Microbial fuel cell cathodes: from bottleneck to prime opportunity?

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ABSTRACT

Microbial fuel cells that can generate energy out of wastewaters are close to pilot scale testing. As such, MFC technology is complementary to methane generation due to the possibility to rapidly convert organic acids, polish effluents and work at low substrate concentrations. The main bottleneck perceived at the moment is the cathodic electron transfer. A variety of catalysts has been investigated for the direct transfer of electrons from the cathode to oxygen in the air. Overlooked in this context were bacteria. Bacteria could indeed be worthwhile to replace chemical catalysts. Moreover, their versatility enables us to not only target at oxygen, but also at nitrous oxides and contaminants as possible drivers of electricity generation, nutrient removal and bioremediation. This paper addresses several recent developments in MFC cathode research, and demonstrates that energy generation is but an aspect of this versatile technology.

Key words | biofuel cell, denitrification, electricity, reduction, renewable energy

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INTRODUCTION

Microbial fuel cells provide direct and efficient recovery of the energy comprised in electron donors (Rabaey & Verstraete 2005). Examples of electron donors are organics and reduced sulfur species, as present in wastewater. Bacteria oxidize the electron donors, and subsequently convey the electrons gained to an anodic electrode. From the anode, the electrons flow over a power user towards a cathodic electrode. At this cathode, electrons are transferred towards the terminal electron acceptor. To complete the charge balance, cations, preferably protons, flow from the anode to the cathode through an ion selective membrane. At present, these systems are mainly tested with artificial wastewaters. Based on acetate, Aelterman and coworkers (Aelterman *et al.* 2006) described a power generation equivalent to $258\,W\,m^{-3}$ anode compartment. When using real wastewater, the efficiencies of conversion generally tend to drop due to the more limited biodegradability of the organics present in sewage, the particulate nature of some of the organics and the presence of alternative electron acceptors (Rabaey *et al.* 2005). When considering the overall process, and not taking into account a limited biodegradability of the anodic substrate, the cathodic reaction is, aside from the flux of protons through the cation exchange membrane, the main bottleneck identified at the moment (Logan *et al.* 2006). In order to understand this issue, it is necessary to look at the basic processes that govern the performance of a cathode. Firstly, activation losses occur due to the imperfect catalysis when oxygen is reduced at the cathode. These losses can be described according to the Butler Volmer equation (Bard & Faulkner 2001):

$$i = i_0 \Big[e^{[(1-\beta)nF\frac{\eta}{RT}]} - e^{[(-\beta)nF\frac{\eta}{RT}]} \Big]$$

where i is the electron flux (A), i_0 the exchange current density (A), β a form factor, F Faraday's number (96485 C/mol), n the number of electrons exchanged and η the so-called overpotential (V). The equation learns that losses are dependent on the current density flowing through the electrode, and the intrinsic catalytic properties of the electrode, represented by the i_0 and β. In a recent article

(Rabaey *et al.* 2007) the extent of these losses in function of the current density is described.

Second, the cathodic process is also limited by the influx of electron acceptor towards the electrode, as it needs to diffuse through a boundary layer. Diffusion is determined by the bulk concentration of the electron acceptor, and the resulting concentration gradient, and the mixing conditions. Summarizing, the cathodic process is determined by the electrode surface, its catalytic properties, the mixing in the cathodic compartment and the concentration of the electron acceptor in the bulk liquid.

BACTERIA AS CATALYSTS FOR CATHODES

Oxygen is both in terms of redox potential and availability the foremost electron acceptor for MFCs. There are several issues when oxygen is used (Zhao *et al.* 2006), such as the high overpotential towards oxygen reduction at electrodes and the fact that oxygen has a limited solubility of about 8 mg O_2 per litre. Considering the issues raised in the introduction, mainly electrode catalysis and electrode surface are addressed here. The oxygen concentrations can generally not be increased as oxygen needs to diffuse from the air into a water film, the issues regarding mixing will be dependent on the water flows over the system but have not yet been studied. In order to improve the catalysis, platinum was often added to the cathode (Oh *et al.* 2004) which resulted in significant improvements versus non catalyzed cathodes. As platinum is an expensive and non sustainable catalyst, alternatives such as pyrolyzed iron (II) phtalocyanine (Zhao *et al.* 2005) were added to the cathode. The second issue, changing the electrode surface, has barely been addressed. Increasing the electrode surface can cause significant increases in power density by an MFC, even without catalysts present in the cathode. However, the level of power generation is still insufficient to run a viable process.

