Sensitivity and Bifurcation Analysis of a Differential-Algebraic Equation Model for a Microbial Electrolysis Cell

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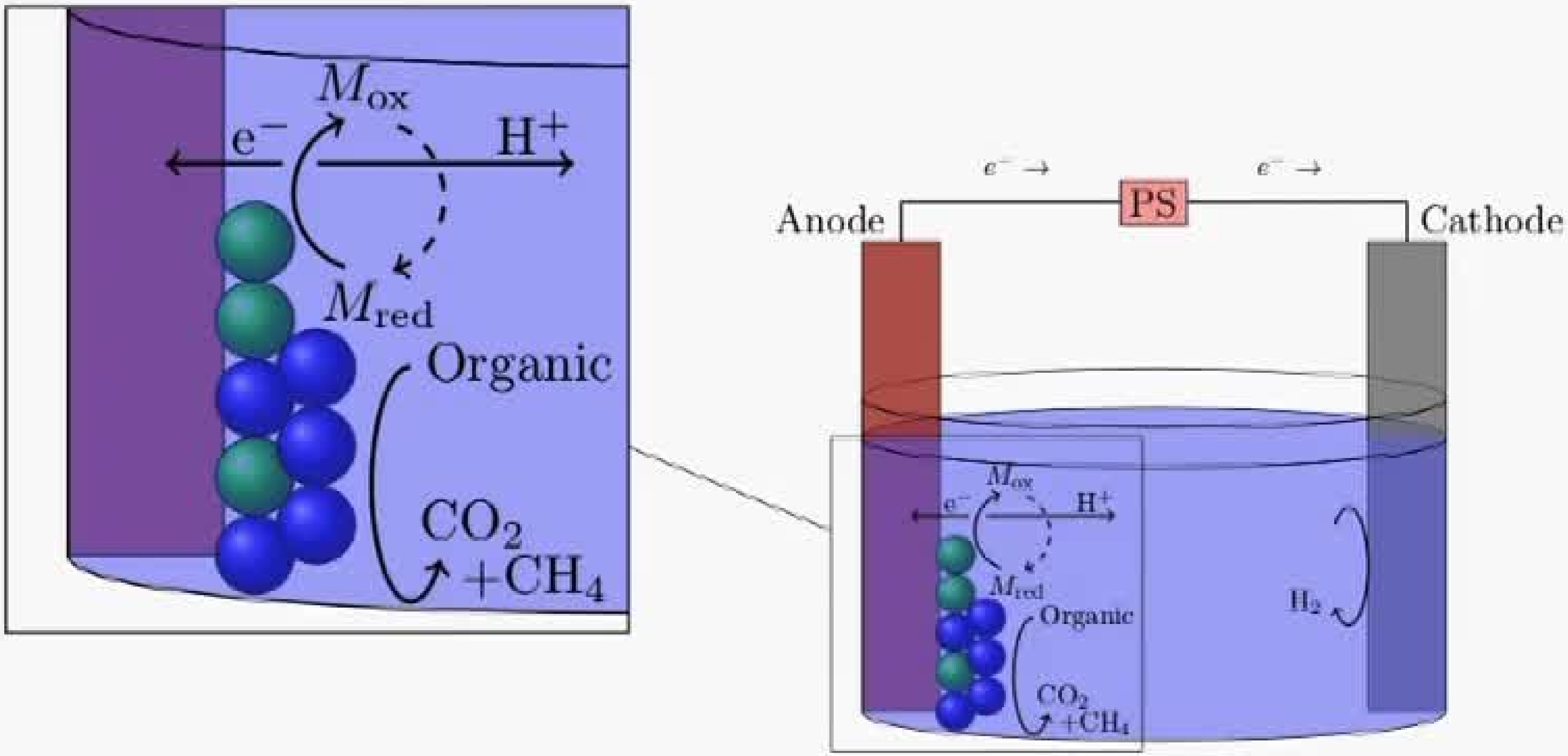
Overview

Introduction

What Are Microbial Electrolysis Cells?

Microbial electrolysis cells (MECs) are biological fuel cells that produce H_2.

