Progress in Computational Fluid Dynamics Simulation of a Microbial Fuel Cell

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Agenda

• Introduction
• About Microbial Fuel Cells
• Mathematical Model
• Validation and Verification
• Results of the Simulations
• Conclusion and Outlook
Introduction - 1

• ~ 80% of global wastewater is released untreated in environment (UN World Water Report 2017)
• High operating costs of wastewater treatment plants
• Transition from major energy consumers to energy neutrality or even net producers?

Expenses of industrial facilities
Survey Industrial WaterWorld Magazine, 2010
Introduction - 2

- Microbial Fuel Cells (MFCs) are one possible technology for sustainable treatment
- Especially promising for selected industrial wastewater (Bierbaum, 2014), where other waste-to-energy technologies are not viable
- One milestone towards upscaling MFC: functional bioanode
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• Electroactive bacteria generate electric current from organic substrates like acetate
• Model organism *Geobacter sulfurreducens* transfers electrons from substrate oxidation to electrode surface through a conductive biofilm matrix
Microbial Fuel Cells - 2

- Sum redox reaction of an MFC with electro active model organism *Geobacter sulfurreducens*:

\[
\text{acetate} + 2\text{O}_2 + \text{H}^+\rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O}
\]

- Splitting into half reactions allows energy harvest as electrons flow from low potential anode to high potential cathode

- For bioanode studies, a potentiostat fixes a defined potential at the anode (eliminates possible limitations by non-ideal cathode)

**bioanode:**
- oxidation of substrate
- electron release

\[
\text{acetate} + 2\text{H}_2\text{O} + \text{H}^+\rightarrow 2\text{CO}_2 + 8\text{e}^- + 8\text{H}^+
\]

**air cathode:**
- reduction of oxygen
- electron consumption

\[
2\text{O}_2 + 8\text{H}^+ + 8\text{e}^-\rightarrow 4\text{H}_2\text{O}
\]
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Mathematical Model - 1

- Balance equations - 1

Flow of water together with acetate $\Omega_{water}$

- Total mass balance equation
- Total momentum balance equation
- Species acetate mass balance equation

Biofilm $\Omega_{biofilm}$

- Species acetate mass balance equation
- Electric potential equation

Anode: Gold electrode $\Omega_{anode}$

- Sink for acetate
- Source for electrons
- Electrical current

Mass flow of acetate
Mathematical Model - 2

- **Balance equations - 2**

\[
\nabla \cdot (\rho_1 \mathbf{v}) = 0 \quad \rho_1 = \frac{1}{\frac{Y_{0,1}}{\rho_{0,1}} + \frac{Y_{1,1}}{\rho_{1,1}}}
\]

\[
\nabla \cdot (\rho_1 \mathbf{v} \otimes \mathbf{v}) = -\nabla p + \nabla \cdot \mathbf{T} \quad \mathbf{T} = \mu_1 \left[ (\nabla \otimes \mathbf{v}) + (\nabla \otimes \mathbf{v})^T - \frac{2}{3} \mathbf{I} \right] \quad \mathbf{I} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}
\]

\[
\nabla \cdot (\rho_1 \mathbf{v} Y_{0,1}) = \nabla \cdot (\rho_1 D_{0,1} \nabla Y_{0,1}) \quad Y_{1,1} = 1 - Y_{0,1}
\]

\[
\rho_1 \quad \text{Density of the water/acetate mixture} \\
Y_{0,1} \quad \text{Mass fraction of acetate in } \Omega_{\text{water}} \\
Y_{1,1} \quad \text{Mass fraction of water in } \Omega_{\text{water}} \\
\mu_1 \quad \text{Viscosity of the water/acetate mixture} \\
D_{0,1} \quad \text{Diffusion coefficient of acetate in water}
\]

\[
\mathbf{v} \quad \text{Velocity vector} \\
\mathbf{I} \quad \text{Identity matrix} \\
\rho_{0,1} \quad \text{Density of acetate in } \Omega_{\text{water}} \\
\rho_{1,1} \quad \text{Density of water in } \Omega_{\text{water}} \\
p \quad \text{Pressure}
\]
### Mathematical Model - 3

#### Balance equations - 3

- **$\rho_2$**: Density of the biomass/acetate mixture
- **$Y_{0,2}$**: Mass fraction of acetate in $\Omega_{biofilm}$
- **$Y_{1,2}$**: Mass fraction of biomass in $\Omega_{biofilm}$
- **$Y_{0,1/2\text{max}}$**: Half-max rate of biomass
- **$C$**: Data fitting constant
- **$\kappa_{bio}$**: Electrical conductivity of the biofilm
- **$F$**: Faradays constant
- **$R$**: Gas constant
- **$T_2$**: Absolut temperature of biofilm
- **$\phi$**: Electric potential
- **$\lambda$**: Acetate to electric current conversion

