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Bioelectricity production from municipal leachate in a microbial fuel cell: Effect of two cathodic catalysts

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ABSTRACT

The objective of this work was to evaluate the effect of the cathodic catalyst (either chalcogenide or Pt) on bioelectricity production from actual municipal leachate in a microbial fuel cell equipped with an anode made of granular graphite (MFC-G) and seeded with an inoculum enriched in Mn(IV)-reducing bacteria.

Each face (I and II) of the MFC-G was characterized by separate (I and II), in series, and parallel connection. Parallel connection of faces increased the maximum volumetric power up to 1239 and 1799 mW m^{-3} for $Ru_xMo_ySe_z$ and Pt, respectively. In general parallel connection of electrode faces significantly decreased the R_{int} (44 and 77 Ω for $Ru_xMo_ySe_z$ and Pt, respectively). In the batch operation where the cells were connected to external resistances (R_{ext}) the average volumetric powers $P_{V\text{-}ave}$ in the second cycle of batch operation were 1005 ± 5 and 1317 ± 687 mW m^{-3} whereas organic matter removal efficiencies of 70 and 85% were registered for the $Ru_xMo_ySe_z$ and Pt, respectively. During the repetitive batch operation of the cells loaded with an actual leachate there was preliminary evidence of an in-cell enrichment process. In principle, the MFC with catalyst $Ru_xMo_ySe_z$ exhibited a performance 24% and 20% lower than that with Pt (on $P_{V\text{-}ave}$ and organic matter removal basis, respectively). This would point to a trade-off or compromise solution, since the cost of $Ru_xMo_ySe_z$ catalyst is 70% lower than that of Pt.

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Introduction

A microbial fuel cell (MFC) is an electro-biochemical reactor capable of directly converting organic matter into electricity [1,2]. Platinum (Pt) has been commonly used as a catalyst of the oxygen reduction reaction (ORR) in MFCs. Yet the high cost of an MFC is mainly due to the high price of this noble metal [3,4]. For instance, Pant et al. [3] have mentioned that material costs constitute a crucial factor in the success of bio-electrochemical systems (BES) technology. According to them, one of the reasons for the existing high cost of BESs is the use of expensive Pt as a catalyst is the electrodes, typically at concentrations of up to 0.5 mg cm^{-2} of electrode surface area. In order to abate high costs, several replacements of Pt have been tested in MFC the last years, such as CoTMPP (0.6 or 1.2 mg cm^{-2}), iron phthalocyanine (1.0 mg cm^{-2}), manganese dioxide (MnO_2), chalcogenides (1.0 mg cm^{-2}), and a low cost activated carbon. In another work [4] the high cost of MFC construction due to the use of platinized electrodes and proton exchange membranes made of Nafion have also been discussed. The authors proposed and successfully tested non-platinized air electrodes that performed satisfactorily in the presence of acetate under MFC conditions of ambient temperature and neutral pH for the oxygen reduction reaction.

The high cost of Pt, in turn, could deter the commercial MFC applications. So, the development of new materials with high catalytic properties to perform oxygen reduction is presently a task of great importance [5–8]. One of the challenges in microbial fuel cells research consists of the application of new electrochemically active catalytic materials (such as $Ru_xMo_ySe_z$ [9] as alternative electrocatalysts to replace the extensive use of the more expensive platinum). Vazquez-Larios et al. [9] evaluated the application of bimetallic chalcogenide $Ru_xMo_ySe_z$, as an ORR catalyst and two anodic materials on the performance of two MFCs fed with synthetic substrate. In that work, they found that the power delivered by the MFC fitted with graphite triangular pieces and chalcogenide catalyst was 43% inferior to that of a similar cell with Pt, although the cost of the first catalyst is significantly lower than that of Pt., *i.e.*, 73% lower, where the cost calculations take into account the different dosages of the catalysts. The use of $Ru_xMo_ySe_z$ as cathodic catalyst in MFC is scarce, to the best of our knowledge. There are, however, a few antecedents that report the use of $Ru_xMo_ySe_z$ as cathodic catalyst in hydrogen fuel cells [10]. In these studies, it was concluded that the maximum performance achieved for the electro-reduction of oxygen was with a loading of 1.0 mg cm^{-2} $Ru_xMo_ySe_z$ 20 wt%/C, arriving to a power density of 240 mW cm^{-2} at 0.3 V and 80 °C [10,11].

