Bioelectrochemical Systems: An Outlook for Practical Applications

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Bioelectrochemical systems (BESs) hold great promise for sustainable production of energy and chemicals. This review addresses the factors that are essential for practical application of BESs. First, we compare benefits (value of products and cleaning of wastewater) with costs (capital and operational costs). Based on this, we analyze the maximum internal resistance (in mΩm²) and current density that is required to make microbial fuel cells (MFCs) and hydrogen-producing microbial electrolysis cells (MECs) cost effective. We compare these maximum resistances to reported internal resistances and current densities with special focus on cathodic resistances. Whereas the current densities of MFCs still need to be increased considerably (i.e., internal resistance needs to be decreased), MECs are closer to application as their current densities can be increased by increasing the applied voltage. For MFCs, the production of high-value products in combination with electricity production and wastewater treatment is a promising route.

1. Introduction

Bioelectrochemical systems (BESs) are electrochemical cells that use microorganisms as the catalyst on one or both electrodes.[1] The reactions occurring at the electrodes are catalyzed by microorganisms, while at the same time electrons are transferred from the oxidized substrate to the anode[2,3] or electrons are accepted from the cathode for a reduction reaction.[4–6] It has only recently been realized that many organisms are electrochemically active, that is, they can grow while exchanging electrons with an electrode.[2,7,8] This realization has led to a rapid increase of research in this area, and BESs hold a great promise for sustainable production of energy or chemicals.[9–13]

BESs can be divided into electron-producing microbial fuel cells (MFCs) and electron-consuming microbial electrolysis cells (MECs). Although the anodic oxidation reactions are similar, the different cathode reactions result in MFCs producing electrical energy as the result of the overall thermodynamically favorable reaction and in MECs requiring additional energy to drive the overall reaction to obtain products.[14,15]

Many possible applications for BESs have been developed over the last couple of years. The first possibility is related to the nature of the oxidation of organic matter and the many different sources of the oxidizable material at the bioanode, such as acetate,[16] cellulose,[17] starch,[18] domestic wastewater,[19] chocolate-industry wastewater,[20] brewery wastewater,[21] and paper-recycling wastewater.[22] These examples of substrates show that the application of BESs comprises a wide variety of substrates and applications for the treatment of wastewaters.

The second possibility of expanding application is related to the cathode of BESs. After discovery of the bioanode, it was realized that microorganisms could also catalyze several cathodic reactions, such as oxygen reduction to water,[23,24] proton reduction to hydrogen,[4,25] nitrate reduction to nitrogen gas,[26] and bicarbonate reduction to methane.[6] Using microorganisms to decrease the activation energy for oxygen reduction and proton reduction would lead to less expensive catalysts compared to the generally applied Pt.[6] In addition to the use of microorganisms as an alternative catalyst, other less expensive catalysts are being explored for the cathode reaction (e.g., nickel, stainless steel and iron[27–29]). Still, many other possible roads for expansion of application of BESs are open.

Many of the new applications for the cathode reaction need an additional energy input, which is determined by thermodynamics of the reactions.[1] This additional energy input is only justified from an economic point of view when the production rate is sufficiently high and products are produced efficiently. The energy efficiency depends on both, the voltage efficiency and the Coulombic efficiency of the reactions proceeding at both electrodes, whereas the current density depends on the internal resistance of the system.[30]

For BESs to become applicable practically, the benefits of the system (value of products and cleaning of wastewater) should be higher than the cost (capital and operational costs). To achieve this, the benefits should be maximized and the capital and operational costs minimized. In general, a high conversion rate (current density) is a prerequisite for low capital...
costs, since a high removal rate allows for a small footprint. At the same time, the conversion rate is limited due to energy losses in the system.

