Review

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Reactor concepts for bioelectrochemical syntheses and energy conversion

Thomas Krieg[1], Anne Sydow[1], Uwe Schröder[2], Jens Schrader[1], and Dirk Holtmann[1]

[1] DECHEMA-Forschungsinstitut, Biochemical Engineering, Theodor-Heuss-Allee 25, 60486 Frankfurt am Main, Germany
[2] Sustainable Chemistry and Energy Research, Institute of Environmental and Sustainable Chemistry, TU-Braunschweig, Hagenring 30, 38106 Braunschweig, Germany

In bioelectrochemical systems (BESs) at least one electrode reaction is catalyzed by microorganisms or isolated enzymes. One of the existing challenges for BESs is shifting the technology towards industrial use and engineering reactor systems at adequate scales. Due to the fact that most BESs are usually deployed in the production of large-volume but low-value products (e.g., energy, fuels, and bulk chemicals), investment and operating costs must be minimized. Recent advances in reactor concepts for different BESs, in particular biofuel cells and electrosynthesis, are summarized in this review including electrode development and first applications on a technical scale. A better understanding of the impact of reactor components on the performance of the reaction system is an important step towards commercialization of BESs.

Merging biotechnology and electrochemistry to create bioelectrochemical systems

Combining the advantages of biological components (e.g., reaction specificity, self-replication) and electrochemical techniques in bioelectrochemical systems (BESs) offers the opportunity to develop novel efficient and sustainable processes for the production of a number of valuable products. In addition to providing fundamental research relating to electron transfer mechanisms and biosensor applications, BESs are potentially of great significance for several industrially relevant fields such as synthesis of fine and bulk chemicals, energy conversion, and storage and remediation processes [1,2]. In general, a distinction is made between separated and non-separated as well as continuous and (fed)-batch reactors (Figure 1). Combining biocatalysts and electrochemical reaction steps to yield a bioelectrochemical process has a number of advantages: the supply of redox equivalents is effectively mass-free, no cosubstrate is required, and therefore no coproducts are formed [3]. Furthermore, electrons are among the cheapest redox equivalents available [4].

To date, one limiting factor for industrial implementation is the low productivity of BESs. A reason for this is that electrode reactions are heterogeneous processes and their productivity is directly proportional to the electrochemically active surface area, which is small for these systems. The main requirements for the technical use of bioelectrochemical processes are: an adequate electrode surface-to-volume ratio, biocompatible surfaces, scalable systems, low-cost and long-term stability of all components, and the absence or reduction of consumables.

Glossary

Anode: is the electrode in the system where electrons are taken up from a compound, which is oxidized.

Benthic microbial fuel cells (BMFCs): are electrochemical devices that gain energy from natural redox gradients between the sediment and water interface. The anode is placed in the anoxic sediment, whereas the cathode is placed in water (oxic zone). Electrons resulting from metabolic activity are transferred to the cathode via an external circuit, where oxygen is reduced and energy can be harvested.

Cathode: is the electrode in the system where electrons are released to a compound, which is reduced.

Counter electrode: every electrochemical process needs a counter reaction, which takes place at the counter electrode. It can be either a cathode or an anode.

Electrolyte: surrounds the electrode and takes up electrons from the electrode or vice versa. Examples for electrolytes are buffers, media, or electroactive compounds (catholyte for cathode, anolyte for anode).

Gas diffusion electrode: are electrodes comprising a solid, a liquid, and a gaseous phase, which contain a catalyst supporting an electrochemical-driven reaction of a gaseous substrate with an electrolyte component.

Mediator: also called electron shuttle, usually are aromatic compounds or metal complexes with delocalized electrons, which can transfer electrons between an electrode and a redox-active substance.

Ohmic losses (IR drop): every electrochemical system has internal resistances, which are caused by wire connections, the conductivity of electrolytes and separators. These resistances cause voltage drops and therefore less energy is available for the electrochemical reaction. The voltage drop can be calculated using Ohm's law and are therefore called 'ohmic losses'.

Reference electrode: enables the setting of a specific potential at the working electrode. Usually silver/silver chloride or calomel electrodes with a known constant potential (versus a standard hydrogen electrode) are used.

Two-electrode system: contains a working electrode, which is connected with a counter electrode as minimum requirement for an electrochemical system. Due to ohmic losses, the applied potential of the working electrode cannot be controlled.

Three-electrode system: in contrast to the two-electrode system this electrochemical system additionally contains a reference electrode, which allows measurement and setting of a specific potential at the working electrode.

Working electrode: the electrode where the reaction of interest takes place in an electrochemical system. It can be either a cathode or an anode.

Corresponding author: Holtmann, D. (holtmann@dechema.de).

