ H^+ + 4e^- \rightarrow 2\ H_2O$ (E_0 = 1.23 V, E_0' = 0.82 at pH 7)

This reaction is strongly pH dependent and is defining the potential. The potential is depending on the oxygen concentration at the cathode surface and is therefore limited by oxygen diffusion (transport). Thus, the velocity of the cathodic reaction affects the inner resistance of the cathodic half cell. To minimise that inner resistance, cathode area or aeration could be increased.

To get a better electron conversion at the cathode, other cathodic reactions could be used, e.g. with potassium hexacyanoferrat(III), which gives larger power output of MFC [SHANTARAM, 2005]. However, this is a toxic substance.

$[Fe(CN)_6]^{3-} + e^- \rightarrow [Fe(CN)_6]^{4-}$ (E_0' = 0.36 V)

Also the cathode material determines the achievable potential. (Furthermore substance overpotentials have to be considered.) Compared to graphite (which was used in the experiments discussed below) platinum has a higher cathodic potential of about 150 mV for the reduction of oxygen. An increased cell power output could be realised by an increased cathodic potential or a decrease of overpotential. Both are pH dependent and could be affected by electrode shape and surface. The cathodic potential can be directly determined by the cathode material or by introduced ions. The following equations give the standard potential of relevant material or ions [SCHWISTER, 1999].

$Fe^{3+} + e^- \rightarrow Fe^{2+}$ (E_0 = 0.77 V)

$Pt^{2+} + 2\ e^- \rightarrow Pt$ (E_0 = 1.20 V)

$MnO_2 + 4\ H^+ + 2\ e^- \rightarrow Mn^{2+} + 2\ H_2O$ (E_0 = 1.28 V)

$Au^+ + e^- \rightarrow Au$ (E_0 = 1.68 V)

Platinum is evidently a good cathodic material. But, the utilization is not recommendable, because of the extreme costs and the large overpotential (Platinum is – like all metals – hydrophilic, which supports formation of a water layer on the surface. That layer strongly restricts H^+ transport to the cathode, thus causing a large overpotential.)

- Anodic Reaction

Aerobic bacteria use oxygen as electron acceptor to mineralise organic compounds and to obtain energy. Though, oxygen is at the terminal end of a long respiration series. In anoxic milieu alternative electron acceptors are used for the oxidation of organic substances. There, the electron acceptor with the largest redox potential of the corresponding redox couple is used first. For this, also presence (solubility) and energy gain have to be considered to assess the probability of the reaction. Tab. 2 summarises information concerning possible electron acceptors. To compare the different biochemical processes, extremely simplified reaction formula are assumed. The organic substance is expressed by the empirical formula $(CH_2O)_{106}(NH_3)_{16}(H_3PO_4)$ [PRACHT, 2001].

Tab. 2: Characteristical parameters of different electron acceptors (according to [BASELT, 2006] and [PRACHT, 2001])

Redox couple	Redox potential at pH 7 E_0' [V]	Gibbs free energy ΔG [kJ/mol $(CH_2O)_{106}(NH_3)_{16}(H_3PO_4)$]
0,5 O_2/H_2O	+ 0,82	- 3190
NO_3^-/N_2	+ 0,74	-3030
Mn^{4+}/Mn^{2+}	+ 0,34	-2920
Fe^{3+}/Fe^{2+}	+ 0,76 (at pH 2)	-1330
$Fe(OH)_3/Fe^{2+}$	+ 0,20	
SO_4^{2-}/H_2S	- 0,22	-380

In sediments, not disturbed by turbulences, a stratification is formed in zones, in which at first nitrate, then manganese(IV), iron(II), sulphate and finally CO_2 is reduced [KEMMLER, 2000].

As alternative electron acceptor some anaerobic bacteria can indeed also use the anode. At certain potentials the anode is the energetically more advantageous electron acceptor compared with those mentioned in Tab. 2. Thus, in MFC with that effect electrons could be obtained directly at the anode.

