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

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U.S. DEPARTMENT OF TRANSPORTATION
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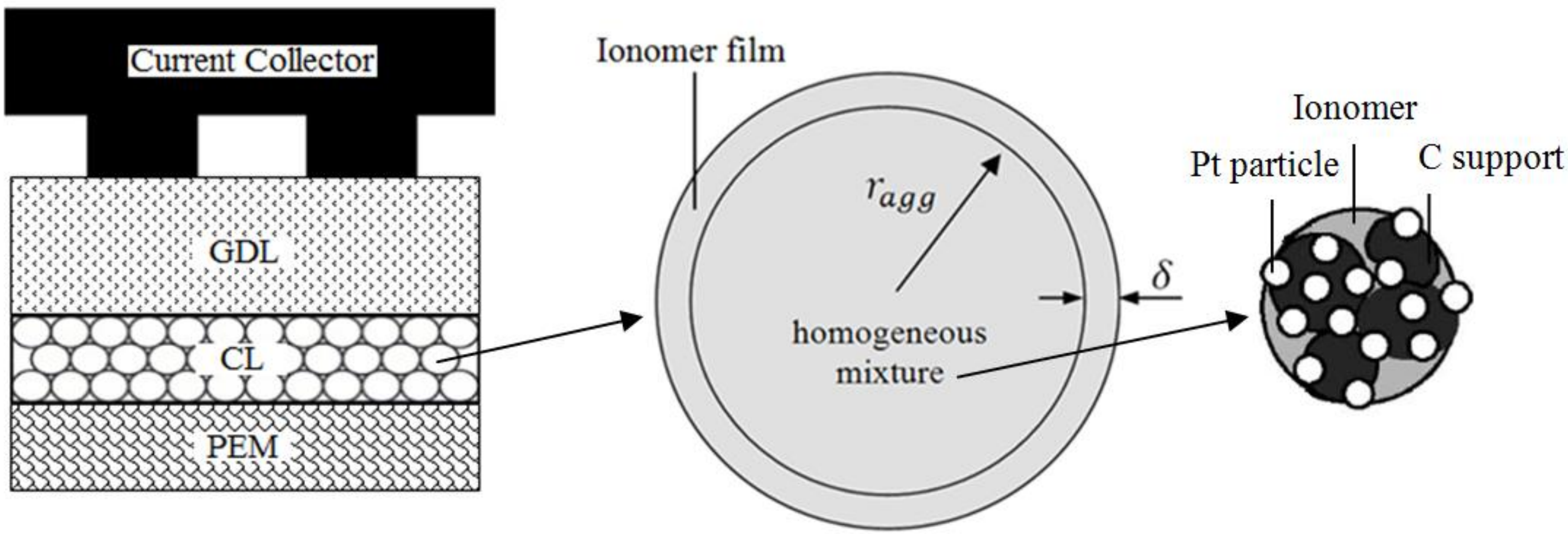
Introduction

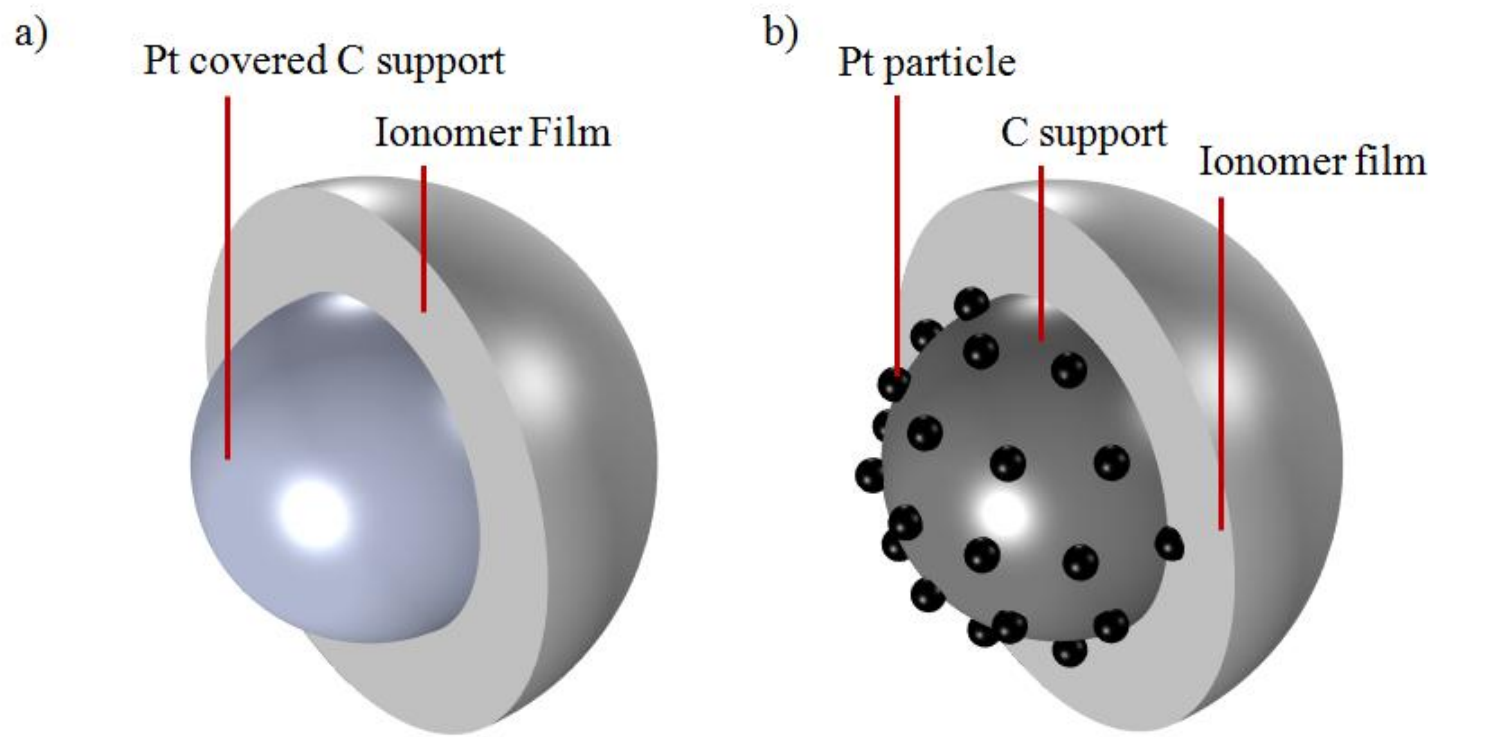
- The catalyst layer (CL) can be seen as the heart of a fuel cell
- Several macro and micro level modeling approaches for CL have been reported in the literature



