Modeling the effect of discrete distributions of Platinum particles in the PEM fuel cell catalyst layer

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Introduction

- The catalyst layer (CL) can be seen as the heart of a fuel cell
- Several macro and micro level modeling approaches for CL have been reported in the literature

**The agglomerate approach (the most comprehensive macro level description of CL)**

- Macro level models mainly consider the whole CL structure with some simplifications and assumptions
Focusing on the micro structure may provide a better understanding of CL.

We compare two models to describe carbon-supported Pt particles (C|Pt).

The main goal is to account for discrete Pt particles in micro level CL models.
Reaction-diffusion phenomena is considered solely based on the geometric parameters of the single catalyst-particle.

- **Dissolution (Henry’s law):** \( C_{O_2,s} = \frac{P_{O_2}}{H} \)
- **Diffusion:** \( \nabla \cdot (D \nabla C_{O_2}) = 0 \)
- **Reaction at active boundaries:** \( \dot{N} = \frac{dC_{O_2}}{dn} = \frac{i}{4F} \)
- **The generated current density (Butler–Volmer):**
  \[
i = i_0 \left[ \frac{C_{O_2}}{C_{O_2,s}} \exp \left( -\frac{\alpha_c F}{RT} \eta \right) - \exp \left( \frac{(1 - \alpha_c) F}{RT} \eta \right) \right]
  \]

- The diffusion equation coupled with a nonlinear flux term at the active boundaries is solved with COMSOL 4.3 by using a stationary parametric solver.
Model Description

- Reaction-diffusion phenomena is considered solely based on the geometric parameters of the single catalyst particle.
- Dissolution (Henry's law):
- Diffusion: \( \nabla \cdot \mathbf{D} \nabla c = 0 \)
- Reaction at active boundaries: 
  \[ i = i_0 \left( \frac{c_{O_2}}{c_{O_2,s}} \right) \exp \left( -\frac{E_a}{RT} \right) \]
- The generated current density (Butler–Volmer):

Note that a logarithmic transformation is applied to the governing equation in order to ensure stability of the diffusion equation and to prevent negative concentration values.

### Table 1. Parameters used for simulating the base case

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>353.15[K]</td>
</tr>
<tr>
<td>Oxygen pressure ( P_{O_2} )</td>
<td>1.5 [atm]</td>
</tr>
<tr>
<td>Henry’s constant ( H )</td>
<td>0.3125 [atmm^3/mol]</td>
</tr>
<tr>
<td>Pt radius ( r_{Pt} )</td>
<td>2 [nm]</td>
</tr>
<tr>
<td>C radius ( r_c )</td>
<td>20 [nm]</td>
</tr>
<tr>
<td>Ionomer film thickness ( \delta )</td>
<td>12 [nm]</td>
</tr>
<tr>
<td>Charge transfer constant ( \alpha_c )</td>
<td>0.5</td>
</tr>
<tr>
<td>Exchange current density ( i_0 )</td>
<td>6e-8[A/cm^2]</td>
</tr>
</tbody>
</table>
Results

- Fuel cell performance comparison: uniform coverage vs. discrete particle approach

- Diffusion loss for the uniform thin Pt layer arises solely from ionomer film

- Additional diffusion loss is imposed by Pt particle interactions
Different responses are obtained for the variation in Pt loading:

For uniform Pt layer case, limiting flux is only dependent on ionomer film

\[ N_{O_2} = D \frac{C_{O_2,s} - C_{O_2,a}}{\delta} \]

Discrete particle approach can capture diffusion losses due to particle interactions as the Pt loading is varied
Effect of catalyst particle size with constant weight and volume fraction:

- Performance improves as catalyst particles become smaller, which is consistent with experiments.
Pt loading can also be varied by changing the number of particles

Effect of number of particles on reactant concentration distribution:

- Reactant consumption increases as the number of particles increases

Concentration contours of reactant in mol/m³ for $\eta = 0.4$ V

- $N_{Pt} = 20$
- $N_{Pt} = 44$
- $N_{Pt} = 104$
Effect of number of Pt particles on polarization curves:

Due to higher reactant consumption, performances improves with increasing number of Pt particles.
Effect of Pt particle distribution: uniform vs. random particle arrangement

Closely clustered particles in the random distribution end up with large dead zones.

This results in local minimum and maximum concentration values.

Concentration contours in mol/m$^3$ for $\eta = 0.4$ V
Effect of Pt particle distribution on performance curves:

The large dead zones observed in the random distribution result in lower overall performance than the uniform case.
Effect of ionomer film thickness on the discrete particle approach:

- Thicker ionomer film leads to greater reactant depletion on the C-support surface due to the film’s higher diffusion resistance.

Concentration contours of reactant in mol/m³ for $\eta = 0.4$ V, $r_c = 20$ nm, $r_{Pt} = 2$ nm.

- $\delta = 6$ nm
- $\delta = 12$ nm
- $\delta = 24$ nm
The effect of ionomer film thickness on the performance curves:

Thicker ionomer film results in an earlier entry into the diffusion-limited region.
Conclusion

The spherical C|Pt particle was considered in two forms:

- Particle interactions affect diffusion losses
- Parametric study with the discrete particle approach showed that
  - Smaller catalyst particle resulted in better performance
  - Uniform distribution of Pt provides better performance
  - Thicker ionomer film causes increased diffusion losses
Acknowledgements

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ANY QUESTIONS