In this Minireview we will address the factors that are essential for BESs to become attractive for practical applications. For this, we make an estimation of costs and revenues for electricity-producing MFCs and for hydrogen-producing MECs. MFCs and MECs are interesting to compare, as they differ in cathode reaction while using the same bioanode (oxidation of organic material). MFCs and MECs have been analyzed before by using life-cycle assessments and compared to several wastewater treatment systems.\(^{[31,32]}\) Here, however, we aim to define operational criteria in terms of internal resistance and current density. Therefore, we compare these criteria to already obtained values for electricity-producing MFCs and for hydrogen-producing MECs both with different types of (bio)catalyzed cathodes. We show that application of MECs is already within reach, whereas the low revenue for electricity limits the application of MFCs.

2. Energy Efficiency and Internal Resistance of BESs

An important parameter that is linked to the internal resistance of a BES is the energy efficiency. The energy efficiency reflects which part of the energy input is recovered as useful energy. The energy efficiency of BESs is the product of Coulombic efficiency and voltage efficiency. The Coulombic efficiency, consisting of anodic and cathodic Coulombic efficiency, indicates which part of the electrons present in the substrate end up as electrons in the electrical circuit (anodic Coulombic efficiency) and which part of the electrons in the electrical circuit end up in the product (cathodic Coulombic efficiency).

The voltage efficiency (η) is defined as

\[
\eta = \frac{E_{\text{cell}}}{E_{\text{app}}} \quad \text{in case of MFCs and} \quad \eta = \frac{-E_{\text{app}}}{E_{\text{app}}} \quad \text{in case of MECs}
\]  

where \(E_{\text{cell}}\) is the derived cell voltage for MFCs, \(E_{\text{app}}\) is the applied voltage in MECs, and \(E_{\text{app}}\) is the thermodynamic voltage determined by the reactions at the electrodes at equal pH. For MFCs, this voltage has a positive value as power is derived from the system, whereas for MECs this voltage has a negative value as power has to be added to the system for the cathode reaction to proceed. The voltage efficiency indicates, which part of the thermodynamic (maximum) energy is actually obtained as electrical energy (in the case of MFCs) or how much energy is added on top of the thermodynamic energy input (in the case of MECs).

For MFCs, the cell voltage (\(E_{\text{cell}}\)) is determined by the thermodynamical potential difference at the electrodes (\(E_{\text{yst}}\)) and the combination of current density and internal resistance of the system (\(R_{\text{int}}\)):

\[
E_{\text{cell}} = E_{\text{yst}} - IR_{\text{int}}
\]  

For an MFC, an increase in current density results in a decrease in cell voltage. The internal resistance determines the maximum current density that can be reached. The power output of an MFC is the product of \(E_{\text{cell}}\) and \(I\). The power thus shows a maximum at a certain current.

For an MEC, however, the maximum current density that can be reached is not limited by the internal resistance. The external power supply offers the possibility to apply more energy to the system than required to overcome the thermodynamic barriers. This suggests that \(E_{\text{app}}\) can be set to a certain value, whereas \(E_{\text{yst}}\) uses the thermodynamically required energy, and the energy that is left over is used to overcome the internal resistance of the system, which is still a function of current. This implies that, in principle, any current can be reached as long as enough power is supplied to the system and as long as the anodic microorganisms can keep up. This fundamental difference between MFCs and MECs shows, why generally MECs produce higher currents than MFCs (Table 1 and 2), but also has direct consequences for the cost effectiveness of both systems.

Although the internal resistance of MECs does not limit the current that can be reached, it does affect the energy efficiency: the higher the internal resistance, the more energy is required on top of the thermodynamic potential to allow for the reactions to be run at the desired rate. Similarly, for MFCs, a high current results in higher energy losses and thus a lower cell voltage.

