

MICROBIAL FUEL CELLS

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Abstract

Microbial fuel cells (MFC) are a promising technology for sustainable production of alternative energy and waste treatment. A microbial fuel cell transformation chemical energy in the chemical bonds in organic compounds to electrical energy through catalytic reactions of microorganisms under anaerobic conditions.

It has been known for many years that it is possible to generate electricity directly by using bacteria to break down organic substrates.

Key words: *microbial fuel cells (mfc), biosensor, wastewater treatment*

1. INTRODUCTION

Microbial production of electricity may become an important form of bioenergy in future because MFCs offer the possibility of extracting electric current from a wide range of soluble or dissolved complex organic wastes and renewable biomass.

Microbial fuel cells (MFCs) have emerged in recent years as a promising yet challenging technology. In a MFC, microorganisms interact with electrodes using electrons, which are either removed or supplied through an electrical circuit (Rabaey et al., 2007). MFCs are the major type of bioelectrochemical systems which convert biomass spontaneously into electricity through the metabolic activity of the microorganisms. MFC is considered to be a promising sustainable technology to meet increasing energy needs, especially using wastewaters as substrates, which can generate electricity and accomplish wastewater treatment simultaneously, thus may offset the operational costs of wastewater treatment plant (Lu et al., 2009).

MFCs can be classified into three subgroups: catalytic, enzymatic, and microbial. Since the turn of the century, the research on microbial fuel cells (MFCs) has experienced rapid increases. MFCs are unique in their ability to utilize microorganisms, rather than an enzyme or inorganic molecule, as catalysts for converting the chemical energy of feedstock directly into electricity (Rismani-Yazdia 2008).

Over the past years, MFCs as a new source of bioenergy have been extensively reviewed. Substrate is important for any biological process as it serves as carbon (nutrient) and energy source. The efficiency and economic viability of converting organic wastes to bioenergy depend on the characteristics and components of the waste material. (Angenent and Wrenn, 2008). (Pant et al., 2010) in their review article on all substrates that have been used in MFCs so far. The substrate influences not only the integral composition of the bacterial community in the anode biofilm, but also the MFC performance including the power density and Coulombic efficiency (CE) (Chae et al., 2009).

MFCs often consist of two compartments, the anode and cathode, which are often separated by a proton-exchange membrane (PEM) (Fig. 1). The anode chamber contains microorganisms that oxidize the available substrate (i.e., the electron donor). The anaerobic oxidation is coupled with liberation of electrons which are transported through the cellular respiratory chain ultimately to the anode. Substrates used in MFC research vary from sugars and organic acids such as glucose or acetate to complex polymers such as starch and cellulose. Domestic, industrial, and animal waste streams have been used as feedstock for generating electricity in MFCs (Rismani-Yazdia 2008).

The other main type of bioelectrochemical systems is the microbial electrolysis cell (MEC) which is a modified MFC for generating hydrogen from acetate and other fermentation end products by electrohydrogenesis.

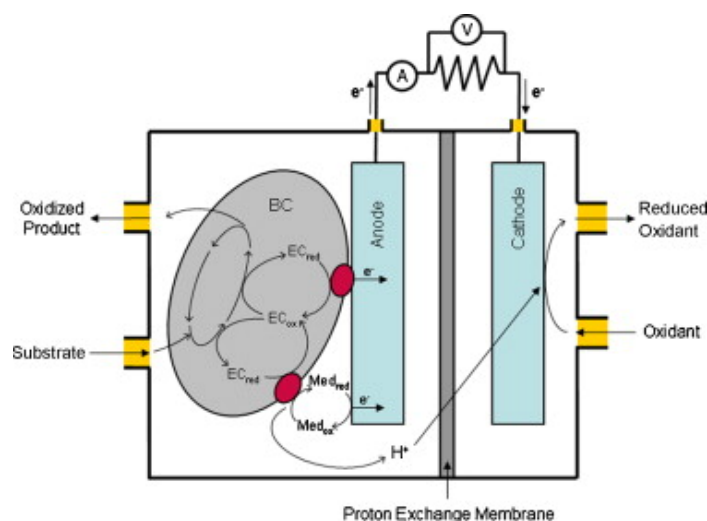


Fig.1. A schematic of a microbial fuel cell containing a model bacterial cell (BC). Electron transport involves oxidized and reduced electron carriers (ECred and ECo_x), and mediators (Medox and Medred).

