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Outlook: Research directions and new applications for BES

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22.1 BES RESEARCH – FOCUS ON THE APPLICATION

As the previous chapters in this book extensively demonstrate, there is substantial scope for application of BESs in the future. However, it is also clear that there is still a major need for ongoing and, in fact, expanded research in this area. This chapter will try to highlight some of the key areas where such R&D efforts could be concentrated on. We will deliberately take a broader view than just the fundamental scientific research since the successful application of this technology will require considerably more research and development work than is currently being undertaken. As with any new or re-discovered technology field, the fundamental principles and processes need to be reassessed to deliver

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an understanding of the underlying factors affecting the performance and the behaviour, before the technology can then be used for more applied research.

In this context, we argue that the BES area is now at the stage where the emphasis should be increased on applied research and development aspects. Basic scientific research should still be continued, though, but its directions could be more influenced by the application-oriented needs and challenges. Significant breakthroughs are likely possible in the pursuit of such activities.

22.2 FUNDAMENTAL RESEARCH DIRECTIONS

22.2.1 Understanding bioelectrochemical process fundamentals

There is no doubt that the fundamental research activities into BESs will continue, and that there is good justification for this ongoing effort. For one, the underlying processes in BESs are scientifically highly novel and in many ways still not well understood. Bacteria directly transferring electrons to and from a solid matrix pose quite a unique situation that has not been investigated thoroughly until fairly recently (see Chapters 4 and 5). Such biologically mediated processes can occur at the anode or cathode of a BES, with a range of substrates and products in different phases (gaseous, liquid, solid) and under many different conditions. The closest analogy for the anodic oxidation of organics is extracellular electron transfer towards insoluble metal oxides. Here, BESs offer the opportunity to gain a much more comprehensive insight into the physiology of extracellular electron transfer, as BESs allow to: (i) control the potential of the electron acceptor; (ii) control the flow/flux of electrons within the system; and (iii) to maintain chemically consistent conditions during the experimental period. We have barely scratched the surface of microbial physiology towards extracellular electron transfer, especially on the cathode side, and are likely to see a number of unexpected processes occurring at these electrodes.

One particular question that remains to be explored is the range of microorganisms capable of direct electron transfer, and the associated versatility in electron transfer strategies. This not only concerns different phyla of the bacterial domain, but most interestingly, also representatives of other domains, such as Archaea, fungi, etc. Recently, it was suggested that Archaea could directly receive electrons from cathodes (Cheng *et al.* 2009), while mediated electron transfer from a yeast to an anode was also established (Chiao *et al.* 2006). Are these organisms capable of direct electron transfer, or maybe able to use some assisted

transfer methods, such as mediators produced by other organisms within the biofilm? Their role has thus far been all but unexplored, and warrants further attention given the unique processes that some of the members of these domains are able to perform, e.g. methanogenesis. What role could they possibly play in an integrated consortium with bacterial cells? Given the highly specialized enzymes that some fungi have, they could possibly also contribute to the breakdown and electrochemical conversion of some of the more recalcitrant compounds, which is particularly attractive for BESs aiming at (lingo)cellulosic biomass as feedstock.

Furthermore, there is the equally fascinating science of the actual extracellular electron transfer mechanisms. Which roles do mediators or potentially nano-wires play and where are they actually most beneficial in an electrode-bound biofilm? How do they enable or affect the interactions between different microorganisms in the biofilm and the electrode itself? It has been suggested that bacteria can form a complex grid, electrically linking organisms over long distances (Ntarlagiannis *et al.* 2007). As is the case in many complex consortia, there is likely not one single transfer mechanism that is most efficient in all situations. In fact, there may well be a co-existence of several of these mechanisms in the electrochemically active biofilm, as indicated earlier by Rabaey and coworkers (Rabaey *et al.* 2004). We need to carefully explore the various factors that may influence the establishment of such mechanisms within the biofilm, which would most likely include a multitude of physical and chemical parameters, such as distance to the electrode, convective vs. diffusive mass transfer, electrical potential gradients within the biofilm, substrate and product gradients and their effects, such as the localized pH conditions, etc. Understanding extracellular electron transfer on a genomic and proteomic level will allow modifying organisms that were previously not capable of extracellular electron transfer, or introducing novel capabilities in electrochemically active bacteria.

Interestingly, many of these electrochemical processes and mechanisms may even occur in systems other than the BESs. One example that is potentially highly relevant is external electron transfer in fermentative anaerobic systems. It is generally accepted that fermenting organisms function best in very close proximity with hydrogen utilizing methanogens as the fermentation processes produce hydrogen (Batstone *et al.* 2006). However, given that hydrogen production and consumption is primarily a mechanism for electron transfer between these different synergistic partners, the question remains whether hydrogen is actually produced and transferred to the hydrogen-utilizing organisms, or whether they could just transfer the electrons directly from one cell to the neighbouring one. This would shift the process from 'interspecies

hydrogen transfer' to 'interspecies electron transfer'. Recent work by Ishii *et al.* has focused on the interaction between *Pelotomaculum* and *Methanothermobacter* (Ishii *et al.* 2005), which coaggregate using a pilus, suggested to be conductive (Gorby *et al.* 2006). Interestingly, such syntrophic associations can be highly specific between two organisms (Shimoyama *et al.* 2009), and as yet there is no information whether such specificity is upheld within BES biofilms. Beside this example, there might be numerous other systems where the extracellular electron transfer facilitates direct interactions between different organisms in a biofilm or also within flocs or cellular conglomerates.