3. Cost and Revenue Calculations

The costs for BESs consist of capital and operational costs. The operational costs are estimated at 0.05 € kg\(_{\text{COD}}^{-1}\) (COD = chemical oxygen demand, removed) and include all other costs.\(^{[33]}\) For MECs, costs for electricity are included (0.06 € kWh\(^{-1}\), www.ecn.nl). Capital costs are estimated at 100 € m\(^{-2}\), which is close to the already optimistic future estimate made by Rozendal et al.\(^{[34]}\) This estimate includes electrode materials, current collectors, and membranes with a specific surface area of 100 m\(^2\) m\(^{-2}\). Furthermore, an interest rate of 6% over a payback time of 10 years is assumed.\(^{[35]}\) If membranes are used, a membrane pH gradient will build up, generally leading to a pH increase in the cathode from 7 to 13. This pH difference of 6 units will lead to an extra 300 mV energy loss and is included in our calculation.

The revenue of both systems consists of 0.35 € kg\(_{\text{COD}}^{-1}\) for the treatment of wastewater (adapted from Ref.\([35]\)). For MFCs, again a price of 0.06 € kWh\(^{-1}\) of produced electricity is used, and a price of 0.35 € m\(^{-3}\) of locally produced pure H\(_2\) is used for MECs.\(^{[36]}\) This hydrogen is assumed to be produced at a cathodic Coulombic efficiency (ratio between the amount of electrons from the electrical circuit and the amount of electrons that end up in the final desired product) of 90% and an applied voltage of 1 V.

Costs are calculated at current densities between 0 and 50 A m\(^{-2}\). Although 50 A m\(^{-2}\) is a high current density compared to reported current densities, this range is considered
because it will be hard to reach cost effectiveness at the current densities reported so far.

These assumptions and estimations are based on large-scale applications of BESs. However, since no full-scale system has been constructed yet, actual costs will differ from these assumed here. When the costs are different, the general landscape will not change. Instead, there will be changes in the maximum allowable internal resistance, and the required current density will also change. Despite the uncertainties in the cost estimates, the general implications will not change.

4. Internal Resistance and Current Density Determine Practical Applicability of BESs

For practical applications of BESs, cost effectiveness is essential. BESs are cost effective when the value of the products and of wastewater cleaning (revenues) is higher than the capital and operational costs. Revenues and costs for MECs and MFCs differ significantly from one another as a result of their different products and operational properties.

An example for the costs of an MEC and for an MFC are shown in Figure 1. All costs are expressed in euro per kg of COD removed (\(\text{€ kg}_{\text{COD}}^{-1}\)) via the anode, so that the costs are independent of the type of wastewater and also of anodic Coulombic efficiencies.

For both systems, the capital costs can be assumed similar, as both systems consist of similar materials and have the same configuration. The capital costs, expressed in € per unit BES are independent of current density. When expressed in €kg_{\text{COD}}^{-1}, however, capital costs decrease with increasing current density because the rate of COD removal increases at higher current densities. Although capital costs are the same for both systems, the operational costs are different for MECs and MFCs. For MECs, the electrical energy input needs to be increased to achieve a higher rate of product formation (at constant cathodic Coulombic efficiency), whereas the operational costs are independent of current densities for MFCs. The total costs for MECs thus have a minimum determined by the current density and the internal resistance, whereas the total costs for MFCs decrease with increasing current density.

The costs and revenues of MECs at different internal resistances and current densities, again expressed in €kg_{\text{COD}}^{-1}, are shown in Figure 2. For an MEC, the revenue per kg of COD removed is constant (at constant applied voltage and constant cathodic Coulombic efficiency) because the amount of hydrogen that can be produced per kg of COD is determined stoichiometrically. The costs show a minimum at a certain current density, and the costs decrease with decreasing internal resistance. The area for which costs are lower than revenue is the area where practical application of MECs becomes feasible. In Figure 2 we see that MECs need to have an internal resistance lower than 80 mΩ m\(^{-2}\) at a current density of \(\approx 20 \text{ A m}^{-2}\) for the revenues to become higher than the costs.

