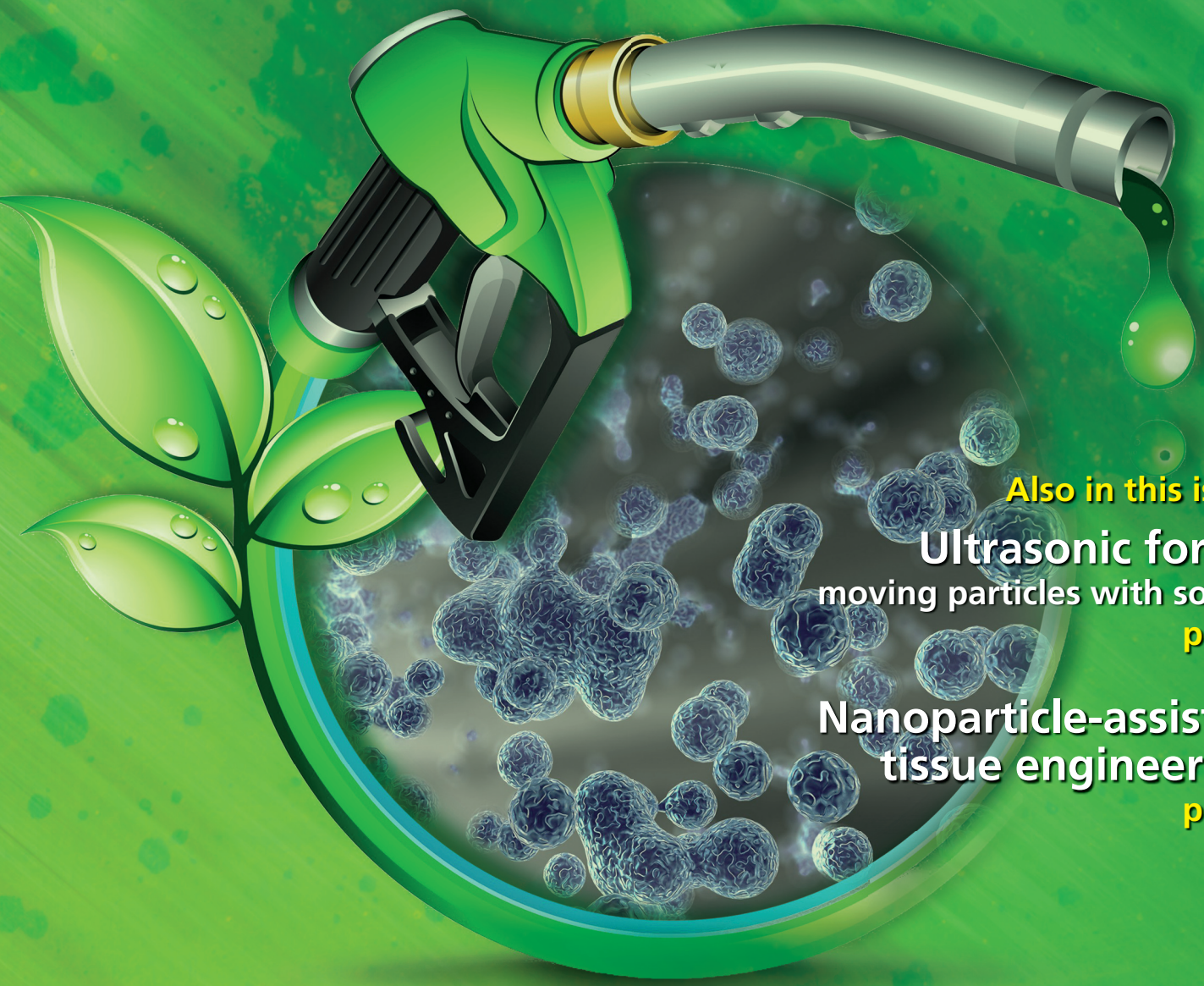
Volume 22 • June 2010 • 20 €

BIO TECH international

THE EUROPEAN MAGAZINE FOR THE LIFE SCIENCES INDUSTRY

Microbial electrosynthesis:
from electricity to biofuels



Also in this issue

Weekly news updates now on www.biotech-online.com

Microbial electrosynthesis
From electricity to biofuels and biochemicals

Korneel Rabaey*, Angela Johnstone, Alexander Wise, Suzanne Read, René A Rozendal

Advanced Water Management Centre, The University of Queensland, Brisbane QLD4072, Australia; *Corresponding author email: k.rabaey@uq.edu.au