22.2.2 Practically inspired fundamental research areas

There is also a range of practically inspired challenges to be explored on a more fundamental level. One such example is the selection and enrichment of acidophilic or alkaliphilic electro-active organisms that could operate well in an anode under very low pH or in a cathode at a high pH. From this perspective, fungi could again be attractive as many are known to have very low or high pH optima. Bacteria may be attractive due to their genetic tractability, allowing straightforward modification to achieve a desired process, e.g. bioproduction of chemicals at the cathode. This in turn could considerably help to operate BESs more efficiently due to the inherently strong proton production or consumption processes at the anode or cathode, respectively.

Another example in this context is the specific oxidation or reduction of metal ions to extract or at least immobilize them from contaminated soils and groundwater streams. Substantial work on the removal of uranium has been performed (Gregory and Lovley 2005). Further fundamental work needs to be undertaken to investigate the often complex redox processes of these metal ions within the complex matrix they are usually found in. These findings can then be tested again in practical applications, such as *in-situ* bio-remediation (see Section 22.6).

The use of selected isolates of microorganisms, or even genetically modified organisms (GMOs), could be a further fundamental development to address specific practical limitations, as elegantly discussed in Chapter 6. The application of this strategy will mainly be viable for the cathodic processes, given that the anodic reactions primarily consist of oxidation of organic substrates to CO₂ and water. This can be efficiently achieved by a wide range of organisms and is also suitable for use with non-sterile organic feeds, such as wastewater streams. Given the separation of the cathodic compartments through an ion-permeable membrane, the use of pure cultures or GMOs is certainly a practically relevant option, even when wastewater is used as the electron-supply in the anode. There may be a surprisingly large range of cathodic reduction processes possible.

One example might be the selective reduction of glycerol (typical byproduct or waste product of bio-diesel production) to 1,2- or 1,3-propanediol, which are widely used organic base chemicals. To be cost-effective, it is likely necessary to develop highly optimized cultures of organisms capable of these selective transformations, or even the creation of GMOs specifically suited for these processes. This approach will likely need a long-term, well-funded project that requires the close collaboration between highly experienced genetic engineering researchers and more application oriented biotechnologists or process engineers to achieve the required selectivity and turnover.

22.3 APPLIED RESEARCH OPPORTUNITIES

22.3.1 Contributions and limitations of current research activities

Given the proliferation of publications on MFCs and BES in the last few years (see Chapter 1), it is valuable to evaluate what aspects are covered well and what knowledge gaps exist. This is focused mainly on the more applied research papers as much of the literature in recent times is in this area.

From a practical viewpoint there have been a number of key innovations and breakthroughs made in the last few years. Some of the major ones include:

- the use of relatively low-cost materials for electrodes and membranes, such as graphite felt (Chaudhuri and Lovley 2003) or granules (Rabaey *et al.* 2005), carbon fibre brushes (Logan *et al.* 2007) or the Ultrex cation exchange membrane (Rabaey *et al.* 2003);
- development of open-air cathodes with metal catalysts (Cheng *et al.* 2006; Zhao *et al.* 2005) or even biologically catalysed (Clauwaert *et al.* 2007b);
- development of the Microbial Electrolysis Cell, aiming at hydrogen production (Liu *et al.* 2005c; Logan *et al.* 2008; Rozendal *et al.* 2006b);
- development of stacked MFC modules to gain higher voltages (Aelterman *et al.* 2006);
- discovery of denitrification processes in the cathode of BES, and biocathodes in general (Clauwaert *et al.* 2007a; Gregory *et al.* 2004);
- demonstration of selective sulfide oxidation to sulfur on anodes (Dutta *et al.* 2009a; Dutta *et al.* 2008; Rabaey *et al.* 2006);

In terms of process optimization, there have also been substantial achievements made related to improved designs with minimized distances between anode

and cathode as well as modifications in the materials and feed solutions used. On the latter, many experimental studies, however, are now employing unrealistic artificial 'wastewater' compositions, particularly in relation to the phosphate buffer concentrations (Liu *et al.* 2005a). While a high phosphate buffer concentration clearly helps in achieving maximal power outputs due to improved conductivity and high buffering capacity (Rozenal *et al.* 2008), it is also obvious that wastewater streams with phosphate-P concentrations of several hundred mg/l do not exist in any realistic situation. Addition of such levels of phosphate to actual wastewater streams would also be impossible for a number of reasons, not the least the costs and required discharge limits. Therefore, some of these 'high performance' systems have very limited, if any practical relevance.