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)



Carbon support covered with a thin uniform Pt layer

Pt particles modeled discretely on carbon support.

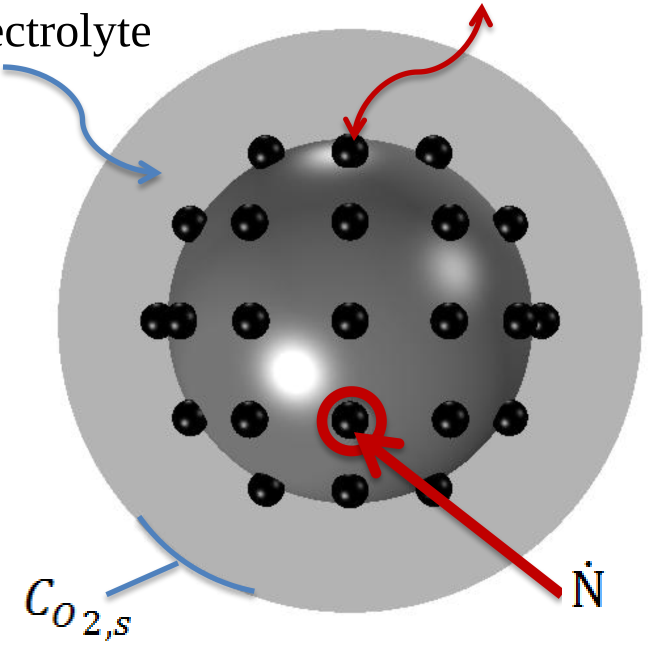
- The main goal is to account for discrete Pt particles in micro level CL models

Model Description

- 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: $\nabla.\left(D\nabla C_{O_2}\right) = 0$
- Reaction at active boundaries: $\dot{N} = \frac{dC_{O_2}}{d\vec{n}} = \frac{i}{4F}$
- 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

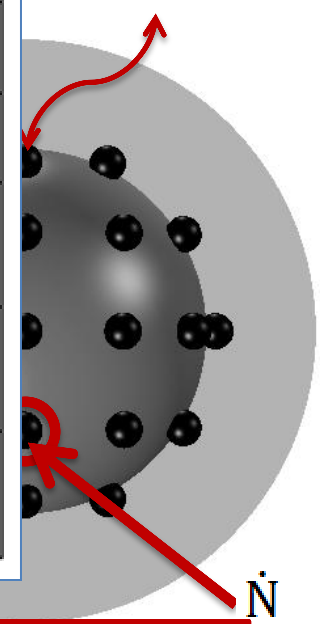
- Reaction-diffu ... netric parameters of

Table 1. Parameters used for simulating the base case

Temperature	T	353.15[K]
Oxygen pressure	P_{O_2}	1.5 [atm]
Henry's constant	H	0.3125 [atmm³/mol]
Pt radius	r_{Pt}	2 [nm]
C radius	r_C	20 [nm]
Ionomer film thickness	δ	12 [nm]
Charge transfer constant	α_c	0.5
Exchange current density	i_0	6e-8[A/cm²]

