Steady-state performance and chemical efficiency of Microbial Electrolysis Cells

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ABSTRACT

The objective of this paper was to study MEC performance at steady-state conditions in continuous mode and to analyse MEC performance in terms of chemical efficiency. At steady-state operation, a current density of 10.2 A m^{-2} (applied voltage 1.0 V) for a set-up with an AEM was produced, compared to 7.2 A m^{-2} for a set-up with a CEM. For all applied voltages, total internal resistance for the AEM configuration was lower than or the CEM configuration. Therefore, energy input for the AEM configuration is lower than for the CEM configuration. In case a CEM is used, the conductivity in the cathode reaches high values: >130 mS cm^{-1}. This conductivity is mainly caused by the presence of Na$^+$ (7.8 g L^{-1}), K$^+$ (12.2 g L^{-1}) and OH$^-$ (8.3 g L^{-1}). Furthermore, MECs perform better at high buffer and electrolyte concentrations. However, as current density does not increase proportionally with increase in chemicals, the effectiveness of chemical addition decreases when more chemicals are added. Therefore, addition of chemicals and buffer does not necessarily enhance performance but increases operational costs.

1. Introduction

Organic material in waste streams is a suitable source for the production of renewable energy and chemicals [1]. Bio-electrochemical systems (BES) are a promising technology to extract the energy from these waste streams to produce a variety of products like, for example, hydrogen gas [2,3]. The bioanode, at which microorganisms convert the chemical energy in organic material to electrical energy, forms the basis of most BESs. Depending on the cathode reaction, these systems are referred to as Microbial Fuel Cells (MFCs) when electricity is produced or Microbial Electrolysis Cells (MECs) when extra energy is added to the electrons to produce products at the cathode (e.g. hydrogen, methane) [4–8].

The challenge to bring BES research further towards application lies in the integration of the many different fields that are relevant for the topic: from electrochemistry, to biotechnology, to microbiology, to modelling, and process technology. This combination of fields makes BES research challenging, and the need for standardization of electro-chemical measurements and experimental design has been recently acknowledged [9,10]. Essential in BES research is that results are obtained under conditions that are relevant for practical application of the technology, i.e. relevant electro-lytes (low conductivity, neutral pH at the anode), continuous mode, and stable current generation. Moreover, addition of high concentrations of phosphate buffers should be avoided [9] as it is not feasible in practice [3].

In contrast, many long term studies on BESs have been performed and their analysis has been done in a situation where only a steady current density has been reached [11,12]. A true steady-state situation however, is not only reflected in stable current generation, but also includes stable pH, conductivity, and ion concentrations in both electrolytes. In most cases the concentration of ions, and thus the conductivity, in anolyte and catholyte still changes even though the current has equilibrated, and therefore a shift within the internal resistance still takes place.

Our objective in this study was twofold: (i) to study MEC performance at steady-state conditions in continuous mode, and (ii) to use a novel method to analyse MEC performance in terms of chemical efficiency.

To study steady-state performance, our approach was to monitor all variables that are required to obtain a true steady-state. Once this steady-state was reached, we analysed the performance and partial internal resistances of systems operated with an AEM and a CEM.

To analyse MEC performance in terms of chemical efficiency, we compared the input of chemicals in the form of buffer to the produced current.

2. Materials and methods

2.1. Microbial Electrolysis Cell

The MEC consisted of an anode and cathode compartment first separated by a CEM (Fumasep® FKE, FuMa-Tech GmbH, Germany) and later by an AEM (AEM; AMX – Neosepta, Tokuyama Corp., Japan). The anode compartment contained a 1 mm thick carbon felt (Technical Fibre Products Ltd., Kendal, United Kingdom) which was separated from the membrane by spacer material (PETEX 07-4000/64, Sefar BV, Goor, The Netherlands) to enable a perpendicular forced flow through the anode [13]. The cathode compartment contained a platinum coated ($50 \, g \, m^{-2}$) titanium mesh (thickness 1 mm, specific surface area $1.7 \, m^2 \, m^{-2}$ – Magneto Special Anodes BV, Schiedam, The Netherlands). Both anode and cathode had a working volume of 280 mL and the anolyte and catholyte were circulated over the compartment at a flow rate of $340 \, mL \, min^{-1}$. The hydraulic retention time of the anode compartment was 0.9 h. Anode, cathode and membrane all had a projected surface area of $250 \, cm^2$. Potentials of anode and cathode were measured using Ag/AgCl reference electrodes (+0.200 V vs NHE. ProSense QiS, Oosterhout, The Netherlands) which were connected to the cell using capillaries filled with 3 M of KCl solution separated from the electrolyte by an agar salt bridge. The cell voltage was applied (0.6, 0.8 and 1.0 V) by an adjustable power supply (ES 03-5, Delta Electronica BV, Zierikzee, The Netherlands). All experiments were performed at 303 K.

