Selectivity versus Mobility: Separation of Anode and Cathode in Microbial Bioelectrochemical Systems

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During the operation of a microbial bioelectrochemical system, charge balance must be maintained between the anode and the cathode. In an ideal scenario, the charge balance would be realized by the unhindered migration of H⁺ or OH⁻. At the same time, any kind of diffusion (crossover) between both electrode compartments should be avoided. However, as several studies have demonstrated, the experimental reality does not match this ideal picture. Crossover processes occur and H⁺/OH⁻ migration only plays an inferior role in the charge-balancing ion transfer, which results in significant losses in the performance of the microbial bioelectrochemical system. This Minireview summarizes the conflict of selectivity versus mobility and discusses principle strategies to cope with the resulting constraints, including pH-static operation and the use of different separator materials and membrane-free systems. Finally, we show that every setup compromises either selectivity or mobility, and no apparent ideal solution currently exists.

1. Introduction

In any electrochemical system, the spatial separation of anodic and cathodic half cell reactions and the accompanying electron flow through the external circuit result in an unbalanced charge distribution between both electrodes. This charge separation produces an electric field gradient between the anode and cathode, which is a major source of free energy. As nature strives for free-energy minimization, the system seeks for local charge neutrality. The electron flow through the external electrical circuit is thus accompanied by the charge-balancing flow of ionic charge between the anode and cathode. To maintain a constant system composition, this charge-balancing ion transfer should be carried out exclusively by ions that are liberated and consumed during the electrochemical oxidation and reduction reactions.

In order to achieve a maximum electric current across the external circuit, the migrative ion transport (driven by electric field gradients) should be realized at the lowest possible resistance. On the other hand, the diffusive movement (driven by the concentration gradients) of the other substances across the separator, especially of fuel and oxygen, should be prevented.

The described ideal scenario is already difficult to achieve in chemical fuel cells and electrolyzers.[1] This is an even greater challenge in the “uncommon” electrochemical operating conditions in microbial bioelectrochemical systems (BES), such as microbial fuel cells (MFCs) and microbial electrolysis cells (MECs). These conditions, which are governed by the growth conditions of the microorganisms, comprise ambient temperature, a low concentration of supporting electrolyte (i.e., low ionic strength), and a physiological pH.[2]

This Minireview summarizes recent insights into migrative and diffusive transfer processes across a separator, and explains their effect on the performance of bioelectrochemical devices. Subsequently, different approaches to overcome this conflict of selectivity versus mobility are discussed.

2. Effects of nonideal separators

2.1. Migration-related effects

2.1.1. pH splitting

The majority of BES-related biological oxidation and reduction reactions involve the liberation or consumption of protons. In most cases, the number of involved protons is equal to the number of transferred electrons, as shown for the bioelectrocatalytic oxidation of carbohydrates, hydrocarbons, and hydrogen at the anode [Equation (1)] and the cathodic oxygen reduction reaction [Equation (2)]:

\[
\text{C}_6\text{H}_5\text{O}_2 + (2x - z)\text{H}_2\text{O} \rightarrow x\text{CO}_2 + (y + 4x - 2z)\text{H}^+ + (y + 4x - 2z)\text{e}^- \tag{1}
\]

\[
\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O} \tag{2}
\]

Consequently, to maintain constant ion concentrations at the anode and cathode during operation, only H⁺ (from the anode to the cathode) or OH⁻ (in the reverse direction) should conduct the charge-balancing ion transfer. Ion transfer by cations or anions other than H⁺ and OH⁻ will result in a buildup of unfavorable concentration gradients, particularly of a pH gradient between both electrodes. Several authors have reported this exact scenario: the pH declines in the anode chamber and rises at the cathode during operation, while the charge-balancing ion transfer is almost exclusively achieved by the other electrolyte constituents.[3-5] This may be surprising because the often-employed proton exchange membranes (PEMs) are considered to be highly selective for proton con-

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duction. However, in a typical microbial bioelectrochemical system, the concentration of protons is about $10^{-7}$ mol L$^{-1}$, whereas that of the alkali ions (Na$^+$ and K$^+$) is about $10^{-1}$–$10^{-3}$ mol L$^{-1}$, and the relative (preferential) conductivity of Nafion-117 (the PEM archetype) for the transfer of H$^+$ to Na$^+$ and K$^+$ is only 3.4 and 6.2, respectively. These values are insufficient for a selective proton transfer in these environments.

Recent experimental and theoretical studies found that it is important to consider the general occurrence of a pH gradient between the anode and cathode for the use of any separator.[7, 8] However, its actual characteristic is a function of the separator (i.e., its type, thickness, and surface area), the composition of the electrolyte solution, and the current density (related to the membrane surface area). In either case, the consequences of this pH shift are severe.

