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Review

Electrokinetic analyses in biofilm anodes: Ohmic conduction of extracellular electron transfer

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ABSTRACT

This review explores electron transfer kinetics from an electron donor to the anode in electrically conductive biofilm anodes. Intracellular electron transfer (IET) from the donor to the anode is well described with the Monod equation. In comparison, mechanisms of extracellular electron transfer (EET) conduction are unclear yet, complicating EET kinetics. However, in biofilm anodes where potential gradient to saturated current density is less than ~300 mV, Ohmic conduction successfully describe conductive EET mainly with biofilm conductivity (K_{bio}) and biofilm thickness (L_f). High K_{bio} essential for production of high current density is found in *Geobacter* pure or enriched biofilm anodes, but other exoelectrogens could make biofilms electrically conductive. IET is rate-limiting for current density in conductive biofilms, and biofilm density of active exoelectrogens and L_f are operating parameters that can be optimized further to improve current density.

1. Introduction

Extracellular electron transfer (EET) is essential for the bacteria using solids as the terminal electron sink in respiration (called, exoelectrogens), such as *Geobacter* and *Shewanella*. EET has been found in a diversity of microorganisms, broadening EET's significance to microbial metabolism in natural environment (Holmes et al., 2017; Lovley, 2017). For instance, metal reducers could donate electrons to methanogens, called direct interspecies electron transfer via electrical pili (Lovley, 2017); alternatively, the syntrophic interaction between *Geobacter* and hydrogenotrophic methanogens was found using intermediate compounds, potentially H_2 or formate (Gao et al., 2017a). These discoveries imply that in natural environment EET can provide a niche for microorganisms to have syntrophy by sharing reducing powers together through EET, which supports more comprehensive significance of EET. Like natural environment, EET plays an important role in biofilm anodes of microbial electrochemical cells (MxCs), which can influences current density, energy loss and probably biofilm community. High current density and small energy loss should be realized for application of MxCs: recovering value-added products from waste biomass and used water (Lee et al., 2010; Dhar et al., 2015), monitoring toxic or organic compounds in water (Gao et al., 2017b; Fraiwan et al., 2013; Dávila et al., 2011) or cleaning used water in more economical fashions (Cui et al., 2014, 2017). Hence, electron transfer kinetics from donor substrate to the anode are detrimental for driving commercialization of MxCs in field. Substrate-utilization rate for exoelectrogens has been described well with the Monod equation (Torres et al., 2008, 2010; Lee et al., 2009, 2016; Dhar et al., 2016a, 2017). In comparison, the information of EET rate is limited. Multiple EET mechanisms and heterogeneous biofilm environments add more complexity in understanding EET kinetics.

In this review, electron transfer rate from an electron donor to the anode was discussed for biofilm anodes. There are several EET mechanisms, but here conductive EET involving high current density was primarily reviewed in parallel with intracellular electron transfer (IET). Finally, implication of Ohmic EET to MxC application was summarized.

2. Intracellular electron transfer (IET)

Electron transfer from donor substrate to the anode can be classified into IET and EET, as shown in Fig. 1. The boundary of IET is from an electron donor to an intracellular terminal electron acceptor. Outer membrane proteins (e.g., cytochrome *c*-like proteins) would be the terminal electron acceptor for IET (Lee et al., 2016; Torres et al., 2010). IET is different from EET for several aspects. First, IET exclusively occurs inside of cells. Second, exoelectrogens would mainly generate and conserve energy in IET; in comparison, energy would be dissipated in EET. More research is actually required to prove energy dissipation in EET, but no studies have demonstrated energy generation and conservation in EET yet. Finally, the relationship between anode potential and IET kinetics is unclear, although anode potential can affect biofilm structures (Torres et al., 2010; Dhar et al., 2016b).

