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Analysis of a microbial electrochemical cell using the proton condition in biofilm (PCBIOFILM) model

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ABSTRACT

Common to all microbial electrochemical cells (MXCs) are the anode-respiring bacteria (ARB), which transfer electrons to an anode and release protons that must transport out of the biofilm. Here, we develop a novel modeling platform, Proton Condition in BIOFILM (PCBIOFILM), with a structure geared towards mechanistically explaining: (1) how the ARB half reaction produces enough acid to inhibit the ARB by low pH; (2) how the diffusion of alkalinity carriers (phosphates and carbonates) control the pH gradients in the biofilm anode; (3) how increasing alkalinity attenuates pH gradients and increases current; and (4) why carbonates enable higher current density than phosphates. Analysis of literature data using PCBIOFILM supports the hypothesis that alkalinity limits the maximum current density for MXCs. An alkalinity criterion for eliminating low-pH limitation – 12 mg $CaCO_3$/mg BOD – implies that a practical MXC can achieve a maximum current density with an effluent quality comparable to anaerobic digestion.

1. Introduction

A microbial electrochemical cell (MXC) provides social benefits by using reactions by anode-respiring bacteria (ARB) to produce electrical current from the oxidation of organic compounds at an anode. The two most well-recognized examples of MXCs are the microbial "F"uel cell for generating electrical power and the microbial "E"lectrolytic cell for generating hydrogen gas or other chemical products at the cathode. Working from bench-top to pilot scales, MXC researchers are considering a wide range of applications, including treating wastewater, producing renewable hydrogen gas, and generating electrical energy from sediments (Logan et al., 2006; Rittmann et al., 2008).

Despite diverse applications, MXCs share common phenomena that can be understood in a systematic and quantitative way by considering the ARB, because all MXCs use ARB at the anode. ARB ultimately transfer electrons to an anode and gain energy by respiring electrons to a conductive solid (Torres et al., 2007; Rittmann et al., 2008). The biofilm community on the anode is collectively referred to as the biofilm anode, because the biofilm conducts to the anode electrons that originate in organic substrates (Marcus et al., 2007; Parameswaran et al., 2009).

In any biofilm, the coupling of reaction with transport can cause gradients in the concentrations of rate-limiting substrates (Wanner et al., 2006). The common rate-limiting substrates are the electron donor and acceptor. For ARB, the analogs are the electron donor and the anode potential (Marcus et al., 2007; Rittmann et al., 2008). Recent studies demonstrate that pH also has a gradient in a biofilm anode and is critically important for controlling the activity of ARB (Torres et al., 2008a; Franks et al., 2009).

Examining the reaction stoichiometry for ARB illustrates why pH (related to the concentration of protons (H^+)) is especially important for ARB. In respiratory metabolism, bacteria gain energy by transferring electrons from a donor to an acceptor. The electron donor generates electrons in an oxidation half reaction, while the electron acceptor consumes the electrons in a reduction half reaction. Normally, the bacteria combine the two half reactions stoichiometrically to form an overall balanced reaction. For ARB, however, only the donor half reaction occurs, and this makes the biofilm anode unique with respect to pH.

An important example of the half reaction for ARB is acetate oxidation:

$$CH_3COO^- + 4H_2O \rightarrow 2H_2CO_3 + 7H^+ + 8e^- \quad (1)$$

which liberates chemical products (i.e., $2H_2CO_3$ and $7H^+$) and $8e^-$. For respiration, the ARB transfer the electrons to the anode, such as inert graphite. In accepting electrons, the inert electrode merely provides passage for the electrons through conduction, without changing oxidation state. Hence, the ARB reaction lacks its partner reduction half reaction. As a result, the electron-donor's oxidation half reaction becomes the overall reaction for ARB in the biofilm anode.

Because the anode accepts only the electrons and leaves the chemical products in the aqueous phase, the ARB reaction yields an excess of $7H^+$. This can lead to a large accumulation of H^+ and

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lower the pH, which can be inhibitory to ARB (Torres et al., 2008a; Franks et al., 2009), as ARB appear to have an optimal activity above neutral pH.

To prevent a major pH drop in the biofilm anode, the basic form of a buffer must combine with H^+ to form a weaker acid that is transported out of the biofilm. Eq. (2) shows an acid–base equilibrium reaction of a buffer that is represented alkalinity (Alk^-), which combines with H^+ to produce protonated-alkalinity (HAlk).

$$Alk^- + H^+ \leftrightarrow HAlk \quad \text{or} \quad HCO_3^- + H^+ \leftrightarrow H_2CO_3 \tag{2}$$

Alk^- equates to HCO_3^- when no other buffer species is present, since inorganic C is present in all natural waters. Because the alkalinity reaction (Eq. (2)) is orders of magnitude faster than the ARB reaction (Eq. (1)), it can be represented as being at equilibrium (Snoeyink and Jenkins, 1980; VanBriesen and Rittmann, 1999). The law of mass action shows that Alk^- maintains the pH near its acid dissociation constant pK_a (around 6.3 for HCO_3^-) by shifting H^+ to the pool of the weaker acid (i.e., HAlk):

$$pH = pKa + \log\left(\frac{[Alk^-]}{[HAlk]}\right) \tag{3}$$

The role that alkalinity plays in transporting H^+ from a biofilm to the bulk liquid has been long recognized (Szwerinski et al., 1986). Fig. 1 illustrates the alkalinity-dependent pH-maintenance mechanism for a biofilm anode. To prevent a significant pH drop inside the biofilm anode, HAlk must transport H^+ out of the biofilm rapidly, and Alk^- must transport into the biofilm to replenish the Alk^- converted to HAlk. A sluggish mass-transport process for HAlk and/or Alk^- means that large gradients are needed to drive the fluxes of HAlk and Alk. Large gradients lead to a low pH in the biofilm anode and strong low-pH inhibition, especially for the bacteria residing in its interior (Fig. 1a).