2.1.1.1. The inhibition of biological reactions

The acidification of the anode compartment and the pH increase at the cathode result in nonphysiological conditions that lead to a decrease of the bioelectrocatalytic activity (due to metabolic changes in the microorganisms) up to the point of complete deactivation of the microbial activity. For example, the inhibiting effect of a low pH on the microbial-assisted anodic substrate oxidation has already been shown by several authors.[9, 10] Recently, Torres et al.[11] showed in a theoretical study that already the proton gradient within a microbial biofilm may limit the anode performance.

2.1.1.2. The decrease of the thermodynamic cell potential

As shown in Equations (1) and (2), most anode and cathode reactions are pH dependent, with a ratio of protons to transferred electrons of 1. As a consequence, the anode potential is increased (∼59 mV per pH unit) whereas the cathode potential is decreased (∼59 mV per pH unit). In sum, both effects lead to the decrease in cell potential.

2.1.2. Ohmic resistance

Similar to the external load for the electron flow, the membrane represents a resistor for the charge-balancing ion flux between the electrodes and thus contributes to the overall internal resistance of the bioelectrochemical system. Except for the bipolar ion-exchange membranes (see Section 3.3), the resistance of the separator can be described as ohmic. For different types of separators, the ohmic potential drop is strongly dependent on the electrolyte composition.[7, 8] Remarkably, the resistance of the membrane material showed a stronger dependence on the electrolyte composition than the resistance of the electrolyte solution itself. For Nafion, the electrolyte resistance of a pH 7, 10 mM, phosphate buffer solution was 70 times higher than that of 100 mM HNO$_3$ solution (Table 1). At the same time, the specific resistance of a membrane immersed in the respective electrolyte solution increased by a factor of 700. It was shown that the membrane resistance increases (exponentially) with decreasing electrolyte concentrations, which are typical for waste water systems.

To determine the internal resistance of a bioelectrochemical system, different methods, requiring varying levels of experimental expertise, provide different depths of information.[12] To evaluate the sole contribution of the membrane within a complex BES, high-performance methods such as impedance spectroscopy are required.[13] To study the sole membrane effect, an abiotic setup may be advantageous.[14]

2.2. Diffusion-related effects

Common to the above discussed effects of the charge-balancing ion transfer is their driving force, which is the electric field gradient. In addition to this migrative ion movement that is necessary for the operation of the bioelectrochemical device, diffusion processes have to be considered. Diffusion results from concentration gradients of anions, cations, and uncharged substances between the anode compartment and the cathode. These concentration gradients can already be present or they can build up due to the nonideal charge-balancing ion transfer. The diffusive flux of most of the ions is only a minor issue, as their movement (in reverse direction to the migration) aims to adjust the ion distribution to the initial setup. However, the diffusion of some particular compounds from one electrode compartment to the other may cause a severe decrease of the performance of the bioelectrochemical device. Most mentionable are the penetration of oxygen into the anaerobic anode chamber and the crossover of fuel (organic substrate) to the cathode. As discussed below, both effects lead to "parasitic" processes.

In addition to ohmic resistance (Section 2.1.2.), the occurrence of a potential difference across the separator due to concentration gradients between the anode and cathode should be considered. In general, this potential gradient can be calculated for electrolyte solutions of various compositions according to the Goldmann–Hodgkin–Katz equation [Equation (3)]:

$$E = \frac{RT}{2F} \ln \left( \frac{\Sigma a_i}{\Sigma a_v} \right)$$

where $a_i$ and $a_v$ are the activities of each ionic species in compartments I and II, respectively. Equation (3) considers the activities of all present ionic species that can permeate to any

<table>
<thead>
<tr>
<th>Electrolyte solution</th>
<th>$\rho_{\text{membrane}}$ [Ω cm]</th>
<th>$\rho_{\text{electrolyte}}$ [Ω cm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 1 (0.1 M HNO$_3$)</td>
<td>180</td>
<td>10.0</td>
</tr>
<tr>
<td>pH 2.5 (0.1 M HNO$_3$/KNO$_3$)</td>
<td>361</td>
<td>68.5</td>
</tr>
<tr>
<td>pH 7 (0.1 M KNO$_3$)</td>
<td>562</td>
<td>95.2</td>
</tr>
<tr>
<td>pH 7 (0.1 M KH$_2$PO$_4$/K$_2$HPO$_4$)</td>
<td>503</td>
<td>86.9</td>
</tr>
<tr>
<td>pH 7 (0.05 M KH$_2$PO$_4$/K$_2$HPO$_4$)</td>
<td>574</td>
<td>143</td>
</tr>
<tr>
<td>pH 7 (0.03 M KH$_2$PO$_4$/K$_2$HPO$_4$)</td>
<td>1780</td>
<td>260</td>
</tr>
<tr>
<td>pH 7 (0.01 M KH$_2$PO$_4$/K$_2$HPO$_4$)</td>
<td>12 600</td>
<td>702</td>
</tr>
</tbody>
</table>
extent through a separator, which is analogous to the Donnan equation, however, the latter presumes a selectivity of the membrane material (e.g., for protons using Nafion).

