



Ammonia recycling enables sustainable operation of bioelectrochemical systems



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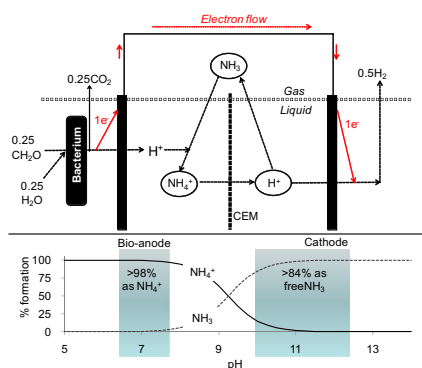
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HIGHLIGHTS

- Anolyte acidification (pH <5.5) severely inhibited current generation.
- Ammonium selectively migrated across a cation exchange membrane to the catholyte.
- Recycling the ammonia to anolyte neutralized the acidity and sustained current.
- Ammonia recycling was achieved without using external carrier gases.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 28 March 2013
 Received in revised form 22 May 2013
 Accepted 25 May 2013
 Available online 31 May 2013

Keywords:

Microbial fuel cells
 Microbial electrolysis cells
 Proton gradient
 pH Split
 Cation exchange membrane

ABSTRACT

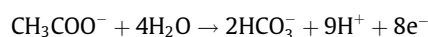
Ammonium (NH_4^+) migration across a cation exchange membrane is commonly observed during the operation of bioelectrochemical systems (BES). This often leads to anolyte acidification (pH <5.5) and complete inactivation of biofilm electroactivity. Without using conventional pH controls (dosage of alkali or pH buffers), the present study revealed that anodic biofilm activity (current) could be sustained if recycling of ammonia (NH_3) was implemented. A simple gas-exchange apparatus was designed to enable continuous recycling of NH_3 (released from the catholyte at pH >10) from the cathodic headspace to the acidified anolyte. Results indicated that current (110 mA or 688 A m⁻³ net anodic chamber volume) was sustained as long as the NH_3 recycling path was enabled, facilitating continuous anolyte neutralization with the recycled NH_3 . Since the microbial current enabled NH_4^+ migration against a strong concentration gradient (~10-fold), a novel way of ammonia recovery from wastewaters could be envisaged.

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1. Introduction

Bioelectrochemical systems (BES) have shown promise for the conversion of organic compounds in wastewaters into valuables (e.g., electricity, fuel gases, chemicals, etc.) (Logan et al., 2008; Rabaey and Verstraete, 2005; Rittmann, 2008). Arguably, the microbial catalyzed anodic reaction is the most critical reaction

in a BES process as it transforms the chemical energy captured in the organics directly into electrical energy. Typically, this reaction not only produces electrons, but also liberates protons (H^+). For instance, anodic oxidation of one mole acetate liberates nine mole H^+ and eight mole electrons according to the following equation (Schroder, 2007):



Since the electrons are continuously scavenged by the anode, the liberated H^+ accumulates and leads to anolyte acidification (Marcus et al., 2011). This has been shown to severely inhibit the

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catalytic activity of anodic biofilms and consequently leading to a complete shutdown of the BES (Cheng et al., 2010; Clauwaert et al., 2007, 2008). In general, a pH neutral condition (pH 7, i.e., $[H^+] = 10^{-7} \text{ mol L}^{-1}$) is essential to sustain optimal anodic microbial activities (He et al., 2008; Patil et al., 2011).

In theory, pH neutral anodic condition can be sustained if the requirement of cation migration (to establish charge balance) is satisfied exclusively by proton migration, resulting in the proton flux from anode to cathode being equal to the electron flow and the proton generation at the anode. However, in reality cations other than protons (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , NH_4^+) are available in much higher concentrations and will hence tend to migrate instead of protons. The higher the concentration of other cations is relative to protons, the lower is the likelihood of proton migration. Under typical experimental conditions the concentration of alkali cations such as Na^+ is orders of magnitudes higher than that of protons resulting in the migration of Na^+ from anode to cathode (Harnisch et al., 2008; Rozendal et al., 2006a). This effect has been suggested to be industrially exploited for the production of caustic soda (Raebaey et al., 2010).

In laboratory trials, the problem of anolyte acidification is often masked by the dosage of pH buffer or alkali (Cheng et al., 2010; Rozendal et al., 2008a). However, these pH control strategies are not sustainable as pH controlling chemicals must be externally added to the process. To approach self-sustaining pH control for CEM-BES without using external chemicals, the migrating cation species across the CEM should possess four properties: (1) it must be an alkaline species neutralizing the excess protons in the anolyte; (2) upon reacting with proton it becomes a cation that migrates across the CEM to the catholyte to maintain charge balance; (3) in the catholyte, it readily dissociates and releases the proton and hence replenishes the proton consumed in the cathodic reaction; and (4) upon releasing the proton in the catholyte, the species can be recycled for neutralizing the anolyte again (Cord-Ruwisch et al., 2011).