In order to see how bacteria could influence cathode catalysis, we have allowed the growth of a biofilm onto an open air cathode (Figure 1) that consisted of carbon tape, covered with a stainless steel current collector. The procedure to obtain this and the underlying mechanisms are not within the scope of this article and will be detailed elsewhere (Rabaey *et al.* in preparation; Freguia *et al.* in preparation).
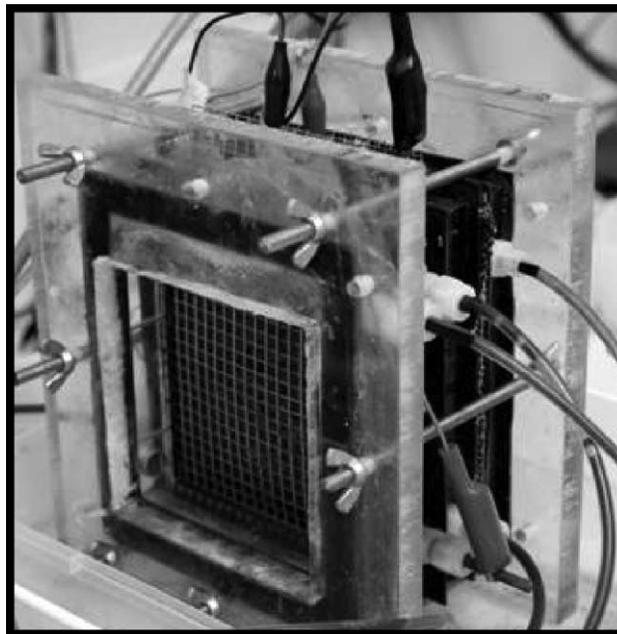

Figure 1 | Open air, biocatalized microbial fuel cells. The cathode comprises of a 1 mm thick carbon tape layer, covered by a stainless steel current collector. Effluent originating from the anode is recirculated over this cathode, which provides a polishing of the effluent and carry over of protons. Bacteria growing on the cathode function as biocatalyst when taking up the electrons originating from the cathode and using them to reduce oxygen.

When no bacteria are present at the cathode, the power output is negligible for these carbon tape based cathodes. After a period of operating the system with a mixed inoculum and conveying the anodic effluent over the cathode, the system generated notably more current than a non catalyzed control (Figure 2). The system was operated over 200 days, and a maximal stable power density (hour based) of 0.28 mA cm^{-2}, which is in the same range as the power densities obtained for open air cathodes catalyzed with platinum. Clearly, bacteria can improve the catalysis at MFC cathodes, by efficiently removing electrons from the surface. Moreover, the fact that the process could be sustained for over 200 days indicates the longevity of this approach.

NUTRIENT REMOVAL AS AN OPPORTUNITY FOR CATHODES IN MFC

Oxygen has the highest redox potential of the commonly available electron acceptors. However, by using oxygen as electron acceptor only oxidative processes at the anode can
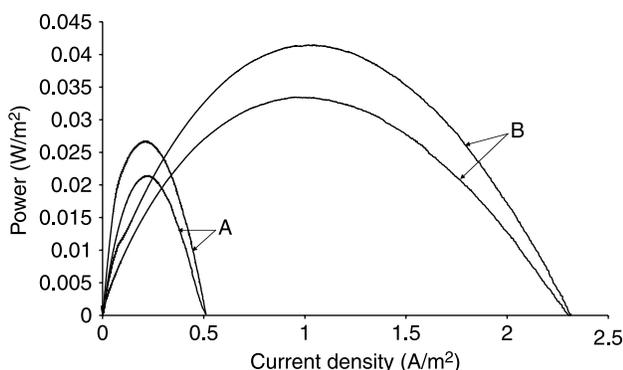
Figure 2 │ Polarization curves for a non-catalyzed (A) and biocatalyzed (B) carbon tape cathode in an open air configuration. A polarization curve expresses the attainable power in function of the current flowing through a system, in this case the microbial fuel cell. A maximal power of 42 mW per m^2 cathode surface could be obtained in this case.

be stimulated, which implies organic substrate and sulfide removal. Nitrogen is often present in problematic concentrations in wastewaters, and therefore needs to be removed as well as the organic substrates. This nitrogen is difficult to remove if the organic substrate concentrations are too low to sustain full denitrification.

When using a cathode as electron donor, the oxidation of the organic donor is physically separated from the reduction process. As such, additional electron donor can easily be added to the system by providing current on top of the organic substrate oxidation which occurs at the anode. A MFC anode will provide an effluent devoid of organics, but still rich in ammonia. This opens up the way for cathodic removal of nitrate, either directly on nitrate rich carbon poor wastewaters, or on anode effluents that underwent an intermediary nitrification step to convert the ammonium into nitrate or nitrite. Taking into account the theoretical considerations stated earlier in the introduction, reducing nitrate is also interesting from a catalytic point of view. The electron acceptor is readily available as solute, and bacteria have a high affinity for this substrate. Bacteria can link up their metabolism to the cathode, which improves the catalysis. Clauwaert and coworkers (Clauwaert et al. 2006) have recently described a MFC that linked up the oxidation of acetate with the reduction of nitrate at the cathode. No additional power was necessary, the system even generated useful power of up to 8 W m^{-3} net cathodic compartment (NCC) and removed up to 0.146 kg NO$_3^-$-N m^{-3} NCC d^{-1}.