For the example in which the anode and cathode solution differ only in the concentration of one electrolyte species by two orders of magnitude (similar to a pH difference of two), the potential drop across the membrane is 118 mV. This type of potential drop has not yet been reported for microbial bio-electrochemical systems, which might be due to the fact that these devices are mostly run with (almost) similar anode and cathode solutions.

### 2.2.1. Parasitic currents

The effect of parasitic currents (also referred to as internal currents) on electrocatalytic materials are well-known for chemical fuel cells,[14] as shown on the example of the oxygen reduction reaction on platinum (Figure 1 a). When oxidizable matter diffuses to the cathode, it can be oxidized at the Pt particle and provide electrons for the oxygen reduction reaction at the same catalyst moiety. This process results in a continuous electron flow and thus, a continuous substrate and oxygen reaction even under open circuit conditions, which can be interpreted as an internal short-circuit reaction (Figure 1 b). Not only is the coulombic efficiency of the device lowered (Figure 1 b), but the formation of a mixed potential, which lies between the redox potential of the oxidant and that of the respective substrate, may also considerably lower the redox potential of the cathode.

To prevent these effects, highly selective electrocatalysts (or bioelectrocatalysts) are employed. For the oxidation reduction reaction (ORR), selective electrocatalysts that do not show catalytic activity for oxidation reactions,[15] such as highly selective enzymes (e.g., laccases),[16] can be used.

### 2.2.2. Parasitic biological processes

Processes similar to the internal currents detected at the chemical electrocatalysts have to be taken into account for the biological components. For the anodic microbial biofilms, the anode serves as the terminal electron acceptor. If oxygen penetrates into the anaerobic anode chamber, different impacts have to be considered.

In the case of facultative anaerobic microorganisms, oxygen can replace the anode as a terminal electron acceptor, which leads to a decrease in coulombic efficiency, typically accompanied by a decrease in the bioelectrocatalytic current density. Continuous oxygen crossover can enhance this effect by allowing an increasing growth of aerobic microorganisms at the aerobic/anaerobic interface, respective in the bacterial solution. In addition, the adaptation to oxygen as a terminal electron acceptor may lead to an adjustment of the enzymatic machinery of the microbial cells. The consequence would be an increase of the redox potential within a single biological catalytic entity. However, these complex processes are not as straightforward as the formation of the electrochemical mixed potentials discussed in Section 2.2.1. The consequence on a macroscopic scale is analogous and represented by a positive shift of the anode potential.

Special cases are biofilms consisting of strictly anaerobic microorganisms. The poisonous oxygen kills the bacterial cells, which leads to the shutdown of the entire device.

However, the presence of oxygen in the anode chamber of a BES cannot be fully generalized as adverse. Some authors have shown that traces of oxygen enable microorganisms to utilize complex substrates that they are not able to exploit in a completely anaerobic environment, which increases the performance of a microbial driven device.[17, 18] In addition, the presence of oxygen may inhibit methanogens in the cathode chamber of an MEC.[19] These effects may also apply to biological cathodes, when organic substrates, crossing over from the anode compartment to the cathode, serve as an alternative electron donor; however, there have been no such reports on this topic.

### 3. Technological conceptions

The first phenomenological study on the influence of the membrane on the MFC performance (Figure 3 a) was presented by Oh and Logan for two chamber MFCs.[20] Since then, different approaches have been proposed to overcome the above summarized problems caused by the separation of anode and cathode. These different concepts and their principal applications in microbial bioelectrochemical devices are discussed.

#### 3.1. The use of pH-static control

The charge-balancing ion transfer in microbial bioelectrochemical systems is almost exclusively based on alkali ions and electrolyte anions, which was also shown by Rozendal and co-workers who analyzed the operation of a MFC system with and without pH-static control in the cathode chamber.[4] Consequently, for every mole of electron flow, one mole of OH– had to be added to the anode chamber and one mole of H+ to the cathode. One may now consider that the total oxidation of 1 kg biochemical oxygen demand (BOD) is equivalent to about 125 mol of transferred electrons. To maintain the pH in both electrode chambers, 7 kg of potassium hydroxide for the
anode compartment and about 3.3 L of concentrated sulfuric acid for the cathode would be used during the pH titration. From this calculation, it can be determined that a pH-static operation requires an extensive application of energy-consuming produced chemicals and thus cannot be considered economical or feasible.