Amongst all cation species typically found in wastewaters (e.g., Na^+ , K^+ , Ca^{2+} , Mg^{2+} , NH_4^+), ammonium (NH_4^+) is the only species that fulfils all the above criteria. It has a characteristic acid-dissociation

constant (pK_a value) of 9.25 (25 °C). Hence, once it has migrated across a CEM to the catholyte, where the localized pH exceeds 9.25, it dissociates predominantly as free volatile ammonia (NH_3) which can be recovered as a gas (Fig. 1). The concept of using NH_4^+ as a proton shuttle in a CEM-equipped BES (CEM-BES) has been evaluated in our recent work (Cord-Ruwisch et al., 2011). The ammonia recycling was achieved by continuously stripping the catholyte with nitrogen (N_2), which was directed through the acidified anolyte to close the loop. N_2 was used to maintain the anaerobic condition required for the microbial anodic reaction. However, N_2 stripping is impractical as it incurs substantial energy input and creates large volume of low-value off-gas. In order to use the very effective principle of ammonia recycling for the sustainable operation of BES, a simple low energy input approach is required.

This work examined a new approach to sustain the current generation in a CEM-BES by internal ammonia recycling without using N_2 stripping. The idea is based on the well-known phenomenon where under anaerobic and highly reducing conditions (e.g., $\leq -500 \text{ mV vs. Ag/AgCl}$), a BES cathode produces hydrogen gas. This gas stream is in principle a vector that could help driving the volatilized ammonia out of the cathodic half cell (Liu et al., 2005; Logan et al., 2008; Rozendal et al., 2006b, 2008b). The aim of this study was to develop an effective way of sustaining BES operation by maintaining suitable anodic pH levels using ammonia from the cathode as the alkalinity carrier. In contrast to our previous work (Cord-Ruwisch et al., 2011), a more efficient (10-fold higher current density) anodic biofilm was used to demonstrate the concept of ammonia recycling in a BES.

2. Methods

2.1. Bioelectrochemical system configuration and process monitoring

A two-chamber CEM-BES was used in this study. It was made of transparent Perspex and has a similar configuration as the one described in an earlier work (Cheng et al., 2008). The two half cells

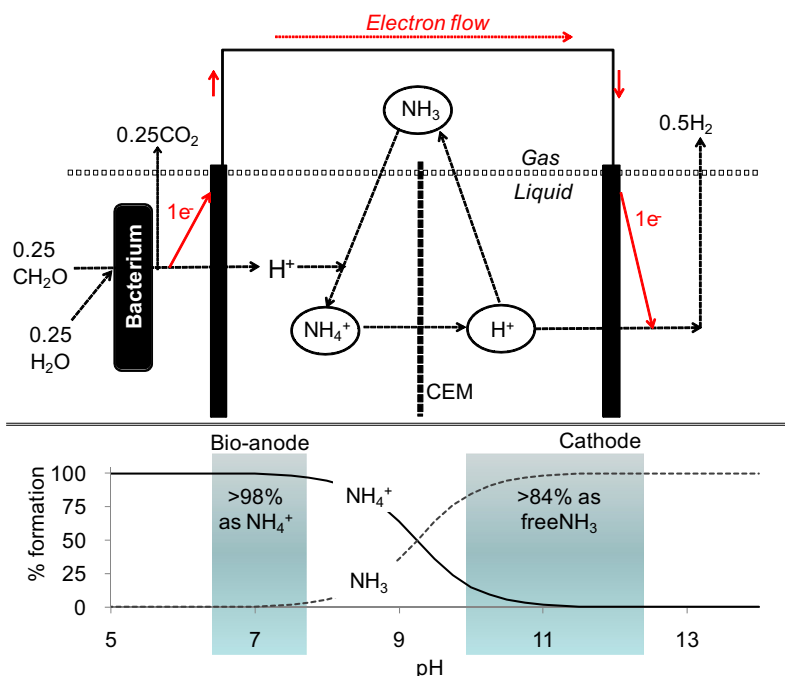


Fig. 1. The principle of using ammonium/ammonia as a proton shuttle in a CEM-BES. Here, the cathode is anaerobically operated enabling abiotic hydrogen gas formation. At neutral anolyte pH (pH 6.5–7.5), ammonia predominantly exists as NH_4^+ , whereas free volatile NH_3 dominates in the catholyte (pH >10).

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