- Dissolution (H
- Diffusion: ∇
- Reaction at ac
- The generated

$$i = i_0 \left[\frac{C_{O_2}}{C_{O_{2,s}}} \exp \right.$$

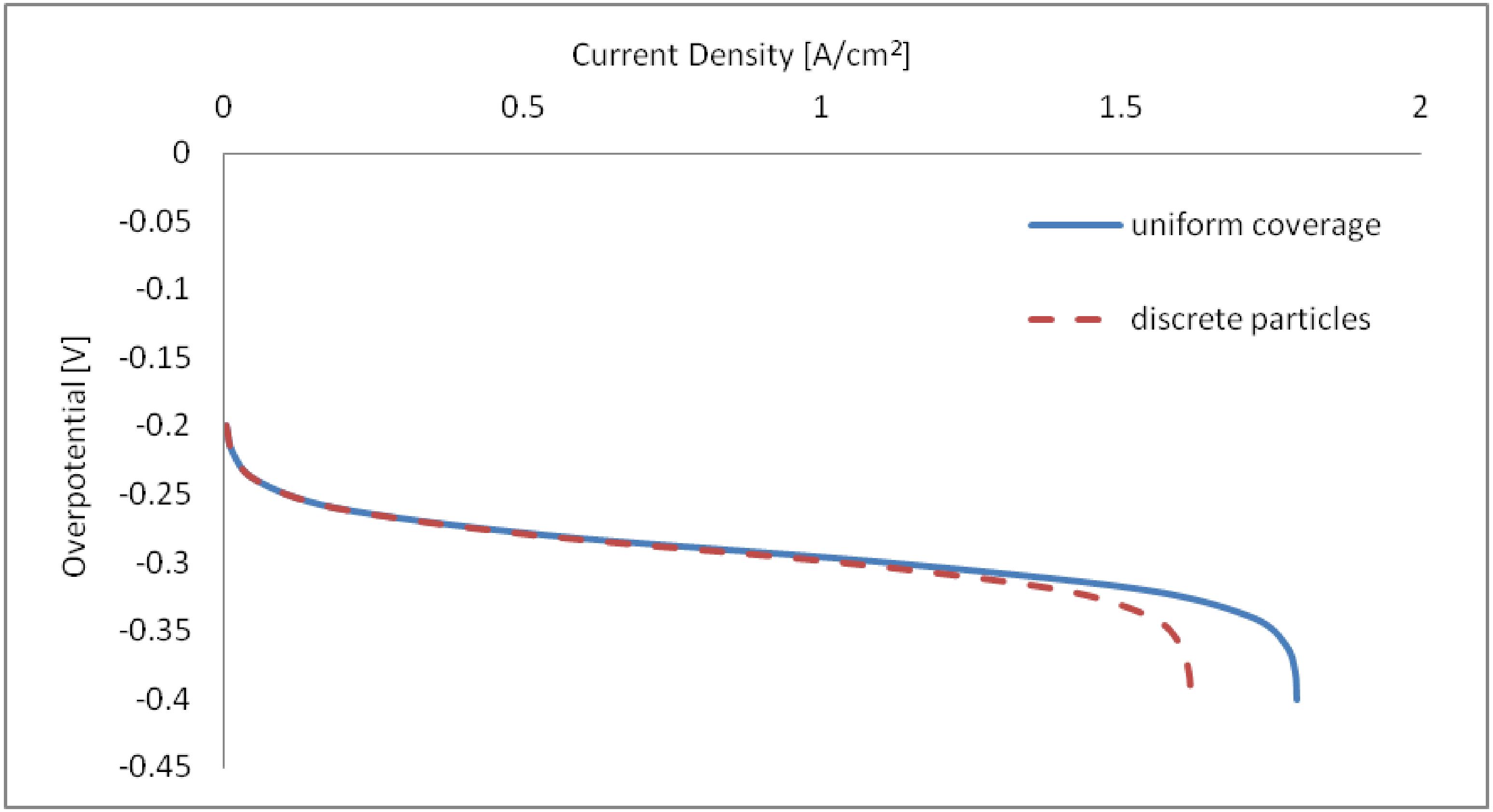


- The ... es is solv

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

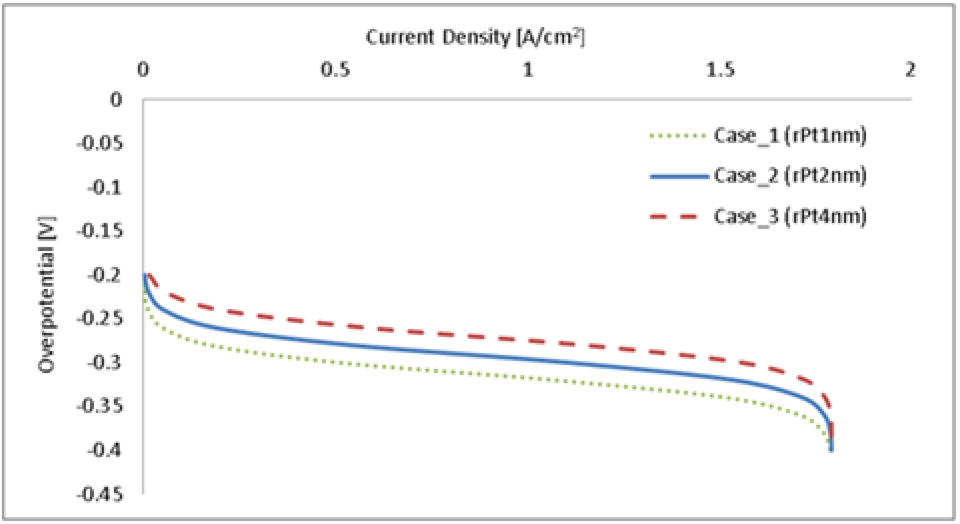
Results

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

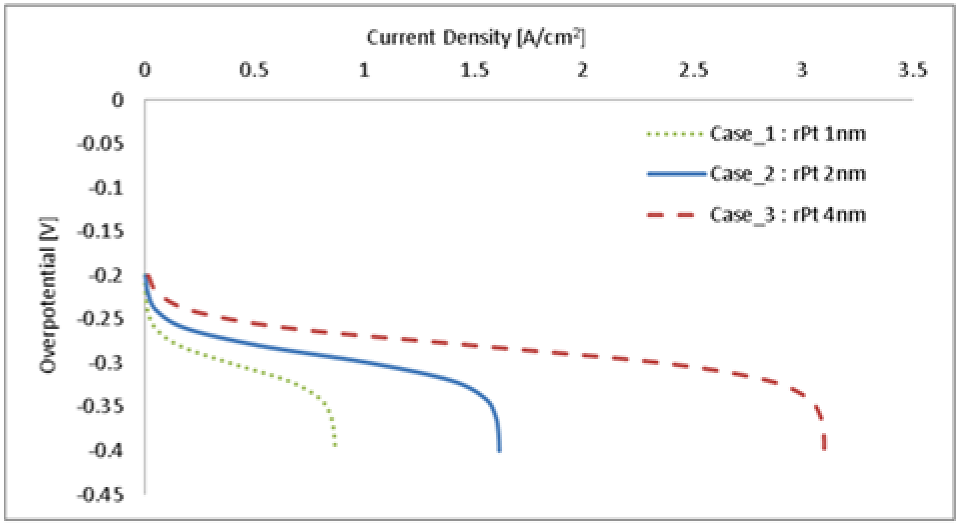


- Diffusion loss for the uniform thin Pt layer arises solely from ionomer film
- Additional diffusion loss is imposed by Pt particle interactions