On the other hand, Pt has been used as the catalyst of choice of the ORR in a plethora works of microbial fuel cells [12–23]. In this set of references, the concentration of Pt used in the cathode was 0.5 mg cm^{-2}. In another work, Cheng et al. [21] evaluated the effect of Pt concentration in the cathode on MFC performance, in the range 0.1 to 2.0 mg Pt cm^{-2}. They observed that when the Pt loading on cathode was reduced from 2 to 0.1 mg cm^{-2}, the maximum power density of MFC decreased by *ca.* 19%. Based on the above results, and as a trade-off, the dose of choice would be 0.5 mg Pt cm^{-2} that would save up to 75% costs of Pt (compared to the dose 2 mg cm^{-2}) with a reduction of cell performance less than 19%.

On the other hand, municipal leachate is an aggressive effluent with relatively high concentration of organic matter [24,25]. Leachate from sanitary landfills is of concern in Mexico City, since very recently the Bordo Poniente mega landfill has been closed and it is known that it generates large amounts of both fresh and aged leachates. So far, the available information on treatment of municipal leachate in MFCs loaded with inoculum enriched in Mn (IV)-reducing bacteria is still scarce. Previous works have demonstrated the feasibility of using leachate as substrate in MFCs. Yet, the powers delivered were in the low-to-mid side of the range. Greenman et al. [26] demonstrated that it was possible to generate electricity and simultaneously treat landfill leachate in MFC columns; they observed a power density of 1.35 mW m^{-2} and 43% BOD removal. Gálvez et al. [27] operated three MFCs hydraulically connected in series for simultaneous leachate treatment and electricity generation. The system when configured into a loop was able to remove 79% of COD and 82% of BOD_5 after 4 days. Ganesh & Jambeck [28] treated landfill leachate in cylindrical single air-cathode without inoculation; they observed a volumetric power (P_V) of 699 mW m^{-3} and 74% COD removal. Tugtas et al. [29] investigated the treatment of anaerobically pre-treated landfill leachate in batch and continuous-flow two-chambered MFCs. They reported a P_V of 2482 mW m^{-3} and 90% COD removal. On the other hand, Puig et al. [30] evaluated an air-cathode MFC fed with landfill leachate, the P_V was 344 mW m^{-3} whereas the COD removal was 70%. It can be seen that, in general, volumetric powers obtained in MFC fed with leachate were in the low-to-mid part of the power range reported in the literature.

We hypothesized that organic substances contained in leachates would be likely recovered as bioelectricity in a MFC. Thus, the objective of this work was to evaluate the use of an inoculum enriched in Mn(IV)-reducing bacteria as well as the effect of the cathodic catalyst (either chalcogenide or Pt) on bioelectricity production from actual municipal leachate in a microbial fuel cell equipped with an anode made of granular graphite.

Materials and methods

Microbial fuel cell architecture

The MFC-G (Fig. 1) consisted of a horizontal cylinder built Plexiglass 90 mm long and 57 mm internal diameter. The opposing faces of the cylindrical shell were fitted with corresponding sets of an assemblage of (inside to outside) proton exchange membrane (Nafion 117), a Toray flexible carbon-cloth containing 1 mg cm^{-2} $Ru_xMo_ySe_z$ (20wt%/C) or 0.5 mg cm^{-2} platinum catalyst (Pt 10 wt%/C-ETEK), and a perforated plate of stainless steel 1 mm thickness.

Each assemblage was corresponded with anodes made of granular graphite and a graphite rod as collector (80 mm long and 5 mm diameter). The average separation between cathode-anode in MFC-G was 17.5 mm. The geometric volume of the anodic chamber was 229.7 mL whereas the net volume was 100 mL (geometric volume minus volume of the anodic