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Cast and 3D printed ion exchange membranes for monolithic microbial fuel cell fabrication

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HIGHLIGHTS

- 3D printed polymer membranes produce power in MFCs.
- Natural rubber latex achieves similar power output to conventionally used membranes.
- Microscopy shows evidence of bacterial degradation/resistance to biofouling.
- pH and conductivity of anolyte play a significant role in performance of MFCs.
- Novel polymer membranes cost less than conventional cation exchange membrane.

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ABSTRACT

We present novel solutions to a key challenge in microbial fuel cell (MFC) technology; greater power density through increased relative surface area of the ion exchange membrane that separates the anode and cathode electrodes. The first use of a 3D printed polymer and a cast latex membrane are compared to a conventionally used cation exchange membrane. These new techniques significantly expand the geometric versatility available to ion exchange membranes in MFCs, which may be instrumental in answering challenges in the design of MFCs including miniaturisation, cost and ease of fabrication.

Under electrical load conditions selected for optimal power transfer, peak power production (mean 10 batch feeds) was 11.39 μW (CEM), 10.51 μW (latex) and 0.92 μW (Tangoplus). Change in conductivity and pH of anolyte were correlated with MFC power production. Digital and environmental scanning electron microscopy show structural changes to and biological precipitation on membrane materials following long term use in an MFC. The cost of the novel membranes was lower than the conventional CEM. The efficacy of two novel membranes for ion exchange indicates that further characterisation of these materials and their fabrication techniques, shows great potential to significantly increase the range and type of MFCs that can be produced.

1. Introduction

The emergence of MFC as a promising renewable energy technology is dependent on optimisation strategies to maximise the power generated using such devices. The theoretical maximum redox potential generated by an MFC is 1.14 V [1], with real systems producing operating voltages significantly lower than this. Proposed strategies for voltage multiplication such as stacking MFCs [2], have driven an increased need for miniaturisation and low cost, rapid fabrication of multiple units, in the design of MFCs. Additionally, past studies have identified one of the greatest challenges in MFC technology as being the design of scalable architectures with large surface areas for oxygen reduction at the cathode and bacteria growth on the anode resulting in higher power density [3]. However, versatility of the design of systems addressing these needs is severely limited by the materials currently used for the ion exchange membrane in an MFC.

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The ion exchange membrane electrically isolates the anode and cathode electrodes while facilitating the proton transport necessary for the redox reaction that generates the cell potential, with the exception of single chamber MFCs which use distal electrodes for this separation. Furthermore, it maximises the coulombic efficiency of the MFC by preventing oxygen diffusion to the anode electrode. Most MFC technology relies on the use of expensive commercial membranes such as Nafion (Dupont) and cation exchange membranes (CEM) which are designed for chemical fuel cells. The planar form of these materials provides low geometric versatility in the design of MFC architectures. Previous work has shown that for a fixed electrode size and anode chamber volume, power density of MFCs scales with ion exchange surface area [3]. Past research has attributed enlarged specific area of the ion exchange surface, facilitating greater ionic conductivity, to a decrease in MFC internal resistance, resulting in higher power density [4] and [5], with areas smaller than that of the electrodes significantly increasing MFC internal resistance [6]. This is particularly applicable to small MFCs which may be preferable when stacking multiple units.

Hence, 3D printed and cast, ionically conductive, monolithic structures present a natural solution to the challenges of increasing the specific ion exchange area for a given anode chamber volume and reducing the overall dimensions of the MFC by decreasing the need for supporting structural material. New ion exchange membrane materials with rapid fabrication processes such as casting and 3D printing significantly expands the range of possible MFC geometries and improves the ease of fabrication and assembly of multiple units.

Recent research has demonstrated the ability of novel, soft materials such as latex condom [7] to exceed the power output of conventional CEM membranes in conventional two chamber analytical style MFCs. Furthermore, functionality of materials such as pre-fabricated latex gloves [8] and cast ceramics [9] for ion exchange and simultaneous structural support has increased the scope of available MFC geometries. Fabrication techniques available to latex such as casting could be used to further expand the range of available architectures beyond those of commercially available pre-fabricated components (condoms and gloves) investigated previously. Cast latex could be used to produce MFCs with high geometric versatility, high power output, fast production rate and optimal materials properties such as high fracture and impact tolerance, and low cost and environmental impact. Hence, this study considers a user-fabricated membrane in contrast to previous studies documenting the use of latex as an IEM.