The bacteria cultivated in MFC are predominantly dissimilative sulphate reducers. Some of these bacteria are able to exercise extra-cellular electron transport (cf. 2.2). It can be assumed, that in the sediment samples, used in the experiments, sulphate reducing bacteria species are present. Some of those bacteria (referred to in 2.2) are common in anaerobic sediments.

3 First Simple Experiments

3.1 Simple Experimental Set-up and Materials

For the first preliminary experiments the very simple set-up described in [BOND ET AL., 2002] was used in principle. A cylindrical container, with a volume of about 50 l and a height of about 50 cm, was filled with (anaerobic) sludgy sediment to a height of about 25 cm. This was taken from the Zwickau pond

"Schwanenteich" ("Swans Lake") from a depth of about one metre. On the sediment layer, tap water was poured, to give a total height of sediment and water of about 45 cm. The experimental set-up is illustrated in Fig. 3.

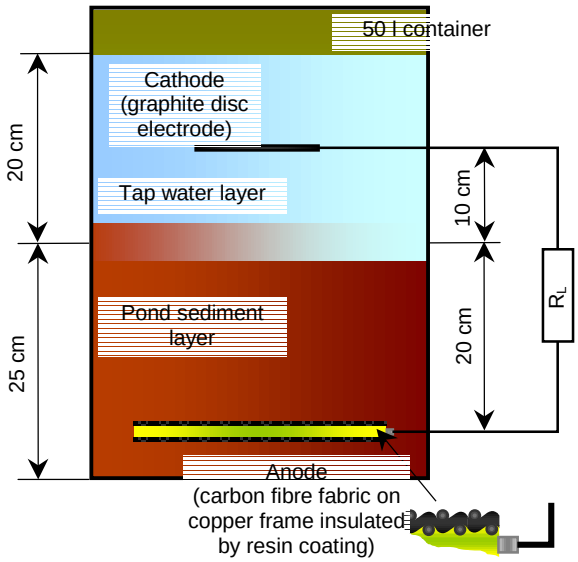

Fig. 3: Experimental set-up (one-chamber cell with pond sediment and tap water)

The anode with an area of about 400 cm^2 (consisting of carbon fibre fabric mounted on an insulated copper frame) was placed about 5 cm from bottom (i.e. with another 20 cm of sediment above it). Up to four graphite disc electrodes (with an area of about 140 cm^2 each) where used as cathode in the tap water, about 10 cm above the sediment layer. During the first tests only temperature, pH and electrode voltage over a high resistance were continuously measured (Fig. 4). Electrode voltage was registered by a data acquisition system (CASSY-C module 667814, Leybold Didactic GmbH) every 5 minutes.

The cathode was aerated during the whole test. The anode sediment was fed once with a glucose solution.

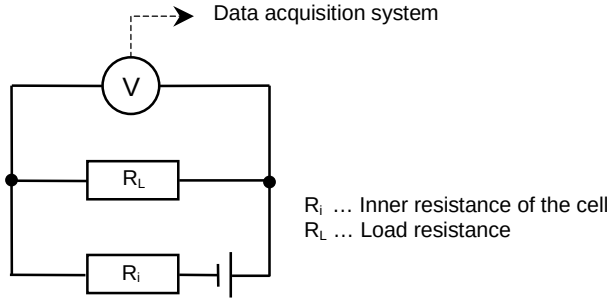

Fig. 4: Electrical flow scheme for the simple test MFC [SPIEGEL, 2006]

3.2 Results and Discussion

In Fig. 5 the terminal electrode voltage between cathode and anode is depicted for a 27 days test. This voltage is a good indicator of cell and individual electrode voltage behaviour, because already after some four days cathode voltage was practically constant. (In some comparable experiments, cathode voltage was about 0.4 V to 0.5 V, anode voltage about - 0.1 V to - 0.2 V [BASELT, 2006].)

The water pH was almost constant during the test at a value of 7.5.