Soluble artificial mediators are often applied to enhance the electron transfer from living cells to an anode in microbial fuel cells. Recently, was reported that the *Candida melibiosica* 2491 yeast strain possesses electrogenic properties and can be used as a biocatalyst in yeast-based fuel cells even in the absence of artificial mediators. To enhance the generated electrical power, the potential application of several organic compounds as mediators in a *C. melibiosica*-based fuel cell was examined. The choice of compounds was based upon observed cyclic voltammetry reversible electrochemical behavior at potentials appropriate for mediated electron transfer. Among the studied mediators, methylene blue, methyl orange, methyl red and neutral red significantly increased the current and power outputs in comparison with those obtained with a mediatorless yeast-based fuel cell (Babanova S. et al., 2011).

The improvement of the electron transfer from the microorganisms to the anode is considered to be one of the most important factors for increasing the biofuel cell efficiency. In study of Hubenova et al. (2011), significant improvement of the yeast-biofuel cell output was achieved by application of Ni-modified carbon felt anodes. In this study, the electrocatalytic properties of new nanomodified carbon materials were investigated. Nickel-iron and nickel-iron-phosphorous nanostructures was electrodeposited on carbon felt by means of pulse plating technique. The produced materials was analyzed for cytotoxicity and applied as anodes in a double-chamber mediatorless yeast-biofuel cell. The use of all modified electrodes resulted in increase of the biofuel cell outputs in comparison with those obtained with non-modified carbon felt; however, higher maximum power density values, exceeding up to 5-folds that of the control, was achieved with NiFeP-carbon felt anodes. The observed electrocatalytic effects were connected with the particular elemental content, size distribution, and morphology of modified materials as well as with a hypothesis for switching on adaptive mechanisms as a response to Ni and Fe presence, resulting in facilitated electron transfer across the cell membrane (Hubenova et al. 2011).

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In their article Mitov et al. mention that microbial electrolysis cells (MECs) provide an innovative bioelectrochemical approach for hydrogen production using microorganisms as biocatalysts. The development of cost-effective cathodes for near-neutral pH and ambient temperature conditions is the

most critical challenge for the practical application of MEC technology. In this study their, the electrocatalytic properties of electrodeposited onto carbon felt NiFe-, NiFeP- and NiFeCoP-nanostructures towards HER in neutral and weak acidic solutions they studied. The voltage needed to initiate hydrogen production and the current production rates have been estimated from obtained linear voltammograms. The developed composite materials possess much higher catalytic activity than bare carbon felt. The highest current production rate corresponding to $1.7 \pm 0.1 \text{ m}^3\text{H}_2/\text{day}/\text{m}^2$ was achieved with NiFeCoP/carbon felt electrodes. In addition, the applied modifications result in improvement of the corrosion resistance. Obtained by the authors results indicate that Ni-based nanomodified materials are promising electrocatalysts for HER in near-neutral electrolytes and could be applied as cathodes in MECs (Mitov, M. et al., 2012).

2. MICROBES USED IN MFCS

Many microorganisms possess the ability to transfer the electrons derived from the metabolism of organic matters to the anode. A list of them is shown in Table 1 together with their substrates. Marine sediment, soil, wastewater, fresh water sediment and activated sludge are all rich sources for these microorganisms (Niessen et al., 2006 and Zhang et al., 2006). These publications are discussed the screening and identification of microbes and the construction of a chromosome library for microorganisms that are able to generate electricity from degrading organic matters (Logan et al., 2005, Holmes et al., 2004 and Back et al., 2004) (Zhuwei Du et al., 2007)

Table 1. Microbes used in MFCs (Zhuwei Du et al., 2007)

