Anode and cathode materials characterization for a microbial fuel cell in half cell configuration

Deepak Pant, Gilbert Van Bogaert, Christof Porto-Carrero, Ludo Diels and Karolien Vanbroekhoven

ABSTRACT

Microbial fuel cells (MFCs) are novel bioelectrochemical devices for spontaneous conversion of biomass into electricity through the metabolic activity of the bacteria. Microbial production of electricity may become an important source of bioenergy in future because MFCs offer the possibility of extracting electric current from a wide range of soluble or dissolved complex organic wastes and renewable biomass. However, the materials used in these devices are still not economic and researchers use different materials as cathode and anode in MFCs. This results in variable performance which is difficult to compare. We tested several commercially available materials for their suitability as anode in an acetate fed MFC. Besides, a novel non-platinized activated carbon (AC) based, gas porous air cathode was also tested. Both the anode and cathode were tested in a half cell configuration. Carbon cloth, graphite cloth and dynamically stable anode (DSA) served as ideal anode material with carbon cloth and graphite mesh reaching the open circuit voltage (OCV) of acetate oxidation (−500 mV vs. Ag/AgCl). The effect of increasing concentration of acetate on anode OCV was also investigated and results showed that on increasing the acetate concentration from 10 mM to 40 mM has no adverse impact on the anodic activity towards electrochemical oxidation of acetate. The AC cathode showed stable current (−1.2 mA/cm^2) over a period of 100 days.

Key words | anode, cathode, current density, microbial fuel cells

Deepak Pant (corresponding author)
Gilbert Van Bogaert
Christof Porto-Carrero
Ludo Diels
Karolien Vanbroekhoven
Separation & Conversion Technologies,
VITO - Flemish Institute for Technological Research,
Boeretang 200,
2400 Mol
Belgium
E-mail: *deepak.pant@vito.be*;
pantonline@gmail.com

INTRODUCTION

Energy from wastewater as a renewable energy source is one of the key issues being explored currently in order to reduce mankind's dependence on non-renewable sources such as fossil fuels. Microbial fuel cells (MFCs) have gained a lot of attention in recent years as a mode of converting organic waste including low-strength wastewaters and lignocellulosic biomass into electricity (Logan 2009; Pant *et al.* 2010a). Municipal sewage is an example of an abundant low-strength wastewater which contains a wide variety of organic compounds and is dominated by compounds that occur in food, including carbohydrates (25 to 50%), protein (40 to 60%), and fats and oils (10%). The high concentrations of protein and fat relative to carbohydrates and the overall low substrate concentrations make municipal wastewater a poor candidate for production of liquid biofuels, which are produced by direct fermentation of carbohydrates and are relatively difficult to separate from the water (Angenent and Wrenn 2008). Acetate is an ideal substrate for such a system, and the recalcitrance of many types of wastewater makes them more difficult to be utilized in MFC than acetate (Sun *et al.* 2009).

A simultaneous wastewater treatment and electricity production using MFCs is a likely short-term application, however, at this moment, limited by low power densities using the existing design (Rismani-Yazdi *et al.* 2008). Furthermore, MFCs basically rely on the use of, both expensive, platinum

doi: 10.2166/wst.2011.217

as a catalyst in the electrode and a proton exchange membrane (PEM) between the cathode and anode. Besides, Pt faces future unavailability (Yu *et al.* 2007) and the PEM Nafion has a too high permeability to oxygen (Chae *et al.* 2008). Also from the anode materials perspective, a variety of materials have been tested with varying results (Feng *et al.* 2010). Half cell measurements are an efficient and rapid way of characterizing large number of electrodes in short time. Recently, a similar approach was used to understand the factors affecting the performance of MFCs for sulfur pollutants removal (Zhao *et al.* 2009).

