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Microbial electrolysis cell performance using non-buffered and low conductivity wastewaters

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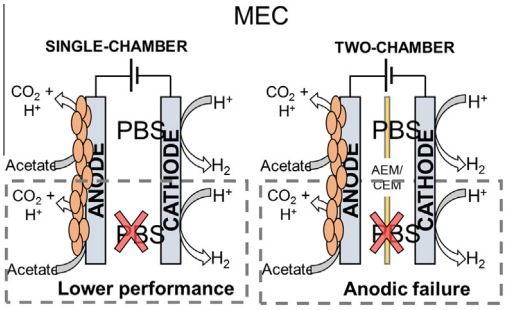
HIGHLIGHTS

- MEC performance is evaluated with non-buffered and/or low-conductivity media.
- Cathodic overpotentials increased with lack of buffer in single-chamber MEC.
- Anodic failure is caused by non-buffered medium in two-chamber MEC.
- Lowering conductivity did not have a relevant role at such low current intensities.

GRAPHICAL ABSTRACT



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ABSTRACT

Microbial electrolysis cells (MEC) are a novel technology aiming at producing hydrogen from wastewater. MEC performance gives successful results in lab-scale experiments with well buffered media and synthetically-increased conductivity, thus preventing operational problems and reducing the internal resistance of the cell. This is especially important in two-chamber configuration where membranes cause potential losses associated to the pH gradients across them. However, domestic and many industrial wastewaters have a limited buffer capacity and low conductivity. In this study, the performance of an MEC with a culture medium more like a real wastewater, in terms of buffer capacity and conductivity, was assessed in both single-chamber and two-chamber configurations and compared to that of a well-buffered cell. Single-chamber MEC tests demonstrated that the lack of buffer affected both the overpotentials of the anode and the cathode, although the overpotential of the latter was significantly higher. In two-chamber configuration, the non-buffered cell failed as a result of a high pH drop in the anode, which harmed the anodic biofilm. The conductivity increase from low (4 mS/cm) to high values (13 mS/cm) did not improve significantly any configuration tested.

1. Introduction

Concerns about climate change coupled to the fossil fuel shortage lead to the necessity to investigate in new renewable energy resources. In this framework, bioelectrochemical systems (BES) have emerged as a promising technology with the advantage that a double goal is accomplished: energy production and wastewater treatment. BES are based on the capability of anode respiring bacteria (ARB) to transfer electrons out of the cell, thus coupling their metabolic pathways to external electron acceptors. In BES, ARB oxidize organic matter from wastewater and use a solid anode as electron acceptor and as a support for growth under anaerobic conditions. The electrons obtained from the oxidation reaction flow through an electric circuit to the cathode, where a reduction reac-

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tion takes place. BES in which the overall process is thermodynamically favoured, thus producing electrical energy, are known as microbial fuel cells (MFC), whereas BES in which an applied electrical energy is necessary to drive the reactions are known as microbial electrolysis cells (MEC). Examples of cathodic reactions for MFC and MEC are the reduction of oxygen to water and the reduction of protons to hydrogen, respectively.

At this stage of research, most studies in BES have been conducted with high buffer concentrations, including phosphate and bicarbonate [1]. The use of buffers in BES helps preventing operational problems such as proton-transport limitations inside the biofilm [2,3] and provides conductivity to the culture medium. This, in turn, reduces the internal resistance of the cells and therefore, increases the attainable power output in MFC or reduces the applied voltage requirements in MEC. Buffers become even more important in two-chamber configuration, since they decrease the pH changes amplified by the presence of an ion exchange membrane and therefore, prevent, to some extent, potential losses [4,5]. During the degradation of organic matter, not only electrons but also protons are produced. Therefore, the transport of electrons from the anode to the cathode needs to be balanced to meet electroneutrality. Ideally, protons and hydroxyls would be responsible for maintaining electroneutrality in a two-chamber BES. However, in reality, electroneutrality condition is mostly reached by other ions such as Na^+, K^+, NH_4^+, Cl^- or S^{2-} as they are present in a much higher concentration [5]. The accumulation of protons and hydroxyls leads to a pH drop in the anodic chamber and a pH increase in the cathodic chamber [4,5]. The theoretical anodic and cathodic potentials are function of pH and hence, both the cathodic pH rise and the anodic pH drop lead to a power decrease in MFC or to an increase of energetic requirements in MEC.

Real wastewaters have a relatively low buffer capacity (the equivalent to 1–4 mM phosphate buffer) in addition to lower conductivities (around 1 mS/cm) compared to those used in most BES lab-scale studies [6,7]. Although the use of high buffer concentrations would decrease pH changes, its use in large-scale systems is, however, unrealistic. So far, several studies have been conducted with non-buffered catholytes, in which the performance of saline solutions [8,9] or acids such as sulfuric and hydrochloric [10] were evaluated as catholytes. Carbon dioxide addition to the cathode of MFC was also studied [11,12]. Carbon dioxide reacts with hydroxyls to form carbonate species, which in turn, are transported to the anodic chamber through an ion exchange membrane, thus sustaining the cathodic pH, while reducing the anodic pH decrease. Moreover, this strategy was reported to be successful for reducing the local cathodic pH at high current intensities [13].