Microbes	Substrate	Applications
<i>Actinobacillus succinogenes</i>	Glucose	Neutral red or thionin as electron mediator (Park and Zeikus, 2000, Park and Zeikus, 1999 and Park et al., 1999)
<i>Aeromonas hydrophila</i>	Acetate	Mediator-less MFC Pham et al. (2003)
<i>Alcaligenes faecalis</i> , <i>Enterococcus gallinarum</i> , <i>Pseudomonas aeruginosa</i>	Glucose	Self-mediate consortia isolated from MFC with a maximal level of 4.31 W m^{-2} . Rabaey (2004)
<i>Clostridium beijerinckii</i>	Starch, glucose, lactate, molasses	Fermentative bacterium Niessen et al. (2004)
<i>Clostridium butyricum</i>	Starch, glucose, lactate, molasses	Fermentative bacterium (Niessen et al., 2004b and Park et al., 2001)
<i>Desulfovibrio desulfuricans</i>	Sucrose	Sulphate/sulphide as mediator (Ieropoulos et al., 2005a and Park et al., 1997)
<i>Erwinia dissolven</i>	Glucose	Ferric chelate complex as mediators Vega and Fernandez, (1987)
<i>Escherichia coli</i>	Glucose, sucrose	Mediators such as methylene blue needed. (Schroder et al., 2003, Ieropoulos et al., 2005a and Grzebyk and Pozniak, 2005)
<i>Geobacter</i>	Acetate	Mediator-less MFC Min et al. (2005)

<i>metallireducens</i>		
<i>Geobacter sulfurreducens</i>	Acetate	Mediator-less MFC (Bond and Lovley, 2003 and Bond et al., 2002)
<i>Gluconobacter oxydans</i>	Glucose	Mediator (HNQ, resazurin or thionine) needed Lee et al. (2002)
<i>Klebsiella pneumoniae</i>	Glucose	HNQ as mediator biomineralized manganese as electron acceptor (Rhoads et al., 2005 and Menicucci et al., 2006)
<i>Lactobacillus plantarum</i>	Glucose	Ferric chelate complex as mediators (Vega and Fernandez, 1987)
<i>Proteus mirabilis</i>	Glucose	Thionin as mediator (Choi et al., 2003 and Thurston et al., 1985)
<i>Pseudomonas aeruginosa</i>	Glucose	Pyocyanin and phenazine-1-carboxamide as mediator (Rabaey et al., 2004 and Rabaey et al., 2005a)
<i>Rhodoferrax ferrireducens</i>	Glucose, xylose, sucrose, maltose	Mediator-less MFC (Chaudhuri and Lovley, 2003 and Liu et al., 2006)
<i>Shewanella oneidensis</i>	Lactate	Anthraquinone-2,6-disulfonate (AQDS) as mediator (Ringeisen et al., 2006)
<i>Shewanella putrefaciens</i>	Lactate, pyruvate, acetate, glucose	Mediator-less MFC (Kim et al., 1999a and Kim et al., 1999b); but incorporating an electron mediator like Mn(IV) or NR into the anode enhanced the electricity production (Park and Zeikus, 2002)
<i>Streptococcus lactis</i>	Glucose	Ferric chelate complex as mediators (Vega and Fernandez, 1987)

3. WASTEWATER TREATMENT

The MFCs were considered to be used for treating waste water early in 1991 (Habermann and Pommer, 1991). Municipal wastewater contains a multitude of organic compounds that can fuel MFCs. The amount of power generated by MFCs in the wastewater treatment process can potentially halve the electricity needed in a conventional treatment process that consumes a lot of electric power aerating activated sludges. MFCs yield 50–90% less solids to be disposed of (Holzman, 2005). Furthermore, organic molecules such as acetate, propionate, butyrate can be thoroughly broken down to CO₂ and H₂O (Zhuwei, Du et al., (2007).

Wastewater from breweries has been a favorite among researchers as a substrate in MFCs, primarily because of its low strength. Besides, it is suitable for electricity generation in MFCs due to the food-derived nature of the organic matter and the lack of high concentrations of inhibitory substances (for example, ammonia in animal wastewaters) (Feng et al., 2008). Although the concentration of brewery wastewater varies, it is typically in the range of 3000–5000 mg of COD/L which is approximately 10 times more concentrated than domestic wastewater (Vijayaraghavan et al., 2006). It could also be an ideal substrate for MFCs due to its nature of high carbohydrate content and low ammonium nitrogen concentration (Pant, D. Et al., 2010).