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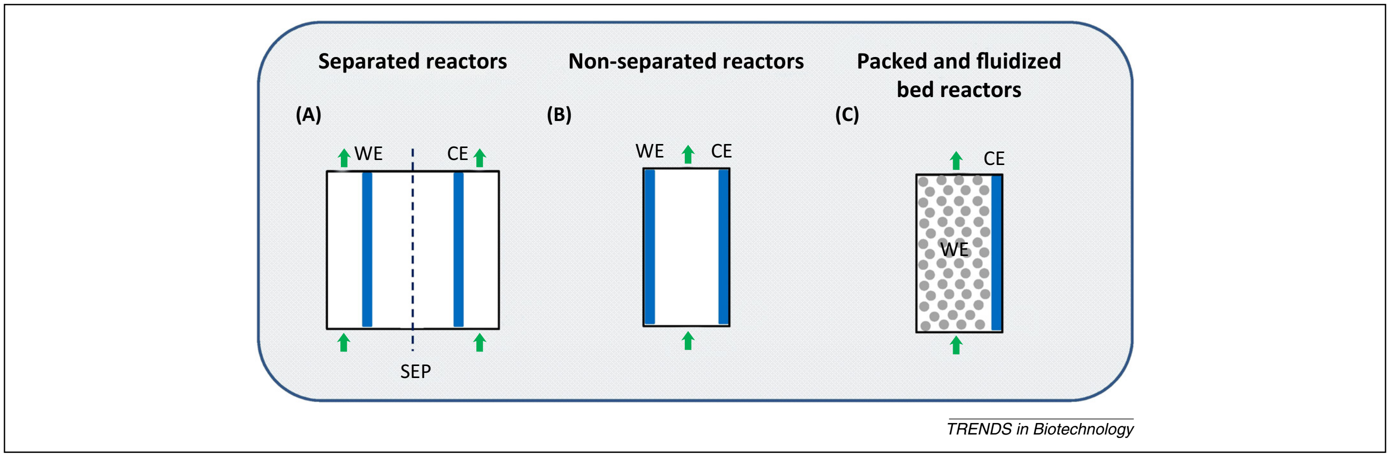

Figure 1. Basic reactor concepts for bioelectrochemical systems (BESs) divided into separated **(A)**, non-separated **(B)**, and packed or fluidized bed **(C)** reactors. Reactors can be operated in continuous mode as well as in (fed)-batch mode. Reactors usually include a reference electrode to set or measure a specific potential at the working or counter electrode (not shown). The different reactors can be used in different geometries such as flat plate or tubular setups. Abbreviations: WE, working electrode; CE, counter electrode; SEP, separator (e.g., ion exchange membranes).

In terms of the biological component, two different electron transfer mechanisms can be distinguished: direct and mediated electron transfer [5]. In direct electron transfer (DET), electrons are exchanged between the biological component and the electrode by direct contact. DET therefore requires direct contact between the active site of an enzyme or the electron transfer components of microorganisms (e.g., cytochromes or pili) and the electrode surface. To date, only a few enzymes and microorganisms can be applied in DET-based reactors. Mediated electron transfer (MET) requires the presence of soluble, redox-active shuttles (e.g., flavins). These components are able to transfer electrons between electrodes and microorganisms or enzymes and can be used in different BESs.

Microbial fuel cells (MFCs) are devices that utilize microorganisms to break down (mainly) organic fuels to produce electricity. MFCs have been utilized for wastewater treatment, where organic pollutants are degraded by the microorganisms with concomitant production of energy [6]. The use of electrochemically active bacteria to break down organic material can be combined with the application of a low external voltage in microbial electrolysis cells (MECs) to achieve a sufficient potential for improved cathodic hydrogen production [7]. Another type of biofuel cell is the enzymatic fuel cell (EFC). Here, isolated enzymes are in direct contact with the substrate during operation, in contrast to MFCs, in which the microbial cell wall or cell membrane prevents direct contact of enzymes with substrates [8]. The discovery that electrical current can also drive microbial metabolism has led to a new application for these systems, called microbial electrosynthesis (MES) [9,10]. MES can be defined as electrically-driven or influenced microbial product synthesis from different sources (e.g., CO_2, wastewater feedstocks) providing a highly attractive and novel route for the generation of valuable products [11–13]. In electroenzymatic processes (or enzymatic electrosynthesis), the electrochemical step is used for the generation of reactants as well as the regeneration or substitution of cofactors [3,14–16]. The combination of enzyme catalysis with electrode processes for cofactor regeneration or substitution often enables cosubstrate- and coproduct-free reaction setups [3].

This review focuses on materials and reactor systems for the conversion of energy (from organic sources to electrical) and the synthesis of fine and bulk products supported by electrical energy. In all applications, scalable reactor concepts are needed. At present, only scaled-up systems for MFCs are available [17]. The aim of this review is to demonstrate that a number of reactor concepts and components can be used in different fields of BES applications. In addition to scaled-up reactors, different smaller systems at ml- and μl-scale are also discussed, which are required to better understand the mechanisms involved and can be used as screening tools for evaluating different biocatalysts or reaction conditions.

Effect of specific components in bioelectrochemical reactors and their positioning

Independent of the reactor system itself, the components are crucial for BES performance. In general, BESs are composed of electrodes, often a separator and the casing (Figure 1). Knowledge about the components and their interactions with each other is crucial because they are responsible for the overall performance of a BES. Therefore, we will examine the use of specific components such as electrode materials or structure, surface modifications of electrodes, separators, and spatial positioning of these components in more detail.

Electrode materials and modifications

The choice of the electrode material has a great impact on the performance of BESs. In addition to the redox process at the electrodes, interactions of biocatalysts with electrodes (e.g., enzyme denaturation or biofouling) need to be considered. A screening system to evaluate up to six electrode materials at the same time using a fixed biological component has been developed ($V = 1$ l) to test the influence of different electrode materials [18]. Several materials (e.g., carbon cloth and felt, graphite foil and felt) were compared with this screening system, using *Shewanella oneidensis* [19]. This organism is well known for its ability to utilize both DET and MET with secreted flavins [20]. Due to these mediating compounds, *S. oneidensis* can access pores in electrode materials down to the