- Different responses are obtained for the variation in Pt loading:



Uniform Pt layer approach



Discrete Pt particle approach

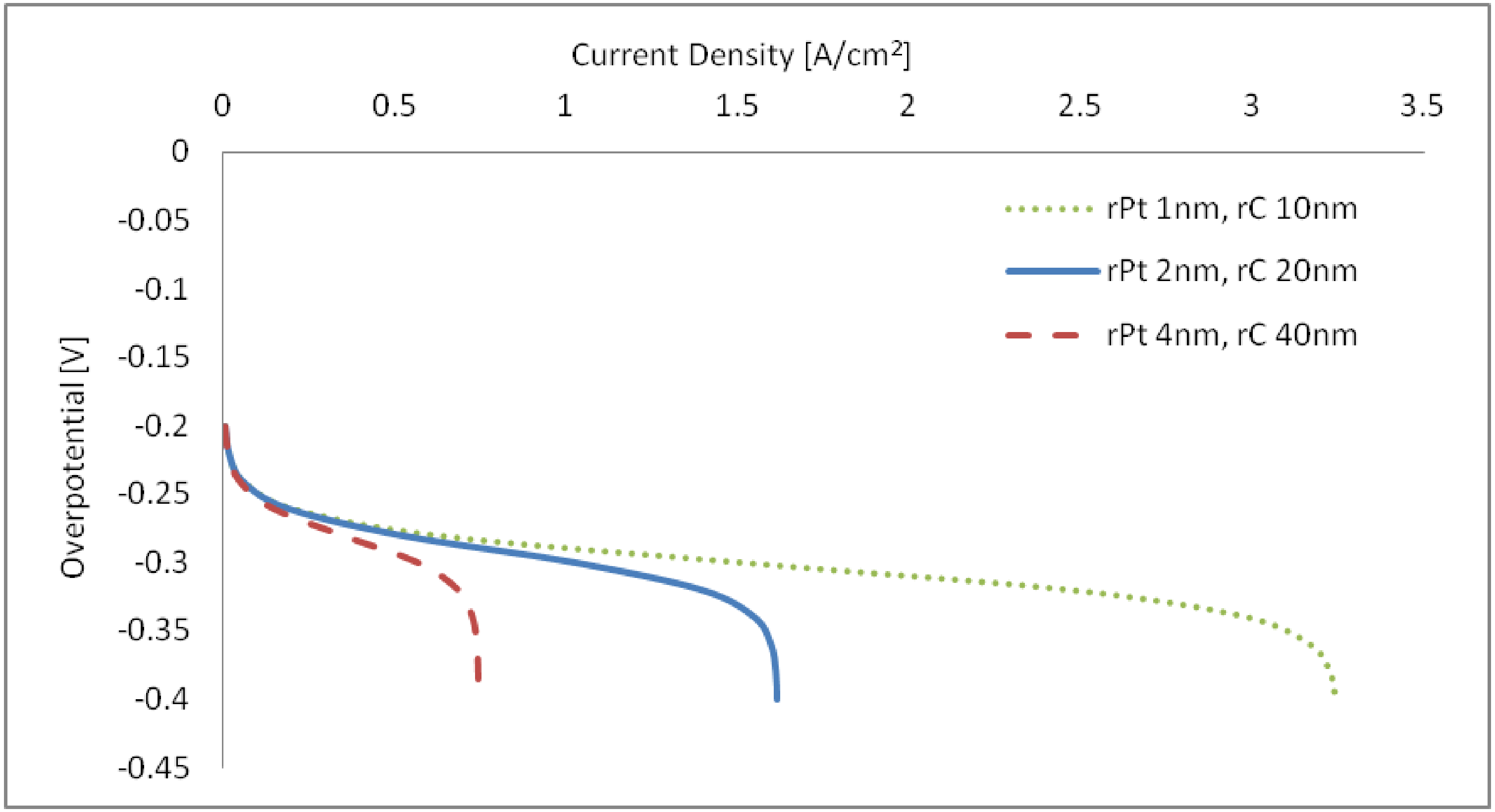
- For uniform Pt layer case, limiting flux is only dependent on ionomer film

Fick's law: $$N_{O_2} = D\frac{C_{O_{2,s}} - C_{O_{2,a}}}{\delta}$$

- Discrete particle approach can capture diffusion losses due to particle interactions as the Pt loading is varied