Starch processing wastewater (SPW) contains a relatively high content of carbohydrates (2300–3500 mg/L), sugars (0.65–1.18%), protein (0.12–0.15%) and starch (1500–2600 mg/L), representing an important energy-rich resource, which can be potentially converted to a wide variety of useful products (Jin et al., 1998). SPW was used as a fuel to enrich a microbial consortium generating

electricity and current generation (0.044 mA/cm²) was coupled to a fall in COD from over 1700 mg/L to 50 mg/L in 6 weeks (Kim et al., 2004). Lu et al. (2009) operated a MFC with SPW containing 4900 mg/L of COD over four cycles and obtained a maximum voltage output and power density of 490.8 mV and 239.4 mW/m² in the third cycle. However, the CE was only 7%. They attributed this low CE to oxygen diffusion to the anode compartment resulting in oxidization of other electron acceptors, biomass production and fermentation (Pant, D. et al., 2010).

4. CONCLUSIONS

Microbial fuel cells are evolving to become a simple, robust technology. Certainly in the field of wastewater treatment, middle term application can be foreseen at market value prices. Provided the biological understanding increases, the electrochemical technology advances and the overall electrode prices decrease, this technology might qualify as a new core technology for conversion of complex substrates present in wastewaters to electricity in years to come.

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REFERENCES

- Angenent, L., B.A. Wrenn, Optimizing mixed-culture bioprocessing to convert wastes into bioenergy, Bioenergy, ASM Press, Herndon, VA, USA (2008), pp. 179–194
- Back, J., M.S. Kim, H. Cho, I.S. Chang, J. Lee, K.S. Kim, *et al.*, Construction of bacterial artificial chromosome library from electrochemical microorganisms, FEMS Microbiol Lett, 238 (2004), pp. 65–70
- Bond, D., D.E. Holmes, L.M. Tender, D.R. Lovley, Electrode-reducing microorganisms that harvest energy from marine sediments, Science, 295 (2002), pp. 483–485
- Bond, D., D.R. Lovley, Electricity production by *Geobacter sulfurreducens* attached to electrodes Appl Environ Microbiol, 69 (2003), pp. 1548–1555
- Chae, K.-J., M.-J. Choi, J.-W. Lee, K.-Y. Kim, I.S. Kim, Effect of different substrates on the performance, bacterial diversity, and bacterial viability in microbial fuel cells, Biores. Technol., 100 (2009), pp. 3518–3525
- Chaudhuri S., D.R. Lovley, Electricity generation by direct oxidation of glucose in mediatorless microbial fuel cells, Nat Biotechnol, 21 (2003), pp. 1229–1232
- Choi, Y., E. Jung, S. Kim, S. Jung, Membrane fluidity sensing microbial fuel cell, Bioelectrochemistry, 59 (2003), pp. 121–127
- Feng, Y., X. Wang, B.E. Logan, H. Lee, Brewery wastewater treatment using air-cathode microbial fuel cells, Appl. Microbiol. Biotechnol., 78 (2008), pp. 873–880
- Grzebyk M., G. Pozniak, Microbial fuel cells (MFCs) with interpolymers cation exchange membranes Sep Purif Technol, 41 (2005), pp. 321–328
- Holmes, D., D.R. Bond, R.A. O’Neil, C.E. Reimers, L.R. Tender, D.R. Lovley, Microbial communities associated with electrodes harvesting electricity from a variety of aquatic sediments, Microbial Ecol, 48 (2004), pp. 178–190
- Hubenova, Y., R. Rashkov, V. Buchvarov, S. Babanova, M. Mitov, Nanomodified NiFe- and NiFeP-carbon felt as anode electrocatalysts in yeast-biofuel cell, J Mater Sci (2011) 46:7074–7081

