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Reduced overpotentials in microbial electrolysis cells through improved design, operation, and electrochemical characterization

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HIGHLIGHTS

• Individual overpotentials in MECs were characterized.

• Cathode-related phenomena were found to result in the highest overpotentials.

• CO₂ addition to the cathode reduced the applied voltage by reducing the pH.

• Ohmic overpotential was <0.1 V through improved design and membrane selection.

• High cathode overpotentials resulted despite using Ni catalyst.

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ABSTRACT

One of the main performance challenges in microbial electrochemical cells (MXCs) is the low voltage efficiency in comparison to other fuel and electrolysis cells. In this study, we aimed to improve the design and operation of microbial electrolysis cells (MECs) to achieve current densities >10 A m⁻² with reduced applied voltages, using a thorough analytical framework involving electrochemical techniques such as chronoamperometry, voltammetry and electrochemical impedance spectroscopy. We developed a design that allows high surface area for the anode using carbon fibers, but without creating a large distance between the anode and the cathode (<0.5 cm) to reduce Ohmic overpotential. We determined that Ohmic overpotential, at current densities >10 A m⁻² remained <0.1 V even when using an anion exchange membrane to separate the anode and the cathode. We observed the largest overpotential from cathode related phenomena. The increase in pH in the cathode chamber, often to \sim 13, results in >0.3 V of Nernstian concentration overpotential. We showed how by adding CO₂ to the cathode, this overpotential could be reduced to negligible. We also tested two different cathode materials - stainless steel and nickel - to compare the cathode activation overpotentials. Overall, through our design and operation improvements, we were able to reduce the applied voltages from 1.1 to \sim 0.85 V, at 10 A m⁻². Our results also provide important guidelines for further optimizations of MXCs.

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1. Introduction

Microbial electrochemical cells (MXCs) represent a promising technology for the recovery of energy from waste organics either as electrical power or for production of useful chemicals such as hydrogen (H₂), hydrogen peroxide (H₂O₂) and many others [1-5]. In MXCs, anode-respiring bacteria (ARB) oxidize waste organics, and generate an electrical current on the anode [6–8]. In the simplest form of anode respiration, acetate, a common product of anaerobic metabolism, is used as the electron donor (Eq. (1)).

$$CH_3COO^- + 4H_2O \rightarrow 2HCO_3^- + 9H^+ + 8e^-$$
 (1)

At the cathode, these electrons reduce oxygen (O_2) to water or H_2O_2 in microbial fuel cells (MFCs) (Eq. (2)), or water to H_2 in microbial electrolysis cells (MECs) (Eq. (3)), which requires a small voltage input [2,9].

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \text{ or } O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$$
 (2)





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(3)

$$2H_2O+2e^- \rightarrow H_2+2OH^-$$

Several different aspects of MXC processes have shown major progress in the last few years, including understanding extracellular electron transport (EET) in ARB [10-13], managing microbial communities to achieve high Coulombic efficiencies [14-17], and developing new, cheaper materials for electrodes and separators [18–20]. However, one of the major limitations still hindering the application of MXCs is the low voltage efficiency [3,21]. In the case of MFCs, a theoretical maximum of 1.1 V is available when coupling acetate oxidation at the anode to O₂ reduction at the cathode. Yet, at current densities of >5 A m⁻², only <0.3 V is produced, representing >0.8 V of overpotential [17,19,22]. Similarly, although the theoretical applied voltage in MECs is only 0.14 V, the actual applied voltage can be as high as 1.2 V, representing close to 1 V of overpotential [23–26]. Such large overpotentials are in stark contrast with most other fuel cells or electrolysis cells, where orders of magnitude higher current densities are possible at lower overpotentials [27,28]. There is thus a need to consider design and operation tactics for MXCs that help reduce the overall overpotential in the system.

Overpotentials in electrochemical systems are always classified into three major types: activation, Ohmic, and concentration overpotentials [29]. Activation overpotential is related to the activation barrier for a given electrochemical reaction, and the properties of the catalysts in overcoming the activation barrier. In the case of the anode reaction in MXCs, activation overpotential relates to the energy lost in the oxidation of the electron donor by the ARB to metabolism. Likewise, cathode activation overpotential relates to the energy loss at cathode during reduction of O_2 to water or H₂O₂ in MFCs or of water to H₂ in MECs. Ohmic overpotential is related to the transport of ions between the anode and the cathode, and depends on the conductivity of the electrolyte. In the case of MXCs, low conductivity solutions are used for the growth of ARB, and thus this results in high Ohmic overpotential if the distance between the two electrodes is large. Thus, to reduce Ohmic overpotential, it is imperative that we reduce distances between the anode and the cathode, as previously suggested by many other studies [23,30-32].