The aim of this paper is to investigate different materials for their suitability for use as an anode in MFCs, both in terms of chemical oxygen demand (COD) removal as well as current production. The influence of the substrate concentration was investigated by increasing the COD in MFCs with different anode materials. Most experiments have been performed with a COD of approximately 700 mg/l or 10 mM acetate. In this study, the MFC performance was determined in function of increasing COD in the influent. The purpose is to determine the highest COD level which can be applied without a drop in efficiency. Besides, a novel non-platinized activated carbon (AC) based, gas porous cathode developed in our laboratory was also tested for its stability for oxygen reduction when used as an air cathode in a half cell configuration.

MATERIALS AND METHODS

Anode and cathode materials and surface area measurement

Activated carbon cloth was obtained from Ballard, USA. Expanded graphite cloth was supplied by Zibo Duocheng Co., Ltd., Shandong, China. DSA electrode was procured from Vlaamse instelling voor technologisch onderzoek, VITO's materials group. The AC cathode was developed at VITO, Belgium itself. The Brunauer, Emmett and Teller (BET) surface area was measured using Quantachrome NovaWin 2 (Version 2.2) using nitrogen as analysis gas.

Experimental set-up

Both the anode and cathode were tested in a half cell configuration where the anode/cathode was the working electrode, Ag/AgCl – 3 M KCl (+199 mV vs. SHE) was the reference electrode (Radiometer Analytical, France) and a Pt disk laser welded on a Titanium (Ti) plate served as the counter electrode (CE). To prevent interference of gases (O_2 or H_2) which can be produced at the counter electrode during the polarization measurements, an ion permeable separator, Zirfon® was placed between the working electrode and the CE.

Both anode and cathode half cells were operated in a recycled flow batch mode (Figure 1). Acetate (sodium acetate, 2 M stock solution) was periodically added to the feed bottle until a concentration of 10–40 mM was reached, when the COD/acetate dropped below 150 mg/L resulting in a concomitant increase in OCV.

The cells were inoculated from a previously running MFC in our lab that has been in operation for 12 months with acetate as substrate. Phosphate buffer solution (PBS) was composed of (mM): NH_4Cl (3.7), NaCl (6.8), $MgCl_2.6\ H_2O$ (1.0), KH_2PO_4 (3.7) and yeast extract (10 mg L^{-1}). The pH was adjusted to 7.0 and the buffer was autoclaved afterwards. Ultrapure (Mili Q) filtered water was used for solution preparation, and all chemicals and reagents used were of analytical grade.

Analytical methods

Polarization curves were obtained by imposing a linear potential decrease of −1 mV/s from the open circuit voltage (OCV) potential to a cell potential of 0 mV followed by a linear voltage increase of 1 mV/s of the cell potential to the original OCV by a potentiostat type PRT 20-2 (Tacussel Electronique, France) connected to a function generator type GSTP (Tacussel Electronique, France). Parameters like pH, electrical conductivity (EC), dissolved oxygen (DO), open circuit voltage (OCV), internal resistance and COD

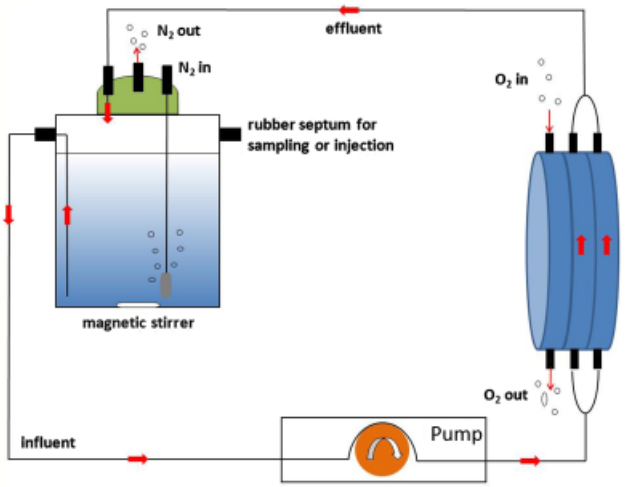

Figure 1 | Schematic drawing of the MFC half cell in recycled batch flow mode.