- Ieropoulos, I., J. Greenman, C. Melhuish, J. Hart, Comparative study of three types of microbial fuel cell Enzyme Microb Tech, 37 (2005), pp. 238–245
- Jin, B., H.J. van Leeuwen, B. Patel, Q. YU, Utilisation of starch processing wastewater for production of microbial biomass protein and fungal α -amylase by *Aspergillus oryzae*, Biores. Technol., 66 (1998), p. 201–206
- Kim B., H.J. Kim, M.S. Hyun, D.H. Park, Direct electrode reaction of Fe(III)-reducing bacterium, *Shewanella putrefaciens*, J Microbiol Biotechnol, 9 (1999), pp. 127–131
- Kim, B.H., H.S. Park, H.J. Kim, G.T. Kim, I.S. Chang, J. Lee, N.T. Phung, Enrichment of microbial community generating electricity using a fuel cell-type electrochemical cell, Appl. Microbiol. Biotechnol., 63 (2004), pp. 672–681
- Lee, S., Y. Choi, S. Jung, S. Kim, Effect of initial carbon sources on the electrochemical detection of glucose by *Gluconobacter oxydans*, Bioelectrochemistry, 57 (2002), pp. 173–178
- Liu, Z., J. Lian, Z.W. Du, H.R. Li, Construction of sugar-based microbial fuel cells by dissimilatory metal reduction bacteria, Chin J Biotech, 21 (2006), pp. 131–137
- Logan, B., C. Murano, K. Scott, N.D. Gray, I.M. Head, Electricity generation from cysteine in a microbial fuel cell, Water Res, 39 (2005), pp. 942–952
- Lu, N., S.-G. Zhou, L. Zhuang, J.-T. Zhnag, J.-R. Ni, Electricity generation from starch processing wastewater using microbial fuel cell technology, Biochem. Eng. J., 43 (2009), pp. 246–251
- Menicucci, J., H. Beyenal, E. Marsili, R.A. Veluchamy, G. Demir, Z. Lewandowski, Procedure for determining maximum sustainable power generated by microbial fuel cells, Environ Sci Technol, 40 (2006), pp. 1062–1068
- Min, B., S. Cheng, B.E. Logan, Electricity generation using membrane and salt bridge microbial fuel cells Water Res, 39 (2005), pp. 1675–1686
- Mitov, M., Elitsa Chorbazhiyska, Rashko Rashkov, Yolina Hubenova, Novel nanostructured electrocatalysts for hydrogen evolution reaction in neutral and weak acidic solutions, International Journal of Hydrogen Energy 37(2012), pp 16522–16526
- Niessen, J., F. Harnisch, M. Rosenbaum, U. Schroder, F. Scholz, Heat treated soil as convenient and versatile source of bacterial communities for microbial electricity generation, Electrochem Commun, 8 (2006), pp. 869–873
- Niessen, J., U. Schroder, F. Scholz, Exploiting complex carbohydrates for microbial electricity generation — a bacterial fuel cell operating on starch, Electrochem Commun, 6 (2004), pp. 955–958
- Pant, D., Gilbert Van Bogaert, Ludo Diels, Karolien Vanbroekhoven, A review of the substrates used in microbial fuel cells (MFCs) for sustainable energy production, Bioresource Technology, Vol. 101, 6 (2010), pp. 1533–1543
- Park D., J.G. Zeikus, Impact of electrode composition on electricity generation in a single-compartment fuel cell using *Shewanella putrefaciens*, Appl Microbiol Biotechnol, 59 (2002), pp. 58–61
- Park, D., J.G. Zeikus, Electricity generation in microbial fuel cells using neutral red as an electronophore Appl Environ Microb, 66 (2000), pp. 1292–1297
- Park, D., J.G. Zeikus, Utilization of electrically reduced neutral red by *Actinobacillus succinogenes*: physiological function of neutral red in membrane-driven fumarate reduction and energy conservation, J Bacteriol, 181 (1999), pp. 2403–2410
- Park, H., B.H. Kim, H.S. Kim, H.J. Kim, G.T. Kim, M. Kim, *et al.*, A novel electrochemically active and Fe(III)-reducing bacterium phylogenetically related to *Clostridium butyricum* isolated from a microbial fuel cell, Anaerobe, 7 (2001), pp. 297–306