One solution for overcoming mass-transport resistance is to increase the concentration of Alk^- (Fig. 1b), which increases pH everywhere in the biofilm without needing to make the pH high in the bulk liquid. Torres et al. (2008a) used an MXC to demonstrate the benefit of Alk^- for overcoming slow H^+ out-transport, a primary limitation for generating electrical current using a biofilm anode.

In the past, Rittmann and co-workers (VanBriesen and Rittmann, 1999; Banaszak et al., 1998; Rittmann et al., 2002, 2003; Willett and Rittmann, 2003; Schwarz and Rittmann, 2007a,b) developed a modeling platform, CCBATCH, to understand systems that have characteristics of a biofilm anode: biological oxidation reactions driving abiotic geochemical reactions and mass transport. However, modeling a biofilm anode requires a major step beyond the phenomena included in CCBATCH. The difference derives from the biofilm anode's high biomass density, restricted mass transport, and intense generation of protons. Modeling a biofilm anode with the framework of CCBATCH demands a comprehensive, systematic, and properly oriented approach.

Here we develop an advanced modeling platform – the Proton Condition in BIOFILM (PCBIOFILM) model – to integrate and critically examine the processes that control ARB activity in a biofilm anode. The platform is founded on the framework of CCBATCH, but has new features essential for representing the biofilm anode. PCBIOFILM can be used to represent any biofilm, but its special features are most valuable for a biofilm anode.

Here, we first describe the new features of PCBIOFILM necessary for representing a biofilm anode. Second, we apply PCBIOFILM for understanding the reaction and transport processes within the biofilm anode of an MXC. Finally, we establish a criterion for taking full advantage of organic substrate supplied to the anode by studying the relationship between alkalinity and current density.

2. PCBIOFILM formulation

The foundation for PCBIOFILM is CCBATCH, which was originally developed to link slow microbial reactions to fast aqueous acid/base and complexation reactions (VanBriesen and Rittmann, 1999). To meet the demands of new applications, CCBATCH was expanded to include precipitation-dissolution reactions (Banaszak et al., 1998; Rittmann et al., 2002, 2003); slow aqueous complexation reactions (Willett and Rittmann, 2003); and transport and the latest knowledge on extracellular polymeric substances (EPS), soluble microbial products (SMP), surface complexation, and bioprecipitation (Schwarz and Rittmann, 2007a,b). A key feature of CCBATCH is its use of the Proton Condition (PC) – a special mass balance on H^+ – as the keystone for linking processes that involve production of acid or base. This PC-based organization is a special benefit when modeling the biofilm anode, in which the ARB reaction produces a large amount of acid. Because of our approach introduces the PC to biofilm modeling, we name our new model PCBIOFILM.

Here we describe PCBIOFILM in three parts: (1) components and their reactions; (2) the PC and its relation to electrical neutrality; and (3) the coupling of slow reactions and transport. For each part, our strategy is to introduce general model equations first and then follow with details that are specific to describing the experimental biofilm anode in Torres et al. (2008a).

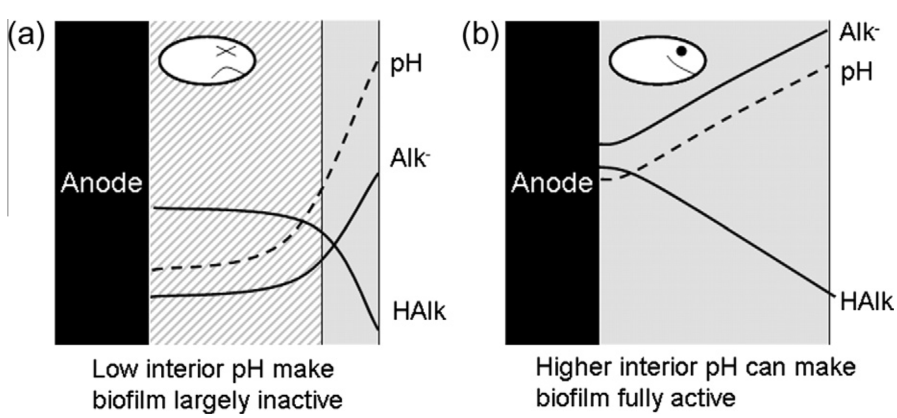

Fig. 1. An illustration of H^+ removal from a biofilm anode by alkalinity in order to maintain pH that is favorable for ARB activity. Active ARB are shown as solid grey, and inactive ARB are shown as dotted grey. The concentration of alkalinity (Alk^-) decreases and protonated-alkalinity decreases (HAlk) to drive inward and outward fluxes of the respective species. (a) Under a sluggish mass-transport condition, a large concentration gradient significantly decreases the pH in the biofilm and makes ARB largely inactive. (b) One solution is to increase alkalinity, so that pH becomes higher throughout the biofilm, especially in the interior of the biofilm, which remains active.