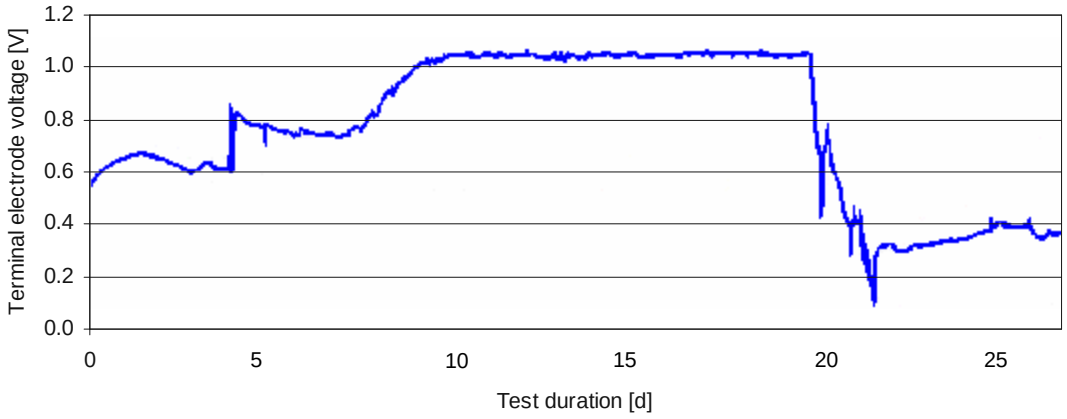

Fig. 5: Terminal electrode voltage of test MFC during a 27 days test with pond sediment and tap water [SPIEGEL, 2006]

During the first four days a relatively stable electrode voltage difference of about 0.6 V was measured. This might obviously be the result of electrochemical reactions – both on cathode and on anode. Microbial metabolism in the anaerobic sediment has just to be re-established after disturbing pond milieu conditions and adapting to the glucose substrate. In the almost pure tap water ("free of microorganisms" and substrate) – i.e. at the cathode – microbial activity is very probably negligible, at least not or poorly detectable.

To find out, whether the voltage stagnation is a problem of microbial growth lag or a problem of having not enough electrode transfer area, at day four, three further cathode electrodes were mounted, giving now a fourfold area compared to the beginning. After a sharp, but logically not fourfold, increase to about 0.8 V, voltage again remained constant or even dropped slightly for another three to four days. Thus cathode (microbial and) electrochemical behaviour came to a certain stable state. It obviously does not very much affect the real microbial mechanisms and derived voltages.

Only then, after about eight test days the voltage difference increased again to about 1 V and remained on that level for about further eight days. Referring to the two preceding step-wise constant periods, that voltage increase obviously hints to a metabolism at the anode (in the anodic part, i.e. the sediment). Indeed metabolism of anaerobic species really starts and stabilises only after lag times of some five to ten days. A further hint for that metabolism was also given by the examination of the sludgy sediment after the sharp drop of voltage at day 19. A smell of hydrogen sulphide (or of fouled eggs) indicated the anaerobic microbial activity. However, the pH value of about 6.5 showed also, that this might not be a stable anaerobic milieu and possibly due to intrusion of oxygen into the sediment. This might be caused by the mass transfer and diffusion of oxygen from the water above into the sediment pore water, due to agitation and aeration at the cathodes.

Further problems arose from the partly destruction of the insulation at the anode electrode frame, leaving copper frame spots just blank. This might be probably mainly caused by the anaerobic milieu conditions, maybe also by moving in the sediment. The copper spots might affect the cell either by short cutting the electrical circuit or releasing some toxic copper ions or by both simultaneously.

Though, it was tried to dilute the substrate (giving some small improvements in voltage and pH value), the large amount of oxygen, introduced in the anodic part with the diluting water, consequently led to a further voltage drop, apparently to a total non-recoverable state.

In general the first preliminary experiments gave the reassurance, that even very simple constructions and natural biomass (microorganisms) with simple substrates can produce a usable voltage difference. Improving the substrate feeding and aeration conditions as well as cell construction should further stabilise the process. Obviously an electrode area increase will improve the cell current output. It has yet to be studied, in which manner (progression) and to which extent. In addition, the electrode material and surface (e. g. for microbial growth or adsorption) has to be investigated definitely.

