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Scaled-up continuous up-flow microbial fuel cell based on novel embedded ionic liquid-type membrane-cathode assembly

M.J. Salar-García [a, *], V.M. Ortiz-Martínez [a, *], Z. Baicha [b], A.P. de los Ríos [c], F.J. Hernández-Fernández [a]

[a] Polytechnic University of Cartagena, Chemical and Environmental Engineering Department, Campus Muralla del Mar, C/Doctor Fleming S/N, E-30202 Cartagena, Murcia, Spain
[b] Mohammed V University, Laboratory of Mechanics and Industrial Processes, Chemical Sciences Research Team, ENSET, E-10100, Rabat, Morocco
[c] University of Murcia, Chemical Engineering Department, Campus de Espinardo, E-30071, Murcia, Spain

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ABSTRACT

The capacity of MFCs (microbial fuel cells) to produce electricity from various substrates and wastes has drawn the attention of the scientific community in the last decades. Thus, this technology has become the focus of many research studies trying to improve its performance by investigating alternative materials and determining optimal operating conditions. In this work, a new single-chamber air-cathode microbial fuel cell configuration has been developed to operate in continuous mode with vertical up-flow. This design incorporates a novel embedded ionic liquid-based membrane-cathode assembly working as separator. The ionic liquids selected for the present work are triisobutyl(methyl)phosphoniumtosylate, [$P^{+}_{i4,i4,i4,1}$][TOS^{-}], and methyltrioctylammonium chloride, [$MTOA^{+}$][Cl^{-}]. MFC performance is investigated in terms of electricity production and wastewater treatment for various feed flow rates. The results show that [$P^{+}_{i4,i4,i4,1}$][TOS^{-}] outperforms [$MTOA^{+}$][Cl^{-}] when used as part of the separator due the conductivity of its anion and cation. For a feed flow rate of 0.25 mL min^{-1}, [$P^{+}_{i4,i4,i4,1}$][TOS^{-}] offers a maximum power density of 12.3 W m^{-3}_{anode} versus 6.8 W m^{-3}_{anode} achieved by the [$MTOA^{+}$][Cl^{-}]-based MFC, and also provided the highest percentage of chemical oxygen demand removal (60%). For the same ionic liquid, MFC power output increases as feed flow decreases.

1. Introduction

MFCs (microbial fuel cells) are an emerging biotechnology that could contribute to overcome the current energy crisis and meet water needs in developing world countries. A MFC is a device that transforms the chemical energy present in a substrate into electrical current [1–3]. Simple substrates such as acetate or lactate can be used as fuel, but the real potential of this technology lies in employing different types of wastes as fuel, usually domestic or industrial wastewater [4,5]. In this way, microbial fuel cells would allow these effluents to be treated while simultaneously generating electricity, offering a two-fold benefit [6]. Bacteria present in wastewater are responsible for performing the oxidation of organic matter and transferring the electrons released to the anode. Then, these electrons are led from the anode to the cathode through an external circuit, where they are consumed by an electron acceptor such as oxygen. The reduced oxygen combines with protons coming from the anode compartment, which usually cross a semi-permeable membrane, to form water [7].

However, the scaling-up of this technology poses some limitations due to its low performance and high construction costs, besides the technical difficulties in adapting lab-scale designs. Many studies have been undertaken to try to improve MFC performance and reduce their cost. For instance, researcher have focused on finding new electrode materials such as PANI (polyaniline) composite or Fe^{+3}-graphite anodes, molybdenum disulphide, nickel alloys or phthalocyanine (FePc) cathodes. Furthermore, wastes such as brewery or starch processing effluents have been analyzed as substrates to improve the practical implementation of MFCs [8].

The use of alternative high-conductivity separators is an effective way to enhance the electrical performance of MFCs. Several reports have shown the potential use of ionic liquids in exchange

* Corresponding authors. Tel.: +34 968 325551.
E-mail addresses: mariajose.salar@upct.es (M.J. Salar-García), victor.ortiz@upct.es (V.M. Ortiz-Martínez).

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membranes for their application in fuel cells [9]. Ionic liquids are well known for their great properties such as electrochemical and thermal stability, negligible volatility and high ionic conductivity, among others. They are organic salts that remain liquid at room temperature. Their unique properties make them ideal solvents for catalysis, synthesis or extraction processes. The major advantage of using ionic liquids is that their properties can be adapted to a specific process by changing the anion or the cation. Among the existing ionic liquids, the most used are those containing ammonium and phosphonium cations due to their wide application range [9,10].

MFC configuration and operation mode are other key factors that affect the performance of this technology. The simpler the design of a MFC, the easier its implementation for industrial applications. Single chamber air-cathode is the most common MFC set-up as it offers the simplest design. As regards operation mode, microbial fuel cells can work in batch or continuous flow mode [11], however, only the last option is able to produce a continuous electrical current, which widens the range of the practical applications of this technology. There are other important factors that affect MFC power generation in continuous mode such as the nature of the substrate used, pH, temperature, ionic strength, HRT (hydraulic retention time) and electrode and catalyst materials. Thus, the selection of optimal materials and operating conditions is crucial for the feasibility of this technology [12–16].

