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Increase life time and performance of Microbial Fuel Cells by limiting excess oxygen to the cathodes

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ABSTRACT

The cathodes of MFCs are the main bottleneck for practical application; undesired cathode biofilms often cause their breakdown. The goal of this study was to extend cathode life time. Membranes were applied on the air side of the cathodes to limit oxygen penetration and reduce biofilm formation. Two single chamber MFC designs with an electrode spacing of 120 mm (HRT ~1 week) and 15 mm (HRT 24 h) were investigated in batch operation using a synthetic blackwater at room temperature (23 ±3 °C). At high electrode spacing cathode life time was increased to 217%, with a significantly increase in power densities over time. The Power densities at 15 mm electrode spacing reached 1155 ± 41 mW m^{-2} with the membrane applied; compared to 460 ± 32 m Wm^{-2} without membrane. TOC degradation relative to the anode surface at close electrode spacing was near equal at 6.8 ± 2.3 and 7.2 ± 3.0 gm^{-2} d^{-1}; however, the Coulomb Efficiency with a membrane increased from 28 ± 10% to 54 ± 13%. CV analysis after operation showed considerably higher ORR activity of the cathodes covered by a membrane.

Nomenclature

c	Molar concentration (mol l^{-1})
c_m	Mass concentration (g l^{-1})
$c_{m,L}$	Saturation concentration (g l^{-1})
E	Half-cell potential (V)
E^0	Standard potential of a half-cell reaction (V)
F	Faraday constant (C mol^{-1})
$I_{A,max}$	Maximum surface specific current density (A m^{-2})
$K_{L,A}$	Surface specific mass transfer coefficient (cm s^{-1})
M_{O2}	Molar mass of oxygen (g mol^{-1})
OTR_A	Surface specific mass transfer rate (mg cm^{-2} s^{-1})
R	Gas constant (J mol^{-1} K^{-1})
T	Temperature (K)
z_e	Number of electrons participating in a reaction (–)

1. Introduction

Microbial Fuel Cells (MFC) mostly rely on the catalyzed cathodic reduction of oxygen (Oxygen Reduction Reaction, ORR) as complementary reaction to the microbial oxidation of organic compounds at the anode. The ORR is the same in a MFC and a conventional H_2-FC or Direct Methanol FC (DMFC). Therefore, conventional FC cathodes are often used in MFC research or serve as model for self-made cathode designs [1]. In a single chamber MFC the cathode is in direct contact with air on one side and the substrate medium on the other side, enabling the unhindered diffusion of ions, e.g., H^+, from the anode to the cathode. The catalytically active layer of the cathode, typically facing the inside of a MFC, is hydrophilic in order to allow the transport of protons through the face boundary interface. This hydrophilicity causes biofilms to grow on the cathode. For suspended microorganisms originating from the anode or substrate (e.g., wastewater), the cathode may offer a thermodynamically more favorable environment than the anode due to its higher potential. The ORR consumes excess protons, stabilizing the pH, and oxygen penetration through the cathode may even provide aerobic conditions. The undesired cathodic biofilm, called biofouling, competes for substrate with the anodic biofilm, reducing the Coulomb Efficiency (CE) of a MFC [2]. However, the additional electrons produced by the microbes at the cathode can promote the ORR, hence; biofouling of the cathode can initially increase power

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densities [3,4]. With the biofilm thickening, the beneficial effect becomes overcompensated by diffusion limitation and the performance of a MFC gradually declines [5].

It is desirable to design MFCs with minimized electrode spacing, as the spacing determines the volume and consequently the volumetric power densities. It has a significant impact on the internal resistance; the closer the spacing the lower the Ohmic losses. Low Dissolved Oxygen (DO) concentrations do not necessarily inhibit power generation of a MFC [2,6]; however, oxygen crossover still demands a minimum spacing to maintain conditions at the anode that favor anode respiration [7]. Substrate and metabolite crossover from the anode can decrease cathode performance significantly due to the formation of mixed potentials and the flow of internal currents [8]. In recent years, separators between anode and cathode experienced a rebirth to deal with the issue of cathode fouling and crossover. Separators must allow a charge balance between the anode and cathode compartment, prevent oxygen and substrate crossover, retain suspended microbes, and have an as low as possible resistance. A wide variety of separator materials have been investigated, including cation exchange membranes, anion exchange membranes, polymer membranes, composite membranes, glass fiber filters, J-cloth, porous earthen plates, and nylon meshes [9,10]. While a separator protects the cathode from fouling, it is exposed to fouling itself [11]; it increases MFC costs and the internal resistance of a MFC, reducing power densities [10].

In order to improve cathode performance and life time different cathode designs, modifications, and coatings were previously investigated. Cheng et al. [12] applied additional PTFE diffusion layers to the air side of conventional cathodes and achieved an increase in power densities by up to 62%. Four PTFE layers proved to result in the best MFC performance. Even 8 layers still resulted in higher power densities than the non-coated cathodes. The layers had no effect on COD (Chemical Oxygen Demand) removal but the CE increased the more layers were applied. Sonatoro et al. [1] investigated different cathode modifications; a two layered cathode comprised of a catalyst layer (CL) and a Gas Diffusion Layer (GDL), a cathode with an additional Micro Porous Layer (MPL) and a cathode with multiple PTFE layers on the air side. The authors proved that a MPL improves cathode performance and reduces biofilm infiltration of the cathode; they also showed that power generation can be increased by applying higher PTFE concentrations in the GDL. Coating the air side of the cathode with four layers of PTFE, similar to the work of Cheng et al. [12], however, caused a reduction in power densities compared to a non-coated cathode. Watson et al. [13] applied different ion exchange polymer coatings on the solution side of the cathode. The coating increased the CE at the cost of decreased power densities. They obtained a similar performance with anion exchange and cation exchange coatings. Yang et al. [14] reported improved MFC performance by applying a Poly(vinylidene fluoride-*co*-hexafluoropropylene) phase inversion coating which had a larger oxygen mass transfer coefficient than conventional Pt/C cathodes. Polyvinyldene fluoride based coatings are a cost-effective alternative to the commonly used PTFE and can improve the CE and power densities of the MFC [15].

