Modeling Bioelectrochemical Systems for (waste)water Treatment and Bioenergy Recovery with COMSOL

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Why is this interesting?

Bioelectrochemical systems (BES) are based on the typical electrochemical system (which convert chemical to electrical energy or vice versa) with the inclusion of microbes, serving as catalysts in transferring electrons to/from external electron acceptors (electrodes). They present a unique potential to provide energy-efficient wastewater treatment, utilize organic waste streams to produce energy, and many important chemicals. However, we are a long way from commercial implementations of BES. A key challenge being the poor understanding of the complex phenomena involved.

Our objective

- Investigating the basic chemical, biological and physical phenomena (especially the mechanisms of extracellular electron transfer and the ecology of the microbial communities) that are critical for the performance of BES using COMSOL Multiphysics.
- Model-based technical evaluation of the different BES applications

Modeling strategy

COMSOL-based modeling framework

COMSOL

Electrochemistry Module
Model structure validation and parameter calibration by electrochemical techniques(e.g. Electrical impedance spectroscopy, cyclic voltammetry etc.)

CFD Module
hydrodynamics of microbial fuel cell (testing different reactor configurations)

Chemical Reaction Engineering Module
linking mass, energy and momentum transport with chemical reactions

LiveLink for MATLAB ⟷

MATLAB
Code for microbial kinetics and ecology, biofilm dynamics, and electron transfer mechanisms

MATLAB code ⟷

LiveLink for Excel ⟷

EXCEL
Model structure definition: Operating, kinetic, and thermodynamic parameters (to be used in both COMSOL and MATLAB)

Microbial Model equations

Case study: Simultaneous cathodic reduction of acetate and butyrate to alcohols and simultaneous anodic oxidations of acetate and hydrogen)

$$I^{an}_{Acox} + I^{an}_{H2ox} = I_{an} = I_{obs} \qquad I^{ca}_{Acred} + I^{ca}_{H+red} + I^{ca}_{Bured} = I_{ca} = I_{obs}$$

$$E^{Bulk}_{Acox} + \eta^{conc}_{Acox} + \eta^{act}_{Acox} = E_{anode} \qquad E^{Bulk}_{Acred} + \eta^{conc}_{Acred} + \eta^{act}_{Acred} = E_{cathode}$$

$$E^{Bulk}_{H2ox} + \eta^{conc}_{H2ox} + \eta^{act}_{H2ox} = E_{anode} \qquad E^{Bulk}_{Bured} + \eta^{conc}_{Bured} + \eta^{act}_{Bured} = E_{cathode}$$

$$\eta^{act}_{ac\_an} = \frac{KsE.I_{ac\_an}}{(I_{ac\_max} - I_{ac\_an})} \qquad E^{Bulk}_{H+red} + \eta^{conc}_{H+red} + \eta^{act}_{H+red} = E_{cathode}$$

$$I^{an}_{Acox} = rS_{Acox}.Y_e.F.\frac{V_{r\_an}}{A_{an}} \qquad rS_{Acox} = q^{max}_{ac\_e}.\frac{S_{ac}}{K_s+S_{ac}}.\frac{S_{in}}{K_{in}+S_{in}}X_{ac\_e}.I_{ph}.\frac{\eta^{act}_{ac}}{KsE+\eta^{act}_{ac}}$$

Where:

$F = Faraday's\ constant\ (C/mol_e)$
$A_{an} = area\ of\ anode(m^2)$
$S_{ac} = conc.of\ acetate(mol_{ac}/m^3)$
$S_{in} = conc.of\ inorganic\ nitrogen(mol_{in}/m^3)$
$KsE = half\ saturation\ activation\ overpotential$ (V)
$\eta^{act}_{ac} = activation\ overpotential\ (V)$
$I_{ph\_an} = pH\ inhibition\ term$ ()
$K_s = acetate\ half\ saturation\ constant\ (mol_{ac}/m^3)$
$rS_{Acox} = anodic\ acetate\ oxidation\ rate\ (mol_{ac}/m^3.s)$
$V_{r\_an} = volume\ of\ anode\ compartment(m^3)$
$Y_e = electron\ yield\ per\ mole\ of\ acetate(mol_e/mol_{ac}$
$q^{max}_{ac\_e} = max.specific\ acetate\ rate\ (mol_{ac}/mol_{ac}.s)$
$K_{in} = half\ saturation\ for\ ammonium\ N(mol_{in}/m^3)$
$X_{ac\_e} = electroactive\ bacteria\ conc.(mol_X/m^3)$
$I_{ac\_max} = max.current\ at\ perfect\ electrocatalysis$

Electrochemical Techniques

Controlled Potential	Controlled Current	Controlled Charge	Impedance methods
Potential Step Potential sweep(Voltammetry) Constant Potential(Bulk Electrolysis)	Chronopotentiometry Coulometry Electrolysis	Charge step(coulostatic methods)	AC voltammetry Electrical Impedance spectroscopy

