



Power generation in microbial fuel cells using platinum group metal-free cathode catalyst: Effect of the catalyst loading on performance and costs



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HIGHLIGHTS

- PGM-free different loadings were investigated in RRDE and MFC.
- In RRDE, increase in loading led to better performance and lower H₂O₂ produced.
- A 2x2e⁻ transfer mechanism can be speculated.
- Power densities in MFCs varied between 90 ± 9 μWcm⁻² and 262 ± 4 μWcm⁻².
- Increase in power density coincides with increase in the loading and in the cost.

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ABSTRACT

Platinum group metal-free (PGM-free) catalyst with different loadings was investigated in air breathing electrodes microbial fuel cells (MFCs). Firstly, the electrocatalytic activity towards oxygen reduction reaction (ORR) of the catalyst was investigated by rotating ring disk electrode (RRDE) setup with different catalyst loadings. The results showed that higher loading led to an increased in the half wave potential and the limiting current and to a further decrease in the peroxide production. The electrons transferred also slightly increased with the catalyst loading up to the value of ≈ 3.75. This variation probably indicates that the catalyst investigated follow a 2x2e⁻ transfer mechanism. The catalyst was integrated within activated carbon pellet-like air-breathing cathode in eight different loadings varying between 0.1 mgcm⁻² and 10 mgcm⁻². Performance were enhanced gradually with the increase in catalyst content. Power densities varied between 90 ± 9 μWcm⁻² and 262 ± 4 μWcm⁻² with catalyst loading of 0.1 mgcm⁻² and 10 mgcm⁻² respectively. Cost assessments related to the catalyst performance are presented. An increase in catalyst utilization led to an increase in power generated with a substantial increase in the whole costs. Also a decrease in performance due to cathode/catalyst deterioration over time led to a further increase in the costs.

1. Introduction

Cathode reduction is the bottleneck reaction in several of the electrochemical and bio-electrochemical systems [1–4]. Despite several oxidants are proposed and used [5], the majority of those systems utilize oxygen as final electron acceptor due to unique characteristics that it possesses such as high potential towards the reduction reaction, natural high availability, low cost and the fact that is continuously naturally provided to the cathode without the necessity of supplying or substituting it. The oxygen reduction reaction (ORR) suffers of several

kinetic problems that were well described previously [1–3]. The situation gets even worse when working in neutral media in which H⁺ and OH⁻ that are main participants within the reaction are in an extremely low concentration (10⁻⁷ M) [6,7]. Therefore, the reaction kinetic needs to be accelerated with supplement of catalysts. Biotic and abiotic catalysts are usually used in neutral conditions. Biotic catalysts are mainly enzymes and bacteria. Despite enzymes are extremely active and selective in neutral media [8–11], they are expensive and not durable in harsh and polluted environments [12]. Bacteria catalysis for ORR is slow and electron transfer mechanisms are not fully understood

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[13–16]. Abiotic catalysis instead is more used and based of utilization of high surface area carbonaceous materials, platinum group metal (PGM) catalysts and platinum group metals-free (PGM-free) catalysts. Few reviews summarize the achievements on the catalysis in neutral media [17–22]. The first choice is quite utilized lately due to the material low cost, durability and the relatively high electrocatalytic activity towards ORR [21–28]. In the recent years, activated carbon (AC) is by far the most adopted catalyst in microbial fuel cells (MFCs). Platinum catalyst was heavily adopted for MFCs application but recently abandoned due to the high cost that hinder large scale applications and then MFC commercialization and also due to the low durability in polluted environment containing anions such as sulfur, chloride, etc [29–32]. The application of PGM-free catalysts for MFCs applications had a steep increase in the recent years due to the material low cost and higher ORR catalytic activity compared to AC and Pt [1,17].

Different categories of PGM-free named i) metal oxides [33–37]; ii) Fe, Co, Ni metal center macrocyclic organic compounds [38–46]; iii) metal and organic compounds subject to high temperature treatment [47–56] have been largely explored and investigated. In more details, the first category is composed by materials based on metal oxides with transition metals such as Fe, Co, Ni, Mn, etc [33–37]. The second category is based on macrocyclic organic compounds with Fe, Co, Ni, Mn, etc as metal center integrated in the structure [38–46]. The main organic structures are porphyrins and phthalocyanine and this type of PGM-free does not go through a high temperature (pyrolysis) process. The last category is a synthetic method that adopt high-temperature in which the precursors (organic based and metal based) are pyrolyzed at a temperature above 800–900 °C [47–56].

Metal-nitrogen-carbon (M-N-C) PGM-free catalysts are based on atomically dispersed transition metal onto a nitrogen rich carbon substrate. Several successful examples with excellent performance are presented in literature utilizing Fe [38,51,57–60], Co [61,62], Ni [33–63] and Mn [34,35]. The catalysts are then incorporated into air-breathing cathodes and integrated into MFCs. The high durability of PGM-free catalysts working in MFCs was also presented [29,30,51,64]. It was recently shown that PGM-free catalyst can be mixed with AC and polytetrafluorethylene (PTFE) and pressed onto a current collector. PTFE is used as binder and is preferred to Nafion due to the much lower cost and its hydrophobic properties that benefit the performance. Lately, this solution is actually the most used due to the positive combination of cathode structure and high catalyst activity [29,30,64,65]. In fact, AC/PTFE pellet-type air breathing configuration enhances the three phase interface (TPI). Moreover, superior electrocatalytic activity of PGM-free catalysts was also shown using rotating ring disk electrode (RRDE) [64,66].

