



Nernst-ping-pong model for evaluating the effects of the substrate concentration and anode potential on the kinetic characteristics of bioanode



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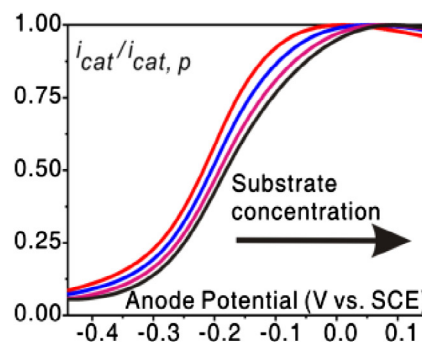
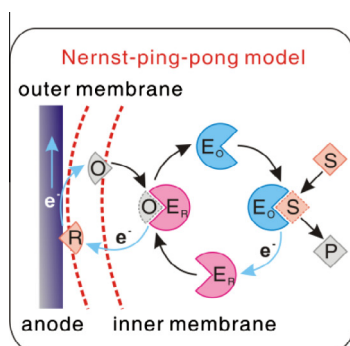
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HIGHLIGHTS

- The Nernst-ping-pong model is newly developed.
- The model describes the kinetics of bioanode in microbial electrolysis cells (MEC).
- Substrate effect on the current of bioanodes in MECs can be precisely evaluated.
- Anodic potential effect on the current of bioanode in MECs can also be evaluated.
- High substrate concentration reduces the overpotential induced anodic energy loss.

GRAPHICAL ABSTRACT

A new kinetic model, the Nernst-ping-pong model, for describing the kinetics of bioanode in a microbial electrolysis cell is developed by considering the intracellular electron transfer mechanisms. This model provides a new insight into the biochemical processes of the bioanode, and for the first time, substrate inhibition of bioanode is well described by this model.



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ABSTRACT

Understanding the electron-transfer mechanism and kinetic characteristics of bioanodes is greatly significant to enhance the electron-generating efficiencies in bioelectrochemical systems (BESs). A Nernst-ping-pong model is proposed here to investigate the kinetics and biochemical processes of bioanodes in a microbial electrolysis cell. This model can accurately describe the effects of the substrate (including substrate inhibition) and the anode potential on the current of bioanodes. Results show that the half-wave potential positively shifts as the substrate concentration increases, indicating that the rate-determining steps of anodic processes change from substrate oxidation to intracellular electron transport reaction. The anode potential has negligible effects on the enzymatic catalysis of anodic microbes in the range of -0.25 V to $+0.1$ V vs. a saturated calomel electrode. It turns out that to reduce the anodic energy loss caused by overpotential, higher substrate concentrations are preferred, if the substrate do not significantly and adversely affect the output current.

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1. Introduction

Bioelectrochemical systems (BESs) such as microbial fuel cell (Logan et al., 2006; Lovley, 2006) and microbial electrolysis cell (MEC) (Liu et al., 2005; Rozendal et al., 2006) are promising energy and environment technologies. BES should contain a bioanode that carries a large number of anode-respiring bacteria (ARB). ARB can oxidize organic matter and transfer intracellular electrons to the insoluble electrode to catalyze the anodic half-reaction. A key issue in BES research is to understand the various biochemical and electrochemical phenomena that drive the half-reaction on the bioanode.

In the bioanode biochemical process, the electrochemically active microbes first anaerobically convert the organic material into carbon dioxide, protons, and electrons in the cytoplasmic matrix. The conversion rate is determined by enzymatic reactions and can be generally described using Michaelis–Menten kinetics. Afterward, the electrons are transported to coenzymes such as NAD⁺ and further to the cytochromes in the periplasm through the extracellular respiration chain on the cytoplasmic membrane (Firer-Sherwood et al., 2008; Kim, 2009). The reduced cytochromes in the periplasm then transfer the electrons to outer membrane-bound cytochromes such as c-type cytochromes (Richter et al., 2009). However, the electron transfer from ARB to the electrode relies on redox components such as soluble mediators (von Canstein et al., 2007), c-type cytochromes (Busalmen et al., 2008), or even conductive pili (Lovley, 2008; Reguera et al., 2006). The electrons are transferred to the anode through the oxidation of the reducible components on the electrode surface; the transfer rate can be described using electron-transfer kinetics such as the Nernst or Butler–Volmer equations (Hamelers et al., 2011; Marcus et al., 2007; Strycharz et al., 2011).