For MFCs, however, the situation is different (Figure 3). As explained above, the costs for MFCs decrease with increasing current density. The revenues (in €kg_{\text{COD}}^{-1}) are a function of the current density and internal resistance. Both the current density and the internal resistance determine the cell voltage [Eq. (2)] and thus the produced power per kg of removed COD. Therefore, with increasing current density and constant internal resistance, the produced power and the revenue decrease. The highest revenues are obtained at the lowest internal resistance as the cell voltage is higher compared to higher internal resistances.
The area where the revenues are higher than costs represents the situations in which practical application is interesting. Figure 3 shows that MFCs require an internal resistance lower than 40 mΩm² at a current density of ≈25 A m⁻².

We see that, for practical applications, the maximum internal resistance of MECs can be a factor two higher than that of MFCs, even at lower current densities. This is mainly the result of the high revenue for hydrogen compared to the low price of electricity produced from fossil fuels. For this reason, production of valuable products seems to be the most promising path for BESs.[37]

When more valuable products are produced at the cathode, as is the case in MECs, the cathodic Coulombic efficiency becomes an especially important parameter, which in our calculations was assumed to be constant. The cathodic Coulombic efficiency will be lower than 100% as a result of competing processes that consume electrons at the cathode. These competing processes increase the required specific energy input for the desired product and, therefore, the cost effectiveness of the system.

5. Analysis of Internal Resistances leads to a Maximum Allowed Cathodic Resistance

The energy losses in BESs are determined by their internal resistance. Our analysis of cost effectiveness showed that MECs can have a maximum internal resistance of 80 mΩm² whereas MFCs can have a maximum internal resistance of 40 mΩm². This total internal resistance consists of several partial resistances, namely the anode resistance, the resistance of the electrolyte, the resistance for ion transport through the membrane, and the cathode resistance. Also, the pH gradient between anode and cathode can be considered as an additional resistance,[38] however, as the pH affects the potential at which the reactions at the electrode proceed, it is more appropriate to include this effect in the $E_{\text{corr}}$. Therefore, in our analysis of cost effectiveness, this potential loss is already included in the performance of the system (cell voltage for MFCs and required energy input for MECs). Because the difference between MFCs and MECs lies in the cathode and the cathode is often considered as the main contributor to the total internal resistance, we analyzed the maximum allowed internal resistance for the cathode. We calculated this maximum allowed resistance by using reported values of well-designed and well-operating cell parts were neglected. Only in terms of current density, we see that almost all reported cathode internal resistances in combination with current densities to compare the obtained values with the requirements for practical applications.

6. Cathode Performance in MECs and MFCs

To compare the state-of-the-art performance of MECs and MFCs and to provide an outlook for practical applications of both systems, it is useful to analyze the total and cathode internal resistance in combination with current density. For MECs, the cathode internal resistance was calculated by dividing the cathode overpotential by the current density (according to Ohm’s law; $E = IR$). As shown above, the target for MECs to be cost effective is a total internal resistance of 80 mΩm², in combination with a cathode internal resistance of 66 mΩm² at a current density of ≈20 A m⁻². In Table 1, only MEC studies that reported both, current density and cathode overpotential, were used to enable calculation of the cathode resistance. Although studies in this table have been performed at different applied voltages, calculation of the internal resistance makes comparison possible as MECs show a linear response in current-density production for applied voltages $> 0.4 \, V$. [49]

The cathode resistances ranging between 4 and 68 mΩm² are shown in Table 1. Cell resistances range between 36 and 189 mΩm², whereas current densities range between 3.3 and 23 A m⁻². In terms of cathode resistance, we see that almost all studies revealed internal resistance lower than the required internal resistance of 66 mΩm². In terms of total internal resistance, more than half of the studies show values that are low enough. This is because, in some of these studies, the focus was only on improving the cathode resistance and the other cell parts were neglected. Only in terms of current density, considerable improvements are required, although the target...
value of 20 \, \text{A/m}^2 \text{ has already been shown to be feasible in two studies.}^{[27,48]}

For MFCs, the result is shown in Table 2. To be able to make a comparison of current densities and to specifically study the effect of cathodes, we used the following approach: (i) only studies that aimed at studying and improving cathode performance have been used; (ii) the current has been normalized to the (projected) cathode surface area, or when cathode surface area was not reported, the current was normalized to the membrane surface area; and (iii) the current density at maximum power density was used, as this is the most important point when aiming to use MFCs for electricity production, whereas the maximum current density (short circuit current) will lead to zero energy production.