A further main focus has been the demonstration of a range of organic substrates that could be used in the anode of a BES (Cheng and Logan 2007; Rabaey *et al.* 2005). This provides some useful contributions to determine the possible application areas of such systems. Based on these studies, it is evident now that most soluble, easily biodegradable organic substrates can be used in a BES anode. For instance, simple Volatile Fatty Acids (VFAs), such as acetate, propionate and possibly butyrate, are clearly preferable substrates (Liu *et al.* 2005b). Moreover, many other substrates would likely be converted through fermentation processes in the anode compartment or biofilm to these preferred substrates (Freguia *et al.* 2008b). Thus, they are usually also suitable, although possibly at reduced conversion rates. The use of more slowly degradable organics, including particulates, is still a major challenge for BES anodes. Typically these are either washed through the anode compartment, or may be captured and then slowly hydrolysed and fermented before being used by the electro-active bacteria.

Any of these fermentable substrates can, however, give rise to another major challenge in the BES operation: methanogenesis. Due to the long solids retention time in the anodic biofilm and the fact that hydrogen is generated in fermentation processes, it is very difficult to avoid or limit the growth of hydrogen-utilizing methanogens in these compartments. Several studies with 'realistic' wastewater sources have highlighted this problem (Freguia *et al.* 2007; He *et al.* 2005; Lee *et al.* 2008; Torres *et al.* 2007). Given the strong greenhouse gas effects of methane (approximately 21 times as strong as CO₂), this methane production must be kept to a minimum, or the methane needs to be captured. Operation at low pH (typically below pH 5) may inhibit the growth of methanogens sufficiently to avoid the problem (Kim *et al.* 2004). However, at these low pH levels, most electro-active bacteria at the anode are also severely inhibited (Rabaey *et al.* 2003), limiting the performance of the system considerably.

Due to the loss of chemical oxygen demand (COD) in the form of methane from the anodic compartment, the actual COD converted to electric current will be reduced. This COD loss, together with other, often not explicitly studied factors, such as biomass growth and loss via secondary metabolites, seems responsible for the reported low coulombic efficiencies, frequently in the range of 10–50% (Freguia *et al.* 2007). This is clearly a major challenge for any practical application since the overall energy conversion efficiency in such cases would be typically well below 20%. This is not even half the energy conversion efficiency that is achievable in anaerobic processes with methane conversion to electric power via gas engines or turbines (Ross *et al.* 1996). In order for an MFC to be seriously considered for any energy generating application, the coulombic efficiency would have to be above 90% in general, which would still likely only give an energy conversion efficiency of less than 50% given the substantial internal resistance and potential losses at the anode and cathode. Therefore, any research that is focusing on energy recovery as a main objective has to achieve a very high coulombic efficiency, while also trying to minimize the internal resistance and overpotential losses at the electrodes.

22.3.2 BESs for wastewater treatment?

While the MFC can be considered primarily as a wastewater treatment process, its performance needs to be compared to the existing main technologies for this application, the aerobic (activated sludge) and anaerobic (methanogenic) processes. Table 22.1 makes a generalized comparison between these technologies to highlight the major advantages and challenges of the MFC technology. MFC technologies share with anaerobic processes the benefits of low sludge production and net energy generation, but they require a post-treatment to achieve a better effluent quality (mainly oxidized, not reduced compounds). The possible loading rate of MFCs is higher than aerobic processes, but currently still much lower than the anaerobic technologies. The single-stage process (including energy generation) is a significant advantage of the MFC technology, while the modular scale-up approach can be advantageous for smaller applications, but will not benefit greatly from economy-of-scale advantages compared to the traditional technologies. The major hurdle though is the capital cost of a MFC, which is currently much higher than the existing technologies, mainly due to the need for expensive electrodes, membrane and current collectors within the many cells that make up an MFC. In a recent review (Rozendal *et al.* 2008), these costs and their likely future reductions are analysed in detail, leading to the conclusion that these high capital costs severely limit the commercial application of MFCs as a wastewater treatment technology.

Table 22.1. Generic comparison between main wastewater treatment technologies and MFC (Adapted from Freguia 2007)

	Aerobic (Activated sludge)	Anaerobic (UASB)	MFC
Removal rate $\text{kg}_{\text{COD}}\text{m}^{-3}\text{d}^{-1}$	1	20	3
Sludge production ($\text{kg}_{\text{COD}}/\text{kg}_{\text{COD}}$)	0.4–0.6	0.01–0.14	0.01–0.3
Energy production ($\text{kWh}/\text{kg}_{\text{COD}}$)	–1.2	3.8 (heat) or 1.5 (electrical)	0.8 (today) 4.4 (theor.)
Effluent quality	Good	Poor	Good
Gas treatment	No	Likely	No
Stages of treatment	Single	Multiple	Single
Reactor scale-up	Volume	Volume	Modular
Capital cost	Medium (high volume cost)	Medium (high peripheral cost)	High

