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Exploring the use of cost-effective membrane materials for Microbial Fuel Cell based sensors

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ABSTRACT

Microbial fuel cells show great potential as a self-powered, real time and on-site technology for monitoring the labile organic carbon content (e.g. Biochemical Oxygen Demand, BOD) in water systems. By drastically reducing their cost of manufacture, MFCs can become an important tool for water quality monitoring, accessible also in the poorest and most remote areas of the world. To enable this, this study investigates for the first time the use of two low cost membrane materials: a natural polymer (eggshell membrane), and a synthetic polymer (polydimethylsiloxane, PDMS). The energy generation and sensing capability of the resulting devices were compared with a membrane-less device, while the well-known Nafion® membrane was used as a control. For each device, the effect of electrode spacing on performance was also investigated. The use of PDMS led to a power density similar to the case of the much more expensive Nafion® membrane. The electrode spacing affected the output power, but it had a negligible effect on the BOD sensing capability of the devices. In particular, for the case of the eggshell membrane and the membrane-less devices, the higher the electrode spacing the better the power performance. The opposite trend was observed when a synthetic membrane was used. Finally, although more unstable than the other devices, the eggshell membrane devices were associated with the lowest internal resistances and the highest sensitivity. In conclusion, this study not only demonstrates the use of inexpensive membranes in MFCs, but it also provides guidelines on design, in terms of electrode spacing and cross-sectional area, according to the material used.

1. Introduction

The biological oxygen demand (BOD) is a measure of the labile organic carbon content in water and is used as an index for sizing wastewater treatment plants and measuring the efficacy of wastewater treatments. [1] The standard method to determine BOD, the 5-day BOD test (BOD_5), is, however, time consuming and not compatible with rapid and on-site monitoring needs. [2] As a result, in the past decades, a lot of effort has been dedicated to the search for technologies that are less time-consuming and more reliable. [3] Table 1S-S*n* in the Supplementary Information, reports a selection of available BOD biosensors in the literature, and highlights their performance and limitations. In principle, all these biosensors show promise for rapid online monitoring of BOD in water with response times ranging from 3 up to 120 minutes. The majority of them, however, present very poor operational stability, low substrate versatility and a small measuring range. Moreover, those that rely on single microbial strains have low accuracy, due to the limited range of biodegradable compounds that they can detect.

Recently, the microbial fuel cell (MFC) has proven to be an attractive technology for BOD monitoring. The striking features of MFC-based BOD sensors are their simplicity, short period of analysis, wide measurement range, low maintenance, and the ability to work online and on-site. [4–8] When a microbial consortium is used as the bio-recognition element, rather than a single species, MFCs can detect a diverse range of biodegradable compounds in water. Moreover, the several types of MFC-based BOD sensors reported in the literature demonstrate appreciable long term stabilities and good correlation between the BOD

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content of the water and current output generated by the MFC sensor. [5,6] Most of these devices employ a two-chamber configuration. [9,10] Single chamber designs are, however, preferable because of lower operational costs, higher design simplicity and, therefore, better possibilities for industrial scale-up. [11–15]

Despite recent design efforts, reducing operational costs remains a key factor in the commercialisation of MFCs. The majority of the MFCs reported in the literature employ platinum as the catalyst at the cathode and expensive membranes, such as Nafion®. [5,6,16–18] To address these issues, catalyst-free devices have been reported, and recently the use of biomass-derived carbon materials has been investigated as a sustainable and cost-effective alternative to platinum. [19–21] Several studies on exploring the use of alternative membranes and separators have been also reported. These include: cation exchange membranes, such as sulfonated poly-ether ether ketone (SPEEK), [22] sulfonated polystyrene-ethylene-butylene-polystyrene (SPSEBS), [23] CMI-7000, [24] and Hyflon Ion; [25] anion exchange membranes, such as AMI-7000; [24,26] salt bridges; [27] and porous materials such as J-Cloth, [9,28] glass fibre filters and nylon, [29] non-woven cloth, [30] earthenware pot, [31] ceramic and terracotta, [32] compostable bags [33] and latex glove and condoms. [34,35] Although cheaper than Nafion®, some of these materials, are still relatively expensive, can be difficult to handle and can be associated with low power performance due to high internal resistances. [18] Membrane-less designs, where a biofilm at the cathode acts as the catalyst and as a living separator, have also been suggested. [36,37] In batch mode, however, these MFCs suffer from reduced power outputs over time, due to biofilm overgrowth at the cathode that reduces the efficacy of electron trasfer. [36] The focus for the majority of these studies has been on the improvement of power performance. The use of alternative membranes in MFCs has also been explored for sensing applications. Examples are the single chamber MFC-based BOD sensors that use a SPEEK membrane [38] or a microporous filter paper membrane. [15] Lastly, an MFC based on flat filter paper, where the paper acted as both the membrane material and the support for the anode and cathode, was tested to detect chromium and nickel. [39]

In order to pursue the development of cost-effective MFC-based sensors, this work looks towards the use of low cost membranes, which would further reduce the manufacturing costs of miniature MFC devices. It is expected that practical applications require the simultaneous use of more than one MFC unit. This approach would allow either increasing the current baseline, when the units are electrically connected to each other, [40] or providing multiple readings for better reliability, when the units are electrically isolated from each other. [14,41] As such, it is important to minimise, as much as possible, the cost of a single MFC device.