Virdis and coworkers (Virdis et al. In preparation) nitrified the effluent of an acetate fed MFC anode in a passively aerated reactor. The effluent of the nitrification reactor was subsequently fed to the cathode compartment of the MFC. Strikingly, this enabled to generate substantially larger power outputs. The maximal power output obtained was 42 W m^3 net cathodic compartment (NCC) (23 W m^3 total cathodic compartment (TCC), corresponding to a removal of 0.41 kg NO$_3^-$-N d^1 m^3 NCC (0.22 kg NO$_3^-$-N d^1 m^3 TCC).

CATHODIC PROCESSES AS *THE* ADDED VALUE OF MFC?

Cathode driven processes carry a number of advantages:

- the supply of electron donors can be continuously controlled both in terms of current and potential
- no chemicals need to be added for electron supply, which omits the need for transport, storage, dosing and post-treatment
- the dosing of the electron donor occurs *in situ*. Due to the high surface area of the cathodic electrodes a disperse supply is possible
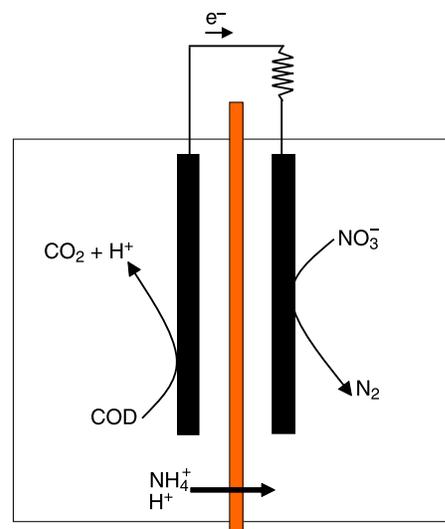

Figure 3 │ Schematic representation of cathodic denitrification, driven by the anodic oxidation of acetate. The anodic process delivers electrons at a potential which is low enough to harvest power at the external resistor and still allow for the cathodic process. This implies that denitrifying bacteria can use an insoluble electron donor with a potential of around 0 mV.
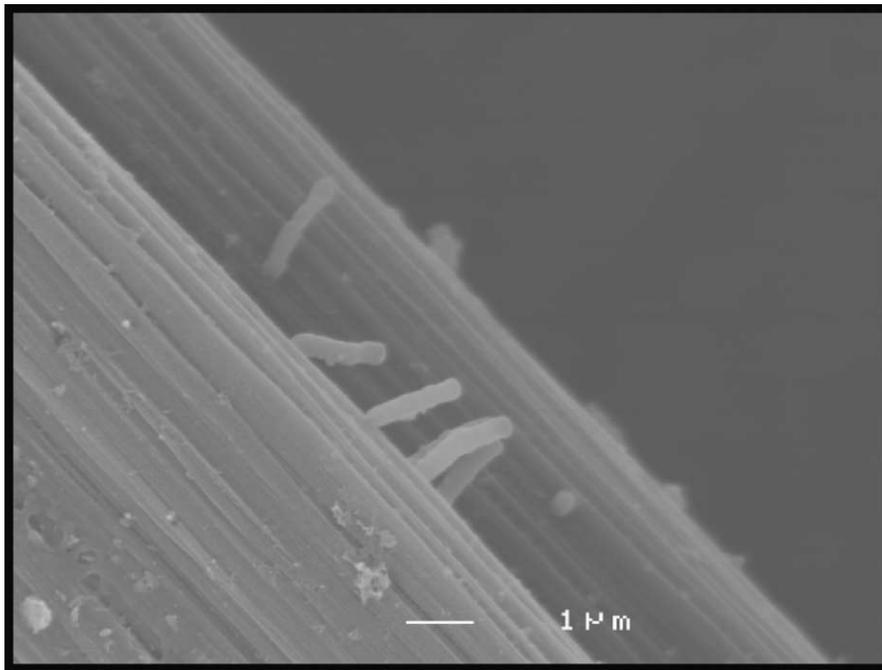
Figure 4 │ Scanning electron microscopy image of a carbon fibre on which bacteria attach perpendicularly. This demonstrates that the carbon fibre surface is too smooth for bacteria to adhere to. Functionalizing the surface or selecting alternative carbon based structures may alleviate this.

- exceptionally low values of the redox potential can be achieved on short term

Cathodes will find their way into a number of applications in the field of bioremediation. The possibility of perchlorate removal has been presented (Thrash et al. 2007), as well as the reduction of hexavalent uranium to the tetravalent form, which precipitates out on the cathode.

