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A critical revisit of the key parameters used to describe microbial electrochemical systems

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ABSTRACT

Many microorganisms have the innate capability to discharge and/or receive electrons to and from solid state materials such as electrodes. This ability is now used towards innovative processes in wastewater treatment, power generation, production of fuels and biochemicals, bioremediation, desalination and resource recovery, among others. Despite being a dynamic field in science and technology, significant challenges remain towards industrial implementation which include representation of judicious performance indicators. This critical review outlines the progress in current density evaluated per projected surface area of electrodes, the most wide-spread performance indicator. It also proposes guidelines to correct current and exchange current per porous surface area, biofilm covered area, electrochemically- or bioelectrochemically- active surface area, of the electrodes. Recommendations for indicators to describe the environmental and electrochemical robustness of electrochemically-active biofilms are portrayed, including preservation of the predominant functionality as well as electrochemical mechanistic and phenomenological features. A few additional key elements for industrial processing are depicted. Whereas Microbial Fuel Cells (MFCs) are the main focus, some important parameters for reporting on cathodic bioproduction performance are also discussed. This critical revision aims to provide key parameters to compare the whole spectrum of microbial electrochemical systems in a consistent way.

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1. Introduction to microbial electrocatalysis

Microbial electrocatalysis refers to the direct or indirect catalysis of electrode surface reactions by whole microorganisms. It relies on the innate capability of many organisms to transport electrons in and out of the cell. While in nature this is used to e.g. reduce minerals, it can be exploited in a so-called microbial bioelectrochemical system (BES) to generate electricity from or to provide electricity to microorganisms [1]. All BESs consist of an anode where the oxidation reaction occurs and a cathode for the reductive reaction, where at least one of these is microbially catalyzed, leading to the terms microbial bioanode and biocathode [2]. In bioanodes, bacteria called exoelectrogens oxidize organic or inorganic matter anaerobically to discharge electrons which are transferred through the electron transport chain to the electrode directly or indirectly. In biocathodes, bacteria called electrotrophs receive the electrons from the cathode directly or via some redox mediators to reduce compounds like organics, CO_2, sulfate or nitrate [2].

A wide range of bioelectrochemical processes has been developed from electrical power generation to the production of biofuels and biochemicals. The most-studied microbial

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electrocatalysis-based process so far is the production of electricity in microbial fuel cells (MFCs). MFCs hitherto produce power densities up to 17-19 W m^{-2} with respect to electrode surface area or volumetric power densities up to 2.87 kW m^{-3}, admittedly at very small scale and artificial conditions [3–5]. Apart from energy recovery from wastewater, MFCs have also been investigated for other applications such as biosensors and energy-neutral desalination [6,7]. The major technological breakthrough which expanded the application range for microbial electrocatalysis has been the possibility to apply electricity as the driving force to catalyze the production of high value chemicals such as hydrogen gas, caustic soda or hydrogen peroxide at the cathode, at a lower energy cost compared to more classical electrochemical production processes [8–10]. Electricity, now increasingly available at low cost from renewable sources, enables driving microbial conversions that are otherwise thermodynamically not feasible. The higher value of these reduced final products relative to electricity makes the so-called microbial electrolysis cells more economically attractive. Subsequently, electricity-driven processes have also been applied and widely explored in the context of bioremediation and inorganic/resource recovery [11–13].

The ability of some microorganisms to catalyze the production of a wide range of biofuels and biochemicals from CO_2 or substrate organics, such as glycerol, at the cathode of an electrolysis cell at a low energy investment cost has further broadened the application range of BESs. Such electricity-driven bioproduction processes are referred to as microbial electrosynthesis (MES). Although the fundamental processes and microbe-cathode interactions are less well understood compared to bioanodes, several proof-of-concept studies have already been reported for MES [14–16]. The possibility to obtain higher value products from waste streams and to integrate these processes easily into the existing biorefineries make MES processes extremely appealing [17,18].