Because of the great advantages offered by continuous mode, several design options have been reported in the literature. Zhuang et al. [17] scaled up five tubular air-cathode stacked MFCs using swine wastewater as fuel, manganese dioxide (MnO_2) as catalyst on carbon fiber cloth (cathode) and graphite felt as anode. They obtained a maximum power density of 14.38 W m^{-3}_{anode} with each single cell with an organic load rate of 1.2 Kg COD (chemical oxygen demand) m^{-3} d^{-1}. Wei et al. [18] designed a double Plexiglas MFC with chambers separated by Nafion-based membrane and carbon paper using graphite rods as cathode and anode, respectively. With this configuration, they achieved a maximum power density of 66.83 mW m^{-3}_{anode} with a sucrose concentration of 3.5 g L^{-1} and 10 h of HRT (hydraulic retention time). Choi and Ahn [19] also studied the effect of electrode connection and hydraulic flow mode in single-chamber air-cathode MFCs, reaching a maximum power density of 12.8 W m^{-3}_{anode} and 44% of COD removal by connecting the electrodes of two stacked MFC in parallel at 30 °C and using platinum as catalyst and graphite brush/titanium as anode. More recently, Lay et al. (2015) investigated the influence of feeding mode on the performance of an up-flow MFC using synthetic wastewater enriched with xylose. They compared the power output of a double chamber MFC in fed-batch and continuous modes. They achieved to increase the maximum power density generated up to 2.86 W m^{-3}_{anode} in continuous mode using a commercial anion exchange membrane and graphite-based electrodes [20]. These studies are only an example of the current interest in the optimization of the performance of MFCs through the development of continuous systems more and more efficient and economically feasible.

Ionic liquid-based PIMs (polymer inclusion membranes) are a good alternative to commercial membranes, such as Nafion or Ultrex, for their use in MFCs since the selection of an appropriate ionic liquid could increase the conductivity of the separator and reduce the internal resistance of these systems [21]. In the case of air-cathode single-chamber MFCs, the standard configuration consists of placing the membrane and the cathode together. However, the resistance of the system associated to the movement of the ions of interest from the anode to the cathode is directly proportional to the thickness of the membrane plus the cathode. Recently, Ortiz-Martínez et al. [22], achieved to reduce the thickness of this configuration by embedding the membrane into a cathode made of carbon cloth. They demonstrated that this novel and more compact configuration allow MFC performance to be increased in batch mode.

In this work, an air-cathode single-chamber up-flow MFC has been designed to operate in continuous mode. It incorporates a novel embedded ionic liquid-based membrane-cathode assembly as separator. The performance of this new configuration was assessed in terms of electricity production and COD (chemical oxygen demand) removal for two ionic liquids at two feed flows, respectively. This design also implies the scaling-up -in continuous mode- of the batch-mode small capacity MFCs (150 mL) previously reported by our group [22]. The scaling-up of such MFCs in continuous mode allows a significant increase in power generation.

2. Experimental

2.1. Fuel and chemical

Wastewater from an industrial factory was used as source of organic matter and microorganisms in the continuous mode essays, being the initial COD (chemical oxygen demand) 1200 mg L^{-1}.

Two polymer inclusion membranes based on different ionic liquids were embedded into carbon cloth cathodes by casting method and tested as separators in MFCs. Respective mixtures of the ILs triisobutyl(methyl)phosphonium tosylate, $[P^{+}_{i4,i4,i4,1}][TOS]$, and methyltrioctylammonium chloride, $[MTOA^{+}][Cl^{-}]$, with PVC (polyvinyl chloride) and THF (tetrahydrofuran) were poured directly onto carbon cloth cathodes. The amount of ionic liquid in both cases was 70% w/w of the PVC/IL mixture. The solvent was allowed to evaporate overnight. The method followed to prepare this embedded membrane-cathode assembly is in accordance with the procedure proposed by our group [22]. Fig. 1 shows a scheme of the method of preparation of this type of separator. As demonstrated in such work, this design allows higher power densities to be obtained when compared with a typical configuration of membrane and cathode in direct contact after being manufactured separately. The cathode was made of 10% wet proofing carbon cloth (Fuel cell earth, EEUU) sprayed with platinum solution (0.5 mg cm^{-2}). The anodes consisted of a combination of graphite bar and carbon granules.

2.1.1. Ionic liquids

Triisobutyl(methyl)phosphonium tosylate, $[P^{+}_{i4,i4,i4,1}][TOS^{-}]$, and methyltrioctylammonium chloride, $[MTOA^{+}][Cl^{-}]$, were selected to prepare the PIMs (polymer inclusion membranes). These types of novel separators are stable at room temperature with a flexible and non-adhesive appearance and have high conductivity [21]. These two PIMs were embedded into the cathodes forming respective membrane-cathode assemblies with a final thickness of 0.5 mm for both ionic liquids. The final weight was 20.1 and 21.3 g for $[MTOA^{+}][Cl^{-}]$ and $[P^{+}_{i4,i4,i4,1}][TOS^{-}]$-based assemblies, respectively. The performance of the MFCs using both separators was compared in terms of maximum power output. Table 1 shows the structure of the anions and cations of the ionic liquids selected.

2.2. Microbial fuel cell configuration

A cylindrical PVC (polyvinylchloride)-methacrylate up-flow reactor was used as single chamber air-cathode microbial fuel cell, with a total volume of 1.7 L. Fig. 2 shows the main components of the reactor.

A PVC-filter containing carbon granules is placed inside a methacrylate housing, with a plastic cap on the top of the reactor with three holes. The first hole is used to feed the MFC with