Several critical issues remain. Further work is certainly needed to improve the power output of the biocatalyzed cathodes. Both oxygen reduction and denitrification still occur at rates which are too low to warrant sufficient power production or nutrient removal in relation to existing technologies. Important in this context is the finding that the bacterial densities on the carbon tape are still very low (Figure 4). Strikingly, most of the bacteria exist as single bacteria, oriented perpendicularly towards the surface. This indicates that the bacteria have difficulty to attach to the very smooth carbon surface. Surface treatments, both through functionalizing or roughening, would possibly alleviate this low success rate for bacterial attachment. Also changing the materials choice to graphite increases the power output, due to the higher reactivity of

the surface and the higher conductivity of the material itself. Both measures can increase the bacterial densities on the surface and facilitate the conduction of the produced electrons – leading to higher current densities and decreased voltage losses.

Furthermore, in order to develop adequate biofilm driven processes, it is necessary to understand how bacteria receive electrons from electrodes. In a study by Thrash et al. (Thrash et al. 2007) hydrogen was being produced at the cathode, which was subsequently oxidized by the bacteria. Also the addition of redox shuttles (AQDS) enabled the reduction of perchlorate. This was substantially different than the findings of Gregory et al. (Gregory et al. 2004) who found that a hydrogen uptake negative mutant of Geobacter sp. was still able to retrieve electrons from the cathode.

CONCLUSIONS

Microbial fuel cells have in recent years primarily been oriented towards energy generation. Using bacteria both in

the anode and in the cathode compartment provides the opportunity to render the process more sustainable and cost efficient, as no catalysts need addition to the system. Moreover, tuning the cathodic process towards nutrient removal and contaminant removal creates a variety of novel applications that have merit by themselves – and not by the possible energy generated.

REFERENCES

Aelterman, P., Rabaey, K., The Palm, H., Boon, N. & Verstraete, W. 2006 Continuous electricity generation at high voltages and currents using stacked microbial fuel cells. *Environ. Sci. Technol.* **40**, 3388–3394.

Bard, A. J. & Faulkner, L. R. 2001 *Electrochemical methods: Fundamentals and applications*, 2nd edn. John Wiley & Sons, New York.

Clauwaert, P., Rabaey, K., Aelterman, P., De Schamphelaire, L., The Pham, H., Boeckx, P., Boon, N. & Verstraete, W. 2006 Biological denitrification driven by microbial fuel cells. *Environ. Sci. Technol.*, Accepted.

Gregory, K. B., Bond, D. R. & Lovley, D. R. 2004 Graphite electrodes as electron donors for anaerobic respiration. *Environ. Microbiol.* **6**, 596–604.

Logan, B., Aelterman, P., Hamelers, B., Rozendal, R., Schroder, U., Keller, J., Freguia, S., Verstraete, W. & Rabaey, K. 2006 Microbial fuel cells: Methodology and technology. *Environ. Sci. Technol.* **40**, 5181–5192.

Oh, S., Min, B. & Logan, B. E. 2004 Cathode performance as a factor in electricity generation in microbial fuel cells. *Environ. Sci. Technol.* **38**, 4900–4904.

Rabaey, K., Clauwaert, P., Aelterman, P. & Verstraete, W. 2005 Tubular microbial fuel cells for efficient electricity generation. *Environ. Sci. Technol.* **39**, 8077–8082.

Rabaey, K., Rodriguez, J., Blackall, L. L., Keller, J., Batstone, D. J., Verstraete, W. & Nealson, K. H. 2007 Microbial ecology meets electrochemistry: electricity driven and driving communities. *ISME J.* May 2007.

Rabaey, K. & Verstraete, W. 2005 Microbial fuel cells: Novel biotechnology for energy generation. *Trends Biotechnol.* **23**, 291–298.

Thrash, J. C., Vantrump, J. I., Weber, K. A., Miller, E., Achenbach, L. A. & Coates, J. D. 2007 Electrochemical stimulation of microbial perchlorate reduction. *Environ. Sci. Technol.* **41**, 1740–1746.

Virdis, B., Rabaey, K. & Keller, J. (In preparation) Microbial fuel cells for simultaneous carbon and nitrogen removal.

Zhao, F., Harnisch, F., Schroder, U., Scholz, F., Bogdanoff, P. & Herrmann, I. 2005 Application of pyrolysed iron(II) phthalocyanine and CoTMPP based oxygen reduction catalysts as cathode materials in microbial fuel cells. *Electrochem. Comm.* **7**, 1405–1410.

Zhao, F., Harnisch, F., Schroder, U., Scholz, F., Bogdanoff, P. & Herrmann, I. 2006 Challenges and constraints of using oxygen cathodes in microbial fuel cells. *Environ. Sci. Technol.* **40**, 5193–5199.