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Effect of buffer charge on performance of air-cathodes used in microbial fuel cells

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ABSTRACT

In microbial fuel cells (MFCs), buffers are typically used to improve performance by stabilizing the electrode pH and increasing the electrolyte conductivity, but the importance of the buffer net charge at current densities typical of MFCs on cathode performance has received little attention. Current production results in an electric field that drives positive ions towards the cathode, and negative ions to the anode. A series of biological buffers were selected with positive, negative, and neutral charges that had pKas ranging from 5 to 10.8. Cathodic current production using these different buffers in solutions with different pHs and conductivities was compared using linear sweep voltammetry (LSV). At lower pHs, buffers with positive charge increased cathodic current by as much as 95% within certain ranges (potential windows) of cathode potentials. No difference in cathodic current was shown in current for buffers with neutral or negative charge. The reason for this increase with the net positive charge buffers was likely due to a more stable electrode pH produced by electric field driving the positively charged ions towards the cathode. The potential window for the positively charged buffers was positively correlated to the concentration of cationic buffer in the electrolyte. At a pH higher than 9, no improvement in cathodic current was shown for buffers with positive charge, indicating at these higher pHs diffusion dominated buffer transport.

1. Introduction

A microbial fuel cell (MFC) is a promising technology for wastewater treatment as it can be used to simultaneously extract electricity from organic compounds using bacteria as well as treat the wastewater [1]. The power produced by a single-chamber MFC is usually limited by the cathode due to the poorly catalyzed oxygen reduction reaction under near-neutral pH conditions needed by the bacteria, with the optimal pH reported to range from 6.5 to 10 [2–4]. In single-chamber MFCs there is no net change in pH due to current production, as protons released at the anode due to oxidation of organic matter are neutralized by OH^- ions produced at the cathode [4]. The local pH around the electrodes can vary, with the anode becoming more acidic than the bulk solution, and the cathode more alkaline. In order to avoid deleterious impacts of pH on the bacteria or electrode reactions, phosphate [5,6], bicarbonate [7], or Good's buffers [8] are usually added into the medium to avoid pH changes. For wastewaters, natural alkalinity can help avoid net pH changes [7].

The addition of a buffer to a medium not only enables control of the pH near the pKa of the buffer, but it also increases solution conductivity which can improve performance. For example, an increase in the concentration of a phosphate buffer in a single-chamber MFC from 100 to 400 mM nearly doubled power production [9]. In two-chamber MFCs, the use of a cation exchange membrane between the electrodes can result in large pH differences in the electrolytes unless high concentrations of buffer are used. In tests with a 10 mM phosphate buffer there was a 75% decrease in power (after 96 h) due to the increase in the catholyte pH, as this pH change increased the cathode overpotential [10]. In a comparison of several different Good's buffers, that were either neutrally or negatively charged, it was shown that conductivity was more important than buffer type when buffers were all added at the same concentration [8].

The importance of the net charge of the buffer on cathode performance has received little attention in bioelectrochemical systems compared to the studies on effect of the buffer pKa. The solution in an MFC is not usually mixed, and so ion transport can be described by the extended Nernst-Planck Equation [11], in terms of

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concentration, chemical activities, and the electric field, as:

$$J_i = -D_i\nabla(c_i) - D_i\frac{z_iF}{RT}c_i\nabla(\mathrm{V}) - D_ic_i\nabla(\ln\gamma_i) \quad (1)$$

where J is the chemical flux, i indicates the specific chemical species, c is the concentration, V the potential, γ the activity coefficient, T the temperature, D the diffusivity, R the gas constant, and z the charge of the species. In an MFC, the electrical field draws cations to the cathode, and anions towards the anode (Fig. 1). Most buffers examined to date in single-chamber MFCs have had a negative charge. A comparison of several different catholyte salts and buffers (NaCl, $NaHCO_3$, NH_4HCO_3, PBS, and NH_4Cl) in gas diffusion half cells, however, showed that positively charged NH_4^+ worked better than the other chemicals examined [12]. The predominant reaction at the cathode is the dissociation of water and release of OH^- ions [13]. In MFCs and other bioelectrochemical systems, the pH near the cathode can become more alkaline with increased current. The improved performance using NH_4^+ by Popat et al. [12] was therefore attributed to its pKa of 9.2 and effective buffering of the hydroxide ion, consistent with other studies demonstrating the importance of the buffer pKa relative to the solution pH on cathode performance [14,15]. It was estimated, using the model PCBIOFILM, that an electrical field could impact current produced by the anode by as much as 15%, but the impact on the cathode was not examined [16]. In other bioelectrochemical systems, such as microbial reverse electrolysis cells (MRECs), it has also been shown that cathode performance is improved in the presence of ammonium bicarbonate, compared to sodium bicarbonate buffer [17]. The importance of the charge of the ion on cathode performance in MFCs or MECs, however, has not been specifically examined in these studies.