- Park, D., B.H. Kim, B. Moore, H.A.O. Hill, M.K. Song, H.W. Rhee, Electrode reaction of *Desulfovibrio desulfuricans* modified with organic conductive compounds, *Biotechnol Tech*, 11 (1997), pp. 145–158
- Pham, C., S.J. Jung, N.T. Phung, J. Lee, I.S. Chang, B.H. Kim, *et al.*, A novel electrochemically active and Fe(III)-reducing bacterium phylogenetically related to *Aeromonas hydrophila*, isolated from a microbial fuel cell FEMS Microbiol Lett, 223 (2003), pp. 129–134
- Rabaey, K., J. Rodríguez, L.L. Blackall, J. Keller, P. Gross, D. Batstone, W. Verstraete, K.H. Nealon, Microbial ecology meets electrochemistry: electricity-driven and driving communities ISME J., 1 (2007), pp. 9–18
- Rabaey, K., N. Boon, M. Hofte, W. Verstraete, Microbial phenazine production enhances electron transfer in biofuel cells, *Environ Sci Technol*, 39 (2005), pp. 3401–3408
- Rabaey, K., N. Boon, S.D. Siciliano, M. Verhaege, W. Verstraete, Biofuel cells select for microbial consortia that self-mediate electron transfer *Appl Environ Microb*, 70 (2004), pp. 5373–5382
- Rhoads, A., H. Beyenal, Z. Lewandowski, Microbial fuel cell using anaerobic respiration as an anodic reaction and biomineralized manganese as a cathodic reactant, *Environ Sci Technol*, 39 (2005), pp. 4666–4671
- Ringeisen, B., E. Henderson, P.K. Wu, J. Pietron, R. Ray, B. Little, *et al.*, High power density from a miniature microbial fuel cell using *Shewanella oneidensis* DSP10, *Environ Sci Technol*, 40 (2006), pp. 2629–2634
- Rismani-Yazdi, H., Sarah M. Carver, Ann D. Christy, Olli H. Tuovinen, Cathodic limitations in microbial fuel cells: An overview, *Journal of Power Sources*, Vol. 180, Issue 2, 1 June 2008, pp. 683–694
- Schroder, U., J. Nieben, F. Scholz, A generation of microbial fuel cells with current outputs boosted by more than one order of magnitude, *Angew Chem Int Ed*, 42 (2003), pp. 2880–2883
- Sofia Babanova, Yolina Hubanova, and Mario Mitov, Influence of artificial mediators on yeast-based fuel cell performance, *Journal of Bioscience and Bioengineering*, Vol. 112 No. 4, 379–387, 2011
- Thurston, C., H.P. Bennetto, G.M. Delaney, J.R. Mason, S.D. Roller, J.L. Stirling, Glucose metabolism in a microbial fuel cell. Stoichiometry of product formation in a thionine-mediated *Proteus vulgaris* fuel cell and its relation to Coulombic yields, *J Gen Microbiol*, 131 (1985), pp. 1393–1401
- Vega C., I. Fernandez, Mediating effect of ferric chelate compounds in microbial fuel cells with *Lactobacillus plantarum*, *Streptococcus lactis*, and *Erwinia dissolvens*, *Bioelectrochem Bioenerg*, 17 (1987), pp. 217–222
- Vijayaraghavan, K., D. Ahmad, R. Lesa, Electrolytic treatment of beer brewery wastewater, *Ind. Eng. Chem. Res.*, 45 (2006), pp. 6854–6859
- Zhang, E., W. Xu, G. Diao, C. Shuang, Electricity generation from acetate and glucose by sedimentary bacterium attached to electrode in microbial-anode fuel cells, *J Power Sources*, 161 (2006), pp. 820–825
- Zhuwei Du, Haoran Li, Tingyue Gu, A state of the art review on microbial fuel cells: A promising technology for wastewater treatment and bioenergy, *Biotechnology Advances* Vol. 25, Issue 5, 2007, Pages 464–482