As shown above, the target for MFCs to be cost effective is a total internal resistance of 40 \, \text{m}2\text{m}^{-2}, in combination with a cathode internal resistance of 26 \, \text{m}2\text{m}^{-2} at a current density of \approx 25 \, \text{A/m}^2. According to Table 2, it is striking, first of all, that considerable differences in open circuit cathode potential are found. The theoretical potential for oxygen reduction to water at pH 7 and a partial pressure of \( p_{O_2} = 0.2 \) is +0.60 V versus Ag/AgCl. Every unit decrease in catholyte pH results in

\[
\text{Table 2. Performance of MFC cathodes at maximum power density reported in literature. Selected studies did not make use of a ferricyanide cathode; these studies aimed at improvement of cathode performance and cathode potential was reported versus current density. All values have been normalized to cathode surface or membrane surface when the cathode area was not reported.}
\]

<table>
<thead>
<tr>
<th>Cathode material and catalyst</th>
<th>OCP\textsuperscript{[a]} \text{[V] vs. Ag/AgCl}</th>
<th>Resistance Cathode \text{[m}2\text{m}^{-2}]</th>
<th>Cell Maximum power density \text{[W}2\text{m}^{-2}]</th>
<th>Current density at ( P_{max} \text{[A/m}^2])</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu\textsuperscript{2+} and \text{O}_2 on graphite; pH 3</td>
<td>0.18</td>
<td>37</td>
<td>105</td>
<td>0.8</td>
<td>3.2</td>
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<tr>
<td>graphite with biocathode</td>
<td>0.38</td>
<td>481</td>
<td>n.a.\textsuperscript{[b]}</td>
<td>n.a.\textsuperscript{[b]}</td>
<td>n.a.\textsuperscript{[b]}</td>
</tr>
<tr>
<td>Pt-coated Ti with Fe\textsuperscript{3+}/Fe\textsuperscript{2+}; pH 1.6</td>
<td>0.5</td>
<td>85</td>
<td>125</td>
<td>2.0</td>
<td>4.2</td>
</tr>
<tr>
<td>Pt-coated carbon cloth</td>
<td>0.5</td>
<td>557</td>
<td>724</td>
<td>0.26</td>
<td>0.68</td>
</tr>
<tr>
<td>polypropylene/carbon black composite</td>
<td>-0.05</td>
<td>56</td>
<td>n.a.\textsuperscript{[b]}</td>
<td>0.4</td>
<td>1.8</td>
</tr>
<tr>
<td>graphite with Fe-EDTA\textsuperscript{[d]}</td>
<td>0.1</td>
<td>86</td>
<td>n.a.\textsuperscript{[b]}</td>
<td>0.36</td>
<td>n.a.\textsuperscript{[b]}</td>
</tr>
<tr>
<td>graphite fiber brush with biocathode</td>
<td>0.3</td>
<td>513</td>
<td>653</td>
<td>0.53</td>
<td>1.3</td>
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<td>graphite granules with HNO\textsubscript{3} activation</td>
<td>0.6</td>
<td>36</td>
<td>942</td>
<td>0.32</td>
<td>0.48</td>
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<td>Pt-coated Ti; pH 4</td>
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<td>110</td>
<td>130</td>
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<td>2.8</td>
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<td>Pt-coated carbon-air cathode; pH 1</td>
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<td>n.a.\textsuperscript{[b]}</td>
<td>5.0</td>
<td>11</td>
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<td>Pt-coated carbon fiber</td>
<td>n.a.\textsuperscript{[b]}</td>
<td>28</td>
<td>131</td>
<td>0.98</td>
<td>3.6</td>
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<td>carbon with CoTMPP\textsuperscript{[e]}</td>
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<td>193</td>
<td>256</td>
<td>0.73</td>
<td>2.1</td>
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<tr>
<td>carbon felt-pretreated MnO\textsubscript{2} + microorganisms</td>
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<td>n.a.\textsuperscript{[b]}</td>
<td>193</td>
<td>1.7</td>
<td>3.7</td>
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<td>4.5</td>
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<td>pyrolyzed Fepc\textsuperscript{[f]}/modified graphite foil</td>
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<td>0.76</td>
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<td>reticulated vitreous Carbon + MnO\textsubscript{2}</td>
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<td>n.a.\textsuperscript{[b]}</td>
<td>n.a.\textsuperscript{[b]}</td>
<td>0.13\textsuperscript{[i]}</td>
<td>n.a.\textsuperscript{[b]}</td>
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<td>CoTMPP\textsuperscript{[f]}-coated carbon cloth; pH 3.3</td>
<td>0.5</td>
<td>37</td>
<td>85</td>
<td>2.35</td>
<td>3.8</td>
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<td>stainless steel + biocathode; pH 8.2</td>
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<td>630</td>
<td>n.a.\textsuperscript{[b]}</td>
<td>0.32\textsuperscript{[f]}</td>
<td>1.34\textsuperscript{[f]}</td>
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<td>Pt-coated carbon cloth</td>
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<td>180</td>
<td>n.a.\textsuperscript{[b]}</td>
<td>0.49</td>
<td>1.22</td>
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</table>