Nafion is conventionally used as both a membrane in MFCs [10] and as the polymer layer in soft robotic, ionic polymer metal composite (IPMC), actuators [11] due to its ionic conductivity and its function as an electrical insulator. Previous work has documented the use of Tangoplus as a dielectric elastomer (DE) actuator [12], demonstrating the material as an electrical insulator. However, the comparatively low breakdown voltage and small displacements achieved by the actuator compared to polymers more conventionally used as DE actuators suggest the migration of charged particles within the material under electrical stimulus. Hence, by exhibiting similar electro active properties to Nafion, Tangoplus shows potential for use as an ionically conductive electrode separator in an MFC. Furthermore, the hygroscopic nature of the material could be instrumental in providing micro-channels for charged particles to move through. The emergence of 3D printing has made rapid, high precision fabrication of a range of materials, including porous rubber-like polymers such as Tangoplus, widely accessible. Recent work has demonstrated 3D printing as a fabrication method of for complex, novel MFC architectures [13] and electrodes [14]. Hence, the demonstration of a 3D printed polymer as an ion exchange membrane in this study shows that 3D printing can be applied to all components of an MFC and therefore shows the possibility for printing a complete MFC as a single unit.

This study compares the efficacy of two novel materials, Tangoplus 3D printed, acrylic based photo-polymer (Stratasys/Objet Geometries) and natural rubber latex (Tomps) as the ion exchange membrane in a microbial fuel cell, using a conventional material CMI-7000 (CEM) (Membranes International Inc.) as a control population. The work aims to validate the development of MFC systems using the novel materials and fabrication processes described.

2. Experimental method

2.1. MFC design and materials

The performance of novel proton exchange membranes; Tangoplus 3D printed polymer (thickness 116 μm) and natural rubber latex (thickness 100 μm) was compared to that of conventional CEM (thickness 450 μm). The novel materials were obtained in their liquid form and planar membranes of uniform thickness were user-fabricated either by 3D printing (Tangoplus) or by casting the liquid material over a glass surface and using a K-bar (R K Print) to obtain uniform thickness (natural rubber latex) (Figs. 1 and Fig. 2).

An Eden 350V 3D printer (Stratasys/Objet Geometries) was used to print the Tangoplus membranes by photopolymer jetting. A print head was used to deposit Tangoplus acrylate photopolymer resin (Stratasys/Objet Geometries) in 29 μm thick layers. The resin was rapidly cured using UV light from lamps mounted on the sides of the print head and the build platform was lowered prior to deposition of the next layer, on top of the previous, accumulating to the complete 3D print. A gel-like support material was also printed to provide support for overhanging or complex geometries during the print. This was removed using a water jet on completion of the print.

Approximately 50 ml of liquid natural rubber latex was deposited on a glass surface using a syringe. A K Bar (RK Print), comprising a stainless steel rod with a pattern of identically shaped radial grooves, formed by precision drawn, wire windings, was used to draw the wet material across the glass surface. The spacing of the grooves controlled the wet film thickness and a No. 8 bar was used to obtain a membrane thickness of 100 μm. The material was air-cured.

The cuboid, analytical style MFC anode chamber, previously described in Ref. [15] held 25 mL of anolyte, and was open on one side, where a proton exchange membrane with a projected area of 20 cm^2 was attached (Fig. 3). An open to air cathode, with an area of 20 cm^2, made from conductive latex using a method derived from Ref. [8] was used to maintain a continuous redox reaction without

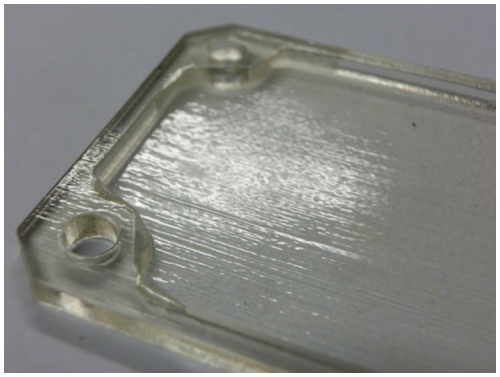

Fig. 1. Tangoplus 3D printed membrane with material grain visible on surface.