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THE ROLE OF METHANOL IN MICROBIAL FUEL CELLS

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Several new technologies based on renewable energy resources are to be developed nowadays. Fuel cells are well-known examples and their enhancement is one of the most important goals of the scientists worldwide. In this work the operation of two fuel cells were compared, which are different in some principles: the microbial fuel cell (MFC) and the direct methanol fuel cell (DMFC). The MFC is a bioreactor converting chemical energy of organic compounds to electrical energy by catalytic reactions of microbes under anaerobic conditions. In the DMFC the liquid methanol (CH_3OH) is oxidized in the presence of water at the anode generating CO_2, H^+ ions and the electrons that travel through the external circuit as the electric output of the fuel cell. The aim of this work was to decide and clarify the role of methanol. Based on the experiments we found that – although the microbes were able to form methanol – the electron flow was the result of the metabolic breakdown of substrates by the microbes in the MFCs.

Keywords: Microbial fuel cell, Direct methanol fuel cell, Microorganisms

Introduction

Microbial fuel cells are electrochemical systems which convert chemical energy directly into electrical energy by microorganisms. In our laboratory multi-culture (mesophilic anaerobic sludge) and mono-culture (*Shewanella putrefaciens)* MFCs were studied. In both systems it seemed sensible to investigate whether the electron transfer in the MFCs occurs according to the "classical" and expected microbiological way or according to the mechanism described in the direct methanol fuel cells, since methanol may be formed during the metabolism of both MFC cultures studied.

In *direct methanol fuel cells* (DMFC) methanol is supplied as an energy source and a polymer membrane is used to separate the two chambers and as an electrolyte. Its scheme is shown in *Fig. 1*. The system eliminates the need for a fuel reformer and allows pure methanol to be used as a fuel.

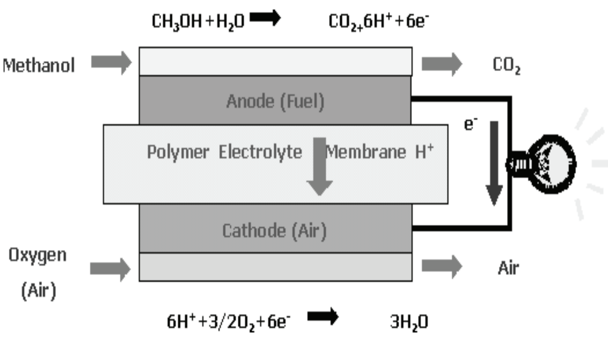

Figure 1: Schematic diagram of a direct methanol fuel cell

The pure methanol is mixed with steam and fed directly into the cell at the anode. Here the methanol is converted to carbon dioxide and hydrogen ions by the catalyst located on the anode. The electrons are then transported through an external circuit to produce electricity (before returning to the cathode) while the hydrogen protons pass across the electrolyte to the cathode, as it occurs in a standard PEM fuel cell. At the cathode the protons and electrons combine with oxygen to produce water [1-3].

The *microbial fuel cells* (MFCs) have generated considerable worldwide interest in recent years. Classic MFCs have two chambers; an anaerobic anode chamber and an aerobic cathode chamber. Microbes in the anodic cell oxidize the substrates generating electrons and protons in the process. Electrons are attracted by the anode and are transported to the cathode through an external circuit (wire), while protons are passing through the membrane and enter the cathode cell where they combine with oxygen to form water [4-8].

Metabolic pathways of microbial consortia converting biomass to acetate include three main biochemical steps [9]:

- hydrolysis of polymeric substances into smaller molecules and residues
- acid formation where not only acidic compounds, but hydrogen, CO_2 and alcohols (methanol!) are formed
- acetogenic phase

The microbial consortia works in the biogas fermenter according to the scheme *(Fig. 2)*, but supplemented with the final steps where acetate and/or $CO_2 + H_2$ are converted to biogas. However this system might be able to produce electric energy, as well. The hundreds of various strains work together in close symbiotic way. In the intracellular space a central NADH → NAD transformations occur during the process providing free electrons [9]. Methanol, however, might be formed as well, as a by-product of the metabolism.

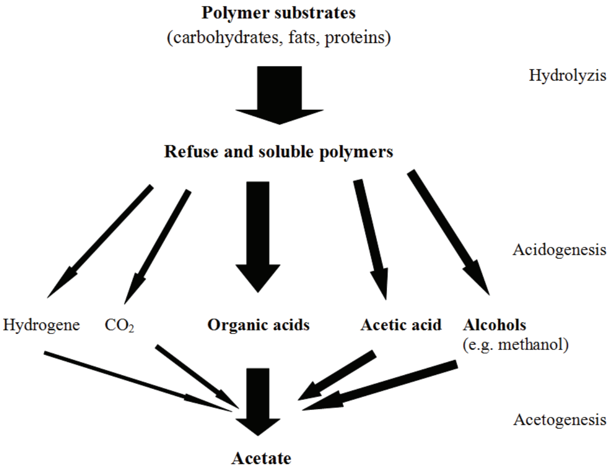

Figure 2: Metabolic routes from biomass to acetate

Shewanella putrefaciens is a Gram-negative, facultative anaerobic bacterium. It has the ability to reduce iron and manganese, hence it can use iron and manganese as the terminal electron acceptor in the electron transport chain [10-15].