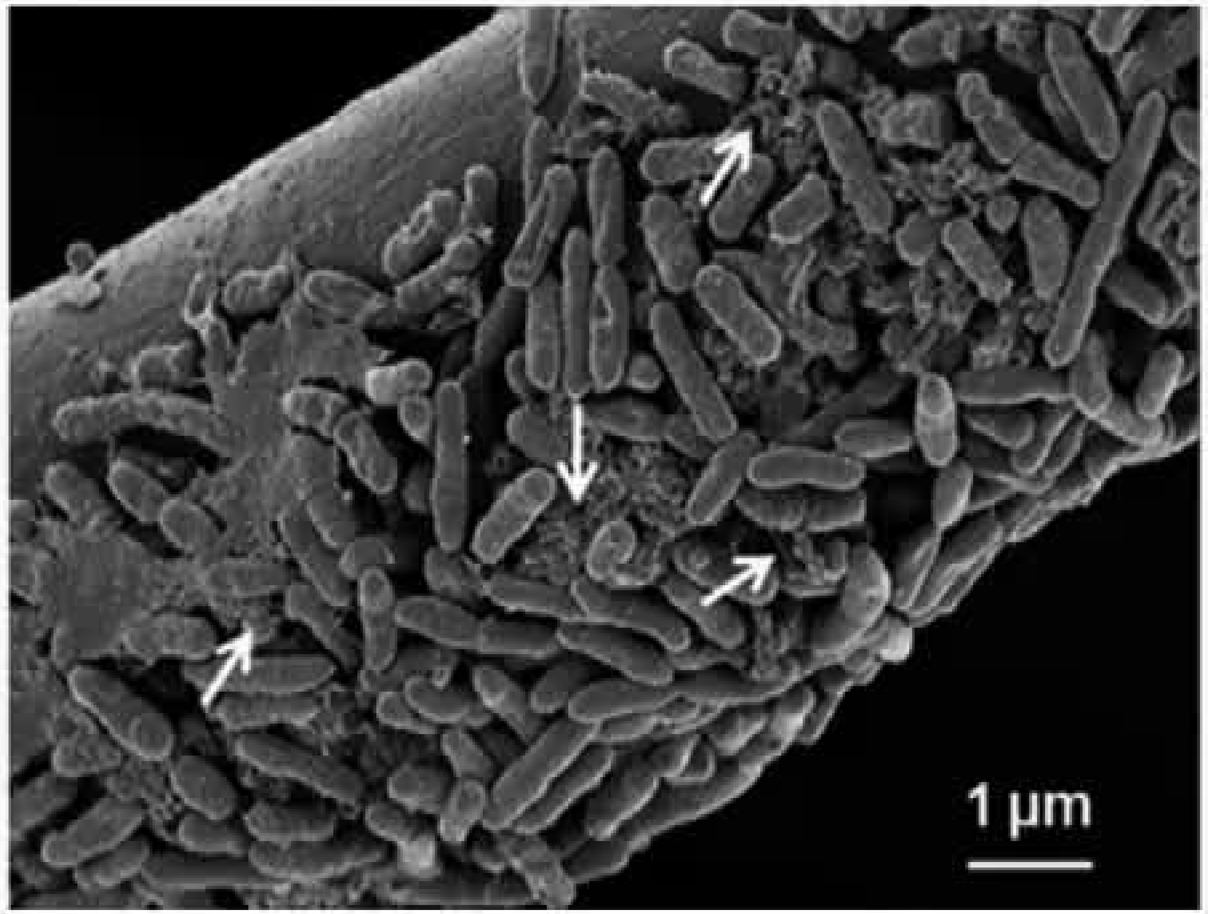


The basic bioelectrochemistry is modeled by

$$S + M_{\text{ox}} \rightarrow M_{\text{red}} + \text{CO}_2,$$
$$M_{\text{red}} \rightarrow M_{\text{ox}} + \text{e}^- + \text{H}^+.$$

e^- Transfer in Anode Biofilm

Microbes form a biofilm on the anode to facilitate electron transfer. Arrows show connections between microorganisms.



[1]Eaktasang et al. Enhanced Current Production by Electroactive Biofilm of Sulfate-Reducing Bacteria in the Microbial Fuel Cell. *Environ Eng Res* 18(4), 2013.

Differential-Algebraic Equation (DAE)

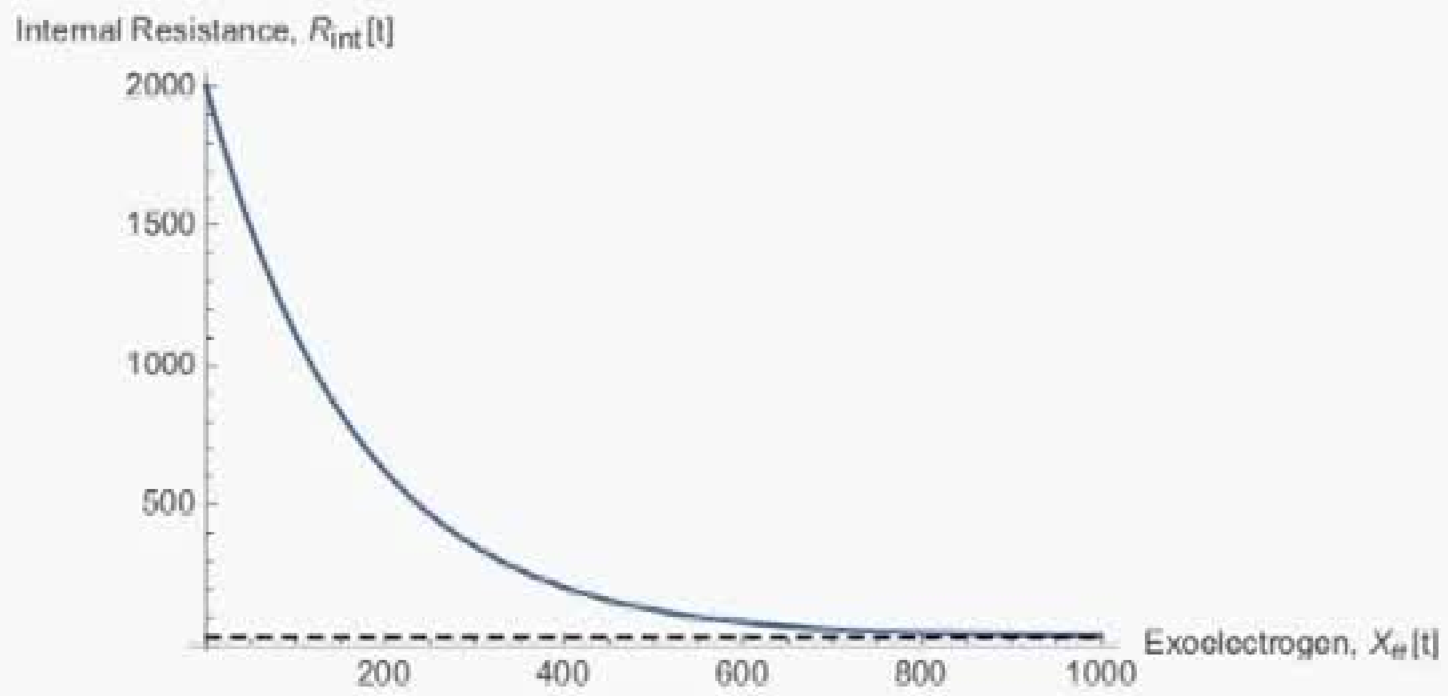
Substrate, microorganism, and oxidized mediator concentrations and current are given by the following DAE:

$$
\begin{aligned}
\frac{dS}{dt} &= D[S^{(0)} - S(t)] - q_e(t)X_e(t) - q_m(t)\left[X_{m,1}(t) + X_{m,2}(t)\right], \\
\frac{dX_{m,1}}{dt} &= [\mu_m(t) - K_{d,m} - \alpha_1(t)]X_{m,1}(t), \\
\frac{dX_e}{dt} &= [\mu_e(t) - K_{d,e} - \alpha_2(t)]X_e(t), \\
\frac{dX_{m,2}}{dt} &= [\mu_m(t) - K_{d,m} - \alpha_2(t)]X_{m,2}(t), \\
\frac{dM_{ox}}{dt} &= -Y_M q_e(t)X_e(t) + \frac{\gamma}{VmF} I_{MEC}(t), \\
I_{MEC}(t)R_{int}(t) &= E_{applied} + E_{CEMF} \\
&\quad - \frac{RT}{mF}\left[\ln\left(\frac{M_{total}}{M_{total} - M_{ox}(t)}\right) + \frac{1}{\beta}\operatorname{arcsinh}\left(\frac{I_{MEC}(t)}{A_{sur,A} I_0^{ref}}\right)\right].
\end{aligned}
$$

Internal Resistance

Previously, Pinto et al. obtained the following expression for internal resistance by fitting an exponential curve to their resistance data.

$$R_{\text{int}}(t) = R_{\min} + (R_{\max} - R_{\min})e^{-K_R X_e(t)}.$$

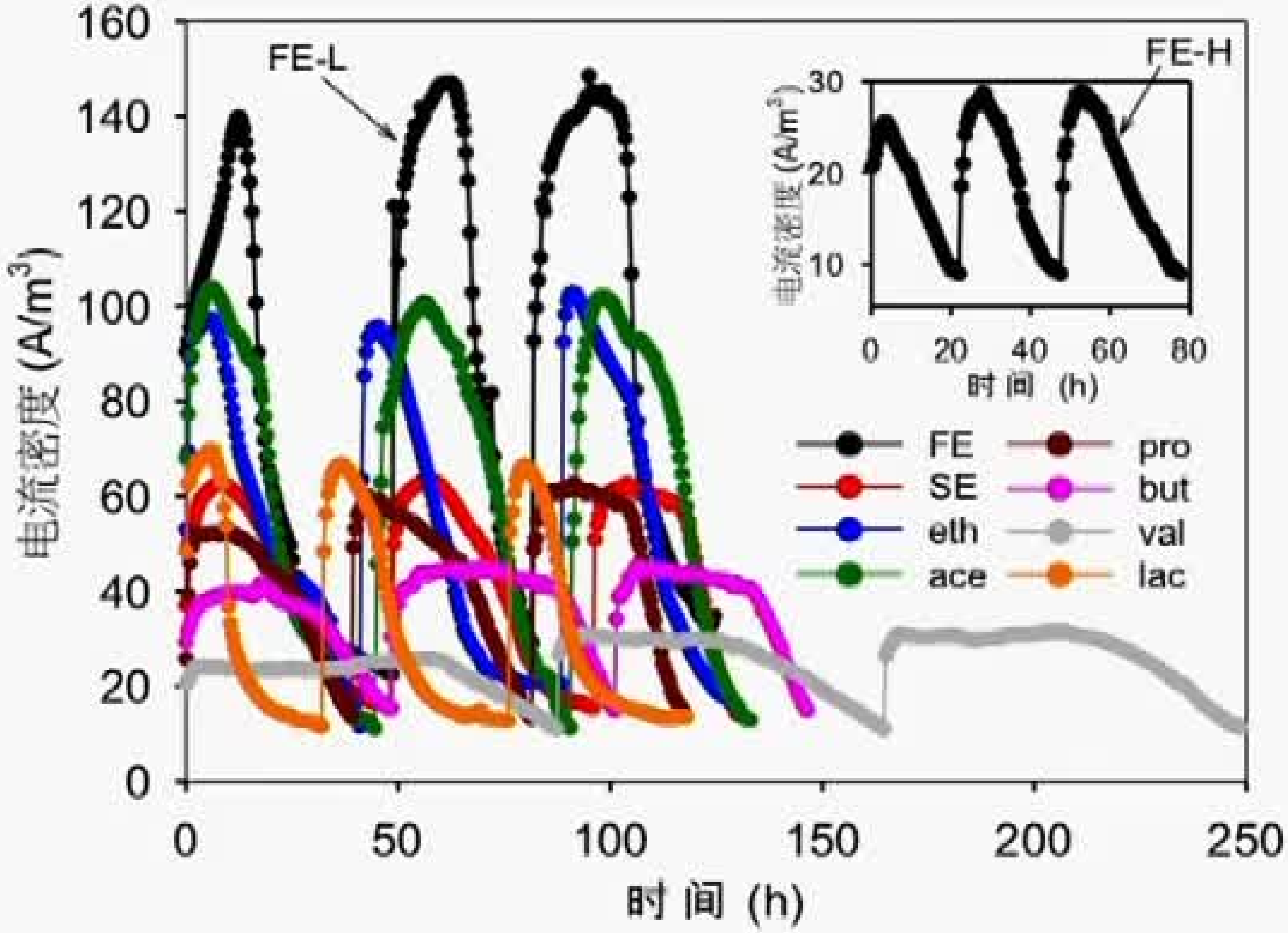


Our data was collected by electrochemical impedance spectroscopy (EIS).