The cathodes rather than the anodes are the main bottleneck of Microbial Fuel Cells. They are the greatest cost factor, especially if noble metal catalysts are used and they are the component with the shortest life time. Increasing the durability of the cathodes is a crucial step for long term MFC research and practical application. Despite some minor inconsistencies in reports, applying additional coatings to MFC cathodes generally has a beneficial effect on MFC operation. In our previous studies, cathode biofouling was the limiting factor for the performance and life time of the MFCs. Preliminary experiments showed promising results from applying a diffusion membrane onto the air side of the cathodes. Both cathode life time and performance increased. Most reported work aimed to improve the structure of the cathodes or to reduce cathode costs. In this study membranes on the air side of the cathode were investigated to control oxygen flux and cathode biofouling as an alternative to coatings and separators inside a MFC. The goal was to investigate the effect and necessity of oxygen limitation on different electrode spacings. The main focus thereby was not to improve the cathode structure or oxygen distribution but to study the effects of oxygen penetration and limitation on cathode biofouling and MFC performance.

2. Materials and methods

2.1. Cell design and operation

All experiments were carried out with single chamber MFCs with air DMFC cathodes (0.5 mg cm^{-2} Pt, Elcomax, Germany). Carbon felt was used as anode material (Sigracell®, KFD 2.5 EA, SGL Group, Germany). The anodes were inoculated via direct anode to anode transfer of microbes from MFCs from previous studies; anaerobic sludge was the primary inoculum for the precursor MFCs. The anaerobic sludge originated from the local Wastewater Treatment Plant; it contained a diverse mixed microbial community [16]. Ubiquitously occurring electroactive microbes and symbiotic/syntrophic co-cultures were enriched on the MFC's anodes due to selection processes and the MFC-to-MFC inoculation. Two different MFC designs were used in this study. The first had an electrode spacing of 120 mm; a net volume of 190 ml, and equally sized electrodes of 12.56 cm^2 (one side). With this design no oxygen crossover is to be expected and anaerobic conditions at the anode can easily be maintained. The second design had an electrode spacing of 15 mm, a net volume of 35 ml and equally sized electrodes of 22.5 cm^2 (one side); oxygen crossover through the highly O_2-permeable DFMC cathode is expected to influence cell performance at such a low electrode spacing.

Synthetic blackwater served as substrate; it was composed of glucose (0.90 g l^{-1}) and NaAc (3.22 g l^{-1}) as carbon sources, the high N concentration of blackwater was set up by Urea (0.56 g l^{-1}). Nutrient salts (33 mg l^{-1} $MgCl \times 6H_2O$, 275 mg l^{-1} $CaCl_2 \times 2H_2O$, 50 mg l^{-1} K_2HPO_4, 75 mg l^{-1} $(NH_4)_2HPO_4$, 34 mg l^{-1} Na_2SO_3, 10 mg l^{-1} $FeSO4 \times 7H_2O$) vitamins (4 μg l^{-1} A, 800 μg l^{-1}C, 120 μg l^{-1} E, 11 μg l^{-1} B1, 14 μg l^{-1} B2, 14 μg l^{-1} B6, 2.5 μg l^{-1} B12, 0.05 μg l^{-1} D3, 0.75 μg l^{-1} K1, 160 μg l^{-1} Niacin, 60 μg l^{-1} Pantothenic acid, 2 μg l^{-1} Folic acid, 0.5 μg l^{-1} Biotin) and trace elements (15 mg l^{-1} $MgSO_4 \times 7H_2O$, 30 mg l^{-1} $MnSO_4 \times H_2O$, 2 mg l^{-1} $CoSO_4 \times 7H_2O$, 2 mg l^{-1} $ZnSO_4 \times 7H_2O$, 0.1 mg l^{-1} $CuSO_4 \times 5H_2O$, 0.2 mg l^{-1} $KAl(SO_4)$ $2 \times 12H_2O$, 0.1 mg l^{-1} H_3BO_3, 0.1 mg l^{-1} $Na_2MoO_4 \times 2H_2O$, 0.25 mg l^{-1} $NiCl_2 \times 6H_2O$, 0.3 mg l^{-1} $Na_2SeO_3 \times 5H_2O$) were added. No particles were simulated in the synthetic blackwater. The C/N/P/S of the substrate solution was 106/28/3/1; the COD/TOC (Chemical Oxygen Demand per Total Organic Carbon) was 2.2, at a COD of 2290 mg l^{-1} and a TOC of 1040 mg l^{-1}. The resulting conductivity was 2.8 mS cm^{-1}. In a MFC, dissolved oxygen and suspended electron acceptors compete with anode respiration. The substrate solution was therefore stored under anaerobic conditions for two days at room temperature (23 ± 3 °C) before it was added to the MFCs. The anaerobic conditioning reduced dissolved oxygen and suspended electron acceptors; COD loss was negligible but the redox potential of the substrate solution thereby dropped by 471 ± 47 mV.

2.2. Measurements and analysis

The cell voltage was logged in 15 min intervals via a multichannel data logger (ALMEMO 5690-2M09, Ahlborn, Germany).