Abstract
Electricity is one of the most widely available forms of energy and can be produced abundantly and sustainably. Microbial electrosynthesis is a new research field, in which renewable electricity can be used to drive microbial production processes. This allows us to produce commodity chemicals by electrically tapping into the plethora of useful biofuels and biochemicals microorganisms can make.

Breathing minerals to survive

To understand how microorganisms can use or produce electrical current, we need to understand how they deal with electrons. All living organisms gain energy by oxidizing an electron donor and reducing an electron acceptor, hence life is driven by electrochemistry. The resulting electron flow, over a potential difference, provides effective power (Watts) to the organism. Typically, organisms will use this power to generate ATP and NAD(P)H, the universal energy and electron carriers for cells. Exactly 100 years ago, it was recognized that microorganisms can link this electrical "circuit" to the outside of the cell – microorganisms achieved the reduction of an electrode (platinum wire) in their environment. In the late 80s it was then discovered that microorganisms effectively manage to transport electrons out of the cell, enabling them to use solid minerals as electron sink. The concept of "extracellular electron transfer" was born.

Extracellular electron transfer (EET) refers to the transport of electrons in and out of the cell, in order to support microbial respiration. Most widely studied is the microbial reduction of solid-state electron acceptors, such as iron and manganese oxides, and also electrodes. These mineral conversions are crucial for the biogeochemical cycles in nature. There are two main strategies for EET, so called direct and indirect (6). Direct transport involves membrane associated protein complexes, predominantly cytochromes, and potentially also nanowires. The latter have been discovered only recently, essentially they are conductive pili ("wires") produced by the cell, in order to transport electrons from the cell to the mineral – or an electrode. The cell is indeed wiring up to its solid electron acceptor. Indirect transport involves the production or use of soluble molecules that can transport the electrons to and from the cell. These molecules are called "electron shuttles", and examples are phenazines, humics and sulfur species. It is important to understand that while many organisms have the capability to perform EET, not many are truly successful – therefore, assisting microorganisms by providing them with electron shuttles provides a means to

artificially achieve EET. In addition, it has been shown that long term culturing of mixed populations or pure cultures lead to increased capability in electron transfer.