3.2. The increase of the buffer capacity

Closely related to the pH-static operation is the increase of the buffer capacity (e.g., by the addition of respective buffer salts such as phosphate or carbonate[21–24] of the anodic and cathodic electrolyte solutions. However, this approach may provide no principle solution and is certainly not practical for large-scale applications, such as a microbial-fuel-cell-based wastewater treatment. This is exemplarily illustrated for the theoretical assumption (see Section 3.3) that bicarbonate accomplishes the entire charge-balancing ion transfer from the cathode through an anion exchange membrane (AEM) to the anode chamber. For every electron flowing from anode to cathode, one molecule of bicarbonate (assuming pH neutral conditions) has to flow in the reverse direction. Analogous to the above calculation (Section 3.1.), one would need 13.2 kg soda ash to achieve the charge balance. Beside the environmental effects of feeding such amounts of chemicals into wastewater treatment systems (e.g., by increased CO₂ released into the atmosphere), such a concept is noneconomical. This is even more pronounced if carbon dioxide enriched air (produced by an energy-consuming process) is used at the cathode.[23]

3.3. The use of different types of separators

As highly sophisticated proton exchange membranes such as Nafion are expensive (i.e., ca. 8000 € m⁻²[25]) and not per-

fect, low-cost alternatives have been proposed for microbial bi-oelectrochemical systems. Among these are different types of cation exchange membranes (CEM) and anion exchange membranes (AEM) that are, together with the PEMs, referred to as monopolar membranes.[4,7,21] Other material classes include size-selective membranes such as ultrafiltration membranes and nanoporous filters, which both can only serve as barriers for mass transport.[21,26,27] Despite the differences in the effective ion flux of the membranes, which is a function of the respective diffusion coefficient, the ion transfer processes (Figure 2a) are similar. Thus, the separators share the same characteristics of concentration gradients and ohmic resistance across the separator (Table 2).

As an alternative, the use of bipolar membranes, which are composed of an anion-exchange membrane and a cation-exchange membrane layer mounted together (Figure 2b), has been proposed.[32] Ideally, the ionic conductivity of the bipolar membranes is not a result of an ion flux across the membrane, but of a water-splitting reaction at the interface of (or in the transition region between) the anion and cation exchange membrane. The water splitting leads to the formation of protons and hydroxide ions, which then migrate through the CEM and the AEM layer, respectively (see Figure 2b). For this water-splitting reaction, an energy of 22 W h mol⁻¹ is required. This energy corresponds to a membrane polarization of approximately 820 mV (ΔE = dG = ΔG/F). Due to the nonideal properties of

Table 2. Ohmic resistances of selected separators used in studies of BES. 

<table>
<thead>
<tr>
<th>Type</th>
<th>BES systems</th>
<th>Separator material</th>
<th>Resistance [Ω cm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>proton exchange membrane</td>
<td>Ref. [27],[28]</td>
<td>Nafion</td>
<td>81[30]</td>
</tr>
<tr>
<td>cation exchange membrane</td>
<td>Ref. [28],[29]</td>
<td>Ultrex</td>
<td>65.7[4,c]</td>
</tr>
<tr>
<td>anion exchange membrane</td>
<td>Ref. [21],[28]</td>
<td>fumasep-FAD</td>
<td>80–100[4,c]</td>
</tr>
<tr>
<td>size-selective membrane</td>
<td>Ref. [21],[27]</td>
<td>cutoff of 20 kDa</td>
<td>100[4,4]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>cutoff of 10 kDa</td>
<td>1912[4,4]</td>
</tr>
</tbody>
</table>

[a] Manufacturer information. [b] AC measurement, 0.5 M NaCl. [c] 0.5 M NaCl[30] [d] 0.1 M NaCl[30]
the anion and cation exchange layers and the resulting permeability for the electrolyte salts, the transition area (or interface) between the AEM and the CEM under equilibrium conditions always contains a certain concentration of electrolyte salts. By applying an electric field, the electrolyte anions migrate through the AEM toward the anode, and the cations through the CEM toward the cathode (Figure 2b). This ion flux is often referred to as a leakage current,[34] and is not based on water dissociation. When all electrolyte ions are removed from the transition area (i.e., when the rate of ion migration out of the transition area exceeds that of the electrolyte diffusion into the transition area), the membrane polarization increases and the water-spli-}

ting reaction commences. The total ion flux is then composed of the contributions from the leakage current and water splitting.