Sensitivity and Batch Fed MECs

Data

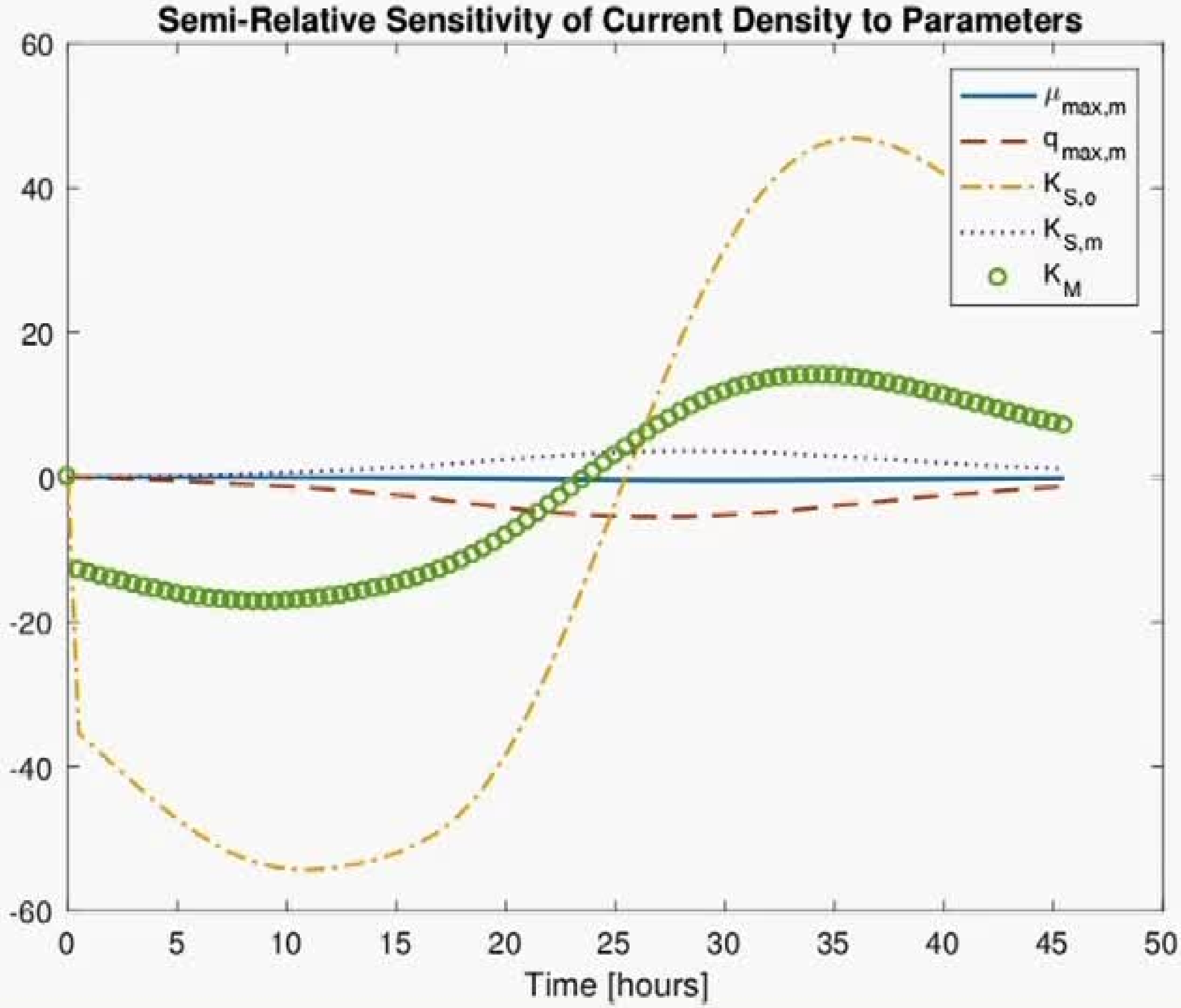
We have data for MEC current over time for various substrates. Each curve has three peaks corresponding to different experiments run in series.



Although we have focused on single substrates so far, a combination of substrates such as fermentation effluent (FE-L) may be most effective.

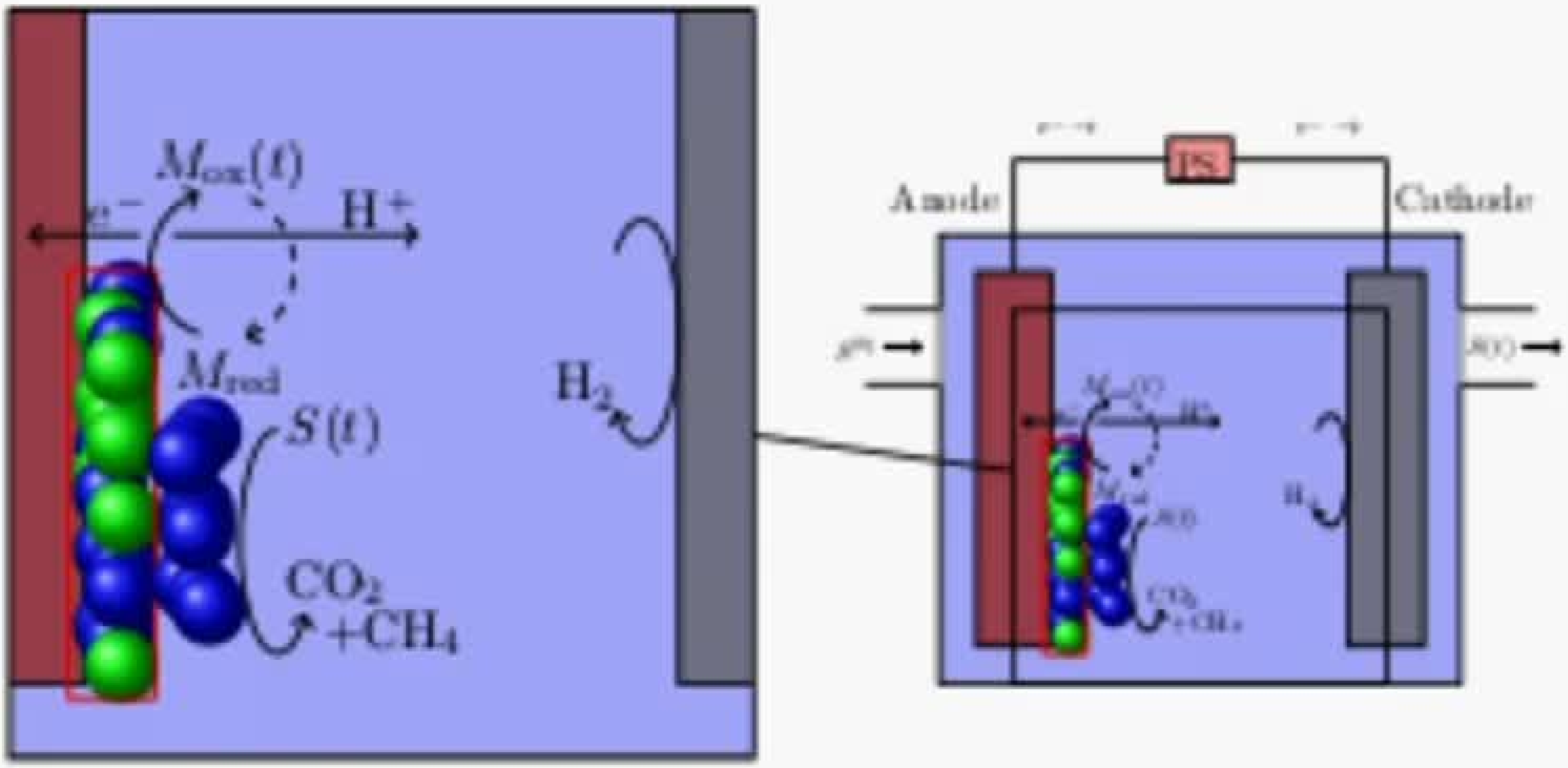
Semi-Relative Sensitivity for Other Parameters