22.3.3 Is power the best product from BESs?

Achieving a practically valuable energy conversion in a MFC is thus a major challenge due to the inherent constraints in the process (see previous sections). For benthic MFCs, this limitation does not impede application, as the required power densities off shore are limited and the cost per unit power is not drastically constrained. However, reactor based (terrestrial) BESs need to successfully compete with well-established wastewater treatment technologies, most notably the anaerobic digestion process that also has a net energy generation potential. The key advantage of the BES in this context is the ability to operate efficiently at room temperature while methanogenic processes work best above 30°C (Pham *et al.* 2006). Furthermore, BESs likely work better under lower influent COD concentrations (Freguia *et al.* 2008a) in contrast to anaerobic processes. Moreover, at low COD concentrations anaerobic digesters particularly suffer from significant methane losses in the treated effluent due to the relatively high solubility of methane and the overall low methane production per volume of wastewater. Certainly at lower temperatures (ambient) this methane solubility can become problematic. Given these major limitations and the severe cost constraints outlined above, it appears that alternative products to electric power may need to be generated in a BES type approach rather than a strict MFC approach. This may create an efficient, cost-competitive application successful in the ‘clean-tech’ market place.

22.4 POTENTIAL NEW BES APPLICATIONS

The electrochemical nature of the BES processes offers the unique ability to control two separate (bio-)chemical reactions in the two half-cells. While the oxidation at the anode may be primarily used for the oxidation of organics in wastewater, the reduction processes at the cathode offer a wide range of possible applications. These are particularly interesting since the (bio-)electrochemical reactions at the cathode can be carefully controlled to achieve selective reduction conditions, which is usually not possible in anaerobic biological processes. Furthermore, if a membrane is used to separate the anode and cathode compartments (which is typically the case) then the cathode reactions can be largely independent of the anode processes except for the electron and cation transfers. This means that, for example, biological processes utilizing pure cultures can be established in the cathode, while wastewater is fed to the anode. This creates unique opportunities for a wide range of products to be generated at the cathode.

22.4.1 Novel options for cathodic reductions

There is likely a wide range of novel biologically or chemically mediated reduction processes possible at the cathode, leading to products of far greater value than the power generated by a MFC. While many of the electrochemical processes have already been demonstrated in principle (e.g. reduction of CO₂ to form hydrocarbons (Gattrell *et al.* 2006)), the bioelectrochemical reactions are largely unexplored.

In all of these applications, power input rather than power generation is required, which slightly adds to the operating costs but also enables these processes to proceed at quite rapid rates. The latter is possible because the applied voltage over the cell can compensate for internal resistance and overpotential losses. Typically these additional voltages are only in the range of several hundred millivolts plus the thermodynamic potentials of the specific reactions (Rozendal *et al.* 2006b), but they enable considerably higher process rates compared to the MFCs. The generation of hydrogen (H₂) gas at the cathode is not further discussed in this section as it is already quite well investigated and covered in detail in Chapter 13.

One of the most straightforward cathodic processes is based in part on the fact that the selectivity of the proton/cation exchange membranes is far from perfect (Rozendal *et al.* 2006a). Due to the much higher concentration of metallic cations than protons, the former are preferably transferred. Typically sodium ions (Na⁺) are most abundant in the wastewater stream, and thus are

substantially transferred to the cathode. The concurrent generation of hydroxide anions (OH^-) at the cathode create suitable conditions for the formation of sodium hydroxide solutions in the cathode compartment. This cathode should be able to achieve NaOH solutions up to several weight-%, but the process is still under development at present.

A further modification of the above process can be achieved by stabilizing hydrogen peroxide, formed during oxygen reduction, at the cathode. Hydrogen peroxide (H_2O_2) is a widely used chemical for bleaching purposes in paper and pulp industries, disinfection and advanced oxidation processes (together with UV irradiation or ferric addition). The concentration that can be achieved in such a cathodic reaction is unclear at present, but needs to reach at least around 3–5% to be of practical relevance in most applications. This solution will also have a high concentration of NaOH, which helps to stabilize the H_2O_2 and in many applications is directly useful, particularly in paper and pulp bleaching (Foller and Bombard 1995).

Both of the above mentioned products are potentially far more valuable than power generated in a MFC or even hydrogen formed in a MEC. Further research will be needed to elucidate the attainable production rates, quality of the end product(s) and the stability of the process itself.

Further prospective cathode reactions may include the selective reduction of glycerol to 1,2- and 1,3-propanediol. Glycerol is a by-product of the bio-diesel production, which is generated in increasingly large quantities and has very limited value due to the contamination with salt and water. On the other hand, propanediols are major basic building blocks of the large-scale organic chemistry industry, and therefore could be readily utilized (after appropriate clean-up/separation) in the industry. However, there are several major hurdles to overcome, particularly the selective production of 1,3- or 1,2-propanediol, the possible interferences of the impurities in the glycerol from biodiesel production, the selection of suitable biological or chemical (electro) catalysts and not the least suitable reactor configurations to achieve a high concentration of the products to help facilitate the downstream separation processes. This is an application where a well-performing, pure-culture microbial catalyst could be used exclusively in the cathode instead of the typically employed mixed culture populations.