2.2. Experimental procedures and steady-state conditions

The MEC was inoculated with 100 mL of effluent from a working MEC [14]. The anode of the system was continuously fed with synthetic wastewater at a rate of $5 \, mL \, min^{-1}$. The synthetic wastewater contained $1.36 \, g \, L^{-1}$ $NaCH_3COO \cdot 3H_2O$, $0.68 \, g \, L^{-1}$ KH_2PO_4, $0.87 \, g \, L^{-1}$ K_2HPO_4, $0.74 \, g \, L^{-1}$ KCl, $0.58 \, g \, L^{-1}$ NaCl, $0.28 \, g \, L^{-1}$ NH_4Cl, $0.1 \, g \, L^{-1}$ $MgSO_4 \cdot 7H_2O$, $0.1 \, g \, L^{-1}$ $CaCl_2 \cdot 2H_2O$ and $0.1 \, mL \, L^{-1}$ of a trace element mixture [15]. At the start of the experiment the catholyte consisted of 10 mM of phosphate buffer.

The system with the CEM was first operated at an applied voltage of 0.6 V until a steady state in ion transport through the membrane was reached (approximately two weeks depending on the produced current). Steady state was determined by a constant current output, a stable conductivity and pH in anode and cathode and by a constant ion content of both anode and cathode compartment. Constant ion content of both anolyte and catholyte was confirmed by measurement of all ions present. After these steady-state conditions the experiment was repeated at an applied voltage of 0.8 and 1.0 V. In both cases, again it took approximately two weeks to reach steady state. Finally, this whole procedure was repeated with the AEM.

Cation concentrations were determined with inductively coupled plasma-optical emission spectroscopy (ICP-OES, Perkin Elmer Optima 3000XL). Anion concentrations were determined using ion chromatography (Metrohm 761 Compact IC equipped with a conductivity detector and a Metrosep A Supp 5 6.1006.520 column). Acetate concentrations were measured using ion chromatograph (Metrohm 761 Compact IC) equipped with a conductivity detector and an anion column (Metrosep A Supp 5 6.1006.520). Bicarbonate concentrations were determined using a total organic carbon analyzer (Shimadzu TOC-VCPH). Finally, ammonium was measured using a standardized test kit for ammonium (ammonium cuvette test LCK303, XION 500 spectrophotometer, Dr. Lange Nederland B.V., The Netherlands). Conductivity and pH of both electrolytes was measured externally by taking a sample from the compartments (WTW pH/cond 340i, Weilheim, Germany).

2.3. Calculations

The energy input and output of an MEC are determined by the produced current (A) and the applied voltage (V). At a higher applied voltage more current will be produced but also the required energy to produce the product is higher. The applied voltage (E_{cell}) is required to overcome the different internal resistances of the system and to overcome the thermodynamically required energy input for hydrogen production compared to the thermodynamically determined energy gain from the oxidized substrate which is called the equilibrium voltage. The internal resistance includes the ionic resistance of the electrolytes, anode and cathode overpotentials and the membrane transport resistance [16,17]. Summarizing the applied voltage consists of: (i) equilibrium voltage (E_{eq}), (ii) anode overpotential (η_{an}), (iii) cathode overpotential (η_{cat}), (iv) ionic resistance (E_{ionic}) and (v) membrane transport resistance (E_T).

The equilibrium voltage was calculated using the measured conditions with

$$E_{eq} = E_{cat} - E_{an}$$
$$= \left(E_{cat}^0 - \frac{RT}{2F} \ln \frac{pH_2}{\left[H_{cat}^+ \right]^2} \right) - \left(E_{an}^0 - \frac{RT}{8F} \ln \frac{[CH_3COO^-]}{\left[HCO_3^- \right]^2 \left[H_{an}^+ \right]^9} \right)$$

(1)