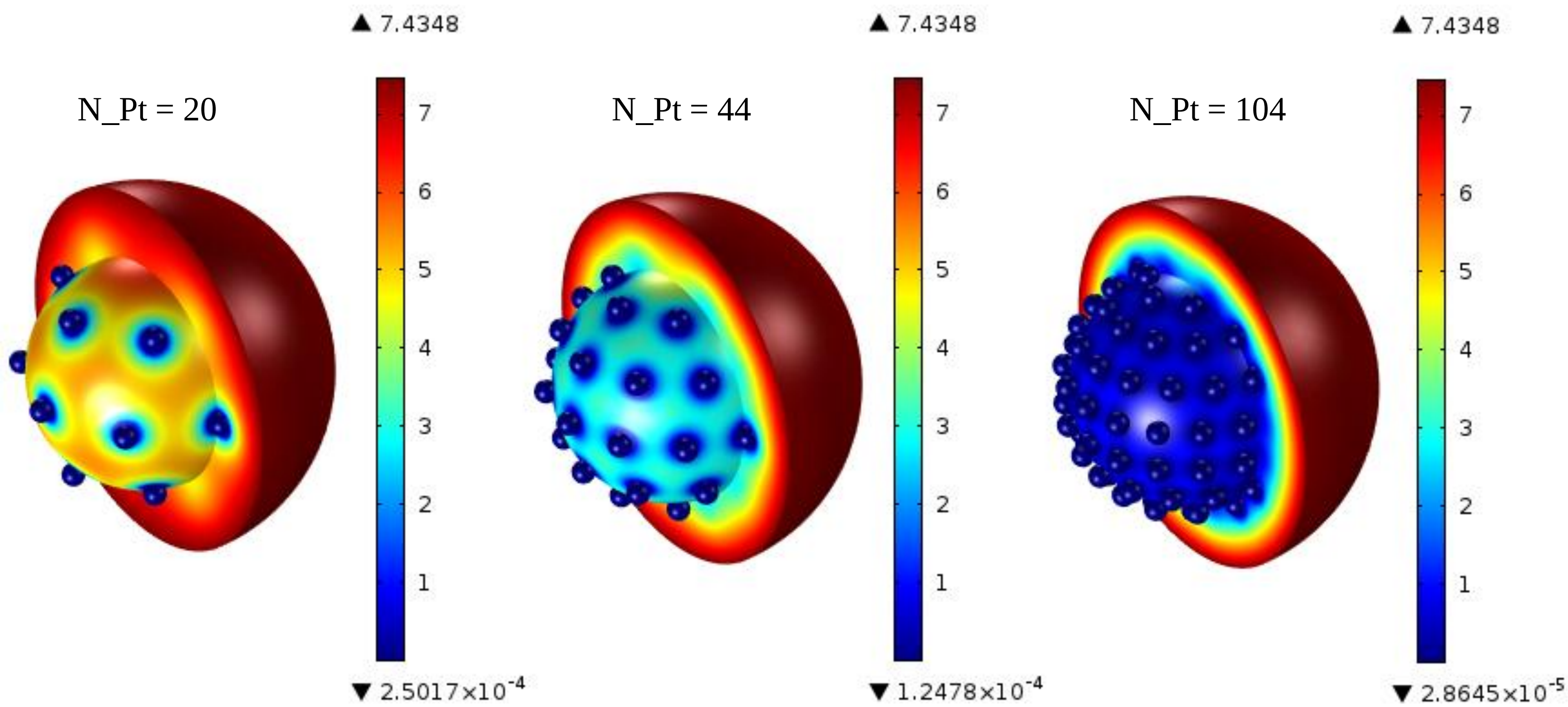
Parametric Study for Discrete Particle Approach

- Effect of catalyst particle size with constant weight and volume fraction:



- Performance improves as catalyst particles become smaller, which is consistent with experiments

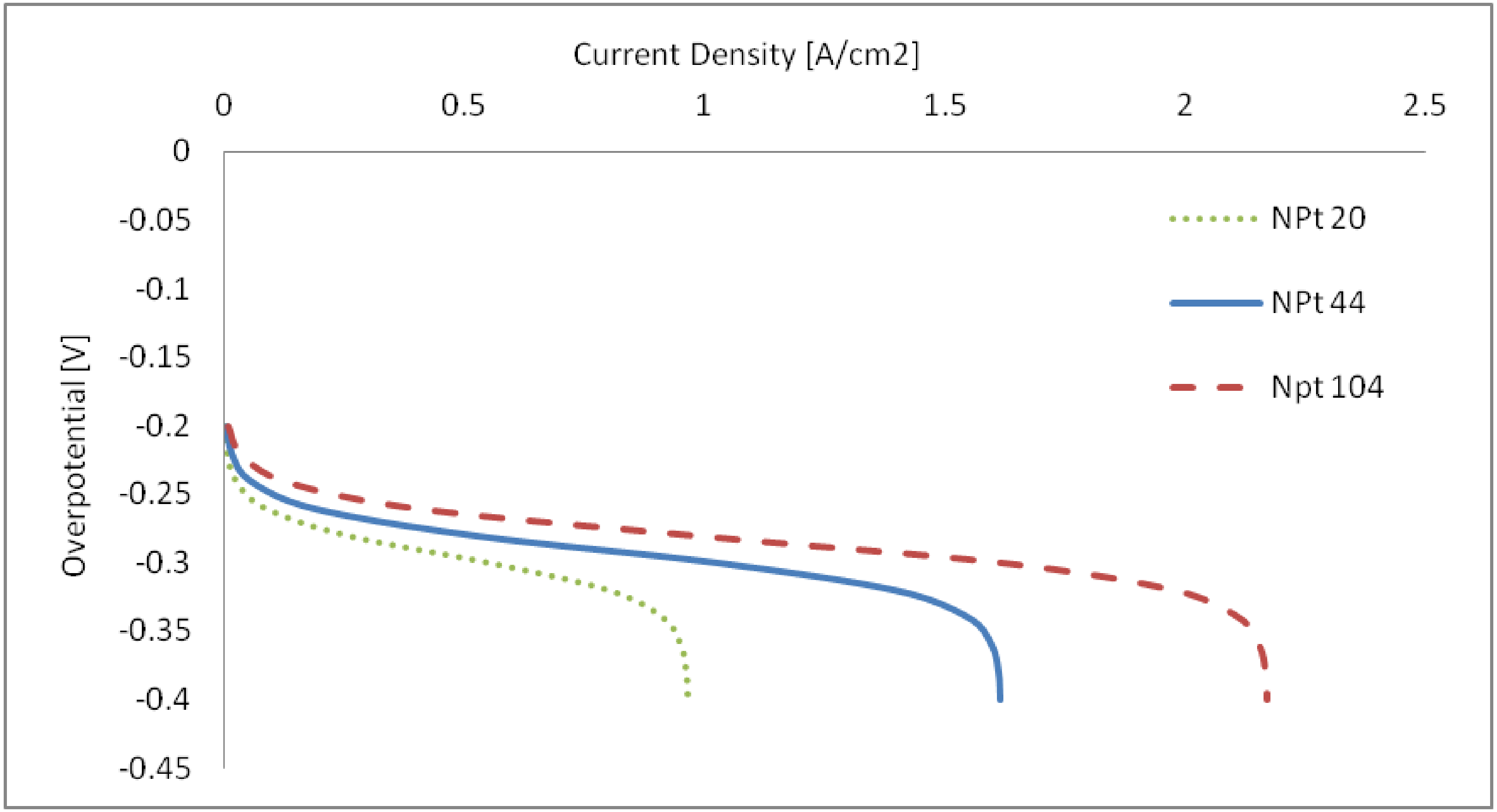
- Pt loading can also be varied by changing the number of particles
- Effect of number of particles on reactant concentration distribution:



Concentration contours of reactant in mol/m^3 for $\eta = 0.4$ V

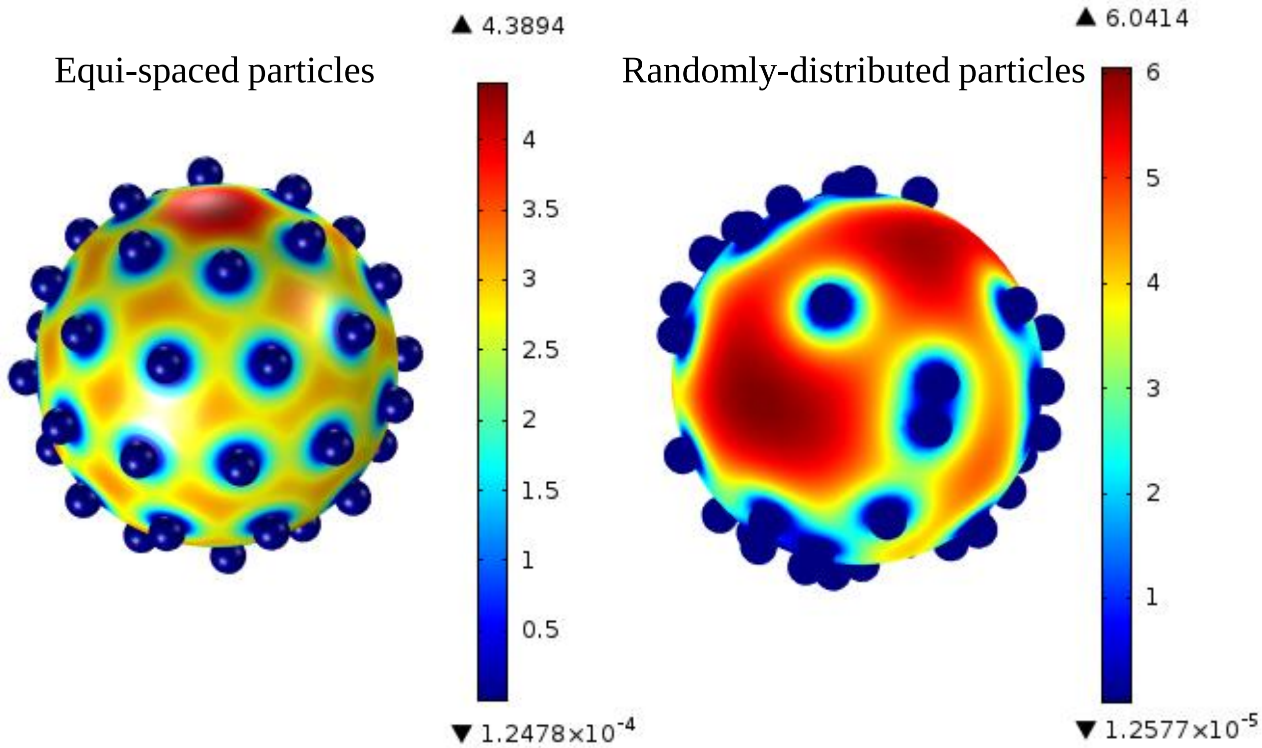
- Reactant consumption increases as the number of particles increases

- Effect of number of Pt particles on polarization curves:



- Due to higher reactant consumption, performances improves with increasing number of Pt particles