These (bio)electrochemical reductions may also be applied for the transformation of strongly oxidized functional groups in persistent chemicals. For example, the nitro-group of nitrobenzene can be selectively reduced to aniline, which can be much more readily degraded in an aerobic biological wastewater treatment process than the original compound (Mu *et al.* unpublished results). Similarly, the azo bond ($-\text{N}=\text{N}-$) of the widely used reactive azo-dyes

is completely non-reactive in aerobic biological processes, but can be slowly reduced under anaerobic conditions. However, using an electrochemical reduction, the azo bond can be readily cleaved to form amine groups and hence break up the molecule and eliminate the colour (Mu *et al.* 2009). The further degradation of the breakdown products will need to be achieved by the (biological) oxidation processes.

22.4.2 Novel options for anodic oxidations

As yet, the use of anodic oxidation for other objectives than power generation is largely unexplored. There is significant scope for the use of anodes beyond the oxidation of wastewater 'bulk' organics. Inorganic compounds, such as sulfides, can be removed, and recovered using an anodic/cathodic switching process (Dutta *et al.* 2009b). Anodes can be used to remove xenobiotics, such as phenol (Luo *et al.* 2009), diesel constituents (Morris *et al.* 2009) and even odorous compounds, as present in, for example, swine wastewater (Kim *et al.* 2008). In the future a consecutive sequence of cathodic reductions and anodic oxidations might even be possible to provide a more comprehensive removal of xenobiotics.

De Schamphelaire and coworkers investigated the use of BESs for the removal of root exudates from rice plants. Removing these exudates may help in decreasing methane emissions of wetlands (De Schamphelaire *et al.* 2008). Likewise, sediment based BESs could even enhance the cycling of manganese, leading to improved degradation of sediment and dissolved (recalcitrant) organics (De Schamphelaire *et al.* 2007).

22.5 BES INTEGRATION INTO PRACTICAL APPLICATIONS

Given the many applications, but also constraints and particularities of the various BES concepts, the proper integration of these processes in practical applications is critically important. One of the major challenges for any novel technology, such as the BES, is to find suitable niches for the initial applications, as these will unlikely be a complete wastewater treatment system replacing existing infrastructure. Therefore, applications are most likely smaller add-on installations to generate new products that can be used on-site or for processing of a smaller stream in parallel to an existing conventional treatment facility.

It is important to note here that BESs will require pre- and post-treatment of the wastewater. The effluent is unlikely to be of discharge quality, especially

when optimized for high production rates, requiring elevated COD concentrations inside the reactor. Moreover, nitrogen and/or phosphorus removal are typically not achieved in the process. Pre-treatments include solids separation (sedimentation, floatation, etc.) and buffer tanks. The composition of the feed stream and achievable effluent quality will largely define how the process is integrated into an existing installation. Generally, the wastewater feed composition should ideally have a balanced COD and buffering capacity (to be able to neutralize the generated protons in the anode directly) (Freguia *et al.* 2008a). Therefore, mainly dilute streams with COD concentrations in the range of 200–600 mg/l are usually suitable. An excellent overview of available streams and their assessment is given in Chapter 18. In case of higher COD concentrations, the use of an anode–cathode recycle could allow us to balance the COD and buffering capacity in the feed water (Freguia *et al.* 2008a), although cross-over of organics from anode to cathode may be difficult to control. The latter could give rise to the formation of a heterotrophic biofilm on the cathode, leading to decreased oxygen availability for the cathodic process. Moreover, this approach is only feasible for MFC applications where the wastewater flows to the anode and then to the air-cathode. In BES applications, aiming at production of valuable chemicals, such a recirculation is not possible, as this would contaminate the product stream. As most wastewaters will have insufficient buffering capacity to remove all the COD, either a post-treatment needs to be provided, or the buffering capacity needs to be enhanced.

Given the above constraints, BES might be integrated as a carbon and sulfide polishing step after a high-rate anaerobic process (see also Chapter 19). There is usually only limited COD remaining, in conjunction with strong buffering capacity, which enable adequate removal at the anode (see Chapter 11). Furthermore, and different from typical aerobic processes, the electrochemical oxidation of sulfide to form elemental sulfur can also be performed at the anode (Rabaey *et al.* 2006), as detailed in Chapter 12. This would allow COD polishing and sulfide removal from the effluent of the anaerobic process, with the sulfur being deposited on the anode from where it can be recovered again (Dutta *et al.* 2009b).

The application of specific cathodic processes may be easier to integrate into existing treatment processes. Nitrate reduction on a biological cathode can be used as final polishing stage of a biological nitrogen removal process that typically has 2–5 mg/L $\text{NO}_3\text{-N}$ remaining in the effluent after treatment (Virdis *et al.* 2008). The electron supply could come from a partial (or side-stream) treatment of the influent flow, which can then be further treated in the existing process train.