This shows $p_i \frac{\partial}{\partial p_i} I_{\text{density}}(t)$ for some of the other parameters.



Continuous Flow MEC

Instead of a batch reactor, we may have a influent substrate.



- Substrate enters at rate $DS^{(0)}$.
- What happens at the stable equilibrium?

Continuous Flow MEC

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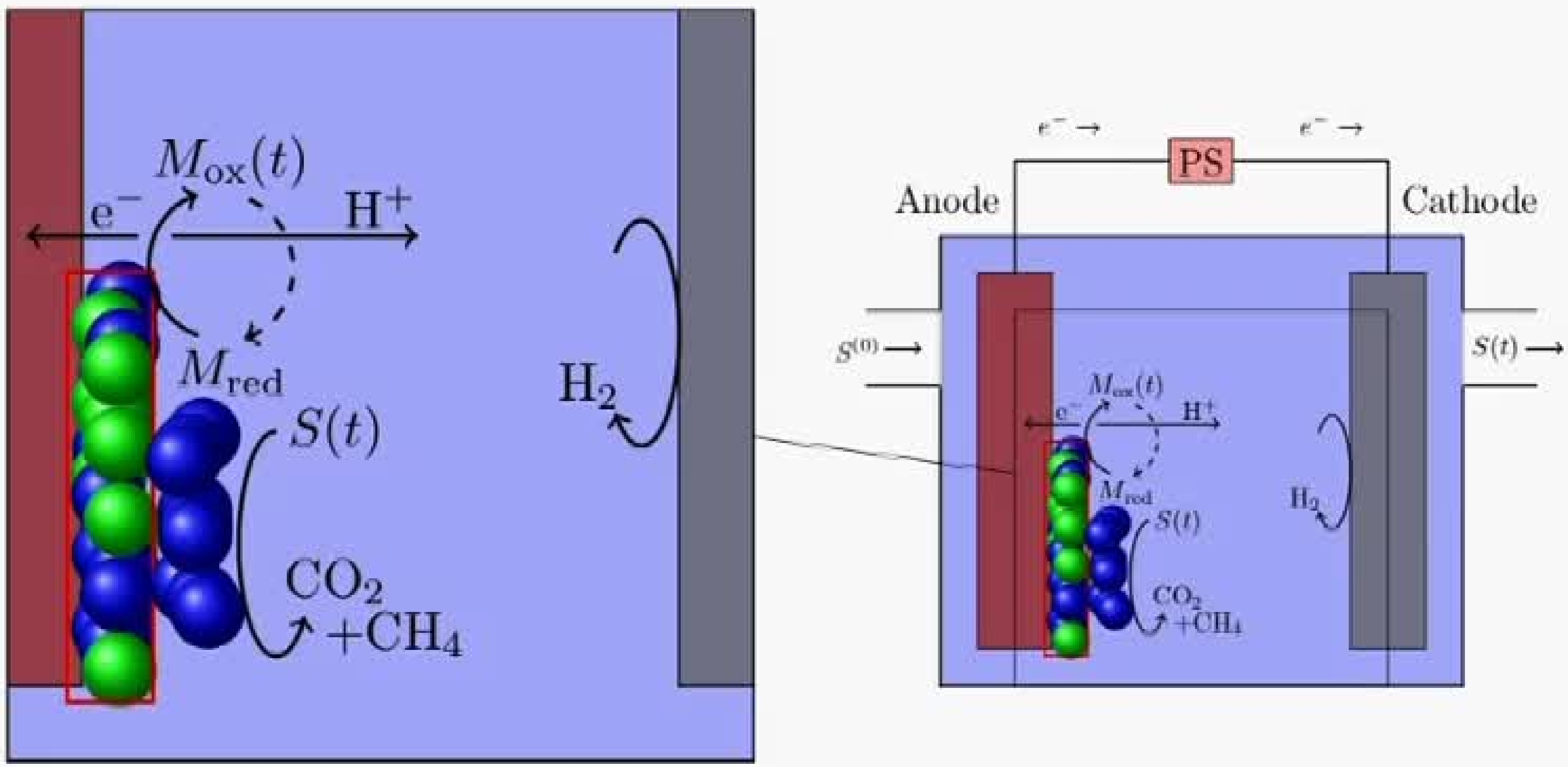


- Substrate enters at rate $DS^{(0)}$.
- What happens at the stable equilibrium?