Concentration overpotential is related to Nernstian and activation losses resulting from not being able to maintain the concentrations of reactants on the electrode surface as well as not removing products from the electrode surface at a fast enough rate. The most common form of concentration overpotential acknowledged for MXCs is due to the pH imbalance that results between the two electrodes when using a membrane to separate the electrodes [2,33]. For every pH unit the cathode pH is higher than the anode pH, a Nernstian concentration overpotential of ~60 mV results. We showed recently that even when bulk concentrations are the same, for e.g. in the absence of a membrane, differences in electrode surface concentrations can still lead to a high concentration overpotential [34].

In this study, we aim to systematically characterize and reduce all overpotentials in an MEC. Although we use an MEC here, the results should directly apply to all other MXCs that use a microbial anode with an inorganic catalyst-based cathode. We started with a logical design for the MEC with reduced distance between the anode and the cathode, and high surface area electrodes. From thereon, based on the characterized individual overpotentials, we modified the materials and the operating conditions we used to reduce the overall overpotential and thus the applied voltage. We show here how it is possible to reduce applied voltages in MECs at a current density of 10 A m⁻², from 1.1 V to ~0.85 V, thus representing only ~0.7 V of overpotential. We also provide a perspective on ways to reduce further overpotentials as well as a limit to the overall voltage efficiency possible in MXCs.

2. Materials and methods

2.1. MEC design and operation

We designed modular flat-plate MECs each with two anodes and two cathodes as described in our previous study [35]. We provide a schematic and photos in Fig. S1. Briefly, the anodes were made of carbon fibers (24K Carbon Tow, FibreGlast, OH, USA) that were woven around a titanium plate that served as current collector (each anode was 10 cm \times 10 cm, geometric area of 100 cm²). A photograph of an assembled anode is shown in Fig. S1(c) in the Supporting information. The two anodes shared a common chamber. We used stainless steel meshes (Type 314, McMaster-Carr, USA) or nickel meshes (Ni 200, Unique Wire Weaving Co., Inc., USA) as the cathodes, and each cathode had a separate individual chamber. We cleaned the assembled anodes with 1 M nitric acid for 3 h, 1 M acetone for 12 h, 1 M ethanol for 3 h, and deionized water (18 M Ω) overnight before using them. We equipped the anode chamber with a reference electrode (Ag/AgCl, MF-2052, Bioanalytical Systems, Inc., USA), which was at a \sim 2 cm distance from each anode. All potentials we report throughout are converted to vs. standard hydrogen electrode (SHE) using a conversion factor of +0.27 V. We determined this conversion factor as previously described for the medium we fed to the MECs [36]. We used the anion exchange membranes AMI-7001 (Membrane International. Glen Rock, NJ) or Fumasep FAA (FuMa-Tech, Germany) to separate the anode and the cathode chambers. We maintained the distance between the anode and cathode at <0.5 cm. The anode chamber volume was \sim 0.5 L and the cathode chamber volume (individual) was \sim 0.1 L (or 0.2 L total). The anode was fed with acetate as the electron donor (see medium composition below), while the cathode was fed with a 100 mM solution of NaCl or NaOH.

We inoculated the MECs with a mixture of anaerobic digested sludge (2 mL, obtained from Mesa Northwest Wastewater Reclamation Plant in Mesa, AZ, USA) and the effluent from a continuously fed MEC in our laboratory fed with acetate as the electron donor (248 mL). We operated the MECs in batch mode initially, followed by continuous flow of the anode medium at a rate of 0.3-0.5 mL min⁻¹, resulting in a hydraulic retention time of 16.7-27.8 h. The anode feed consisted of 50 mM acetate, 100 mM phosphate buffer (PBS, 85 mM of KH₂PO₄ and 15 mM of Na₂HPO₄), 14 mM ammonium chloride, and trace minerals [6]. The pH of the medium was \sim 7.6. We operated the MECs in a temperaturecontrolled room at 30 °C. We sparged the anolyte and catholyte with ultra-high purity nitrogen gas (>99.999%) to remove O₂ before feeding to each chamber. For experiments where we added CO₂ to the cathode (see text in Section 3), we used 100% CO₂ that was sparged into an external chamber containing the catholyte. The CO₂ flow rate was 250 mL min⁻¹ and we recirculated the catholyte within the cathode chambers at 20 mL min⁻¹ flow rate (Fig. S2). We set the anode potential at -0.03 V with a multi-channel potentiostat (VMP3, BioLogic Science Instruments, Knoxville, TN), and recorded current, and anode and cathode potential every 2 min. This anode potential was selected on the basis of a previous study that has shown that the potential is oxidizing enough to allow optimum growth of known ARB [36].

After a stable current was obtained, we developed j–V curves using chronoamperometry starting from the open circuit potential up to the anode potential resulting in the highest saturation current densities, stepping the potential 25 mV for each data point. We waited ~10 min for steady current at each potential before stepping up the anode potential. At the end of each experiment, we performed electrochemical impedance spectroscopy (EIS) measurements at 100 kHz with an amplitude of 10 mV, while using the anode as the working electrode and the cathode as the counter and

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