The importance of the net charge of a buffer on cathode performance was examined here using linear sweep voltammetry (LSV) for buffers that varied in charge, pKa, and molecular diffusivities. It was hypothesized that the use of buffers with net positive charge would improve cathode performance as they are drawn to the cathode surface by the electrical field, while negatively charged ions would be repelled, but the magnitude of this difference in performance was not known. A total of 13 different buffers were selected categorized into three buffer groups with net positive, negative or neutral charge. Cathode performance was examined at several different pHs relative to the pKa of the buffers.

2. Methods

2.1. Buffer selection and solution preparation

Buffers with a range of pKas and net charges were selected from commercially available biologically compatible buffers (Table 1). The buffers were categorized into three groups based on their net neutral, negative, or positive charged. The pKas of these buffers

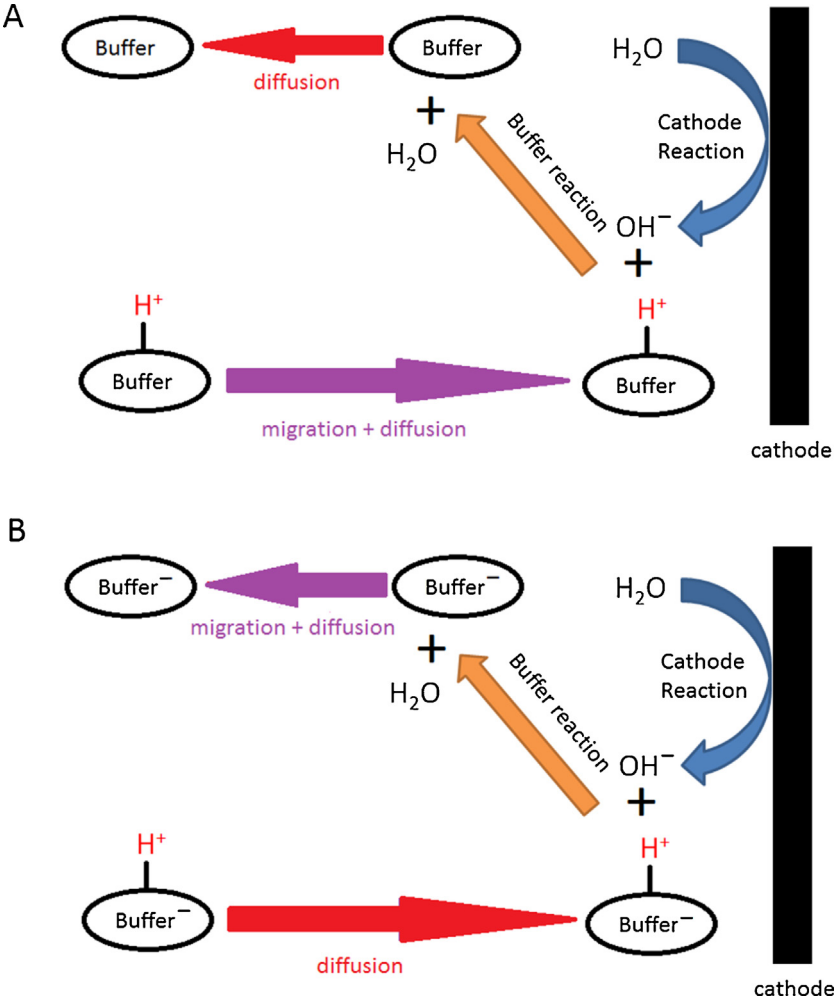

Fig. 1. Diagram of (A) a positively charged and (B) a neutrally charge buffer interfacing with cathode in an MFC.