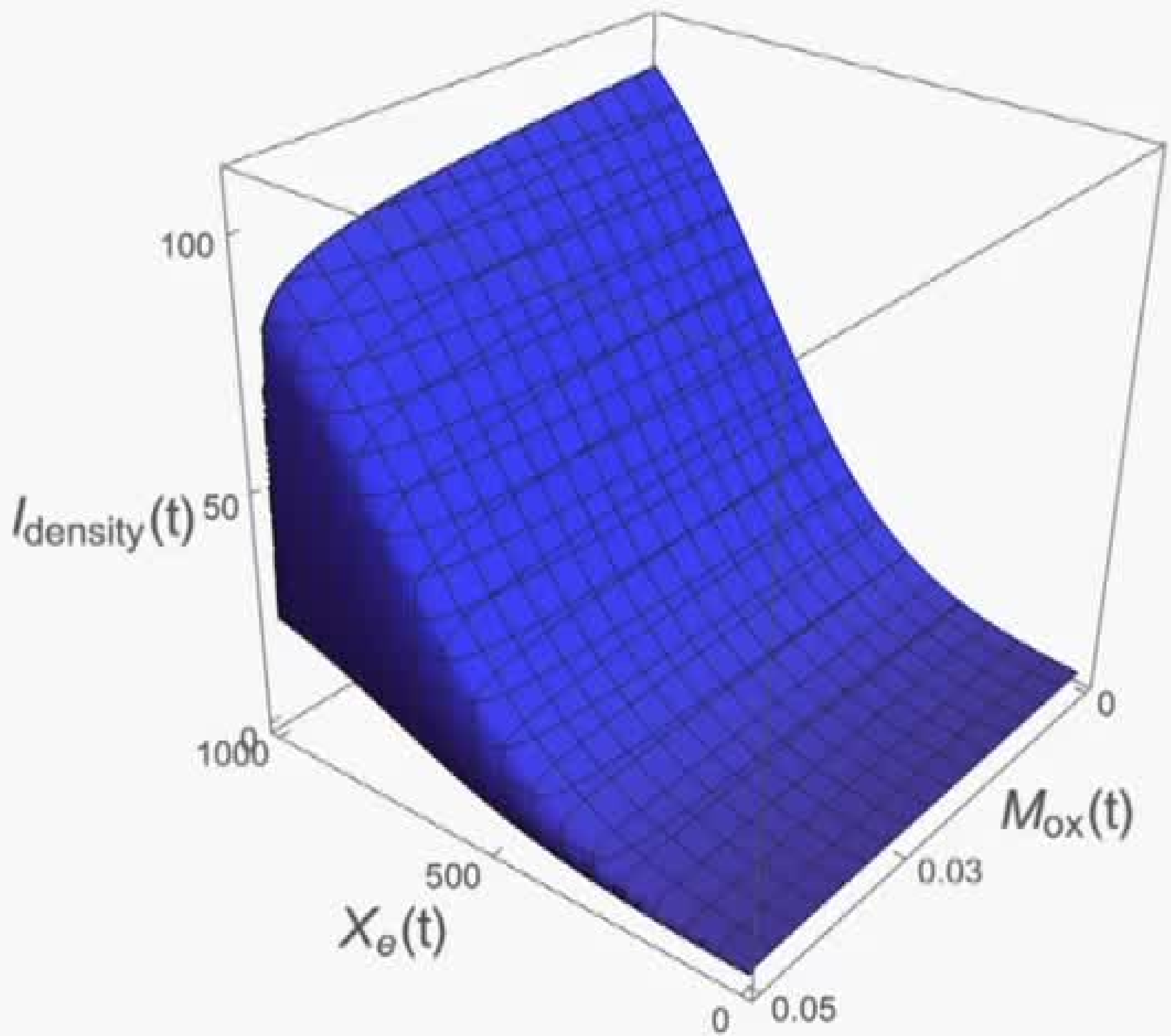
Stability from Matrix Pencil

Theorem (Riaza). Suppose x^* is a regular equilibrium point of the quasilinear DAE $A(x)x' = f(x)$. Then the matrix pencil $\lambda A(x^*) - f'(x^*)$ is regular, and the spectrum of the Jacobian matrix of the reduced ODE equals $\{\lambda \in \mathbb{C} \mid \det(\lambda A(x^*) - f'(x^*)) = 0\}$.

This theorem allows us another way to assess dynamical aspects such as stability of equilibria in DAEs without explicitly calculating the state reduction to an ODE.

Solutions to the Algebraic Equation

We can solve the algebraic equation numerically to generate the following contour plot. This shows where $0 = g(y, z)$.



Bifurcations in Semi-Explicit Index One DAEs

We use the Schur complement in Sotomayor's Theorem to obtain conditions for a transcritical bifurcation.

Suppose that $S = f_y - f_z g_z^{-1} g_y$ has one geometrically simple zero eigenvalue that is the only eigenvalue on the imaginary axis. Furthermore, suppose that this eigenvalue has right eigenvector v and left eigenvector w. Then a transcritical bifurcation occurs in the parameter p at (y^*, z^*, p^*) if

