



Shift of voltage reversal in stacked microbial fuel cells



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HIGHLIGHTS

- Voltage reversal occurred in the stacked MFC 1 having sluggish cathode reaction rate.
- No voltage reversal was observed in the stacked MFC 2 having faster kinetics on the cathode.
- Change in reaction rates on the cathode shifted voltage reversal between two stacked units.
- Voltage reversal can be shifted from the anode to the cathode in stacked MFCs.

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ABSTRACT

We proved that sluggish kinetics on the cathode and the imbalance of cathode kinetics cause voltage reversal in a stacked microbial fuel cell (MFC) equipped with a non-Pt cathode. Catholyte aeration to a unit MFC against passive air diffusion to the cathode in the other unit MFC shifted voltage reversal between the two units, due to improved mass transport and O₂ concentration effects in the aerated MFC. The shifted voltage reversal returned to an original status when catholyte aeration was stopped. A Pt-coated cathode increased the rate of oxygen reduction reaction (ORR) by a factor of ~20, as compared to the non-Pt cathode. As a result, the anodic reaction rate that became slower than the rate on the Pt-cathode limited current density to overpotential in the stacked MFC equipped with the Pt-cathode. This work shows that dominant kinetic bottlenecks, which are the primary cause of voltage reversal, can be shifted between individual MFCs of stacked MFCs or electrodes depending on relative kinetics.

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1. Introduction

Many researchers have attempted to increase voltage by stacking MFCs for their application to energy-efficient wastewater treatment, bio-sensors, and power supplies to small electronic devices [1–3]. Stacking MFCs in series can directly boost voltage and power, but often causes voltage reversal [4–12]. Literature suggests that voltage reversal in stacked MFCs occurs due to significant anode polarization triggered by substrate depletion, the change of microbial community in biofilm anode, or other heterogeneous internal resistance factors [5–12]. The cathode reaction rate in the MFCs that employ efficient noble-metal catalysts (e.g., platinum) or strong liquid oxidants (e.g., potassium ferricyanide) is much faster than the anode reaction rate [5,9,10,13,14]. This phenomenon has resulted in some researchers predicting that

significant anode overpotential leads to voltage reversal in stacked MFCs.

Interestingly, the energy loss on the cathode is typically larger than that on the anode in MFCs. Cathode overpotential is as large as 300–500 mV at the maximum current density (0.12–3 mA cm^{−2}) in MFCs, while anode overpotential is relatively small at 100–270 mV [15–17]. This substantial cathode energy loss contrasts to small cathode overpotentials (100–450 mV) at the extremely high current density of 400–1500 mA cm^{−2} in chemical fuel cells equipped with a 0.1–0.3 mg Pt-cathode similar to that used in MFCs [18,19]. Mass transport limitations and concentration gradients throughout the cathode (hydroxyl ions or O₂) that are significant for MFCs can lead to large cathode overpotential even at small current density in MFCs [17,20]. This unique feature of large cathode overpotential relative to small anode overpotential in MFCs implies that slow cathode kinetics would lead to voltage reversal in stacked MFCs.

An and Lee [7] recently proved that the imbalance in anode

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kinetics over relatively constant kinetics on the cathode causes voltage reversal in stacked MFCs. They suggested that higher heterogeneity on the anode than on the cathode could readily lead to voltage reversal in stacked MFCs, although different cathode kinetics can drive voltage reversal. It is true that cathodic conditions such as relatively uniform catalysts and a single electron acceptor are homogeneous over the anode. However, heterogeneous features of the cathode cannot be avoided in MFCs. For instance, passive air supply to the cathode lacking intensive mixing will increase heterogeneity in mass transport to the cathode, resulting for instance, in different O_2 concentration gradients throughout cathodes for individual MFCs. Heterogeneous mass-transport for protons or hydroxyl ions in the water–cathode interface and the area between the interface and a separator will be substantial due to insufficient advection in air-cathode MFCs [17,20]. This heterogeneous mass transport related to cathodic reaction could limit cathode kinetics, causing voltage reversal in stacked MFCs. Cathode-driven voltage reversal seems to complicate the operation of steady-state stacked MFCs because both anodic and cathodic kinetics can lead to voltage reversal, as suggested by An and Lee [7]. Hence, voltage reversal will readily occur in stacked MFCs caused by relatively sluggish or imbalanced electrode kinetics. This interpretation implies that voltage reversal can be switched between electrodes or individual units in stacked MFCs, exacerbating the performance of stacked MFCs. There are no studies on the voltage reversal caused by cathode kinetics and shift of voltage reversal in stacked MFCs, although understanding them is significant for the success of stacked MFCs.

The goals of this work are three-fold. The first is to confirm the phenomenon of voltage reversal led by sluggish cathode reaction rates in a stacked MFC. The second is to further support cathode-driven voltage reversal by showing the shift of voltage reversal between two individual units of the stacked MFC. The final is to demonstrate that sluggish electrode kinetics mainly leads to voltage reversal in the stacked MFC.