3.4. The use of one-chamber and membrane-free systems

The use of single-chamber microbial fuel cells dates back to 1989, by Sell and co-workers.[35] In a single-chamber BES, the cathode can either be immersed directly in the anode solution or an air cathode separated by a diaphragm.

In the case of an air cathode (Figure 3b), the increased oxygen availability, no longer restricted by the limited oxygen solubility in water, is a great advantage. However, this increased oxygen concentration at the cathode may lead to increased oxygen diffusion to the anode solution, lowering the coulombic efficiency.[36] In microbial electrolyzers, the coulombic efficiency decreasing effect of oxygen penetration does not apply as both electrodes operate under anaerobic conditions. However, in this case, methanogenesis may play a detrimental role.[37, 38]

The oxygen crossover may be restricted by the used diaphragm material, but the more the oxygen diffusion is confined, usually the higher the ohmic resistance of the separator, which decreases the maximum power output for the MFCs[36] or the hydrogen yield of the MEC systems.[36] Strictly speaking, the term “one chamber” MFC for the latter device (Figure 3 b) is accurate only from a technological point of view. Due to the osmotic and the hydrodynamic pressures, a small volume of liquid always penetrates across the separator forming a thin electrolyte layer at the cathode. Thus, the overall process takes place in two volume entities. For the electrolyte layer (adherent to the air cathode), the same pH-splitting phenomena have been observed as for conventional two-compartment cells. Moreover, due to the minute total liquid volume, the occurring pH gradients can become even more pronounced; thus, cathodic pH values of up to 13 have been reported.[28]

In the case where the cathode (embedded in an oxygen diffusion layer) is facing the anode solution, O₂ may directly enter the microbial media (Figure 3C), in which it may act as a final microbial electron acceptor. In addition, organic material that diffuses to the cathode leads to a flow of internal currents. Consequently, the main disadvantage of this low-cost setup is its decreased coulombic efficiency.

In sediment fuel cells, the natural boundary between seawater and sediment serves as a diffusion barrier, and due to the very low current densities and high salt concentrations in seawater, the concentration effects may not be very pronounced.[39, 40]

3.5. The use of the anodic effluent as influent for the cathode chamber

Freguia et al. recently reported a concept in which the aerated effluent of the anode chamber was used as the influent for the cathode (Figure 4).[41] Thus, the pH decline during anodic oxidation was compensated by the proton consumption during the ORR at the cathode. One may refer to this concept as “internal neutralization” or classify it as a one-chamber system, as there is no real separation between the electrodes. Naturally, this setup requires a carefully managed flow (in order to minimize the substrate crossover to the cathode) and aeration regime to maximize its energetic yield.

4. Conclusion and Outlook

In this Minireview, we have summarized the severe issues associated with separation of anode and cathode in microbial bioelectrochemical systems. When pH-static controlled operations and the use of artificial high buffer concentrations are not applicable, different other approaches have to be appreciated. These concepts include the use of alternative separators, a separator-free operation, and the use of internal titration procedures. We have shown that all the concepts share common drawbacks, however, to a varying extent. Every technological setup is a compromise of selectivity and mobility. The main constraints associated with each concept are summarized in Table 3.

Finally, we conclude that no ideal method for the separation of an anode and cathode is currently available and thus, the further development of present and new concepts is of utmost importance.
Table 3. Main constraints of each BES concept.

<table>
<thead>
<tr>
<th>Concept</th>
<th>pH shift</th>
<th>Resistance</th>
<th>Coulombic efficiency[a]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ideal (theoretical) PEM</td>
<td>no</td>
<td>very high</td>
<td>close to 100%</td>
</tr>
<tr>
<td>less selective (real) separator</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>without pH control</td>
<td>yes</td>
<td>medium to high</td>
<td>high (but microbial activity is decreasing)</td>
</tr>
<tr>
<td>with pH-static control</td>
<td>no</td>
<td>medium to high</td>
<td>high</td>
</tr>
<tr>
<td>with a one-chamber air cathode system</td>
<td>yes (increased)</td>
<td>medium to high</td>
<td>high (but microbial activity is decreasing)</td>
</tr>
<tr>
<td>one chamber system</td>
<td>no</td>
<td>low</td>
<td>low</td>
</tr>
</tbody>
</table>

[a] Two-chamber MFC/electrolyzer without pH control, if not stated otherwise. [b] Not considering restrictions of the microbial metabolism. [c] Considering only H⁺ charge-balancing ion transfer.

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