For the production of hydrogen (MEC), NaOH and H₂O₂, a separate (clean) stream of water could be used in the cathode with only limited flow, while a sidestream of the wastewater influent would flow through the anode (see also Chapter 19). Since the full treatment of that stream is not the objective (it serves simply as an electron donor flow for the system), a relatively high flow rate can be applied, hence not depleting the available buffering capacity in the wastewater. One of the major challenges though for this configuration is the scaling in the cathode due to the high pH and the likely presence of cations that precipitate with hydroxide ions (such as Ca²⁺, Mg²⁺). Methods to avoid such scaling need to be developed.

Finally, another proposed implementation route particularly for MFC applications is the installation of complete BES modules into existing treatment tanks (Min and Angelidaki 2008). The advantage of such an approach is the low cost in structural materials required, as existing infrastructure can be retrofitted. However, current collection and the cost-effective provision of sufficient aeration for the air-cathodes are challenging aspects. While any existing aeration system could be used in this case, the energy required for this is likely considerably higher already than the energy generated from the MFC installation. Given the substantial additional costs for such installations, an overall net benefit of such a system might be difficult to achieve.

22.6 CONCLUDING THOUGHTS ON THE FUTURE OF BES

Despite the somewhat negative assessment of the future of MFCs due to the high cost/benefit ratio, the future for BES in general is brighter than ever, notably with respect to bioremediation and bioproduction.

Bioremediation Specific beneficial processes such as nitrate or sulfide removal, (bio)electrochemical oxidation or reduction of recalcitrant chemicals that are difficult to remove by traditional wastewater treatment applications pose highly exciting prospects towards application. Such implementations are typically justified due to the often considerably higher costs of alternative treatments, such as advanced oxidation processes or anaerobic removal requiring substantial amounts of co-substrates.

Bioproduction. The most promising future application in our view, however, is in the area of product formation using the wastewater stream as a free electron supply, while the product generation is performed in the cathode. There is a

wide range of options available that seem to provide very attractive investment returns even in the short-medium term. Most importantly, such applications can typically also be implemented in a staged approach with no or minimal impact on the existing wastewater treatment process, hence drastically lowering the implementation barrier at any potential full-scale site.

Overall, the BESs clearly offer a highly interesting and novel range of processes, both scientifically and from an engineering/application prospect. They enable process options that have not been possible so far and new reactions and applications will certainly be developed in future as well.

REFERENCES

- Aelterman, P., Rabaey, K., Pham, T.H., Boon, N. and Verstraete, W. (2006) Continuous electricity generation at high voltages and currents using stacked microbial fuel cells. *Environ. Sci. Technol.* **40**, 3388–3394.
- Batstone, D.J., Picioreanu, C. and van Loosdrecht, M.C.M. (2006) Multidimensional modelling to investigate interspecies hydrogen transfer in anaerobic biofilms. *Water Res.* **40**(16), 3099–3108.
- Chaudhuri, S.K. and Lovley, D.R. (2003) Electricity generation by direct oxidation of glucose in mediatorless microbial fuel cells. *Nature Biotechnol.* **21**(10), 1229–1232.
- Cheng, S. and Logan, B.E. (2007) Sustainable and efficient biohydrogen production via electrohydrogenesis. *Proc. Nat. Acad. Sci. USA* **104**(47), 18871–18873.
- Cheng, S., Liu, H. and Logan, B.E. (2006) Power densities using different cathode catalysts (Pt and CoTMPP) and polymer binders (Nafion and PTFE) in single chamber microbial fuel cells. *Environ. Sci. Technol.* **40**(1), 364–369.
- Cheng, S., Xing, D., Call, D.F. and Logan, B.E. (2009) Direct biological conversion of electrical current into methane by electromethanogenesis. *Environ. Sci. Technol.* In press.
- Chiao, M., Lam, K.B. and Lin, L.W. (2006) Micromachined microbial and photosynthetic fuel cells. *J. Micromech. Microeng.* **16**(12), 2547–2553.
- Clauwaert, P., Rabaey, K., Aelterman, P., DeSchamphelaire, L., Pham, T.H., Boeckx, P., Boon, N. and Verstraete, W. (2007a) Biological denitrification in microbial fuel cells. *Environ. Sci. Technol.* **41**(9), 3354–3360.
- Clauwaert, P., Van der Ha, D., Boon, N., Verbeken, K., Verhaege, M., Rabaey, K. and Verstraete, W. (2007b) Open air biocathode enables effective electricity generation with microbial fuel cells. *Environ. Sci. Technol.* **41**, 7564–7569.
- De Schamphelaire, L., Rabaey, K., Boon, N., Verstraete, W. and Boeckx, P. (2007) Minireview: The potential of enhanced manganese redox cycling for sediment oxidation. *Geomicrobiol. J.* **24**(7–8), 547–558.
- De Schamphelaire, L., van den Bossche, L., Dang, H.S., Hofte, M., Boon, N., Rabaey, K. and Verstraete, W. (2008) Microbial fuel cells generating electricity from rhizodeposits of rice plants. *Environ. Sci. Technol.* **42**(8), 3053–3058.
- Dutta, P.K., Keller, J., Yuan, Z., Rozendal, R.A. and Rabaey, K. (2009a) Role of sulfur during acetate oxidation in biological anodes. *Environ. Sci. Technol.* **43**(10), 3839–3845.