However, there is very little research on non-buffered anodes, although pH changes would have a significant impact on the anode operation as it is a biological system. In this framework, Sleutels et al. [3] studied the effect of buffer concentration on MEC operation obtaining higher current intensities and coulombic efficiencies for the highest buffer concentration. The performance of both AEM and CEM in a continuous flow two-chamber MEC with a low phosphate buffered saline (PBS) concentration (10 mM) was also evaluated in terms of chemical energy and internal resistance and, in both cases, anion exchange membranes outperformed cation exchange membranes [14,15]. In a further study, Sleutels et al. [16] operated an MEC with an extra ion exchange membrane, creating a middle compartment, which allowed to recover conductivity and alkalinity in the anodic compartment, thus reducing buffer requirements. Rozendal et al. [17] evaluated the effect of different membranes on ion transport to that same PBS concentration and concluded that bipolar membranes could retard the increase of pH in the cathodic chamber. These works show how preventing pH changes in the cell can enhance its performance.

Therefore, a full understanding of the benefits/drawbacks of membrane utilization under these non-ideal conditions will be very helpful in view of posterior design of practical bioelectrochemical applications. In addition, the advantages of choosing anion or cation exchange membranes under non-ideal conditions should also be experimentally assessed. Hence, the aim of this study is the systematic comparison of the MEC performance with a culture medium more like a real wastewater, in terms of buffer capacity and conductivity, with respect to a conventional MEC working with a medium with high buffer capacity and high conductivity. Three different MEC configurations were compared: (i) single-chamber, (ii) two-chamber with anion exchange membrane (AEM) and (iii) two-chamber with cation exchange membrane (CEM), resulting in a wide matrix of experimental results.

2. Materials and methods

2.1. Reactors description and medium composition

Three different MEC were used: buffered (BF), high conductivity (HC) and low conductivity (LC). Bioelectrochemical cells consisted of two 32 mL methacrylate vessels provided with lateral apertures (3.8 cm diameter), so that they could be arranged either as a two-chamber or a single-chamber MEC depending on whether a membrane was placed in between them or not. Two typical membranes applied in bioelectrochemical systems were evaluated, an AEM (AMI-7001, Membranes International INC) and a CEM (Nafion N-117, fuelcellstore.com). The vessel closer to the cathode had a glass cylinder at the top, tightly sealed with a politetrafluoroetylene (PTFE) rubber cap. The glass cylinder was connected to a 0.1 L gas sample bag with a twist type valve (Cali-5-Bond, Ritter), where hydrogen was collected. The anodes were carbon fiber brushes (20 mm diameter × 25 mm length; 0.18 m^2; fibers of 7.2 μm diameter; PANEX®33 160 K, ZOLTEK) [18]. They were thermally treated at 450 °C for 30 min to enhance biomass adhesion [19] and were inoculated in an MFC for approximately a month. The cathodes were carbon cloth coated with carbon powder and platinum suspension on the side facing the anode [20,21] and had an area of 7.07 cm^2. The distance between the electrodes was 6 cm regardless of the cell configuration. This distance was given by cell restrictions in two-chamber configuration. However, it was also maintained in experiments in single-chamber to prevent parameters other than membrane, buffer or conductivity to affect the results.

A constant voltage of 1.0 V (unless otherwise specified) was provided by a power supply (TTI QL355TP). Current intensity was calculated from the monitoring of the voltage across an external resistance of 12 Ω by using a 16-bit data acquisition card (Advantech PCI-1716) connected to a personal computer with software developed in LabWindows CVI 2014 for data acquisition. Current intensity was normalized with respect to the anode surface area, expressing it as current density.

The medium composition was different for each cell. Nevertheless, in all of them, the culture medium contained per liter: 0.2 g NH_4Cl, 4 mg $FeCl_2$, 6 mg NaS_2 and 5 mL of mineral media. The mineral media stock solution contained per liter: 1 g EDTA, 0.164 g $CoCl_2{\cdot}6H_2O$, 0.228 g $CaCl_2{\cdot}2H_2O$, 0.02 g H_3BO_3, 0.04 g $Na_2MoO_4{\cdot}2H_2O$, 0.002 g Na_2SeO_3, 0.02 g $Na_2WO_4{\cdot}2H_2O$, 0.04 g $NiCl_2{\cdot}6H_2O$, 2.32 g $MgCl_2$, 1.18 g $MnCl_2{\cdot}4H_2O$, 0.1 g $ZnCl_2$, 0.02 g $CuSO_4{\cdot}5H_2O$ and 0.02 g $AlK(SO_4)_2$. Moreover, the methanogenic inhibitor 2-bromoethanesulfonate was used at a concentration of 50 mM according to the work of Parameswaran et al. [22] and acetate was added as substrate with an initial concentration of 1–1.5 g/L.

In BF, 172 mL of PBS per liter were also added, so that the final PBS concentration was 100 mM. The PBS stock solution contained 70 g Na_2HPO_4 and 12 g KH_2PO_4 per liter. pH and conductivity of