To the best of our knowledge, till now, there is no work presented in literature in which different PGM-free catalyst loadings added to the AC/CB/PTFE matrix are presented. In this investigation, the electrocatalytic activity of air-breathing cathode having different Fe-based catalyst loadings that varied between 0.25 mgcm⁻² till 10 mg cm⁻² were studied. Electrochemical performance as well as cost analysis are here presented in order to optimize the cathode performance for utilization in MFCs.

2. Materials and method

2.1. Catalyst preparation

Fe-AAPyr cathode catalysts working in MFC was previously reported [54,66–69]. Surface chemistry and morphology of the catalyst were deeply investigated in previously reported literature [29,54,66–69]. Briefly, the catalyst was prepared utilizing sacrificial support method (SSM). Particularly, iron nitrate (Fe(NO₃)₃·9H₂O) and aminoantipyrine were mixed with a dispersion of silica (Cab-O-Sil™ LM150, ~200 m² g⁻¹) used as a template and then manually grounded using a mortar and a pestle. The sample was then inserted into a furnace

in which the temperature was increased with a ramp rate of 25 °C min⁻¹. When reached the temperature of 950 °C, the temperature was kept constant for 30 min and pyrolysis took place. The entire heat treatment was done in inert atmosphere utilizing a constant flow rate (100 mLmin⁻¹) of Ultra High Purity (UHP) nitrogen. The silica used as sacrificial support was then etched using a dilute solution of HF (20% wt). The catalyst was then washed several times using DI water till neutral pH was reached. The catalyst was then dried at 85 °C to remove the excess in water.

2.2. Rotating ring disk electrode experiments

Rotating Ring Disk Electrode (RRDE) experiments were carried out using a glassy carbon electrode (Pine Research, USA) with polycrystalline Pt outer ring. An ink was then prepared and applied on the disk electrode. The ink was formulated using 8.5 parts of IPA:H₂O (isopropanol:water 1:4 ratio) mixture and 1.5 part of 0.5 wt% Nafion with 5 mg of only Fe-AAPyr catalyst. The obtained mixture was ultrasonicated and then shaken for 4 min and 3 min respectively (three times each procedure). A pipette was used for drop casting the ink onto the disk that was then naturally dried in atmospheric environment. Eight different loadings were used during the RRDE investigation. The electrolyte used was 0.1 M potassium phosphate buffer (K-PB) electrolyte solution (pH 7.5) that was inserted into an electrochemical cell and vigorously purged with oxygen for over 20 min. This type of buffer was used to keep the pH stable at 7.5 during the duration of the tests and keep a “clean” solution avoiding the presence of sulfur and other pollutants that might interact directly with the catalyst diminishing its performance in RRDE. Linear sweep voltammetries (LSVs) were run at a scan rate of 5 mVs⁻¹ in the potential range of 500 mV/-700 mV (vs Ag/AgCl). The electrode was kept at constant rotation speed of 1600 RPM. Pine bichannel potentiostat was used with a graphite rod as counter electrode and Ag/AgCl electrode (3 M KCl) as the reference electrode.

The disk current (I_{disk}) and the ring current (I_{ring}) were obtained and used to evaluate the hydrogen peroxide produced (%H₂O₂) using the following equation (1) (eq. (1)):

$$\%H_2O_2 = \frac{200 \times \frac{I_{\text{ring}}}{N}}{I_{\text{disk}} + \frac{I_{\text{ring}}}{N}} \quad (1)$$

The number of electron transferred (n) can be also calculated using equation (2) (eq. (2)):

$$n = \frac{4I_{\text{disk}}}{I_{\text{disk}} + \frac{I_{\text{ring}}}{N}} \quad (2)$$

N is the collection efficiency that was 0.43 as reported by the supplier.

2.3. Cathode preparation

Fe-AAPyr catalyst was then incorporated within an air-breathing cathode. The preparation was described previously in details [54,64]. Particularly, activated carbon (AC, SX Ultra Norit, Sigma Aldrich), carbon black (CB, acetylene 50% compressed, Alfa Aesar) and polytetrafluorethylene (PTFE, 60% emulsion, Sigma-Aldrich) with a percentage in weight of 70%:10%:20% respectively were mixed within a grinder and milled for few minutes. The obtained mixture was then mixed vigorously with the catalyst in different concentration. The total weight added on the circular pellet die was 500 mg. This was due to the fact that a constant total loading of 50 mgcm⁻² was used in order to keep the thickness of the air-breathing cathode constant within the different mixtures. Eight different loading were investigated as reported in Table 1. Each mixture was then pressed on a stainless steel mesh used as current collector at 2 mT for 5 min as previously described [54,64].

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