were monitored on a regular basis which allow to map the changes during the bioelectrochemical process at the electrode. pH and DO were measured using a multimeter (wtw 340i). The EC was measured using a conductivity meter (Knick SE204). The resistance between the electrodes was measured using a milliohm resistance meter (HIOKI 3560 AC mΩ HiTester). COD of the acetate solution in MFC was measured using a COD testing kit (DR LANGE). Acetate in the MFC solution was measured using ion chromatograph (IC) analysis and bicarbonate was measured by a total inorganic carbon analyzer (TIC).

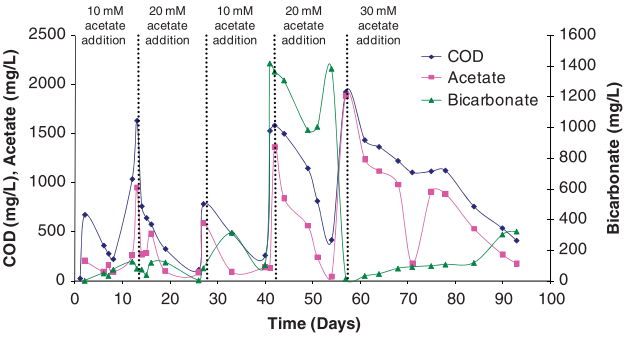

Figure 3 | COD, acetate and bicarbonate crbon cloth anode half cell. The dotted lines indicate the addition of acetate (10 mM acetate corresponds to 700 mg/L COD).

RESULTS AND DISCUSSION

Anode measurements in a half-cell

The DO level in all the anode half cells always remain less than 0.5 mg/L due to continuous flushing of the acetate solution with N_2. However, after a while, the pH in the anode compartment increased from the original 7.0 to > 9.0. This change in pH led to very low current production when a polarization curve was made. It has been proven that pH is one of the important parameters influencing the bacterial activity at the anode of a MFC (Franks *et al.* 2009). When the whole medium was replaced on day 90 the pH dropped to its original level but increased again after a few days until a pH of almost 10 was reached (Figure 2). The reason for this rise is probably the continuous removal of the weak CO_2 acid due to N_2 flushing to maintain the anaerobic conditions. Of course, flushing with N_2/CO_2 would keep the pH at a constant level and currently is being tried in these cells. It also means that the buffer solution does not work effectively enough to keep the pH around 7. Afterwards the pH remained quite stable (between pH 9 and 10). The EC showed a continuous increase due to the deposition of ions (Figure 2). Similar results for pH and EC were also observed for graphite cloth and DSA half cells as well.

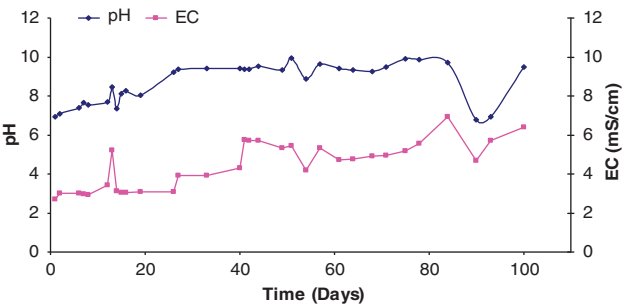

Figure 2 | pH and EC in carbon cloth anode half cell.

DSA are metal mixed oxide coated electrodes that have a wide range of electrochemical applications such as the production of chlorine and sodium hydroxide. Coatings of RuO_2, IrO_2, TiO_2 and Ta_2O_5 on titanium are used for these anodes. The OCV of DSA anode half cell could reach only −300 mV vs. Ag/AgCl.

