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The effect of internal capacitance on power quality and energy efficiency in a tubular microbial fuel cell

Katrin R. Fradler[a], Jung Rae Kim[b,*], Hitesh C. Boghani[a], Richard M. Dinsdale[a], Alan J. Guwy[a], Giuliano C. Premier[a,**]

[a] Sustainable Environment Research Centre (SERC), Faculty of Computing, Engineering and Science, University of South Wales, Pontypridd, Mid-Glamorgan CF37 1DL, UK
[b] School of Chemical and Biomolecular Engineering, Pusan National University (PNU), Busandaehak-ro, 63 Beon-gil, Geumjeong-gu, Busan 609-735, South Korea

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ABSTRACT

The *pseudo*-capacitive behaviour of a high surface area carbon veil electrode in a tubular microbial fuel cell (MFC) was investigated as a mechanism to enhance power quality and energy efficiency. Accumulated charge and energy from the anodic biofilm after prolonged open circuit times (1–120 min) were compared against equivalent periods of steady state loading (R = 100–3000 Ω). A significant difference in the amount of accumulated charge with different loads was observed, resulting in 1.051 C (R = 100 Ω) compared to 0.006 C (R = 3 kΩ). The automated application of short open and closed circuit (0.5–10 s) cycles resulted in an increase of power/current production (closed circuit alone), but presented lower efficiency considering entire open and closed period. The cumulative charge on the carbon veil electrode with biofilm was 39,807 C m^{-2} at 100 Ω. Electrochemical Impedance Spectroscopy (EIS) showed that the Helmholtz layer presented a double layer capacitance of more than ten times the biofilm on electrode. The results indicate that the capacitive behaviour could be utilized to increase the power quality, i.e. its availability/applicability with respect to the operation of low power consuming devices.

1. Introduction

Microbial fuel cells (MFCs) have been investigated extensively for their potential to generate bioenergy and simultaneously achieve energy saving in waste/wastewater treatment. Although the power production of MFCs have been increased three orders of magnitude since late 90 s, through developments in materials and reactor configurations and enrichment of electrogenic bacteria, the low power production (i.e. low cell voltage and current) ascribed to various overpotentials, including mainly mass transport limitations and activation on the electrode, has been acknowledged as a drawback. MFCs are able to generate renewable and sustainable power from various biodegradable organic materials into useful electrical energy. However, the power quality, particularly the low voltage, which derives from the intrinsic limitation of the biological redox reactions, makes it difficult to directly operate even small electronic devices and equipment. Therefore, one of the key challenges in implementing MFCs as self-powering systems is to raise the power quality to the point that it can reliably operate real and available electronic devices.

The theoretical cell potential achievable from MFC while neglecting losses, is calculated by the following electrochemical thermodynamic equilibrium between anode and cathode,

$$E^{\circ} = E^{\circ}_{\text{cathode}}(0.805\,\text{V}) - E^{\circ}_{\text{anode}}(-0.300\,\text{V}) = 1.105\,\text{V}, \quad (1)$$

when assuming an acetate feedstock concentration of 16.9 mM, pH = 7 and an oxygen partial pressure of 0.2 atm. The open circuit voltage (OCV) in a MFC reactor with a Pt catalyst cathode and oxygen reduction is typically limited by cathodic overpotential; therefore it lies between 0.6 and 0.7 V. Previous studies have shown that the OCV depends on several parameters, including organic loading rate [1], cathode catalyst [2] and pH of the electrolyte [3], amongst others. Ohmic, activation and mass transport losses are frequently seen to decrease the cell potential in a MFC to ~0.3 V, when operated with a 100 Ω external load. Hence the cell potential from MFCs in practical operating conditions with current generation is typically 0.3–0.5 V. The cell voltage is therefore marginal or inadequate to power typical low power consuming

* Corresponding author. Tel.: +82 051 510 2393; fax: +82 051 512 8563.
** Corresponding author. Tel.: +44 01443 482333; fax: +44 01443 482169.
E-mail addresses: j.kim@pusan.ac.kr, jrkim0906@gmail.com (J.R. Kim), iano.premier@southwales.ac.uk (G.C. Premier).

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electronics. For example, low power microprocessors requires circa 1.8 W (270 μA, 2.2 V), LEDs require over 2 V (10–20 mA) [4] and photodiodes require 33 mW (10 mA, 3.3 V) [5].

Several approaches to increase the cell potential for improving the power quality of MFCs have been investigated. Serially connected stacks of individual MFC unit cells have been successfully demonstrated [6,7], as have maximum power point tracking (MPPT) methods [8,9]. However, serial connection might present the problem of excessive voltage drop due to a circuit through the electrically conductive liquid phase pathways in module arrangement [6]. A voltage reversal in serial connection has been reported in many MFC stack operations, where cell potentials are likely to vary from unit cell to cell [10]. The initially small difference in potential between cells can eventually dominate and suppress the performance of neighbouring cells. This voltage reversal can detract from the expected total power output in serial connection, and can also deleteriously affect the electrogenic biofilm on the electrode [10]. Grondin et al. [11] used intermittent and periodic connection of the load as an alternative to MPPT operation to match internal and external impedance in order to obtain maximum power transference. Various duty cycles of open and closed circuit operation in benthic MFCs increased power output, but saw little or no effect on the anode community development [12]. They also suggest that the diffusion in these sediment utilizing devices is the limiting factor in delivering power to the circuit, as the mass transport in the anode and cathode surface controls the electrochemical reaction. External capacitors and DC/DC converters have been used to harvest energy by increasing the voltage to a useful power output [13–15]. The efficiency and performance of both methods are significantly affected by electrical operating strategy and power losses.