So far, only a few kinetic models (Hamelers et al., 2011; Lee et al., 2009; Marcus et al., 2007; Pinto et al., 2011; Pinto et al., 2010; Strycharz et al., 2011; Torres et al., 2008) have been proposed to describe the kinetic characteristics of bioanodes. These models are mainly focused on investigating the effects of the anode potential on the anode current (Hamelers et al., 2011; Lee et al., 2009; Marcus et al., 2007; Strycharz et al., 2011; Torres et al., 2008). The Nernst–Monod model proposed by Marcus et al. (Marcus et al., 2007) is efficient in describing the bioanode performance in terms of the effect of the anode potential. However, this model is derived from the multiplicative Monod model for dual donor–acceptors when both substrates are soluble and the solid anode as electron acceptors was considered by connecting the concentration using Nernst equation. Hamelers et al. (Hamelers et al., 2011) developed the Butler–Volmer–Monod model, which combines the enzymatic and Butler–Volmer electron-transfer kinetics, for cases both of the biochemical reaction and/or the electrochemical reaction of the electron transfer could be the rate-determining step (RDS), particularly at low overpotential. By assuming that the redox components act as electron acceptors for substrate oxidation and as electron donors in the electron transfer to the electrode, the Butler–Volmer–Monod model successfully predicts the potential dependency of the apparent Monod constant (K'_m). However, the redox components for substrate oxidation, particularly the anaerobic-respiring enzymes located in the cell, are different from the electron shuttles for electrochemical reactions. Strycharz et al. (Strycharz et al., 2011) clearly distinguished the electron shuttle from the substrate oxidase and proposed a five-step model that involves a direct redox reaction between the microbe and the electron shuttle. However, the intracellular biochemical process, namely, the electron-transport reaction between the substrate oxidase and the electron shuttle, has not been fully discussed to date.

Generally, the intracellular respiration of a microorganism involves two kinds of reactions, namely, substrate oxidation and

electron transport reaction, both of which follow enzymatic kinetics such as that of Michaelis–Menten (Creevey et al., 2008; Durand et al., 2011; Meschi et al., 2010). The two-substrate (bisubstrate, Bi–Bi) enzymatic reaction mechanism (Marangoni, 2003), a reaction catalyzed by an enzyme in which two substrates and two products are involved, can be applied to better understand the electron transfer between the substrate oxidase and the electron shuttles. In addition, the ping–pong mechanism is used as a general tool for analyzing this Bi–Bi reaction. The ping–pong mechanism was experimentally illustrated successfully in the study of enzyme modified-electrode (Casero et al., 2005; Limoges et al., 2006, 2002; Savéant, 2006), another type of bio-electrode which is similar with the bioanode in BES in terms of bioelectrochemical reaction processes. This mechanism is also suitable in analyzing the reactions during the substrate inhibition (Durand et al., 2011), which is probably present in the bioanode process.

In this study, a Nernst–ping–pong model was proposed to evaluate the effects of the substrate and the anode potential on the performance of a bioanode in a MEC. The model involves the introduction of the ping–pong mechanism to describe the biochemical process of ARB. Through mathematical transformation, an analytical solution that yields an expression of the half-wave potential was obtained. The potential dependency of the apparent Monod constant can be predicted by this analytical solution. Moreover, the Nernst–ping–pong model was used to investigate and discuss the effects of substrate concentration on kinetic control and substrate inhibition.

2. Methods

2.1. Model description

In a BES, the electrochemically active ARB functions as a biocatalyst that oxidizes the organic substrate and then transfers the generated electrons to the anode. Two kinds of mechanism were proposed for the anodic extracellular electron transfer, namely, indirect electron transfer (IET) and the direct electron transfer (DET) (Kim et al., 1999; Liu et al., 2010a,b; Marsili et al., 2008; Wrighton et al., 2011). In these two mechanisms, the redox components are oxidized on the anode (for some cases, on the metal-like conductive nanowires). The difference between IET and DET is that the redox components in IET are soluble mediators that shuttle between the anode and the cell. On the other hand, bound cytochromes at the outer cell surface play a key role in DET. Thus, the bioanode reaction can be considered as a three-step process. In the first step, the substrate is catalyzed by an anaerobic respiration oxidase to generate electrons and products (Step 1). The electrons are then transferred to oxidized redox components such as some coenzymes or cytochromes to form the reduced redox component and regenerate the oxidase (Step 2). Finally, the reduced redox component is oxidized in the anodic oxidation reaction, and the electrons are transferred to the electrode (Step 3). Step 3 follows the Nernst equation (Lee et al., 2009; Marcus et al., 2007; Torres et al., 2008) because the bioanode usually performs under more positive potentials than the formal equilibrium potential of the redox component in normal operating conditions.

To develop a simplified scheme in analyzing the kinetic characteristics of the bioanode process, the classic ping–pong mechanism can be used to describe the first two biochemical reactions (Steps 1 and 2), which combine to form a Bi–Bi reaction. As presented in Scheme 1, Steps 1 and 2 occur inside the ARB, whereas the heterogeneous electron transfer (Step 3) occurs on the electrode surface. First, the substrate (S) combines with the oxidized substrate oxidase (E_O) to generate an intermediate-state enzyme $E_O S$, which produces products (P) and a reduced oxidase (E_R). E_R then binds

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