IET can be described with dual-limitation kinetics in which an electron donor and intracellular terminal electron acceptor can affect

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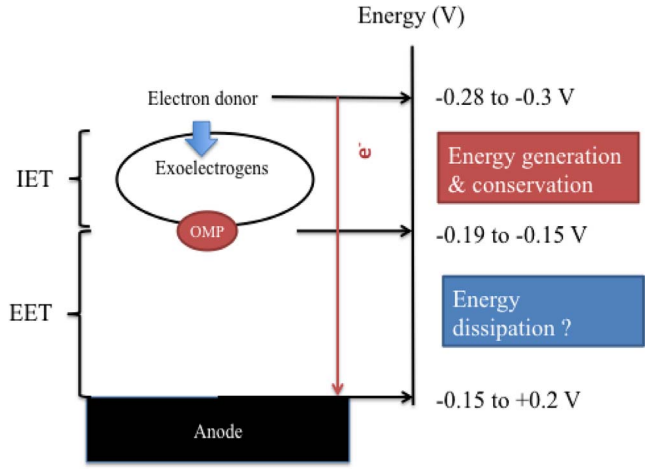

Fig. 1. Schematic diagram of intracellular and extracellular electron transfer for catabolism of exoelectrogens. IET: intracellular electron transfer, EET: extracellular electron transfer, OMP: outer membrane proteins. Typical values of electric potential for electron donor, OMP and the anode were provided to show energy gradients in the electron transfer to the anode.

substrate-utilization rate, as expressed in Eq. (1).

$$-\frac{dS_d}{dt} = f_e^0 q_{max,app} X_a \frac{S_d}{S_d + K_{sd,app}} \frac{S_{a,OMP}}{S_{a,OMP} + K_{sa,app}} \quad (1)$$

where S_d: donor substrate (g COD/m^3), t: reaction time (d), f_e^o is the fraction of electrons used for catabolism, $q_{max,app}$ is the apparent maximum specific substrate utilization rate (g COD/g VS-d), X_a is the concentration of active exoelectrogens (g VS/m^3), $K_{sd,app}$ is the apparent half-saturation concentration of electron donor (g COD/m^3), $S_{a,OMP}$ is concentration of an intracellular terminal electron acceptor (i.e., an outer membrane protein) (g COD/m^3), and $K_{sa,app}$ is the apparent half-saturation concentration of an intracellular terminal electron acceptor (g COD/m^3). Eq. (1) describes substrate-utilization rate for planktonic exoelectrogens, not in biofilm systems.

For steady-state biofilm systems, ($-$dS/dt) term is expressed as flux (g COD/m^2-d) where the X_a term is replaced with X_f (biofilm density of active exoelectrogens, g VS/m^3) and L_f (biofilm thickness, m). This flux is equivalent to current density (A/m^2 of anode geometric surface area) in biofilm anodes, and Eq. (1) becomes:

$$j = 0.14 f_e^o q_{max,app} X_f L_f \frac{S_d}{S_d + K_{sd,app}} \frac{S_{a,OMP}}{S_{a,OMP} + K_{sa,app}} \quad (2)$$

where j is current density (A/m^2) and 0.14 is the conversion factor (0.14 A = 1 g COD/d).

Eq. (2) mathematically describes IET kinetics, and most of thermodynamic and kinetic parameters in Eq. (2) are measurable or estimated. For instance, f_e^o can be quantified with true growth yield of Y (g VS/g COD), providing electron fraction used for cell synthesis (f_s^o); thus, we can experimentally determine f_e^o. In *Geobacter*-enriched biofilm anodes, f_s^o is close to 0.1 (Lee et al., 2008, 2010, 2016, Torres et al., 2008). L_f can be measured with confocal laser scanning microscopy or microsensors (Lee et al., 2016; Dhar et al., 2016a, 2017); a microsensor method described in the literature is highly recommended for measurement of biofilm anodes because intact exoelectrogens in biofilm anodes are well protected during the measurement (Dhar et al., 2016a, 2017).