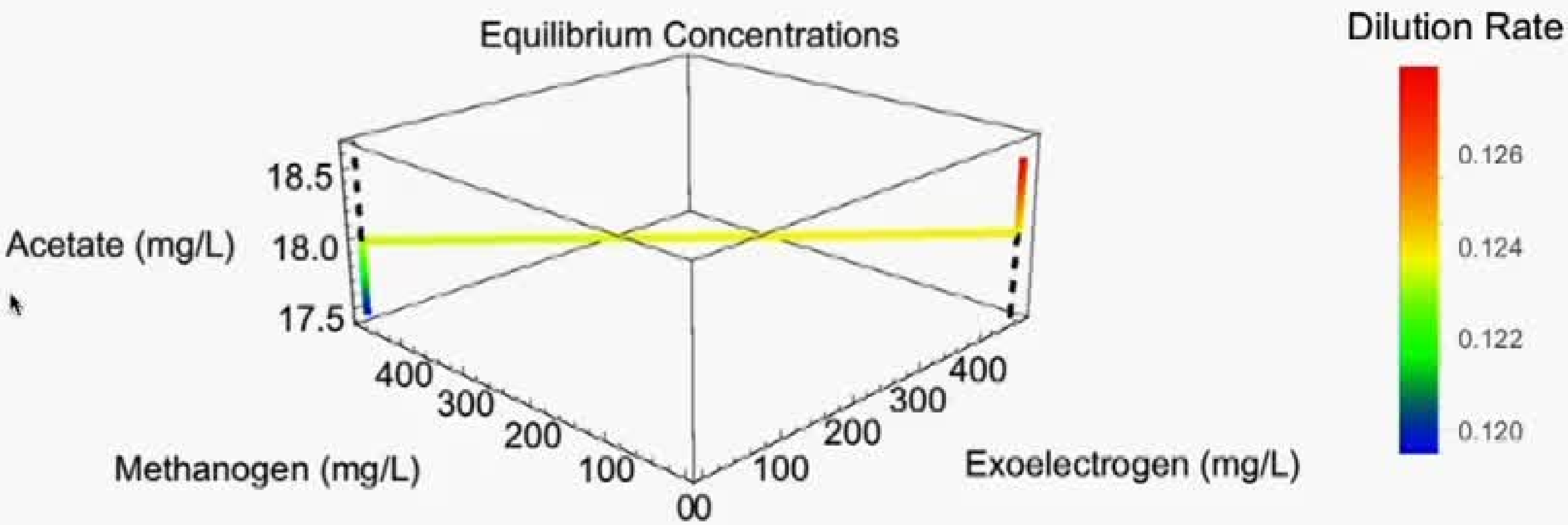
(1) $w^T(f_p - f_z g_z^{-1} g_p) = 0$,

(2) $w^T[(f_p - f_z g_z^{-1} g_p)_y v] \neq 0$, and

(3) $w^T[S_y(v, v)] \neq 0$.

Results

Transcritical bifurcations occur in the dilution rate, at $D = 0.1233388$ and $D = 0.1240194$. This is a flow rate of ≈ 11 mL / day in a 90 mL MEC.



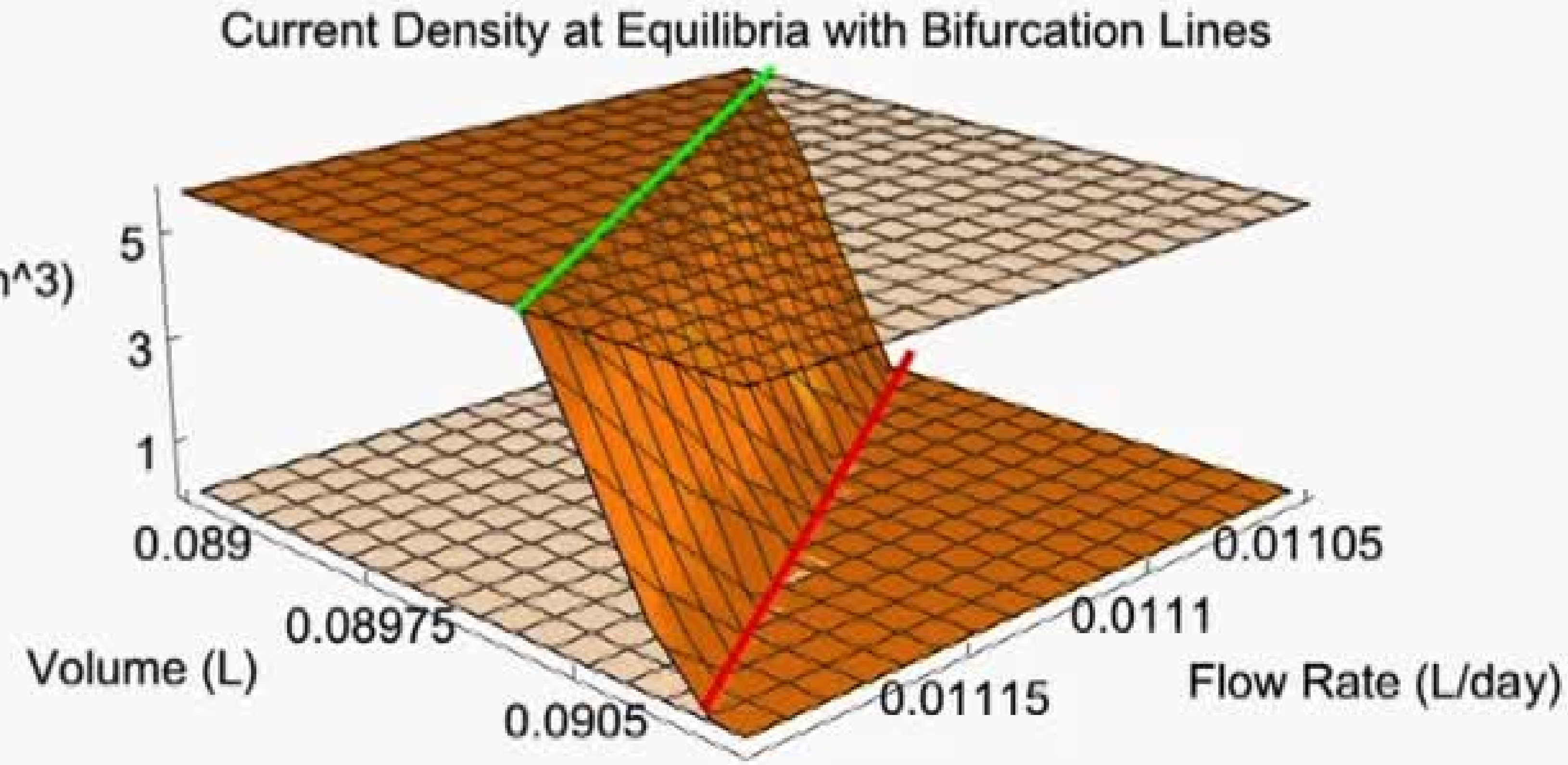
As D increases, the system moves through three regimes:

(1) competitive exclusion by methanogens,

(2) coexistence, and

(3) competitive exclusion by exoelectrogens.