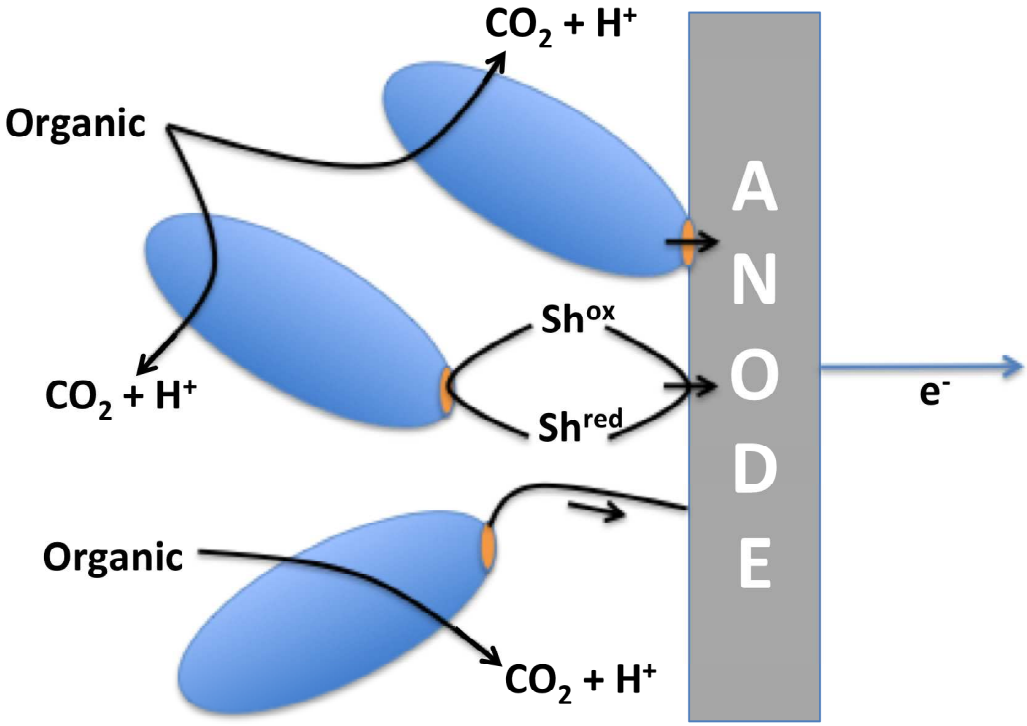


Figure 1. Overview of the different proposed electron transfer pathways from microorganisms to electrodes, using organic compounds as electron donor. Cells can grow attached to the surface of the anode, and transfer electrons through membrane bound complexes (orange symbols) to the electrode, possibly in conjunction with conductive pili/wires, that connect the cell with the anode over longer distances. Alternatively, cells can reduce an electron shuttle (Sh^{ox}) while being in suspension or not in direct contact with the electrode. The reduced shuttle (Sh^{red}) is then oxidized at the anode.

From minerals to electrodes

Interestingly, long before the role of EET in biogeochemical cycles was discovered, it was observed that microorganisms can interact with electrodes. The most studied interaction is that with an anode, where microorganisms can catalyse the oxidation of organics to carbon dioxide, protons, and electrons. Such an electrode is called a bioanode and if linked to a cathode (where reduction occurs) a biocatalyzed electrochemical system is created. As early as 1962, Davis and Yarbrough used this concept to develop the “microbial fuel cell”, capable of using organic substrate for the production of electrical power (1). Indeed, linking microbial metabolism to a low potential anode and then conveying the harvested electrons to a high potential cathode generates net electrical power from the microbial decomposition of organic matter (Figure 2A). This concept has gained considerable momentum in the past few years, due to the interest in microbial fuel cells for energy recovery from wastewater (2). There are also niche applications, such as electricity generation at remote locations, powered by the microorganisms in marine sediments.

In 2003, microbial electrolysis cells were first described. If current is applied to the system instead of extracted, the cathode potential can be driven sufficiently low to electrolyse water (Figure 2B). This allows (i) hydrogen gas to be *indirectly*

produced from any organic feedstock and (ii) hydrogen production at far lower energy requirements than conventional electrolysis (3).