(a) Open circuit potential. (b) Not analyzed. (c) Ethylenediamineteraetraacetic acid. (d) Cobalt tetrathiomolybdenumporphyrin. (e) Iron hexacyanoferrate. (f) No polarization curve was recorded to determine the maximum performance. (g) Anode oxidation reaction was hydrogen oxidation instead of a bioanode.
an increase in cathode potential of 0.06 V, which implies that a cathode potential of +0.96 V versus Ag/AgCl would be expected at pH 1. The highest open circuit cathode potentials are indeed found for solutions with low pH values; however, the measured open circuit values are generally considerably lower (≥ 250 mV) than the theoretical potential (catholyte pH is only mentioned when deviating from 7). In our calculation, this difference between thermodynamic potential and open circuit voltage is not included in the value for internal resistance as we used the slope of the polarization curve. However, in practice it accounts for an extra cathode internal resistance. From the studies that report cathode polarization curves, it can be seen that internal resistances of cathodes vary between 22 and 630 mΩ m² and that there is only one study that reports a cathode internal resistance lower than 26 mΩ m². For the other studies, the total internal resistances vary between 85 and 942 mΩ m², showing that none of these studies fulfilled the requirements. Furthermore, the maximum reported (cathodic) current density of 4.5 A m⁻² shows that the current density is still a factor > 5 lower than the aim of 25 A m⁻².

In conclusion, there have been no reports so far of MFC cathodes that fulfill the criteria to be cost effective, whereas several MECs cathodes already have been proven to be cost effective. This difference in performance can be explained from the fact that current densities in MECs can always be increased by raising the applied voltage, whereas MFCs are limited by the cell voltage, that is, thermodynamically determined, and that the internal resistance determines the reachable current. It is important to mention that the higher currents generally obtained for MECs compared to MFCs (at maximum power density) are a result of the fact that the applied voltage helps to overcome the cathode limitations in the MEC.

7. Implications

The expanding possibilities for BESs hold great promise for their application. Before practical application is in reach, however, BESs should be cost effective. Possible applications of BESs depend on their internal resistance and current density, which also determine the overall energy efficiency. Our analysis shows that the higher product revenue of MECs compared to MFCs allows less stringent design criteria in terms of internal resistance. Furthermore, our analysis of internal resistances and current densities shows that MFCs still need considerable improvement to reach the target values (I ≈ 25 A m⁻² and internal resistance of 40 mΩ m²), whereas MECs have already been proven to be able to produce 23 A m⁻² at an internal resistance below 80 mΩ m². Therefore, MFCs require further improvement. The current in MFCs, however, will always be limited by the maximum thermodynamic cell voltage, whereas limitations in current in MECs can be overcome by adding more external electrical energy to the system. Therefore, for MFCs to become cost effective, a promising route is not only to decrease internal resistance and increase current density, but also the production of high-value products. For example, it has been recently discovered that metals such as Cu⁷¹ and Cr²⁵⁶ can be recovered simultaneously to energy production. When producing a high-value product in MFCs, their internal resistance becomes less important from a cost point of view, as is the case for hydrogen production in MECs.