- Dutta, P.K., Rabaey, K., Yuan, Z.G. and Keller, J. (2008) Spontaneous electrochemical removal of aqueous sulfide. *Water Res.* **42**(20), 4965–4975.
- Dutta, P.K., Rozendal, R.A., Keller, J., Yuan, Z. and Rabaey, K. (2009b) Electrochemical regeneration of sulfur loaded electrodes *Electrochem. Comm.* **11**(7), 1437–1440.
- Foller, P.C. and Bombard, R.T. (1995) Processes for the production of mixtures of caustic soda and hydrogen peroxide via the reduction of oxygen. *J. Appl. Electrochem.* **25**(7), 613–627.
- Freguia, S. (2007) Fundamental studies of anodic and cathodic processes in microbial fuel cells, PhD thesis, Advanced Water Management Centre, The University of Queensland.
- Freguia, S., Rabaey, K., Yuan, Z. and Keller, J. (2007) Electron and carbon balances in microbial fuel cells reveal temporary bacterial storage behavior during electricity generation. *Environ. Sci. Technol.* **41**(8), 2915–2921.
- Freguia, S., Rabaey, K., Yuan, Z. and Keller, J. (2008a) Sequential anode-cathode configuration improves cathodic oxygen reduction and effluent quality of microbial fuel cells. *Water Res.* **42**(6–7), 1387–1396.
- Freguia, S., Rabaey, K., Yuan, Z. and Keller, J. (2008b) Syntrophic processes drive the conversion of glucose in microbial fuel cell anodes. *Environ. Sci. Technol.* **42**(21), 7937–7943.
- Gattrell, M., Gupta, N. and Co, A. (2006) A review of the aqueous electrochemical reduction of CO₂ to hydrocarbons at copper. *J. Electroanal. Chem.* **594**(1), 1–19.
- Gorby, Y.A., Yanina, S., McLean, J.S., Rosso, K.M., Moyles, D., Dohnalkova, A., Beveridge, T.J., Chang, I.S., Kim, B.H., Kim, K.S., Culley, D.E., Reed, S.B., Romine, M.F., Saffarini, D.A., Hill, E.A., Shi, L., Elias, D.A., Kennedy, D.W., Pinchuk, G., Watanabe, K., Ishii, S., Logan, B., Nealson, K.H. and Fredrickson, J.K. (2006) Electrically conductive bacterial nanowires produced by *Shewanella oneidensis* strain MR-1 and other microorganisms. *Proc. Nat. Acad. Sci. USA* **103**(30), 11358–11363.
- Gregory, K.B. and Lovley, D.R. (2005) Remediation and recovery of uranium from contaminated subsurface environments with electrodes. *Environ. Sci. Technol.* **39**(22), 8943–8947.
- Gregory, K.B., Bond, D.R. and Lovley, D.R. (2004) Graphite electrodes as electron donors for anaerobic respiration. *Environ. Microbiol.* **6**(6), 596–604.
- He, Z., Minteer, S.D. and Angenent, L.T. (2005) Electricity generation from artificial wastewater using an upflow microbial fuel cell. *Environ. Sci. Technol.* **39**(14), 5262–5267.
- Ishii, S., Kosaka, T., Hori, K., Hotta, Y. and Watanabe, K. (2005) Coaggregation facilitates interspecies hydrogen transfer between *Pelotomaculum thermopropionicum* and *Methanothermobacter thermautotrophicus*. *Appl. Environ. Microbiol.* **71**(12), 7838–7845.
- Kim, I.S., Hwang, M.H., Jang, N.J., Hyun, S.H. and Lee, S.T. (2004) Effect of low pH on the activity of hydrogen utilizing methanogen in bio-hydrogen process. *Int. J. Hydrogen Energy* **29**(11), 1133–1140.
- Kim, J.R., Dec, J., Bruns, M.A. and Logan, B.E. (2008) Removal of odors from swine wastewater by using microbial fuel cells. *Appl. Environ. Microbiol.* **74**(8), 2540–2543.