Acetate was also measured directly in these cells to confirm that the drop in COD measured was indeed correlated to acetate consumption by the bacteria. Also, in the MFC conditions (phosphate buffer, pH 7), bicarbonate is formed when acetate is consumed. Figure 3 shows the changes in COD, acetate and bicarbonate in carbon cloth anode half cell anode right from the beginning (day 0). It is evident that most of the time, the drop in COD is directly linked to the removal of acetate from the system. At the same time, the reduction in acetate is accompanied by an increase in bicarbonate concentration in the system.

Figure 4 also presents the data from the same cell but from day 20 onwards and shows the evolution of anode open circuit voltage (OCV) as a function of change in COD. Most of the MFC studies so far have used acetate at a concentration of 1–1.5 mM (Logan *et al.* 2007; Dumas *et al.* 2008) which correspond to a COD of 700–1000 mg/L. This study proves

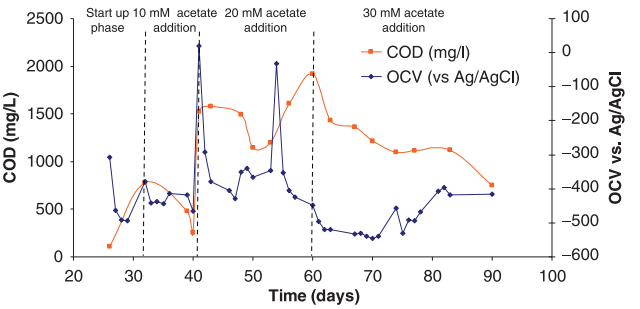

Figure 4 | Influence of increasing acetate concentration on OCV of carbon cloth anode half cell. The dotted lines indicate the addition of acetate (10 mM acetate corresponds to 700 mg/L COD).

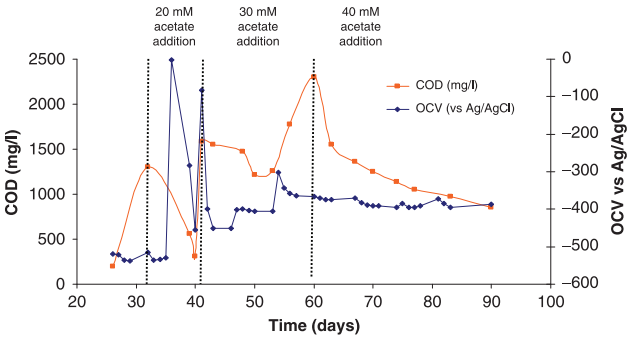

Figure 5 | Influence of increasing acetate concentration on OCV of expanded graphite cloth anode half cell. The dotted lines indicate the addition of acetate (10 mM acetate corresponds to 700 mg/L COD).

that in experimental cells, the concentration of acetate can be increased up to 40 mM. When the acetate concentration is increased, initially, there is an increase in the OCV of anode (it changes from −500 mV vs. Ag/AgCl to 0 mV vs. Ag/AgCl). However, this change is temporary and after a few days only, the OCV recovers to its original state (Figures 4 and 5).

In order to check the electrochemical activity of these electrodes, polarization curves were prepared periodically using linear sweep voltammetry. Figure 6 shows one such curve for expanded graphite cloth anode half cell. At 0 mV vs Ag/AgCl, a current of 0.15 mA/cm^2 was recorded. Earlier, a maximum current density of 0.076 mA/cm^2 was reported for acetate fed MFC with graphite rod electrodes (Lee *et al.* 2008). Using a wastewater amended with acetate (1600 mg/L) as substrate, a maximum current density of 0.09 mA/cm^2 was reported in a submersible microbial fuel cell (Min and Angelidaki 2008). Of course, these studies were carried out in a full cell mode of MFC.