Also for MECs, the range of products is expanding rapidly. From Figure 2 it can be inferred that production of compounds with a higher economic value than hydrogen, such as caustics or hydrogen peroxide,⁶¹,⁶⁷ allows higher internal resistances for the system to become applicable, whereas these systems would require lower current densities at the same time.

We can conclude that on lab scale, MEC performance is already satisfactory. The next step is to show similar performance in pilot-scale installations. Scaling-up BESs poses new challenges, as it may give rise to completely new bottlenecks that are not met when working on lab scale. Recently, three scientific studies have addressed scaling-up MFCs⁵⁶,⁶⁴ and MECs.⁶⁸ Although these studies do point out some serious issues associated with scaling-up (e.g., cell reversal, flow characteristics, and Coulombic efficiency), comparable performance to lab-scale systems has been reported.

Already, considerable effort has been applied to the reduction of the cathode resistance in both MECs and MFCs. This cathode resistance is determined by activation and concentration overpotentials. The activation overpotential can be influenced by using different materials or microorganisms as catalyst (as shown in Table 1 and Table 2), whereas the concentration overpotential can be influenced by increasing the specific surface area,²⁷ increasing the mass transport rate, or adapting the electrolyte solution.³⁹ Finally, it has been shown that cathode limitations can be considerably reduced by increasing the size of the cathode compared to the anode,²⁸ however, the question is whether this can be achieved efficiently on a larger scale.

In addition to the cathode, other limiting parts of BES have been studied, including electrolyte resistance, membrane resistance, buffer requirements, and anode resistance. These resistances, however, have already been reduced to acceptable levels (Figure 4). The electrolyte resistance can become a serious issue especially when wastewaters with a low conductivity are used. However, the distance between electrodes can be reduced through smart engineering so that this resistance is reduced sufficiently. Furthermore, it is important to have sufficient buffer capacity in the anolyte to prevent acidification of the bioanode. In our calculations, we have not included costs for addition of buffer, and moreover, adding buffer to the system is not desirable due to discharge regulations. Recently, several studies have shown that the addition of buffer is not necessary to prevent acidification of the anode. The strategies to prevent acidification of the anode without adding buffer include ensuring good mass transfer³⁹,⁷⁰ or to reuse the buffer capacity that is available in the system.¹³

Finally, the use of a membrane is essential for BESs to achieve high Coulombic efficiencies and to recover a pure product.⁷¹ On the other hand, the membrane adds an extra internal resistance to the system. However, research on different types of membranes, combined with good mass transport in the system, make it possible to reach internal resistances that are acceptable for BESs (<10 mΩ m²). The remaining constraint
for applying membranes lies in the fact that a pH gradient develops between anode and cathode. This pH gradient translates into an additional required applied voltage in MECs or an additional energy loss in MFCs.\(^9\) On the other hand, a high pH value at the cathode enables a lower cathodic resistance for several reactions, such as hydrogen production and oxygen reduction, depending on the type of catalyst used.\(^{60}\) Already some strategies, such as CO\(_2\) addition to the cathode, have been applied to lower this pH gradient.\(^{51,73}\)

The progress achieved by reducing the internal resistance has been established through extensive research by an ever growing and developing research community. Further effort in reducing the cathode resistance by these groups will help to develop the required progress.

When future scale-up studies are combined with these improvements, there is considerable promise for practical applications of MECs in short term and also for MFCs producing valuable compounds on the longer run.

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