With this purpose, the use of a natural polymer, such as eggshell membrane, and of a synthetic polymer, such as polydimethylsiloxane (PDMS) are tested here for the first time. In previous work, eggshell membrane has been used as a template for a 3D fibrous cathode in solid oxide fuel cells, [42] while egg yolk has been tested as a base material for a biodegradable cathode in MFCs. [43] PDMS has been used as a base material for a carbon based cathode constructed around a stainless steel mesh in an MFC, in which the PDMS prevented water leakage from the device and acted as a diffusion layer. [44] This study is, however, the first that investigates the use of these materials as a membrane in an MFC for BOD sensing. The energy generation and sensing capability of the resulting devices are analysed and compared with the case of a membrane-less device, while Nafion® is used as a control. Finally, for each membrane material used, the relevance that the spacing between the anode and cathode had on performance was also investigated.

2. Experimental

2.1. Materials

All reagents used were of analytical grade and purchased from Sigma-Aldrich and Alfa Aesar. All solutions used were prepared with reverse osmosis purified water. Polydimethylsiloxane (PDMS, Dow Corning Sylgard 184) was purchased from Ellsworth Adhesives (UK). Nafion® 117 was purchased from Sigma Aldrich.

Artificial Wastewater (AW) was used as the feedstock containing (per litre): 0.27 g $(NH_4)_2SO_4$, 0.06 g $MgSO_4$.7H2O, 0.006 g $MnSO_4$.H2O, 0.13 g $NaHCO_3$, 0.003 g $FeCl_3$.6H2O, 0.004 $MgCl_2$, 3.1 NaH_2PO_4.H_2O and 10.9 Na_2HPO_4. Potassium acetate was added to the AW (between 0.1–200 mM) and used as the carbon source for the bacteria. The resulting medium was autoclaved prior to use.

2.2. Microbial fuel cells and membrane assembly

The single chamber miniature MFCs were manufactured as previously described. [45] The length of the devices was 8 mm and the width was 4 mm. The height of the MFCs, corresponding to the electrode spacing, was varied from 4 mm (anodic chamber volume, V_A = 128 μL) to 6 mm (V_A = 192 μL) and 8 mm (V_A = 256 μL). Both the anode and cathode were made of carbon cloth (untreated carbon cloth, type-B, E-Tek, USA), and the cathode was opened to the air. Four MFC configurations were manufactured using different membrane materials, Nafion® (MFC_N), eggshell membrane (MFC_E) and PDMS (MFC_P), along with a membrane-less device, where the cathode was directly exposed to the anodic chamber (MFC_M). For each type of MFC, the electrode spacing is denoted by a suffixed number (e.g. MFC_N4 denotes a Nafion® membrane with an electrode spacing of 4 mm). In the case of MFC_N, Nafion® was hot-pressed to the cathode as previously described. [45] For MFC_E, the eggshell membrane was carefully peeled off from the shell of fresh eggs (Figure 1S-S*n*), and thoroughly rinsed with deionised water prior to use. It was then cut into a 15 × 15 mm square and hot pressed to the cathode by applying a pressure of approximately 2.5 bar for 5 minutes at a temperature of 100 °C. For MFC_P, 69 mg cm^{-2} of PDMS was spin coated at 1900 rpm (SCK-100 Spin Coater, Instras Scientific) for 1 min onto the cathode surface and then cured for 40 min at 100 °C (Figure 2S-S*n*). MFC_M used a carbon cloth cathode with no further treatment. All the experiments were conducted using duplicates for each device.

2.3. Operation of MFCs

The MFCs were fed with AW at a flow rate of 0.36 mL min^{-1} (hydraulic retention time of 22 seconds), and their voltage continuously monitored as previously described. [45] An external load was connected to the MFC to polarise the cell, as shown in Figure 3S-*Sn*. Enrichment and further operation of the MFCs was undertaken as previously described, [45] except that AW contained 1% v/v of anaerobic sludge (provided by Wessex Water from a wastewater treatment plant in Avonmouth, UK), and 100 mM potassium acetate was used to enrich the MFCs for a period of 14 days. After enrichment, no sludge was added in the feed solution. The feed solution was kept anaerobic; however, depending on the specific system set-up used, we expect oxygen diffusion through the system *via* the cathode, leading to the formation of an aerobic biofilm at the cathode.

Polarisation experiments and calculations of current, power, and internal resistance were performed as previously described. [45] Current and power densities refer to the macro surface area of the anode (0.32 cm^2) and to the anodic chamber volume