However, a further aspect has to be reflected, when the cell should produce usable electrical current and power: the inner resistance of the cell. For the reported set-up the inner resistance is the sum of the resistance resulting from the medium between the electrodes and the transition resistance of the electrodes themselves. Using similar electrodes transition resistances can be considered as remaining constant for different but analogous set-up. The inner resistance caused by the medium between the

electrodes $R_{i,m}$ could be derived from the following parameters and resulting with equation (1) in the given values:

- electrical conductivity of the used tap water: $\kappa_W \approx 0.487$ mS/cm
- electrical conductivity of the sediment (pore water): $\kappa_S \approx 1.22$ mS/cm
- cathode area (single side): $A_C \approx 70$ cm^2 or 280 cm^2 (for 4 electrodes)
- anode area (single side): $A_A \approx 200$ cm^2
- cell length in tap water ("cathodic part"): $l_W \approx 10$ cm
- cell length in sediment ("anodic part"): $l_S \approx 20$ cm
- inner resistance $R_{i,m} \approx 375$ Ohm or 155 Ohm (for 4 electrodes)

with: $$R_{i,m} = \frac{l_W}{\kappa_W \cdot A_C} + \frac{l_S}{\kappa_S \cdot A_A} \quad (1)$$

With a further decrease of cell lengths (chamber sizes) to the half each, i.e. 5 cm in (cathodic) tap water and 10 cm in (anodic) sediment, the inner resistance caused by conduction in the medium could also be reduced to about the half. However, even this will only result, with the measured voltages, in electrical currents of less than 0.2 mA, and therefore also only in an electrical power of less than 0.05 mW. Obviously a lot has to be done on reducing cell inner resistance and possibly dimensions.

Even then, the utilisation possibilities seem to be limited to very small applications (both in size and in power).

4 Summary and Conclusions

Main types and aspects of microbial fuel cells, as design, main components, microbial species and possible mediators were discussed. After some 40 years of investigation which was even intensified in the last 15 years, a number of microorganisms were found to be active in MFC. While the potential and expectations are large, the actual applications are restricted to small laboratory (or possibly pilot) scale demonstrations. Main reasons are the low electrical currents (of some mA) and power output (of some mW) at electrode areas up to 100 cm^2.

However, with a very simple one-chamber design (adapted from literature), tests were carried out with sludgy pond sediment and tap water in a 50 l container with electrode areas of 140 cm^2 (or fourfold) for the cathode and 400 cm^2 for the anode and an electrode distance of about 30 cm (10 cm in water and 20 cm in sediment). Into the anode part glucose as substrate was added. The electrode potential increased with the cathode area up to 1 V, after a lag time of some 8 days. But, the cell voltage output was not stable, obviously due to inhibition reactions at the anode, caused either by oxygen intrusion and/or toxic metal ions. Because of the relatively high inner cell resistance electrical current or power generation was not measured.

Though just simple and preliminary, some main general conclusions could be derived from the experiments:

- Increase of electrode surface is essential to increase at least voltage and maybe power; but it might not necessarily lead to a proportional increase in cell current and power. Also electrode resistance and double or diffusion layers as well as microbial (or biochemical) milieu conditions have to be considered.
- Determination and measurements of inner cell resistance is obligatory to find out an optimum of cell efficiency and cell size as well as, whether the cell will at all work as stable power source.

Options could be:

- a two-chamber cell with a membrane or porous material as a diffusion barrier with a large resistance for mass (material) flow, i.e. restricting mixing and concentration equalisation of cathodic and anodic chamber electrolytes or
- a two-chamber cell with a salt bridge also with a membrane or diffusion barrier.

However for both options the additionally introduced separating elements should also have very low electrical resistances. Therefore the width (area) of the elements and electrical conductivities of the

electrolytes (salt bridge) should be maximised, whereas length of salt bridge, membrane or barrier thickness (or permeability) and mass flows should be restricted to the necessary minimum.

For further tests the two-chamber cell with salt bridge and membrane barrier was selected. In this variant, cell performance and stability do not as strongly depend on the membrane characteristics alone as they do in a two-chamber cell with membrane separator.

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