Cathode measurements in a half-cell

The performance of these electrodes towards oxygen reduction and in a complete MFC has already been proven (Zhang *et al.* 2009; Pant *et al.* 2010b). In the present study, their

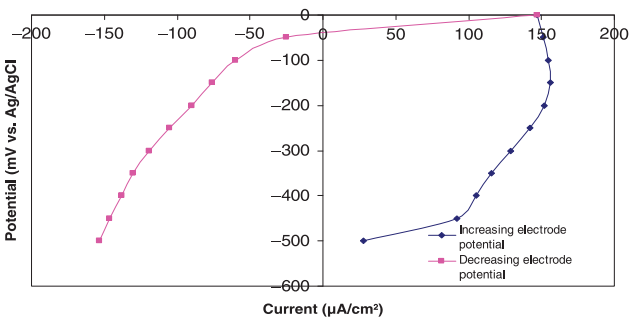

Figure 6 | Polarization curve of expanded graphite cloth anode half cell.

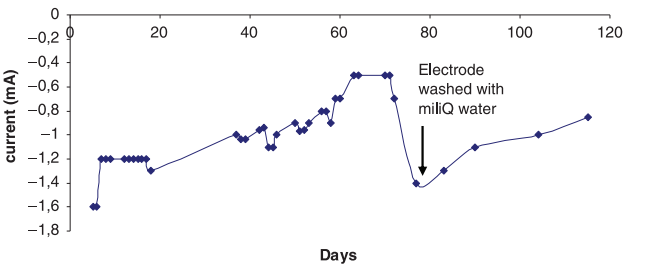

Figure 7 | Current production by 0 wt% Pt AC cathode poised at −100 mV vs Ag/AgCl.

stability was tested. When these electrodes were tested in a half cell configuration, the current was quite stable (Figure 7). After 100 days, the electrodes were cleaned by flushing the cell with demineralized water which resulted in improved performance of these electrodes.

As Table 1 shows, the highest BET surface area among all the electrodes tested was for VITO AC cathode which could account for its high activity towards oxygen reduction. Among the materials tested as MFC anode, the highest BET surface area was for expanded graphite cloth thus makes it the best electrode for acetate oxidation which was also proven in this study. In future, the MFCs based on the electrodes described in this study will be operated using real industrial wastewater and then it will be important to study the pollutant transport models (Chau and Jiyang 2004b) as well as the floc particle size (Chau and Jiyang 2004a) to better understand the impact of different wastewaters on the performance of these electrodes which have so far been tested using a defined substrate.

Table 1 | The BET surface area of the electrodes tested in this study and other commercial electrodes

Sample Type	Specific weight (g/m^2_{PSA})	BET (m^2_{BET}/g)	BET (m^2_{BET}/m^2_{PSA})
Expanded graphite cloth	1012.66	14.854	15042
Carbon cloth	439.52	4.207	1849
Carbon paper	74.33	9.567	711.1
AC (0% Pt) + 10% PTFE (500 μm) active catalyst	675.68	180	121500
Vito graphite electrode (0% Pt)	961.38	101.824	97891
Stainless steel mesh	541.67	1.355	733.96

PSA- Projected Surface area
BET- Brunauer, Emmett and Teller
PTFE- Polytetrafluoroethylene

CONCLUSIONS

In the present study, various electrode materials were tested for their use as anode and cathode in MFCs. The VITO AC electrode without platinum shows good results for current production. The amount of current generated is comparable to that of the more expensive platinized electrodes. Both carbon cloth and expanded graphite cloth show good activity as an anode in acetate fed microbial fuel cell conditions. Further, increasing the acetate concentration have only a temporary effect on the OCV of these anodes and they recover within a few days to reach the optimal OCV of −500 mV vs. Ag/AgCl. All these innovations will result in lower MFC costs and enhanced performance in terms of current production as well as pollutant removal.

ACKNOWLEDGMENTS

This research was supported by a grant from Milieu en Energietechnologie InnovatiePlatform (MIP), Antwerp under the project 'Sewage Plus: Second life of sewage as a matrix for dilution of organic waste streams' (M8463).

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