Significant challenges remain to scale up these BESs for industrial applications and energy generation [19]. An important factor in the evolution towards a mature domain, and towards effective comparison of studies and technological performance, is the availability of adequate data representation [20]. Usually current and cell voltage are reported as main performance indicators along with some other parameters, however this is insufficient to crosswise compare studies. The race of publishing the data without considering other important and critical system performance parameters has consequently affected the rational development and thus delayed the commercialization of BES technologies. Here we evaluate some routinely used performance indicators and propose several alternative ones, especially from an electrochemical perspective, for reporting on BESs performance results.

2. Typical performance indicators

The performance of microbial BESs is mostly governed by factors such as microbial physiology, electrode material and surface properties, redox potentials, electrolyte chemistry, nature of substrate and imposed operational conditions [5,21,22]. Besides, BES bioelectrodes typically utilize bacteria in the form of electrochemically-active biofilms (EABs) as the electrocatalytic unit. The distributed properties of these EABs also have a major impact on the transient current [23]. Current density has been therefore employed as the most typical performance indicator of microbial BESs operated at a set potential [24].

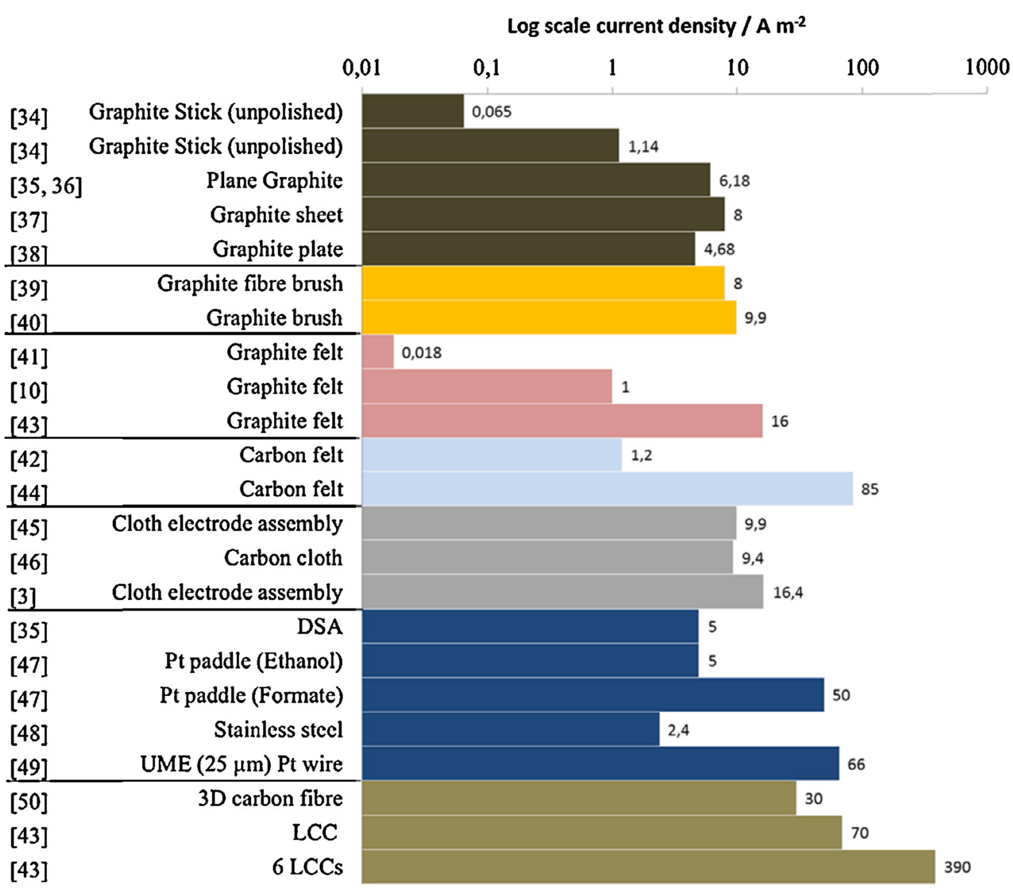

Fig. 1. Evolution of current density per anodic projected surface area (A m^2) through time for diverse bioanodes, as a result of more optimal selection of materials. UME: Ultramicroelectrode; LCC: Layered corrugated carbon. Cloth electrode assembly refers to J-cloth (Associated Brands L.P.) used in an array similar to a membrane electrode assembly (MEA) but the membrane is replaced by a piece of J-cloth itself.