### Biofilm $\Omega_{biofilm}$

\[
0 = \nabla \cdot (\rho_2 D_{0,2} \nabla Y_{0,2}) - C \frac{Y_{0,2}}{Y_{0,1/2\text{max}} + Y_{0,2}} \frac{1}{1 + e^{-\frac{F}{RT_2} \phi}}
\]

\[
Y_{1,2} = 1 - Y_{0,2}
\]

### Anode: Gold electrode $\Omega_{anode}$

\[
0 = \nabla \cdot (\kappa_{bio} \nabla \phi) - \lambda C \frac{Y_{0,2}}{Y_{0,1/2\text{max}} + Y_{0,2}} \frac{1}{1 + e^{-\frac{F}{RT_2} \phi}}
\]

\[
\rho_2 = \frac{1}{\frac{Y_{0,2}}{\rho_{0,2}} + \frac{Y_{1,2}}{\rho_{1,2}}}
\]
Boundary condition on the biofilm

\[ Y_{0,1}^{cell} = Y_{0,1}^{wall} = Y_{0,2}^{wall} = Y_{0,2}^{cell} \]

\[ Y_{wall} = \frac{1}{\rho_2 D_{0,2}} \frac{1}{\Delta s_{water}} Y_{0,1}^{cell} + \frac{1}{\rho_1 D_{0,1}} \frac{1}{\Delta s_{biofilm}} Y_{0,2}^{cell} \]
Mathematical Model - 5

• **Boundary conditions**

**Flow of water together with acetate** $\Omega_{\text{water}}$

- $v = 0$
- $\frac{\partial Y_{0,1}}{\partial n} = 0$
- $v: 21.0 \times 10^{-6} \text{ m/s}, \text{normal to and constant over the surface}$
- $Y_{0,1}: 0.001174867, \text{constant over the surface}$

**Biofilm** $\Omega_{\text{biofilm}}$

- $v = 0$
- $\Gamma_{\text{surface}}$
- $\frac{\partial Y_{0,2}}{\partial n} = 0$
- $\phi_{\text{anode}}$
- $\Gamma_{\text{anode}}$

**Anode: Gold electrode** $\Omega_{\text{anode}}$

- $\Gamma_{\text{anode}}$
- $\phi_{\text{anode}}$
- $\Gamma_{\text{anode}}$

$p: \text{constant over the surface}$
Mathematical Model - 6

- All electrons produced in the biofilm must pass through the anode

Flow of water together with acetate $\Omega_{\text{water}}$

Biofilm $\Omega_{\text{biofilm}}$

\[
J_{\text{anode}} = - \int_{\Omega_{\text{biofilm}}} \lambda C \frac{Y_{0,2}}{Y_{0,1/2\text{max}} + Y_{0,2}} \frac{1}{1 + e^{-\frac{F}{RT}\phi}} dV
\]

Anode: Gold electrode $\Omega_{\text{anode}}$

Electrical current
## Mathematical Model - 7

### Material properties at 30 °C

<table>
<thead>
<tr>
<th>Component</th>
<th>Density $\rho$ in $kg/m^3$</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>$995.65$</td>
<td>Karat et al. (2008)</td>
</tr>
<tr>
<td>Acetate</td>
<td>$995.65$</td>
<td>VDI-Wärmeatlas (2002)</td>
</tr>
<tr>
<td>Water with acetate</td>
<td>$797.35 \cdot 10^{-6}$</td>
<td>Karat et al. (2008)</td>
</tr>
<tr>
<td>Diffusion coefficient</td>
<td>$1.30648 \cdot 10^{-9}$</td>
<td>Compton and Hancock (1999)</td>
</tr>
</tbody>
</table>

### Flow of water together with acetate

\[ \Omega_{water} \]

\[
\begin{align*}
\text{Water: } \rho_{1,1} & = 995.65 \frac{kg}{m^3} \\
\text{Acetate: } \rho_{0,1} & = 995.65 \frac{kg}{m^3} \\
\mu_1 & = 797.35 \cdot 10^{-6} \frac{kg}{ms} \\
D_{0,1} & = 1.30648 \cdot 10^{-9} \frac{m^2}{s}
\end{align*}
\]