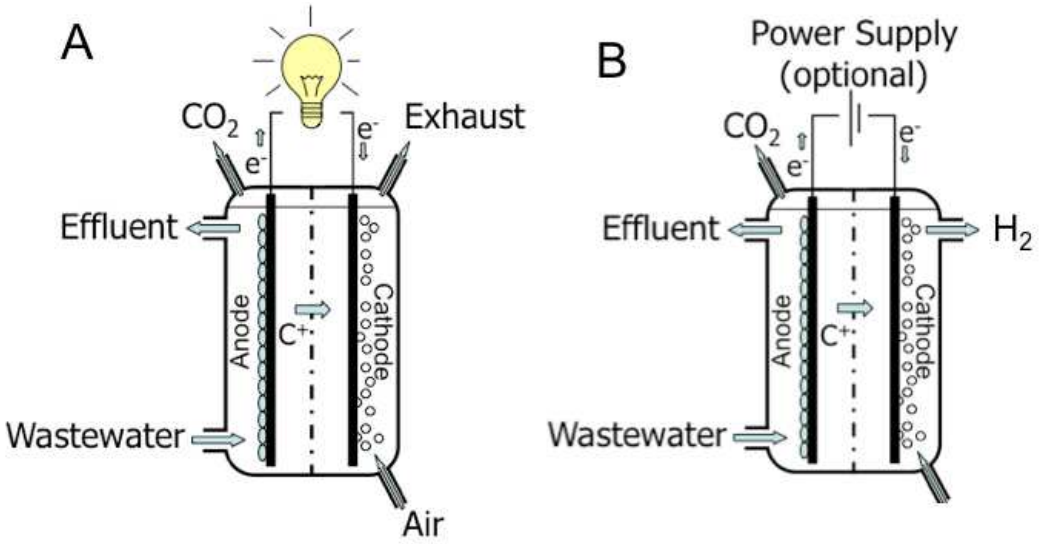


Figure 2. The microbial fuel cell (A) and the microbial electrolysis cell (B). In both cases, microorganisms catalyse the anode reaction. While for the microbial fuel cell, harvesting power is the key objective, for the microbial electrolysis cell valuable products (such as hydrogen) are the desired end product. To achieve the latter, power is in most cases added to the system. C^+: cations; e^-: electrons. Figure redrafted after Rozendal et al (7)

As anodes and cathodes can provide a highly controllable source of oxidizing or reducing power, respectively, they are increasingly used for the biodegradation of recalcitrant xenobiotics or nuisance compounds. Examples of cathodic reduction processes are the removal of nitrobenzene, azo dyes, nitrate and perchlorate, while anodic oxidation was used for the removal of 1,2-dichloroethane and sulfur species.

Coming up – Next Generation Bioelectrochemical Systems

Based on the microbial fuel cell and microbial electrolysis cell concepts, a number of bioelectrochemical production processes were recently put forward. An ion selective membrane typically separates the anode and cathode. In most cases, a cation exchange membrane is used, allowing cations to travel from anode to cathode while anions (like acetate) are retained in the anode. While about one proton is produced for every electron going in the electrical circuit, there are at present no membranes that can transport only protons towards the cathode. The cross-over of other cations such as sodium causes decreasing pH in the anode, and increasing pH in the cathode. Recently, this was exploited to produce alkaline solutions at the cathode (5). This would enable (mainly industry) to produce caustic on site, using the organics available in the wastewater as driver. As a side effect, cations such as sodium and potassium are removed from the wastewater, leading to lower salt discharges in the environment. Similarly, the observation that oxygen reduction at cathodes often leads to hydrogen peroxide formation has now enabled a new process for the production of peroxide, from wastewater. It can be expected that a whole range of microbial production processes, driven by bioelectrochemical current generation, evolve in the coming years.

Coming up – Microbial Electrosynthesis

Non-fossil fuel based production of fuels and chemicals is critical to their future supply. We point out two key aspects of importance:

(i) Electricity can now be produced virtually anywhere, in a sustainable manner. However, electricity is difficult to store at high density.
(ii) Microorganisms can use a tremendous variety of organic or inorganic electron donors to produce a plethora of attractive biofuels or biochemicals.

Considering the two above points, it is clear that a process linking electrical current to product formation is of considerable interest. This observation has lead to a new field of research: microbial electrosynthesis. This field addresses the use of microorganisms as catalysts on cathodes (i.e., biocathodes) to achieve electricity driven synthesis of chemicals and fuels. Recently, the first study linking solar electricity to product formation, starting from CO_2, was published (4).

While not always labelled this way, microbial electrosynthesis has been around for several decades. The first demonstration involved the use of electrical current to increase the glutamic acid yield during fermentation of glucose. Since then, the use of electrical current to modify fermentation pathways has been the main focus. For example, butanol or propionate was produced at higher yields during glucose fermentation when electrical current reduced the medium. In most cases, the link between the electrode and the microorganisms was established by adding a mediator, such as methyl viologen. The question, though, is whether electrons were effectively transported inside the cell, or NADH regeneration was hampered by the provided reducing power. In depth analysis of microbial metabolism and physiology in this context is warranted.

