Influence of platinum group metal-free catalyst synthesis on microbial fuel cell performance

Carlo Santoro[1], Santiago Rojas-Carbonell[1], Roxanne Awais, Rohan Gokhale, Mounika Kodali, Alexey Serov, Kateryna Artyushkova, Plamen Atanassov[*]

Department of Chemical and Biological Engineering, Center for Micro-Engineered Materials (CMEM), University of New Mexico, Albuquerque, NM 87131, USA

HIGHLIGHTS

- Iron-Nicarbazin was synthesized using Sacrificial Support Method.
- Temperature treatment and acid treatment modify the surface chemistry.
- Etching and second pyrolysis affect positively the performances.
- Maximum MFC power output achieved in this work was $214 \pm 5 \ \mu Wcm^{-2}$.
- High reproducibility was detected within three independent batches.

ARTICLE INFO

ABSTRACT

Platinum group metal-free (PGM-free) ORR catalysts from the Fe-N-C family were synthesized using sacrificial support method (SSM) technique. Six experimental steps were used during the synthesis: 1) mixing the precursor, the metal salt, and the silica template; 2) first pyrolysis in hydrogen rich atmosphere; 3) ball milling; 4) etching the silica template using harsh acids environment; 5) the second pyrolysis in ammonia rich atmosphere; 6) final ball milling. Three independent batches were fabricated following the same procedure. The effect of each synthetic parameters on the surface chemistry and the electrocatalytic performance in neutral media was studied. Rotating ring disk electrode (RRDE) experiment showed an increase in half wave potential and limiting current after the pyrolysis steps. The additional improvement was observed after etching and performing the second pyrolysis. A similar trend was seen in microbial fuel cells (MFCs), in which the power output increased from $167 \pm 2 \ \mu W \ cm^{-2}$ to $214 \pm 5 \ \mu W \ cm^{-2}$. X-ray Photoelectron Spectroscopy (XPS) was used to evaluate surface chemistry of catalysts obtained after each synthetic step. The changes in chemical composition were directly correlated with the improvements in performance. We report outstanding reproducibility in both composition and performance among the three different batches.

1. Introduction

Bioelectrochemical systems are fascinating technologies in which electroactive microorganisms consume a variety of organic compounds and release electrons directly on the anode electrode [1,2]. Microbial fuel cell (MFC) is by far the most studied with the perspective of generating electricity for practical applications and removing organics and pollutants from the electrolyte [3,4]. One of the biggest problems related to the electrochemical performances of bioelectrochemical systems (BESs) is certainly the sluggish cathodic reaction. Several oxidants were utilized and studied, but by far oxygen represents the best option

due to several intrinsic characteristics such as high reduction potential and the natural availability without a cost associated with it [5–7]. Oxygen reduction reaction (ORR) suffers from numerous severe limitations when it occurs in neutral media, and therefore an optimization of the catalyst is needed to accelerate the process [8–10]. First, high activation overpotentials exist, being as high as 50–100 mV when enzymes are utilized [11–14], 200–300 mV in the case of platinum based group metal (PGM) catalysts [15,16] or platinum group metal-free (PGM-free) catalysts [17–22], and even larger in the case of bacterial catalyst [23–25] or carbonaceous materials [26–33]. Second, the ORR reaction kinetics is very slow mainly due to the neutral pH, in which

---

both H^+ and OH^- are present in low concentration and both of them participate directly as reactants of ORR, the first one via the acidic pathway and the second one via the alkaline pathway [5,6,25]. Moreover, unfortunately, due to the presence of biotic matter on the anode electrode, the increase in temperature, which can usually be used to enhance the kinetic rate of ORR, cannot be utilized to a full extent as it can degrade the entire microbiological system [34,35]. To be competitive with other energy sources or wastewater treatment systems, the cost of the catalyst in a low current/energy producing system must be considered. Both enzymes and platinum-based electrocatalysts are expensive, and moreover, are not durable at conditions in which pollutants and anions are present in abundance [36–40]. Bacterial catalysts also can not be used due to their low kinetics and high activation overpotentials [23–25], making carbonaceous based and PGM-free catalysts the only suitable candidates to be utilized in catalyzing ORR in MFCs. The application of both types of catalysts is increasing over time as was summarized in a recent review [16,41–43]. Considerable effort was devoted to using commercial high surface area carbonaceous materials such as activated carbon (AC) [44–50], modifying it to increase the surface area or to functionalize it to enhance ORR [44–50]. Moreover, the ongoing research is focused on developing, fabricating and studying new carbonaceous materials such as graphene [23,30,51,52], carbon nanotubes and carbon nanofibers [53,54] etc. All of these materials have outstanding properties such as high surface area, high resistance to corrosion, high mechanical strength, relatively high electrical conductivity in common. Carbonaceous materials demonstrated high durability in long terms operations with losses identified in 15–30% over one-year operations [49,55].