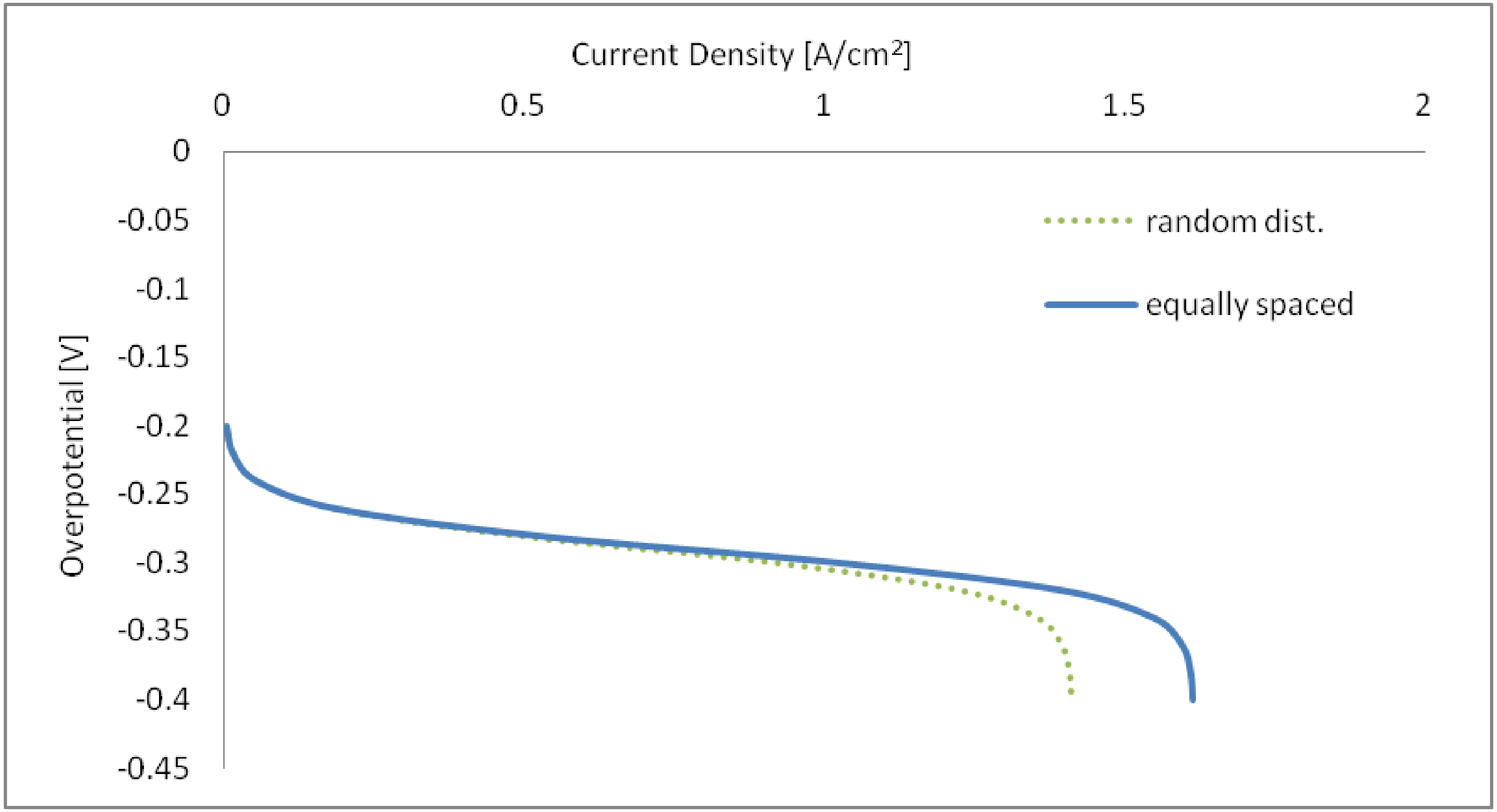
- Effect of Pt particle distribution: uniform vs. random particle arrangement



Concentration contours in mol/m^3 for $\eta = 0.4$ V

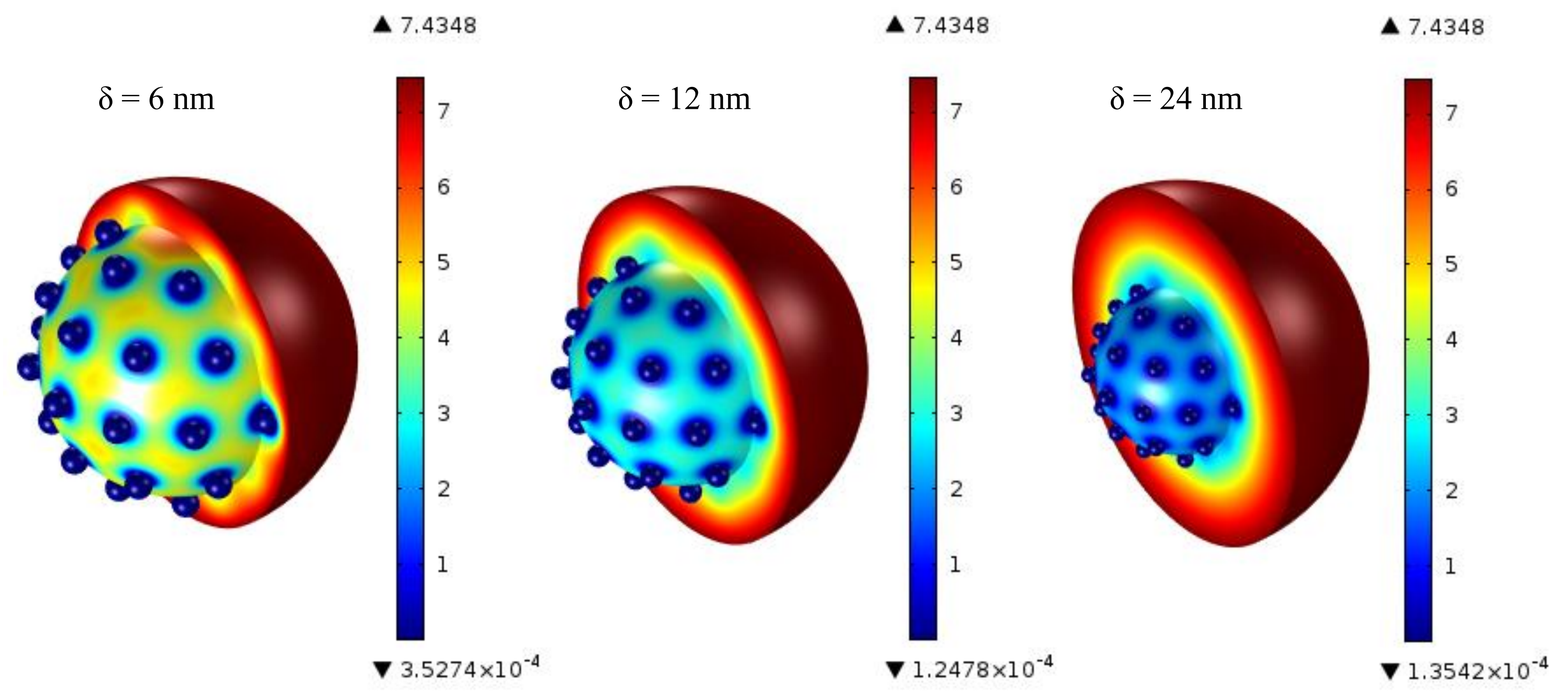
- Closely clustered particles in the random distribution end up with large dead zones
- This results in local minimum and maximum concentration values

