START-UP MONITORING OF MICROBIAL FUEL CELLS WITH CARBON FIBER-BASED ANODES

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Introduction

Microbial fuel cells (MFCs) are bioelectrochemical systems that couple microbial oxidation of organic matter to extracellular electron transfer, enabling simultaneous substrate removal and electrical energy recovery. Their performance depends on reactor configuration, operating conditions, and on the establishment of an electroactive microbial community at the anode. Microbial attachment, selection of electroactive populations and biofilm development occur concurrently during start-up, making this stage critical for obtaining a reproducible bioelectrochemical response before long-term performance evaluation (LOGAN et al., 2006; SANTORO et al., 2017).

Carbonaceous materials are widely employed as MFC anodes due to their electrical conductivity, chemical stability and compatibility with microbial growth. Carbon fiber brushes are particularly attractive because their three-dimensional structure provides a large accessible surface area for biofilm colonization (LOGAN et al., 2007). Surface functionalization can further modify electrode-microorganism interactions. Polydopamine (PDA), formed through oxidative self-polymerization of dopamine under alkaline conditions, produces adherent coatings containing oxygen- and nitrogen-containing functional groups and can be deposited on complex substrates under mild conditions (LEE et al., 2007).

Nevertheless, before assessing the effects of advanced electrode modifications, it is necessary to verify the successful establishment of bioelectrochemical activity under the selected operating conditions. Start-up behavior can be assessed through the development of cell voltage together with substrate consumption over successive operating cycles.

Therefore, this study evaluated the early start-up behavior of two air-cathode MFC configurations: unmodified carbon fiber brush (CFB), and polydopamine-coated carbon fiber brush (PDA/CFB). The analysis focused on inoculum characterization, development of voltage

generation, and chemical oxygen demand (COD) removal during the initial batch period and the first three fed-batch cycles.

Materials and Methods

The 3D-printed single-chamber air-cathode MFCs had a working volume of 140 mL. The distance between anode and cathode was 1 cm and a cation-exchange membrane (CEM) separated the anodic liquid phase from the air-cathode assembly. The cathode consisted of a 200-mesh stainless-steel screen (0.05 mm wire diameter) coupled to a commercial gas-diffusion electrode (ELAT 1400W, De Nora) based on carbon textile with a Pt/C catalyst layer (20 wt% Pt/C; 0.4 mg Pt cm^{-2}). Carbon fiber brush anodes were assembled using carbon fiber filaments (24K) supported by high-purity titanium wire (TA1; nominal purity 99.99%), which served as the current collector.

Two anode configurations were evaluated: unmodified carbon fiber brush (CFB) and polydopamine-coated carbon fiber brush (PDA/CFB). PDA/CFB was developed by coating CFB in PDA by immersion in 0.010 mol L^{-1} dopamine hydrochloride prepared in 50 mmol L^{-1} Tris-HCl buffer at pH 8.5, maintained under magnetic stirring for 6 h, and air-dried for 1 h. The procedure was based on the oxidative self-polymerization of dopamine under mildly alkaline conditions (LEE et al., 2007).

Aerobic activated sludge was collected from a municipal wastewater treatment plant operated by Companhia Catarinense de Águas e Saneamento (CASAN) in Florianópolis, Santa Catarina, Brazil. The sludge was pre-treated to remove impurities by sieving and washing with 0.5 g L^{-1} NaCl solution. Total suspended solids (TSS), fixed suspended solids (FSS), and volatile suspended solids (VSS) were quantified according to Standard Methods for the Examination of Water and Wastewater (APHA; AWWA; WEF, 2017). During start-up, the inoculum was used to achieve the initial biomass concentration of 1.0 g VSS L^{-1}.

Synthetic wastewater, adapted from Lovley and Phillips (1988), contained $NaHCO_3$ (1.00 g L^{-1}), sodium acetate (0.84 g L^{-1}), $(NH_4)_2SO_4$ (0.12 g L^{-1}), KH_2PO_4 (2.94 g L^{-1}), K_2HPO_4 (0.595 g L^{-1}), yeast extract (0.025 g L^{-1}), and a micronutrient solution.