Expected/ Representative Results

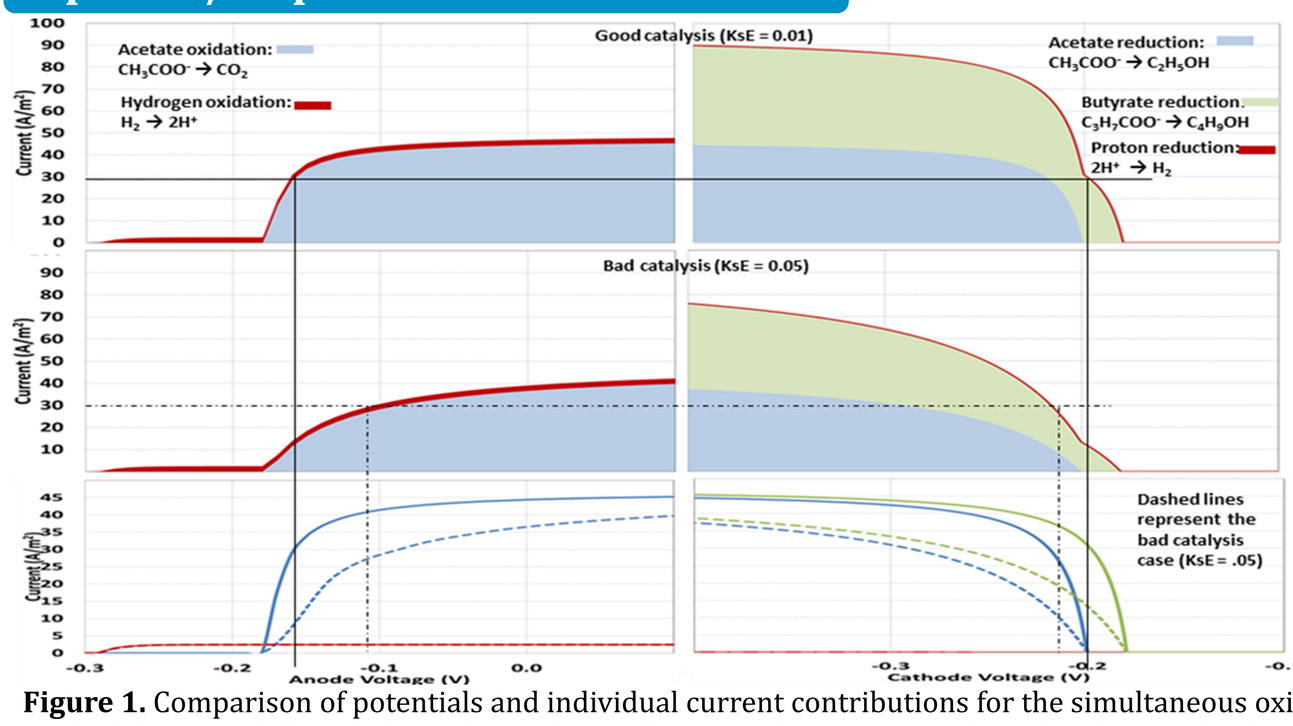

Figure 1. Comparison of potentials and individual current contributions for the simultaneous oxidations of acetate and hydrogen (anode) and reductions of butyrate, acetate and protons (cathode) at two different electrode catalysis efficiencies (KsE = 0.01 and 0.05). Arbitrary fixed cathode and anode bulk liquid concentrations of 0.1M of butyrate and acetate; 0.3mM for dissolved hydrogen and pH 5 are used.

Data from Electrochemical experiments + **COMSOL-based electrochemical and microbial model** = **Chemical, biological and physical parameter calibration**

Figure 1 shows a representative result for an example time snapshot of bulk concentrations in the case study system. At the bottom, the individual current contributions from each reaction are represented for two different bio-electrode catalysis qualities (KsE values); the top figures represent the aggregated (observed) current values for both cases. Note that electrode potentials are unique for all reactions involved. As an example, in order to achieve the same current (30 A/m2) in the worse catalysis case (KsE = 0.05 V), the anode potential has to be placed much higher and the cathode potential much lower requiring more energy supply to make the microbial electrolysis cell process run.

TAKE-HOME INFORMATION

- The proposed model structure provides a platform for elucidating nontrivial interactions between physical, chemical and biological variables using data from **classical electrochemical experiments** which is critical for **commercialization of BES**.
- It can be used to perform **technical evaluations of BES applications** including **wastewater treatment**, **industrial chemical production(bioelectrosynthesis), water desalination and bioremediation** etc.

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REFERENCES

1.Rodriguez, J. and G. Premier, Towards a mathematical description of bioelectrochemical systems, in Bioelectrochemical Systems: From Extracellular Electron Transfer to Biotechnological Application, K. Rabaey, et al., Editors. 2010, IWA Publishing: London, UK.
2.Sharma, M., et al., Bioelectrocatalyzed reduction of acetic and butyric acids via direct electron transfer by a mixed culture of sulfate-reducers drives electrosynthesis of alcohols and acetone. Chem. Commun., 2013.
3. Picioreanu, C., et al., Model based evaluation of the effect of pH and electrode geometry on microbial fuel cell performance. Bioelectrochemistry, 2010. 78(1): p. 8-24.
4. Bard, A.J. and L.R. Faulkner, Electrochemical methods: Fundamentals and applications. Wiley:New York, 2001.
5. Zoski, C.G., Handbook of electrochemistry. Elsevier B.V: Amsterdam, The Netherlands. 2007