Metabolic pathway of *Shewanella putrefaciens* might also include a route to form methanol during the metabolism [16], as it can be seen in *Fig. 3*.

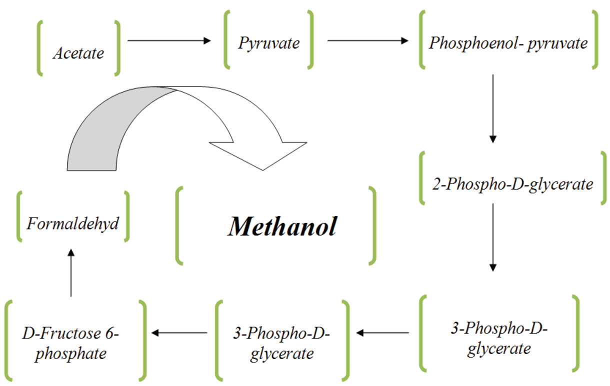

Figure 3: Metabolic pathway of *Shewanella putrefaciens*

In our work it was questioned whether it is truly the metabolic breakdown of the substances by the microorganisms that results in electrons or not. Since methanol formation cannot be entirely excluded in both systems, an electrocatalytic oxidation might take place in the anode space where – according to our assumption – electrons and protons are generated from *methanol*, and the flow of these electrons can be detected by our data collecting system. In this case we cannot talk about MFC rather about a direct methanol fuel cell.

Materials and methods

A two-chamber microbial fuel cell shown in *Fig. 4* was designed and built in our laboratory. The fuel cell had 240 ml anode and cathode chamber volume. In the anode cell graphite electrode and in the cathode space graphite electrode shot by platinum were applied. The surface of the cathode was 46 cm^2 and the surface of the anode was chosen to be first 49 cm^2 and then 91 cm^2. The two cells were separated by a Nafion 0125 type proton selective membrane with the surface of 25 cm^2. The fuel cell was placed in a bio-thermostat in order to keep it at the constant desired temperature. Effectiveness of the cells were determined as electrical power ($P = V \cdot I$) calculated from the measured voltage (V) and the current ($I = V/R$) calculated by the known 10 Ω resistance (R) built in the circuit. The voltage transmitted by the cell was measured and stored by a computerized data collecting system using LabView 8.5 software.

Figure 4: Picture of the used laboratory equipment

In the MFC the liquids in both cells were possible to circulate and stir. In the cathodic cell air was entered continuously into the distilled water by a pump to ensure aerobic environment, while N_2 was sparged through the anodic cell to assure the anaerobic conditions. The MFC reactor was initially inoculated with anaerobic sludge (from a local working biogas plant) in case of the multiculture system, and *Shewanella putrefaciens* in the monoculture system. Then the microorganisms started to operate in the cell and they were allowed to adapt the actual conditions.

Shewanella putrefaciens was grown on the nutrients summarized in *Table 1* [13, 14].

Table 1: The applied nutrients

Nutrients	Concentration (g/100ml)
Meat extract	0.3
Peptone	0.5
Agar	1.5

Results

The aim of this work was to decide and clarify the role of methanol in MFCs. Therefore experiments were carried out in both MFCs by mesophilic anaerobic sludge and *Shewanella putrefaciens,* where the effect of methanol added on the power generation was determined.

The *operation of the multicultural system* was studied and it has turned out that MFC was able to work reliably and generate power for a long period of time (over 60 hours) [17]. The voltage data observed were ~5 mV, while the power density value was around 1 mW/m^2, which was increased up to 2.0–5.1 mW/m^2 by adding nutrients like glucose and acetate.

Based on these experiences another serial of experiments was designed and conducted: methanol was added into the anodic cell *(Fig. 5)*.

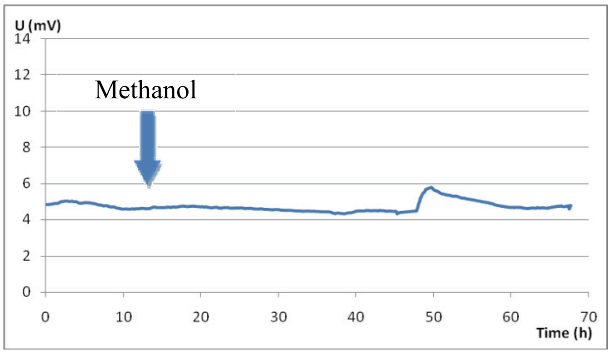

Figure 5: The effect of methanol on the voltage data at multicultural MFC

As it can be seen there was no effect at all on the voltage data, which confirmed that the equipment operates as a MFC.