Reactors were operated under closed-circuit conditions with an external resistance of 1.0 kΩ, and cell voltage was continuously recorded using a data acquisition system (LIU; LOGAN, 2004). Following the initial acclimation batch, the reactors were operated in fed-batch mode by replacing 50% of the anolyte (70 mL) with fresh synthetic wastewater at each feeding. Chemical oxygen demand (COD) was determined at the beginning and end of each operating interval according to APHA, AWWA and WEF (2017), and COD removal efficiency was calculated from the corresponding initial and final concentrations. The present analysis comprised the initial batch and the first three complete fed-batch cycles. Because each anode configuration was represented by a single reactor, the results were interpreted descriptively, and no inferential statistical comparison between anode types was performed.

Results and Discussion

The inoculum average concentrations were 3.68 ± 0.48 g L^{-1} TSS, 0.78 ± 0.03 g L^{-1} FSS and 2.90 ± 0.49 g L^{-1} VSS. Thus, the volatile fraction represented approximately 79% of the suspended solids. Adjustment of the inoculum based on VSS allowed the reactors to begin operation at approximately 1.0 g VSS L^{-1}.

Both MFC configurations subsequently developed a clear electrical response during start-up. On the first day of operation, daily mean voltages were 10.9 mV for CFB and 8.0 mV for PDA/CFB. Voltage remained comparatively low during the first days and increased as acclimation progressed. On day 7, mean values reached 130.8 and 43.5 mV, respectively, increasing to 326.7 and 167.8 mV on day 8. By day 10, mean voltages reached 343.4 mV for CFB and 293.1 mV for PDA/CFB (Figure 1).

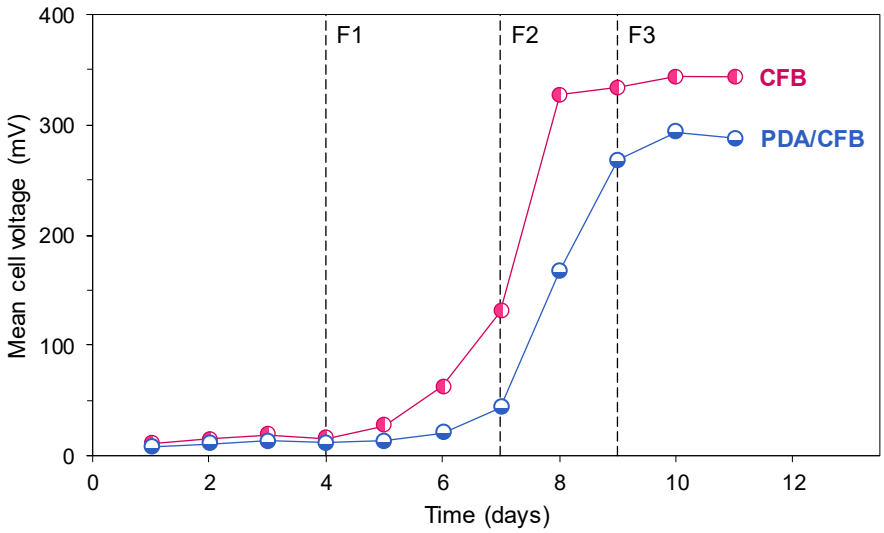

Figure 1. Daily mean cell voltage during the early start-up of microbial fuel cells equipped with CFB and PDA/CFB anodes. Feeding events are indicated as F1-F3.

The profiles shown in Figure 1 indicate distinct temporal dynamics during establishment of the two reactors. The CFB reactor exhibited an earlier increase in voltage, whereas the PDA/CFB reactor showed gradual rise before approaching approximately 300 mV. In MFCs, the progressive development of current or voltage during start-up is commonly associated with acclimation of the inoculum to electrode-respiring conditions and development of electroactive biomass at the anode surface (LOGAN et al., 2006; SANTORO et al., 2017). Electroactive biofilms are central to extracellular electron transfer in MFCs and influence the electrical response of the system (SANTORO et al., 2017).

Start-up duration is not a fixed property of MFCs and may vary with inoculum composition, substrate, buffer conditions and other operational parameters. Reported

substantial differences in MFC start-up times depending on amendments and operating medium, ranging from approximately 110 h to more than 500 h under different conditions. Therefore, the voltage evolution observed here is better interpreted as an acclimation response rather than as steady-state electrode performance (LIU et al., 2011).