It is assumed that an intracellular terminal electron acceptor (e.g., cytochrome *c*) would not limit IET. Several works justified this hypothesis by anode-polarized conditions given that donor substrate mainly limits substrate-utilization rate in highly positive anode potential (Torres et al. 2010; Lee et al., 2016). Then, the electron acceptor term in Eq. (2) can be ignored.

$$j = 0.14 f_e^o q_{max,app} X_f L_f \frac{S_d}{S_d + K_{sd,app}} \quad (3)$$

For a chemostat biofilm anode, the two kinetic parameters of $K_{sd,app}$ and $q_{max,app}X_f$ can be estimated, as current density is monitored to donor substrate concentration. To produce high current density in MxCs, we should enrich exoelectrogens having high $q_{max,app}X_f$ and low $K_{s,app}$, and large L_f (thick biofilm). However, exoelectrogens at an inner biofilm can be metabolically inactive or dead in a thick biofilm mainly due to proton accumulation (Dhar et al., 2017; Sun et al., 2015; Frank et al., 2009). This indicates the requirement of biofilm thickness optimized for maximum current density, not simply keeping a thick biofilm. Table 1 summarizes $K_{sd,app}$ and $q_{max,app}X_f$ values estimated for *Geobacter* enriched biofilm anodes. $K_{s,app}$ ranges from 156 to 274 g COD/L, suggesting that $K_{s,app}$ does not influence current density much. Instead, $q_{max,app}X_f$ is very significant for increasing current density. X_f will be a key engineering parameter to high performance MxCs (i.e., high current density) because engineering exoelectrogens for q_{max} increase is limited. Hence, revisiting the study on X_f related to anode design and enrichment of kinetically efficient exoelectrogens (i.e., *Geobacter* spp.) seems important to accelerate MxC application in field.

3. Extracellular electron transfer (EET)

Three EET mechanisms that include direct contact, utilization of shuttling compounds, and electrical conduction are well known. EET kinetics via electrical conduction is much faster than the other pathways for long-distance EET, such as in biofilm anodes (Torres et al., 2010; Lee et al., 2010, 2016). Hence, understanding electrically conductive EET is important to engineer and control MxC performance. There are two types of electrical conduction of EET. One is redox conduction (called, long-range electron hopping) and the other is Ohmic conduction. Redox conduction of EET describes that electrons would extracellularly transport from an intracellular terminal electron acceptor to the anode via cascade electron hopping in multiple extracellular cofactors throughout biofilm anodes or conductive nanowires of extended outer membrane and periplasm (Strycharz-Glaven et al., 2011; Yates et al., 2016; Phan et al., 2016; Li et al., 2016; Pirbadian et al., 2014); redox conduction of EET in biofilm anodes is to extend electron hopping from a nanometer to a micrometer scale. Quantum mechanics has been used for simulating electron hopping in molecular level (Breuer et al., 2014). Redox conduction of EET occurs from inner and outer biofilms to the anode, which means that the distance of EET is in a few to several dozens of micrometers. Hence, Newtonian physics in a macro-scale can well describe redox conduction of EET, not quantum mechanics. Literature mathematically described the EET with modified

Table 1
Comparison of apparent half-saturation concentration ($K_{s,app}$) and apparent maximum specific substrate utilization rate multiplied with biofilm density ($q_{max,app}Xf$) for biofilm anodes.

$K_{s,app}$ (gCOD/m^3)	$q_{max}X_f$ (g COD/m^3-d)	Anode potential (V vs. SHE)	E_{KA} (V vs. SHE)	j (A/m^2)	L_f (μm)	Reference
168	1.26×10^5	−0.2	−0.246 ± 0.002	1.68 ± 0.06	139 ± 11	Dhar et al., 2016c
156	6.4×10^5	−0.2	−0.230 ± 0.003	2.05 ± 0.05	34 ± 5	Dhar et al., 2016a
274	9.2×10^4	−0.15	−0.230 ± 0	0.82 ± 0.03	100	Lee et al., 2016
184	10^6	−0.2	−0.248 ± 0	8.31	66 ± 16	Lee et al., 2009
N/A	8.6×10^5	−0.2	−0.225 ± 0.002	10	79	Torres et al., 2008

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