In the first experiments with the microbial fuel cell operated with the bacteria strain *Shewanella putrefaciens* growth curve was studied *(Fig. 6)*. We found that at least seven days were necessary to reach the optimal microbe number, this is the minimal adaptation period.

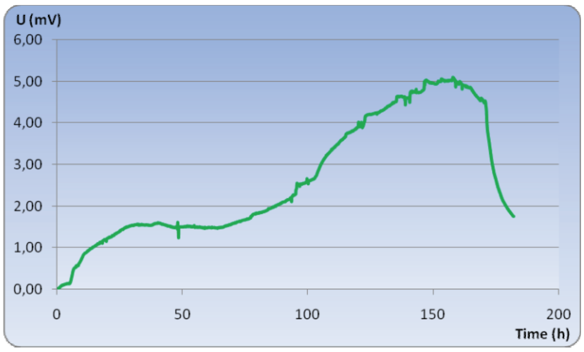

Figure 6: Growth curve of *Shewanella putrefaciens*

Following the necessary incubational stage, the effect of nutrient addition was investigated. First glucose solution was added in the system. – (0.5% final) glucose concentration in the anode space. According to the expectations, the voltage values transmitted by the system showed a sudden increase as an effect of the extra nutrients. This can be clearly seen in *Fig. 7*.

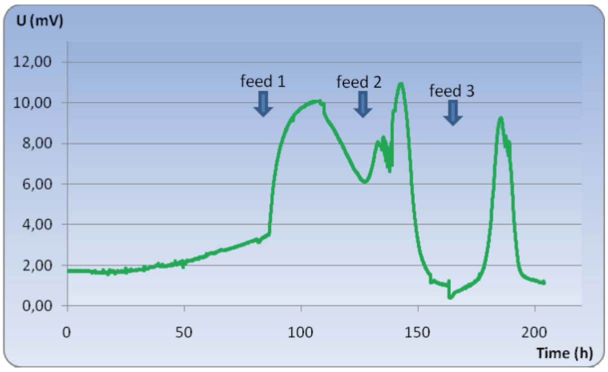

Figure 7: The effect of glucose supply on the voltage data at monocultural MFC

Due to the received data it could not be stated for sure whether the electrons and protons were produced directly by the microorganism from the given nutrients or by the produced methanol. Methanol might also be produced from the added nutrients and the electrons and protons could be then formed in the electrocatalytic transformation of the methanol catalysed by undefined micro polluters present in the system. Therefore, further measurements should be carried out to decide which one of the two options really happens.

As a next step, the effect of the methanol as nutrient solution on the electron production was studied. In this case the amount of the methanol given to the anode chamber was also selected so that the glucose concentration was 0.5% in the liquid phase.

The vital parameters of the fuel cell, such as temperature, cell mass, etc. were monitored and kept constant to reach a fully grown up culture similar to the one previously studied.

As it is seen in *Fig. 8*, the voltage values achieved by the cell significantly decreased right after the methanol was added to the system.

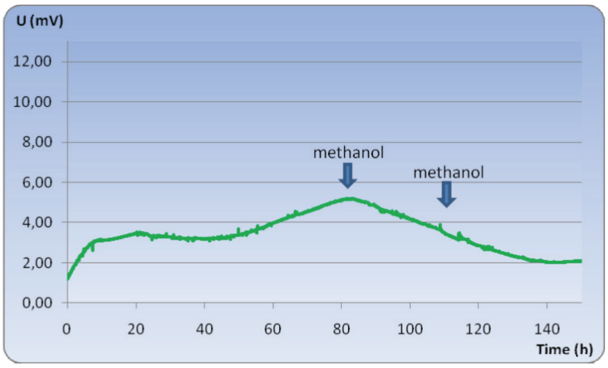

Figure 8: The effect of methanol on the voltage data at monocultural MFC

The data indicate that methanol as a nutrient had a negative effect on the operation of the system. Therefore the methanol cannot be used by the microorganisms for their own metabolic processes.

The determined values show that after adding the methanol solution to the system a decline can be observed instead of stagnation in the voltage data. Hence it is possible that an inhibition phenomenon occurs. In the case of *Shewanella putrefaciens* bacterium, the electrochemical activity of the microorganisms is restrained by methanol.

If methanol could be produced by the microbe the measured voltage would be expected to increase proportionally as an effect of the extra methanol in the system. However in our case, the opposite happens, the process of metabolic increase can be observed in the microbial fuel cells. Therefore it can also be stated that micro polluters that could help the electrocatalytic oxidation of the methanol are not present in the system.

Conclusion

The aim of our investigation was to decide if our systems were MFCs or DMFCs. In our work it was questioned whether it is truly the metabolic breakdown of the microorganisms that results in electron flow.

The values determined show that after adding the methanol solution to the systems there was no effect (multicultural system) or a decline could be observed instead of the voltage stagnation (monocultural system). Thus, the experimental results proved that neither of our systems could be DMFC, but they really work as MFCs.

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