Results (cont...)



From another perspective the three regimes correspond to

(1) zero current,

(2) increasing current, and

(3) current slightly above 5 ampere / m^3.

Discussion

- Dilution rates must be large enough for exoelectrogens to dominate their biofilm and provide greatest possible current density.
- Using the appropriate dilution rate can be an effective approach for maintaining a vibrant exoelectrogenic microbial community and maintaining stable system performance.
- The locations of the bifurcations depend on growth and consumption parameters, so these should be measured or estimated to help guide MEC operation.
- Literature has shown that hydrogen production directly correlates with current generation so the findings presented in the study do represent hydrogen generation from the MEC.

Preliminary Work - Proofs

An Alternative Model

Consider the same model except that biofilm retention is modeled by

$$\alpha_1(t) = \begin{cases} 0, & \text{if } X_{m,1}(t) < X_{\max,1}, \\ \mu_m(t) - K_{d,m}, & \text{otherwise,} \end{cases}$$

and

$$\alpha_2(t) = \begin{cases} 0, & \text{if } X_e(t) + X_{m,2}(t) < X_{\max,2}, \\ \frac{[\mu_e(t) - K_{d,e}]X_e(t) + [\mu_m(t) - K_{d,m}]X_{m,2}(t)}{X_e(t) + X_{m,2}(t)}, & \text{otherwise.} \end{cases}$$

Combined Growth Parameter

The the behavior as $t \to \infty$ is determined by the growth parameters

$$\lambda_m = \frac{K_{S,m}}{\frac{\mu_{\max,m}}{K_{d,m}} - 1} \text{ and } \lambda_e = \frac{K_{S,e}}{\frac{\mu_{\max,e}}{K_{d,e}} - 1}.$$

Lemma

The solutions $S(t)$, $X_{m,1}(t)$, $X_{m,2}(t)$, $X_e(t)$, $M_{ox}(t)$, and $I_{MEC}(t)$ of equations are bounded. With the exception of $I_{MEC}(t)$, they are also positive.

Theorem (Extinction)

If either

(a) $\mu_{max,i} \leq K_{d,i}$ *or*

(b) $\mu_{max,i} > K_{d,i}$ *and* $\lambda_i > S^{(0)}$,

then $\lim_{t\to\infty} X_i(t) = 0$.

Competitive Exclusion

Theorem (Competitive-Exclusion)

Suppose that the microbes are not guaranteed to go extinct by the previous theorem. Limiting behavior of solutions is determined by the smaller λ_i.

(1) *Suppose* $\lambda_m < \lambda_e$. *Then, as* $t \to \infty$, *solutions approach*

$$W = \{(\lambda_m, X_m^*, 0, X_m^*, \tilde{M}_{ox}, 0)\} \tag{2}$$

where

$$X_m^* = \frac{(S^{(0)} - \lambda_m)(K_{S,m} + \lambda_m)D}{q_{max,m}\lambda_m} \tag{3}$$

and

$$\tilde{M} = M_{total}\left(1 - exp\left[-\frac{mF}{RT}(E_{applied} + E_{CEMF})\right]\right). \tag{4}$$

⋮

Competitive Exclusion

Theorem (Competitive-Exclusion (cont...))

(2) *Suppose $\lambda_e < \lambda_m$. Then, as $t \to \infty$, solutions approach*

$$W = \{(\lambda_e, 0, X_e^*, 0, M_{ox}^*, I_{MEC}^*)\}.$$

where

$$X_e^* = \frac{(S^{(0)} - \lambda_e)(K_{S,e} + \lambda_e)D(K_M + M_{ox}^*)}{q_{max,e}\lambda_e M_{ox}^*},$$

$$I_{MEC}^* = DY_M(S^{(0)} - \lambda_{e,1})\frac{VmF}{\gamma} > 0,$$

and

$$M_{ox}^* = M_{total}\left[1 - exp\left(\frac{mF}{RT}\left[-E_{applied} - E_{CEMF} + \dots \right.\right.\right.$$
$$\left.\left.\left.\frac{RT}{\beta mF} arcsinh\left(\frac{I_{MEC}^*}{A_{sur,A} i_0}\right) + I_{MEC}^* R_{int}(X_e^*)\right]\right)\right].$$

Coexistence

Theorem (Coexistence)

Suppose microorganisms are not guaranteed to go extinct and that $\lambda = \lambda_e = \lambda_m$. Then, as $t \to \infty$, solutions approach the largest invariant set in

$$
\begin{aligned}
E = \{ & (\lambda, X_{m,1}, X_e, X_{m,2}, M_{ox}, I_{MEC}) : \\
& D[S^{(0)} - \lambda] = q_{max,m}\left(\frac{\lambda}{K_{S,m}+\lambda}\right)[X_{m,1}(t) + X_{m,2}(t)] \\
& \qquad + q_{max,e}\left(\frac{\lambda}{K_{S,e}+\lambda}\right)\left(\frac{M_{ox}(t)}{K_M + M_{ox}(t)}\right)X_e(t), \\
& \frac{dM}{dt} = \frac{\gamma}{VmF} I_{MEC}(t) - Y_M q_{max,e}\left(\frac{\lambda}{K_{S,e}+\lambda}\right)\left(\frac{M_{ox}(t)}{K_M + M_{ox}(t)}\right)X_e(t), \\
& I_{MEC}(t) R_{int}(t) = E_{applied} + E_{CEMF} \\
& \qquad - \frac{RT}{mF}\left[\ln\left(\frac{M_{total}}{M_{total} - M(t)}\right) - \frac{1}{\beta}\operatorname{arcsinh}\left(\frac{I_{MEC}(t)}{A_{sur,A} i_0}\right)\right]\}.
\end{aligned}
$$