- Lee, H., Parameswaran, P., Kato-Marcus, A., Torres, C.I. and Rittmann, B.E. (2008) Evaluation of energy-conversion efficiencies in microbial fuel cells (MFCs) utilizing fermentable and non-fermentable substrates. *Water Res.* **42**(6–7), 1501–1510.
- Liu, H., Cheng, S.A. and Logan, B.E. (2005a) Power generation in fed-batch microbial fuel cells as a function of ionic strength, temperature, and reactor configuration. *Environ. Sci. Technol.* **39**(14), 5488–5493.
- Liu, H., Cheng, S.A. and Logan, B.E. (2005b) Production of electricity from acetate or butyrate using a single-chamber microbial fuel cell. *Environ. Sci. Technol.* **39**(2), 658–662.
- Liu, H., Grot, S. and Logan, B.E. (2005c) Electrochemically assisted microbial production of hydrogen from acetate. *Environ. Sci. Technol.* **39**(11), 4317–4320.
- Logan, B., Cheng, S., Watson, V. and Estadt, G. (2007) Graphite fiber brush anodes for increased power production in air-cathode microbial fuel cells. *Environ. Sci. Technol.* **41**(9), 3341–3346.
- Logan, B.E., Call, D., Cheng, S., Hamelers, H.V.M., Sleutels, T.H.J.A., Jeremiasse, A.W. and Rozendal, R.A. (2008) Microbial electrolysis cells for high yield hydrogen gas production from organic matter. *Environ. Sci. Technol.* **42**(23), 8630–8640.
- Luo, H.P., Liu, G.L., Zhang, R.D. and Jin, S. (2009) Phenol degradation in microbial fuel cells. *Chem. Eng. J.* **147**(2–3), 259–264.
- Min, B. and Angelidaki, I. (2008) Innovative microbial fuel cell for electricity production from anaerobic reactors. *J. Power Sources* **180**(1), 641–647.
- Morris, J.M., Jin, S., Crimi, B. and Pruden, A. (2009) Microbial fuel cell in enhancing anaerobic biodegradation of diesel. *Chem. Eng. J.* **146**(2), 161–167.
- Mu, Y., Rabaey, K., Rozendal, R.A., Yuan, Z. and Keller, J. (2009) Decolourization of azo dyes in bio-electrochemical systems. Submitted.
- Ntarlagiannis, D., Atekwana, E.A., Hill, E.A. and Gorby, Y. (2007) Microbial nanowires: Is the subsurface “hardwired”? *Geophys. Res. Lett.* **34**.
- Pham, T.H., Rabaey, K., Aelterman, P., Clauwaert, P., De Schamphelaire, L., Boon, N. and Verstraete, W. (2006) Microbial fuel cells in relation to conventional anaerobic digestion technology. *Eng. Life Sci.* **6**(3), 285–292.
- Rabaey, K., Boon, N., Siciliano, S.D., Verhaege, M. and Verstraete, W. (2004) Biofuel cells select for microbial consortia that self-mediate electron transfer. *Appl. Environ. Microbiol.* **70**(9), 5373–5382.
- Rabaey, K., Lissens, G., Siciliano, S.D. and Verstraete, W. (2003) A microbial fuel cell capable of converting glucose to electricity at high rate and efficiency. *Biotechnol. Lett.* **25**(18), 1531–1535.
- Rabaey, K., Ossieur, W., Verhaege, M. and Verstraete, W. (2005) Continuous microbial fuel cells convert carbohydrates to electricity. *Water Sci. Technol.* **52**(1–2), 515–523.
- Rabaey, K., Van de Sompel, K., Maignien, L., Boon, N., Aelterman, P., Clauwaert, P., De Schamphelaire, L., Pham, H.T., Vermeulen, J., Verhaege, M., Lens, P. and Verstraete, W. (2006) Microbial fuel cells for sulfide removal. *Environ. Sci. Technol.* **40**(17), 5218–5224.
- Ross, C., Charles, C., Drake, T.J. and Walsh, J.L. (1996) *Handbook on Biogas Utilization*. 2nd Edition, Muscle Shoals, AL: Southeastern Regional Biomass Energy Program, Tennessee Valley Authority.

- Rozendal, R.A., Hamelers, H.V.M. and Buisman, C.J.N. (2006a) Effects of membrane cation transport on pH and microbial fuel cell performance. *Environ. Sci. Technol.* **40**(17), 5206–5211.
- Rozendal, R.A., Hamelers, H.V.M., Euverink, G.J.W., Metz, S.J. and Buisman, C.J.N. (2006b) Principle and perspectives of hydrogen production through biocatalyzed electrolysis. *Int. J. Hydrogen Energy* **31**(12), 1632–1640.
- Rozendal, R.A., Hamelers, H.V.M., Rabaey, K., Keller, J. and Buisman, C.J.N. (2008) Towards practical implementation of bioelectrochemical wastewater treatment. *Trends Biotechnol.* **26**(8), 450–459.
- Shimoyama, T., Kato, S., Ishii, S. and Watanabe, K. (2009) Flagellum mediates symbiosis. *Science* **323**(5921), 1574–1574.
- Torres, C.I., Kato-Marcus, A. and Rittmann, B.E. (2007) Kinetics of consumption of fermentation products by anode-respiring bacteria. *Appl. Microbiol. Biotechnol.* **77**, 689–697.
- Virdis, B., Rabaey, K., Yuan, Z. and Keller, J. (2008) Microbial fuel cells for simultaneous carbon and nitrogen removal. *Water Res.* **42**(12), 3013–3024.
- Zhao, F., Harnisch, F., Schröder, U., Scholz, F., Bogdanoff, P. and Herrmann, I. (2005) Application of pyrolysed iron(II) phthalocyanine and CoTMPP based oxygen reduction catalysts as cathode materials in microbial fuel cells. *Electrochem. Commun.* **7**(12), 1405–1410.