Dewan et al. [13] showed that the power increased by 111% when an external capacitor was employed and intermittently charged by a MFC compared to continuous electrical operation under fixed load. A similar study resulted in 22–32% higher average current, when the stored electrical energy in a capacitor was discharged on closed circuit operation [14]. Kim et al. [15] charged four capacitors in parallel to avoid voltage reversal in MFC, and by virtue of the serial discharging of the capacitors, voltage could be boosted up to 2.5 V. The work was extended such that the parallel charged capacitors were used to power a Microbial electrolysis cell (MEC) which requires a minimum of 800 mV [16]. Meehan et al. [17] connected a MFC to a charge pump and stored the energy in a super capacitor, before using a boost converter. Other energy management systems tested with MFCs include different DC/DC converter topologies [18] and their combination with MPPT [19]. All of these methods using external capacitance and/or devices could contribute to power increases in bioelectrochemical systems. However, it is necessary to investigate the intrinsic capacitance effect of bioelectrochemical systems as the bio-anode itself usually has a high surface area and a biofilm structure which could also accumulate charge and act as a coulombic capacitor.

Open circuit energy accumulation within an MFC was first observed in sulphate/sulphide mediated MFCs by Ieropoulos et al. [20]. Discontinuous operation was recently used to demonstrate the charge accumulating capabilities of the cellular structure of *Geobacter sulfurreducens* [21] and *Shewanella oneidensis* [22] during open circuit operation. Both strains were found to be capable of direct electron transfer and could store electrons in their extracytoplasmic cytochromes even in the absence of an electron acceptor during open circuit operation. When the anode is available as the terminal electron acceptor (closed circuit operation), the cytochromes are continuously oxidized and release the charge to the anode electrode. Charging can even continue during open circuit operation and theoretically a single *Geobacter* cell was estimated to store 10^7 electrons (1.60×10^{-12} C) [23]. A *pseudo*-capacitor, which combined a double layer capacitor on a conductive surface with *Geobacter sulfurreducens* biofilm has also been investigated. This combination of double layer capacitance (C_{DL}) with the redox active c-type cytochromes present in *Geobacter* increased the capacitance by two orders of magnitude [24]. An alternative perspective is to consider the implementation of capacitive anodes for renewable energy storage in MFC. It has been proposed that electron transfer and storage of electrons in the capacitive anode during current interruption would be maintained, as the anode potential is less rapidly reduced towards the open circuit potential than in a non-capacitive electrode [25]. In this context the effect of different capacitive layer thicknesses was also considered [26].

In this study we investigate the effect of internal capacitance in a tubular MFC. The capacitance of the anode compartment resulted from a combination of both the biofilm and the carbon veil anode with high surface area. The MFC configuration used is arguably closer to an economic MFC, as were the associated operating conditions. The aim of the study was to take advantage of the inherent capacitance which results from both the electrode surface and the electrogenic biofilm on the anode (internal capacitance), to increase the usability of the MFC's power. The additional charge and energy released during the closed circuit (CC) period, which had been accumulated during the preceding open circuit (OC) period, were estimated under differing electrical loads and duty cycle times. In order to study higher frequency of duty cycling, automated short period OC/CC-cycling was applied, aiming to increase the MFCs power output. The scale and origin of the *pseudo*-capacitance, was investigated by evaluating the anode, cathode and cell potentials from transient responses to intermittent current operation under different external ohmic loads. In this investigation, we take *pseudo*-capacitance to include the electrode double layer capacitance in combination with all intra- and extra-cellular electron storage mechanisms and the electrogenic redox-reaction in the biofilm which has discharge dynamics with similar settling times to the duty cycles investigated. Electrochemical impedance spectroscopy was used to investigate the double layer (C_{DL}) and charge transfer/polarization resistance ($R_{CT/P}$) at different anode potentials. An equivalent electrical circuit model was used to distinguish between biofilm derived capacitance and Helmholtz layer (surface morphology) capacitance.

2. Materials and methods

2.1. MFC configuration and operation

A tubular longitudinal MFC reactor, made from polypropylene tube (230 mm long; 40 mm diameter), was constructed using a MEA cathode and a rolled carbon veil anode as previously reported [27]. The anode was fabricated by rolling carbon veil (230 mm × 450 mm; PRF Composite Materials; Dorset, UK) around a central perspex cylinder of 10 mm diameter, which resulted in a projected surface area of 1035 cm^2 for the sheet of veil and a projected surface area of 13 cm^2 for the anode. The cathode membrane assembly consisted of a cation exchange membrane (122 mm × 192 mm; CMI-7000, Membrane International Inc., NJ, USA) assembled with a carbon cloth cathode (163 mm × 82 mm) containing 0.5 mg cm^{-2} Pt. The MEA was placed onto the inner anode tube and fixed with a similar perforated plastic tube [28]. MFC modules with an anode chamber volume of 220 mL were inoculated with anaerobic digester sludge (1:10), in 40 mM acetate in a 50 mM phosphate buffer, vitamins and minerals (χ = 9 mS cm^{-1}) and enriched under a 1 kΩ external load. To demonstrate the reproducibility and to minimize measurement errors, all experiments were carried out simultaneously using two MFC modules. Hence all results present the averaged value from duplicated measurements.

2.2. Charging–discharging experiments with different external loads

In order to investigate the influence of the load on charge accumulation in the tubular reactor, charging–discharging experiments were conducted under different external loads (100 Ω, 500 Ω, 1 kΩ and 3 kΩ) at room temperature and once a stable biofilm had been developed on the anode surface. Prior to each experiment, the anode chamber content was replaced by fresh acetate containing media and the voltage was allowed to stabilize overnight under the corresponding resistive load. The stable current generation was interrupted by subsequent OC charging periods of differing durations, in which the reactor was manually disconnected from the resistor. The resulting CC discharge behaviours at the corresponding loads were