- 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

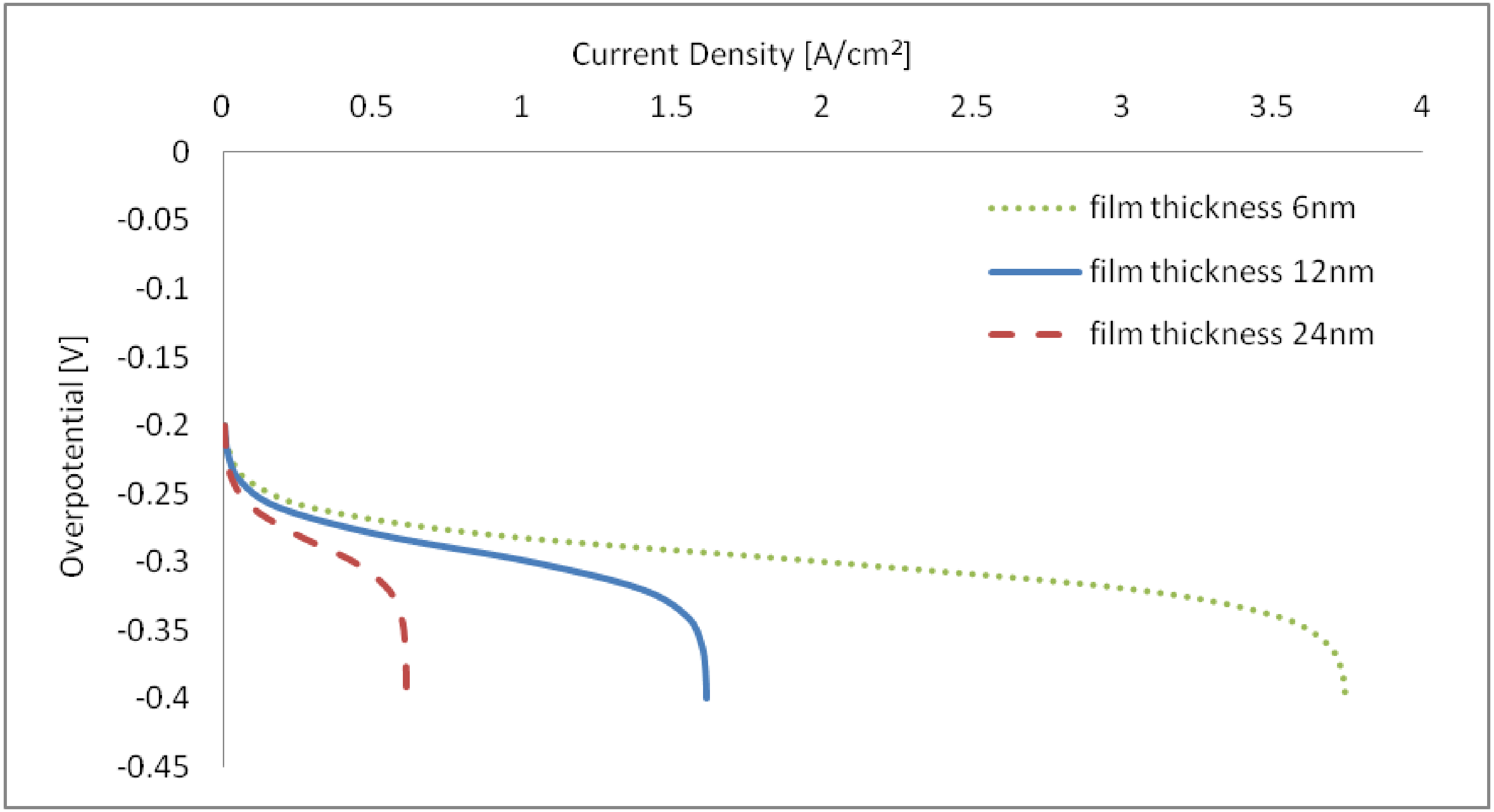
- Effect of ionomer film thickness on the discrete particle approach:



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

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

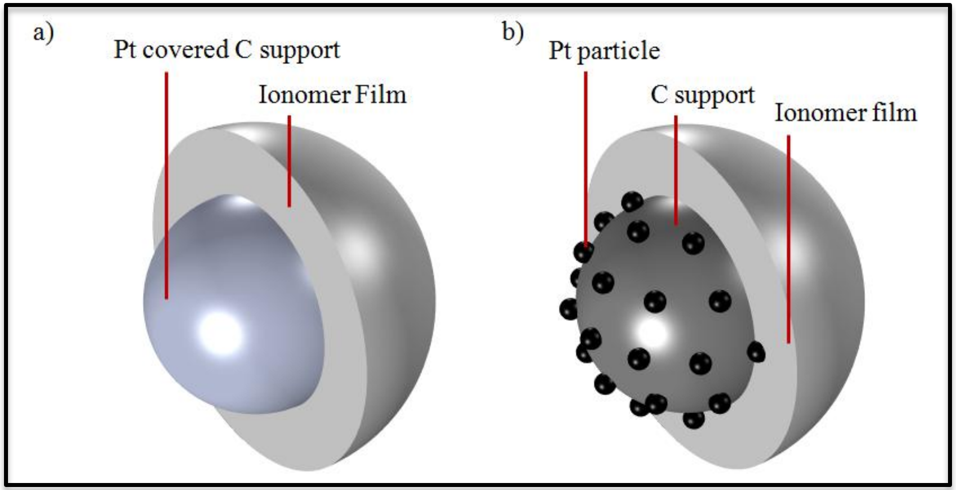
- The effect of ionomer film thickness on the performance curves:



- 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

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ANY QUESTIONS