The observed difference between CFB and PDA/CFB cannot be attributed specifically to PDA coating in the present experiment. Independent reactor replicates were not included, and electrode-specific electrochemical characterization was outside the scope of this preliminary study. The voltage profiles are interpreted descriptively as evidence that both systems developed substantial electrical generation during the evaluated start-up period, rather than as evidence that one anode configuration performed better than the other.

During the initial batch period, COD removals of 83.6% for CFB and 56.7% for PDA/CFB were observed. In the subsequent first, second and third fed-batch cycles, removal efficiencies were 79.7, 91.4 and 55.5% for CFB and 74.0, 70.2 and 80.6% for PDA/CFB, respectively (Figure 2). The first two complete fed-batch intervals lasted approximately 73 and 50 h, and the third 73 h.

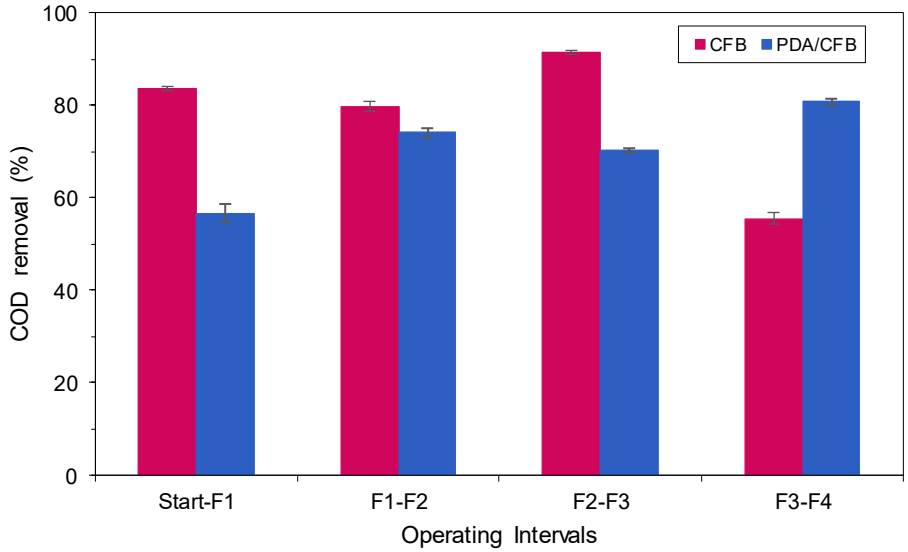

Figure 2. COD removal during the initial batch (Start-F1) and the first three fed-batch cycles (F1-F2, F2-F3 and F3-F4) for microbial fuel cells equipped with CFB and PDA/CFB anodes. Error bars represent propagated standard deviations from replicate COD determinations.

Figure 2 shows that both systems displayed cycle-to-cycle variability, compatible with an early acclimation stage, when the anodic microbial community and electroactive biofilm are still developing and reactor performance has not yet reached a reproducible long-term condition (LIU et al., 2011; SANTORO et al., 2017).

The COD and electrical responses are complementary indicators of reactor establishment, where COD removal confirms consumption of the supplied organic matter, whereas the appearance and subsequent increase of cell voltage demonstrate that electron transfer through the external circuit was occurring. As Coulombic efficiency was not used as a response variable in the present analysis, the fraction of substrate-derived electrons recovered as electrical current cannot be inferred directly from COD removal alone (LOGAN et al., 2006).

The progressive increase in voltage and substantial COD removal are consistent with successful establishment of bioelectrochemical activity in both reactors during the evaluated period. The focus on the start-up stage also avoids conflating these initial acclimation processes with the subsequent evaluation of advanced electrode materials, supporting as an operational baseline for the longer-term study.

Conclusions

The adopted start-up procedure established bioelectrochemical activity in MFCs containing unmodified and PDA-coated carbon fiber brush anodes. Both reactors progressed from low initial voltage to a sustained bioelectrochemical response during the evaluated period while maintaining substantial organic matter removal during the initial batch and subsequent fed-batch operation.

Variability among the first operating cycles indicates that the systems were still undergoing acclimation and supports interpretation of these data as start-up behavior rather than steady-state performance. The established reactors provide an operational baseline for subsequent long-term evaluation of electrode modifications (e.g., functionalization with other particles) and bioelectrochemical performance.

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