Performance of microbial fuel cells with and without Nafion solution as cathode binding agent

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A B S T R A C T

The performance of tubular microbial fuel cells (MFC) with and without Nafion solution as binding agent for the cathode catalyst preparation was investigated using different electrochemical techniques. The current output of both types of MFCs was monitored as a function of time using an external resistor. The current did not change much with time and was higher for the water cell (WC) than for the Nafion cell (NC). Cell voltage (Uc)–current (I) curves were recorded using a potentiodynamic technique. From the Uc–I curves power concentration (P)–I and P–Uc curves were constructed. The water cell (without Nafion) also achieved a higher maximum power output. The internal resistance that was determined from the cell voltage at which the power concentration reached its maximum value was higher for the NC than that for the WC, possibly due to the higher cathodic polarization resistance of the NC cell. The impedance for the cathodes decreased with exposure time for both cells due to increased porosity of the surface layers covering the cathode materials. No changes of the impedance were observed for the WC anode. For the NC anode the impedance spectra changed from a one-time constant system to a two-time constant system at the longer exposure time.

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1. Introduction

Microbial fuel cells (MFC) are bio-electrochemical devices that convert organic materials into electricity using microorganisms as biocatalysts [1–4]. Bacteria have been identified to be capable of generating electricity from the anaerobic oxidation of organic matter [1–5]. Several factors have been identified as limiting the power production of MFCs [6], including (1) fuel oxidation at the anode, (2) electron transfer from microbial cells to the anode, (3) ohmic resistance of the circuit, (4) proton transfer through the membrane, and (5) rate of oxygen reduction at the cathode.

The method of assembling membrane electrodes can significantly affect the MFC performance. Many efforts have been made to apply Pt as a catalyst to improve the oxygen reduction rate at the cathode. Nafion solution, which is a perfluorinated ion-exchange solution, is often used as a binding agent to connect the Pt particles, membrane, and carbon electrode [2,7,8]. A widely used method is that Pt/C powder is mixed with Nafion solution to form a paste, which is then applied by brushing, spraying or dipping onto an ion-exchange membrane [7,8]. Employing binding agents is costly and may increase the polarization resistance of the cathode. It would be of great interest to understand the effect of cathode binding agents on the power output of a MFC in more detail.

In this study, a Nafion solution was used as a model cathode binding agent. The electricity production from two MFCs with and without Nafion solution as cathode binding agent was investigated. Electrochemical impedance spectroscopy (EIS) was employed to characterize the electrochemical properties of the anode and the cathode and provide information concerning the polarization resistances of the anode and cathode electrodes. Current–time curves were recorded as a function of exposure time using an external resistor. Cell voltage–current curves were determined using a potentiodynamic technique. From these curves power concentration–current concentration and power concentration–cell voltage curves were calculated for the water cell (WC) and the Nafion cell (NC).

2. Experimental approach

2.1. MFC configuration and operation

A schematic and a photograph of the laboratory prototype MFC are shown in Fig. 1. The MFCs were made of a tubular cation exchange membrane (CMI-7000, Membrane International Inc., NJ, USA), which had a diameter of 4.8 cm and a length of 14 cm. The total volume was about 250 cm³ and the liquid volume was 150 cm³. The anode that was placed inside the membrane consisted of carbon granules. It was connected to the external circuit by two titanium wires. The cathode...
2.2. Data collection

were conducted by applying a frequency range from 100 kHz to 5 mHz. EIS measurements were taken using a Gamry reference 600 potentiostat (Gamry Instruments, Warminster, PA, USA). An ac voltage signal of 10 mV was applied between the anode and the cathode using a Gamry reference 600 potentiostat (Gamry Instruments, Warminster, PA, USA). The power concentration was obtained at a cell voltage of about 200 mV in both cases as can be seen from the $P-U$ curves in Fig. 3c.

At the cell voltage $U_{\text{max}}$ where maximum power output $P_{\text{max}}$ occurs, $R_{\text{int}} = R_{\text{ext}}$, where $R_{\text{int}}$ is the internal resistance of the MFC and $R_{\text{ext}}$ is the external resistor that is placed between the anode and the cathode to obtain $U_{\text{max}}$. $R_{\text{int}}$ has been defined as [9]:

$$
R_{\text{int}} = R_{\text{an}} + R_{\text{cat}} + R_{\Omega},
$$

where $R_{\text{an}}$ and $R_{\text{cat}}$ are the polarization resistance of the anode and the cathode, respectively and $R_{\Omega}$ contains the ohmic contributions such as the solution resistance between the anode and the cathode, the membrane resistance and the electrical resistance of the electrodes, leads, etc. $R_{\text{int}}$ of the WC was calculated as 117 Ω, while for the NC a value of 195 Ω was obtained. As discussed previously, $R_{\text{int}}$ depends on cell voltage [9].