In parallel, application of PGM-free materials has risen significantly mainly due to the relatively affordable cost of the high performing catalysts that are made out of transitional metals such as Fe, Mn, Ni and Co. Three types of PGM-free materials were recently used in MFCs [16,42,43]. The first type is based on the utilization of transitional metal oxides such as Fe, Co, Ni, etc [56–61]. The improvement compared to AC is certainly important, but still, there are obvious limitations in performance [56–61]. The second type is based on the use of non-pyrolyzed macrocyclic organic compounds such as porphyrins, phthalocyanine, etc. with the incorporation of the metal center such as Fe, Co, Ni [62–70]. Despite the high performances achieved, the main limitation is the high cost of the macrocyclic organic compounds that hinder their introduction in the commercialization world [62–70]. The third type is based on the high-temperature synthetic method in which metal salts and an organic rich in nitrogen precursors are pyrolyzed at a temperature above 900 °C [71–77]. The last type is the most adopted for fabricating catalysts utilized in MFCs [26,42,43]. Fe-based catalysts seem to be the most promising since they perform better than Co-based catalysts [17,18]. Mn-based [17,18] and Ni-based [17,18] had high performances compared with bare AC but their performances were lower compared to Fe- and Co-based catalysts.

The method we adopted to produce our catalyst is based on a technique named Sacrificial Support Method (SSM) [79,80]. This method was used to create catalysts that were previously tested in MFCs [37,38,47,71,74–76,78]. SSM technique consists of mixing metal salt and organics precursors with monodispersed silica acting as a template. The etching of the silica using aggressive acidic conditions allows creating a three-dimensional structure.

In this work, a catalyst was prepared using SSM technique following six steps. The organic precursor (Nicarbazin, N-C source) was mixed with the metal salt (iron nitrate, metal source) and the templating silica particles (step 1). The mixture was then pyrolyzed in reducing atmosphere (step 2). After pyrolysis, the mixture was ball-milled (step 3) and then silica was etched (step 4). The second pyrolysis was applied to the sample (step 5) and then the obtained material was further ball-milled (step 6). Three separate batches were used to fabricate the catalysts. A small quantity of material was saved after every synthesis step. The electrocatalytic activity toward ORR of the catalyst produced after each step in three different batches was evaluated using rotating ring disk electrode (RRDE) in neural media. Those measurements allowed measuring the disk and ring current and identifying the H_2O_2 produced as well as the electron transfer mechanism involved. The catalysts were then incorporated into air-breathing cathodes and tested in working microbial fuel cells. After every synthetic step, the surface chemistry of the catalyst was analyzed by X-ray Photoelectron Spectroscopy (XPS) and it was then related to the electrochemical performance of the catalyst both in RRDE and in MFCs.

2. Materials and method

2.1. Catalyst preparation

Three different batches of the PGM-free catalyst were prepared, and particularly, a sample of the product was collected and saved for testing for each step of the synthesis.

The synthesis consists of six main steps identified as 1) mixing; 2) the first pyrolysis; 3) ball milling; 4) etching; 5) the second pyrolysis; 6) ball milling. The mixing step consists in combining 55.6% (wt./wt.) of the organic precursor (Nicarbazin, Sigma-Aldrich, 98%), 11.0% (wt./wt.) of in-house prepared Stöber spheres, 13.9% of LM-150 fumed silica (Cabot); 13.9% of OX-50 hydrophilic fumed silica (Aerosil) and 5.6% of iron nitrate nonahydrate (Sigma-Aldrich, 99.95%). The mixing was initialized adding deionized water. The obtained mixture was stirred overnight at a constant controlled temperature of 45 °C and 300 RPMs. After becoming a dry solid mixture, a further dry treatment was done using an oven at 85 °C for additional 16 h. The dry mixture was then ball milled with agate glassware at 350RPM for 30 min, and a sample of each batch was collected (labeled A1, A2 and A3 respectively) (Table 1). These three samples were selected for the surface chemistry analysis only, but not for the electrochemical measurements. This decision was dictated by the fact that the mixture was not electrically conductive (organic, inorganic precursors and a substantial amount of non-conductive SiO_2).

After the fine powdered mixture was obtained from the previous step, it was subjected to the first heat treatment (HT). The powder was placed in a porcelain boat and introduced into a quartz tubular furnace. The tubular configuration allowed a reductive atmosphere of 7 at% hydrogen balanced with ultra high purity (UHP) nitrogen flow (100 cm³ min⁻¹). The furnace was preheated at 525 °C, and then the quartz tube containing the sample was placed in the hot zone of the furnace. Then, the temperature was increased to 900 °C by a ramp rate of 75 °C min⁻¹. Once reached the designated point, the temperature

Table 1
Description of the samples studied and the synthesis steps done.

Sample number	1st pyrolysis	Ball milling	etching	2nd pyrolysis	Ball milling	Sample abbreviation
1,2,3						A
4,5,6	x					1P
7,8,9	x	x				1PB
10,11,12	x	x	x			1PBE
13,14,15	x	x	x	x		1PBE2P
16,17,18	x	x	x	x	x	1PBE2PB