### Biofilm

\[ \Omega_{biofilm} \]

\[
\begin{align*}
\text{Biofilm: } \rho_{1,2} & = 1,010.00 \frac{kg}{m^3} \\
\text{Acetate: } \rho_{0,2} & = 995.65 \frac{kg}{m^3}
\end{align*}
\]

\[
\begin{align*}
\text{Zhang and Bishop (1994)}
\end{align*}
\]

\[
\begin{align*}
\text{Karat et al. (2008)}
\end{align*}
\]

\[
\begin{align*}
\text{VDI-Wärmeatlas (2002)}
\end{align*}
\]

### Anode: Gold electrode

\[ \Omega_{anode} \]

\[
\begin{align*}
\text{Anode: Gold electrode}
\end{align*}
\]

\[
\begin{align*}
\text{Karat et al. (2008)}
\end{align*}
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\begin{align*}
\text{VDI-Wärmeatlas (2002)}
\end{align*}
\]
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Validation and Verification - 1

- About validation and verification (parameter fitting)
Validation and Verification - 2

- Geometrical model of the anode compartment from Choi and Chae, 2012

Inlet: $21.0 \times 10^{-6}$ m/s, $Y_{0,1} = 0.001174867$
Validation and Verification - 3

- Numerical mesh: Result of a mesh convergence study
Validation and Verification - 4

- Data ranges for the parameter fitting simulations

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Value and Unit</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C$</td>
<td>$8.7195 \times 10^{-6} - 8.7195 \times 10^{-2}$ kgAcetate/ (m$^3$s)</td>
<td>Assumed</td>
</tr>
<tr>
<td>$D_{0,2}$</td>
<td>$0.05 \ D_{0,1} - 0.5 \ D_{0,1}$</td>
<td>Stewart (2003)</td>
</tr>
<tr>
<td>$Y_{0,1/2max}$</td>
<td>$1.41 \times 10^{-4} - 7.67 \times 10^{-4}$ kgAcetate/kgWater</td>
<td>Liu et al. (2005), Min and Logan (2004)</td>
</tr>
<tr>
<td>$\kappa_{bio}$</td>
<td>$7.5 \times 10^{-3} - 5.0 \times 10^{-1}$ S/m</td>
<td>Malvankar et al. (2011)</td>
</tr>
<tr>
<td>$\phi_{anode}$</td>
<td>$0.0 - 0.7 \ V$</td>
<td>Choi and Chae (2012), (Marcus et al., 2007)</td>
</tr>
</tbody>
</table>

- Target Value: Electrical current of $80 \mu A$
Results of the parameter fitting:

- Strong dependency on $C$
- Weak dependency on $Y_{0,1/2\text{max}}$
- Nearly no dependency on the other values

<table>
<thead>
<tr>
<th>Symbol</th>
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<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C$</td>
<td>$7.5 \times 10^{-3}$</td>
<td>kgAcetate/(m$^3$s)</td>
</tr>
<tr>
<td>$D_{0,2}$</td>
<td>$1.16813 \times 10^{-10}$</td>
<td>m$^2$/s</td>
</tr>
<tr>
<td>$Y_{0,1/2\text{max}}$</td>
<td>$7.23889 \times 10^{-4}$</td>
<td>kgAcetate/kgWater</td>
</tr>
<tr>
<td>$\kappa_{\text{bio}}$</td>
<td>$7.11146 \times 10^{-2}$</td>
<td>S/m</td>
</tr>
<tr>
<td>$\phi_{\text{anode}}$</td>
<td>$0.370417$</td>
<td>V</td>
</tr>
</tbody>
</table>
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Results - 1

- Pathlines of flow (coloured by velocity magnitude)
Results - 2

- Mass fraction of acetate on biofilm and in biofilm
Results - 3

- XY-plot of the electrical potential on a line through the biofilm: approx. 10 V/m
- Measurement Babauta et al. (2012): approx. factor 4 - 5 larger for a comparable current
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• Results of the Simulations and Discussion
• Conclusion and Outlook
A mathematical model of a microliter-sized MFC was developed.

The model was validated and verified against experimental data of Choi and Chae (2012) (parameter fitting).

The model allows an in-depth analysis of the MFC.

The CFD simulations of the fitted model show a very regular flow behaviour.

The slope of the potential along the biofilm height is one order of magnitude smaller than an experimental value.
What comes next: Evaluation of the performance of textile fibre carbon anode configurations

Mass fraction of acetate on biofilm
References