The impedance spectra obtained for the NC and the WC at the open-circuit potential (OCP) for the anode and the cathode during the exposure times of 120 and 140 days are shown in Fig. 4 as Bode-plots in which the logarithm of the impedance modulus $|Z|$ is plotted vs. the logarithm of the applied frequency $f$. The impedance spectra of the NC and the WC cell cathodes are in general agreement with the coating model proposed by Mansfeld et al. [10,11] for the analysis of impedance data for polymer coated metals. The decrease of the impedance of the cathode for both MFCs with the exposure time is considered to be due to a decrease of the thickness of the polymer

3. Results and discussion

Fig. 2 shows an example of the current–time curves that were recorded over extended time periods. The current did not change much with time and the WC produced higher current values than the NC. The performance of the NC and the WC was investigated by the recording $U_{\text{oc}}-I$ curves.

Since the area of the anode was not known, the experimental current and power values were normalized by the liquid volume of the anode compartment which was 150 cm$^3$. Fig. 3a gives a comparison of the current concentration and the power concentration produced by the anode and the WC. The maximum current concentration obtained from the WC (26 µA/cm$^3$) was more than twice that from the NC (12 µA/cm$^3$) (Fig. 3a). Fig. 3b shows the power concentration as a function of the current concentration. The maximum power concentration produced by the WC was about 1.8 µW/cm$^3$ compared to 1.2 µW/cm$^3$ for the NC. The maximum power concentration was obtained at a cell voltage of about 200 mV in both cases as can be seen from the $P-U$ curves in Fig. 3c.

The voltage across a $R_{\text{ext}} = 500$ Ω external resistor was recorded every 30 s using a computer based data acquisition system (Keithley 2700 multimeter). These measurements were only interrupted when impedance spectra or cell voltage–current curves were recorded. Cell voltage ($U_c$)–current ($I$) curves were collected by applying a potentiodynamic scan at a scan rate of 0.1 mV/s from the open-circuit cell voltage $U_{\text{oc}}$ to zero cell voltage $U_0$ using a Gamry reference 600 potentiostat. The power concentration $P$ ($\mu$W/cm$^3$) based on the liquid volume of the MFC was calculated from the $U_{\text{oc}}-I$ curves and plotted as a function of current concentration ($j$) or cell voltage. The impedance spectra were collected at the open-circuit potential (OCP) of the anode and the cathode using a Gamry reference 600 potentiostat (Gamry Instruments, Warminster, PA, USA). An ac voltage signal of 10 mV was applied in a frequency range from 100 kHz to 5 mHz. EIS measurements were conducted by first recording the impedance spectrum of the anode with the cathode acting as counter electrode (CE) followed by recording of the spectrum for the cathode with the anode serving as CE.
layers covering the graphite fibers (increase of high-frequency capacitance) and increased porosity of these layers (decrease of pore resistance at intermediate frequencies) (Fig. 4b). The impedance of the cathode for the NC is higher than that for the WC for both exposure times due to the polymer layers formed during treatment with the NaF solution.

The impedance spectra for the WC anode did not change significantly with time indicating stable behavior (Fig. 4a). The impedance for \( f \sim 10^4 \) Hz is due to the solution resistance and is very low. The impedance for \( f \sim 1 \) Hz is due to the capacitance of the anode. The impedance spectra for the NC anode at 120 days were different from those of the WC at the same exposure time with a significantly lower capacitance value. The spectra changed to a two-time constant system for an exposure time of 140 days. These changes cannot be explained at present, however they point to a complex interaction between the anode and the cathode for the NC.

### 4. Summary and conclusions

The performance of tubular MFCs (Fig. 1) with and without NaFion solution as a binding agent was investigated using different electrochemical techniques. The current–time curves (Fig. 2) and the power concentration–current concentration or power concentration–cell voltage curves that were obtained from the experimental cell voltage–current curves (Fig. 3) have demonstrated that the power production by the water cell is higher than that of the NaFion cell. The internal resistance determined from the power density–cell voltage curves (Fig. 3c) was higher for the NaFion cell. The impedance spectra for the cathodes of the two MFCs suggest that this higher value is due to the higher polarization resistance of the NaFion cell cathode. The ohmic contribution to the internal resistance (Eq. (1)) was very small (Fig. 4). The NaFion polymer layers covering the cathode material (Pt particles and Ni-coated carbon fibers) apparently block access of oxygen and thereby reduce the rate of oxygen reduction.

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References