2. Materials and methods

2.1. MFC configuration and inoculation

Two identical sandwich type MFCs (denoted as MFC 1 and MFC 2) were fabricated with Pyrex glass in the Waterloo Engineering Machine Shop at the University of Waterloo. The MFCs consist of an anode and a cathode chamber, and the working volume of each chamber is 29 mL. Non-Pt carbon cloth (CCP40, Fuel Cell Earth, USA) was used for the anode in the MFCs. Pt/C-coated carbon cloth (3 mg cm^{-2} 40% Pt, Carbon Cloth Electrode EC34019-2, Fuel Cell Earth, USA) and non-Pt carbon cloth (CCP40, Fuel Cell Earth, USA) were tested for the cathode; two cathodes were compared to prove the shift of voltage reversal in a serially stacked MFC. The projected surface areas of the anode and cathode were identical at 9.6 cm^2 . Cation exchange membrane (CMI-7000, Membrane International Inc. USA) was positioned between the electrodes in the MFCs. To prevent solution leakage, a rubber gasket manually cut with a sharp blade was inserted between each electrode and chamber. An Ag/AgCl reference electrode (BAS, MF-2052, USA) was placed at 2 mm distance from the anode in order to monitor electrode potential. MFC 1 and MFC 2 equipped with non-Pt carbon cloth were denoted as MFC-woPt 1 and MFC-woPt 2. In comparison, MFC-wPt indicates the MFC equipped with Pt/C-coated cathode.

MFC-woPt 1 and MFC-woPt 2 were inoculated with recycle activated sludge (29 mL) sampled from a wastewater treatment plant (Waterloo, ON, Canada). Tap water was added to the cathode chambers as catholyte. Air was passively provided through a hole of 8 mm diameter on the top of the cathode chambers, which kept the

concentration of dissolved oxygen (DO) at $\sim 5.42\text{ mg L}^{-1}$ in catholyte during our experiments. We used an external resistor of $120\ \Omega$ during ARB acclimation and fed acetate medium (25 mM acetate) to anode chambers at a flow rate of 0.06 mL min^{-1} using a peristaltic pump (Masterflex, Model 7523-80, USA) over ~ 3 months; hydraulic retention time (HRT) was fixed at 8.1 h in the anode chambers. The tap water in the cathode was replaced daily with a syringe to compensate for evaporated water, and the pH in the cathode ranged from 7.0 to 7.3.

2.2. Polarization tests for individual and stacked MFCs using non-Pt cathode

Polarization tests for MFC-woPt 1 and MFC-woPt 2 were conducted under non-stacked and stacked modes, to prove that voltage reversal can occur due to sluggish cathode reaction rates. Throughout this paper MFC-woPt 1 and -woPt 2 under non-stacked mode were referred to as non-stacked MFC-woPt 1 and MFC-woPt 2 (see Fig. S1(a) in Supplementary material). For stacked mode, MFC-woPt 1 and -woPt 2 connected in series were designated as stacked MFC-woPt, and individual units were denoted as stacked MFC-woPt 1 and stacked MFC-woPt 2, respectively (see Fig. S1(b)). Prior to the polarization tests, individual MFCs connected with an external resistor of $120\ \Omega$ were converted to open circuit mode until OCVs in the MFCs became constant. Then, external resistances were sequentially changed from $518\text{ k}\Omega$ to $56.1\ \Omega$ every 2 min. Closed circuit voltage (CCV) in each MFC was monitored using a multimeter (Keithly 2700, Keithley Instruments, Inc. USA) connected to a personal computer. After the polarization tests for non-stacked mode, the two MFCs were fully recharged in open circuit mode and were serially connected for polarization experiments in stacked mode. Stacked-mode polarization tests were carried out in the same manner as with non-stacked MFCs. The polarization tests for non-stacked and stacked mode were conducted in duplicate (see Supplementary material for duplicate test results). External resistances were changed from $581\text{ k}\Omega$ to $56.1\ \Omega$ every 2 min. CCV in stacked mode was monitored between the cathode of stacked MFC-woPt 1 and the anode of stacked MFC-woPt 2, as illustrated in Fig. S1(b). Current was calculated with Ohm's law, i.e., $I = R_{\text{ext}}/V$ (I : current (A), R_{ext} : external resistance (Ω), and V is voltage (V)). In addition, V -current density (j) curves and potential (P)- j curves were built to analyse voltage reversal phenomena for stacked MFC-woPt.

2.3. Aeration tests for the cathode of the MFC-woPt 1 and MFC-woPt 2 under stacked mode: shift of voltage reversal between individual units

Aeration tests were carried out for the cathode of stacked MFC-woPt 1 and MFC-woPt 2, respectively, to investigate voltage reversal behaviours in response to different cathode reaction rates: shift of voltage reversal between individual MFC units. Aeration in the cathode can increase dissolved oxygen (DO) concentration, and mass transport (i.e., advection) in catholyte.

Both stacked MFC-woPt 1 and 2 were connected with $1.4\ \Omega$ of external resistor, and the voltages in the two MFCs were -13.4 and 14.9 mV , respectively. We aerated the cathode chamber of stacked MFC-woPt 1 using an air blower for 7 min to saturate DO concentration $\sim 6.7\text{ mg L}^{-1}$ in catholyte (see Supplementary material for detailed information on DO measurement). In comparison, air passively diffused to catholyte in stacked MFC-woPt 2 and DO concentration was saturated at $\sim 5.42\text{ mg L}^{-1}$ in the catholyte. Catholyte aeration for stacked MFC-woPt 1 was stopped, while air diffusion to the cathode of stacked MFC-woPt 2 was kept. We then aerated the cathode of stacked MFC-woPt 2 for 7 min in comparison

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