Rather than modifying fermentation pathways, Greg Zeikus' group used electrical current as the sole driver of microbial respiration. For example, they reduced fumarate to succinate at high efficiency by providing *Actinobacillus succinogenes* with electrical current and neutral red as electron shuttle. Cathodes can, as supplier of electrons, be compared with hydrogen gas as electron donor. A wide range of microbial conversions driven by hydrogen, such as biopolymer production from CO_2, and reduction of fatty acids to alcohols, are coming into the picture.

New perspectives for old processes.

Microbial electrosynthesis has been a dormant field for several decades. Pivotal for the development seen in the past few years were the discoveries that microorganisms can directly transfer electrons to electrodes, that they develop multilayered structures (biofilms) and that they improve over time when properly enriched. In the slipstream of the microbial development, improved reactor designs and the use of new materials have enabled developing microbial fuel cells and microbial electrolysis cells to pilot stage. While several hurdles are yet to be overcome, it appears that this technology will find its way to the market in the coming years. The development of microbial electrosynthesis will benefit strongly from these industrial applications. The main hurdle today is again microbiology. The pathways for electron transfer towards microorganisms are poorly understood, and also the impact of material structure (topography) and properties (functional groups, charge density) needs considerable attention by researchers. Once a suitable interface between the cathode and the microorganisms is established, the existing technology can quite easily be adapted for this bioproduction.

One particularly interesting development will be the direct link between solar power and bioproduction. Microbial electrosynthesis principally allows producing biofuels and biochemicals directly on site from solar power. Hence, a method is created to generate valuable products, storing the solar power and making it transportable due to the high energy density that can be achieved. Based on energy densities of microbial photosystems and engineered solar technology, production yields per hectare per annum are potentially an order of magnitude higher than the existing alternatives such as algal fuels and particularly plant-based biofuels. Conversely, this development may boost the installation of solar panels, particularly in remote areas from which at present the transport of electricity is economically not feasible.

Acknowledgements
The research relating to this manuscript is supported by the Australian Research Council (ARC DP0879245) (KR), by a UQ Foundation Research Excellence Award (KR) and a UQ Postdoctoral Research Fellowship (RAR).

References

1. **Davis, J. B., and H. F. Yarbrough. 1962. Preliminary experiments on a microbial fuel cell. Science 137:615-616.**
2. **Logan, B., P. Aelterman, B. Hamelers, R. Rozendal, U. Schroder, J. Keller, S. Freguia, W. Verstraete, and K. Rabaey. 2006. Microbial fuel cells: methodology and technology. Environ. Sci. Technol. 40:5181 - 5192.**
3. **Logan, B. E., D. Call, S. Cheng, H. V. M. Hamelers, T. Sleutels, A. W. Jeremiasse, and R. A. Rozendal. 2008. Microbial Electrolysis Cells for High Yield Hydrogen Gas Production from Organic Matter. Environmental Science & Technology 42:8630-8640.**
4. **Nevin, K. P., T. L. Woodard, A. E. Franks, Z. M. Summers, and D. R. Lovley. 2010. Microbial electrosynthesis: feeding microbes electricity to convert carbon dioxide and water to multicarbon extracellular organic compounds. mBio 1:e00103-10. doi:10.1128/mBio.00103-10.**
5. **Rabaey, K., S. Bützer, S. Brown, J. Keller, and R. A. Rozendal. 2010. High current generation coupled to caustic production using a lamellar bioelectrochemical system. Environ. Sci. Technol. 44 4315-4321.**
6. **Rabaey, K., J. Rodriguez, L. L. Blackall, J. Keller, P. Gross, D. Batstone, W. Verstraete, and K. H. Nealson. 2007. Microbial ecology meets electrochemistry: electricity-driven and driving communities. ISME J 1:9-18.**
7. **Rozendal, R. A., H. V. M. Hamelers, K. Rabaey, J. Keller, and C. J. N. Buisman. 2008. Towards practical implementation of bioelectrochemical wastewater treatment. Trends in Biotechnology 26:450-459.**