

# Multi-scale Modeling of Hydrogen Transport in a Porous Fuel Cell Anode

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## Hydrogen Transport Resistances

Gas transport in proton exchange membrane fuel cells encounters multiple length-scales and phases:

- 1) electrode pores at the length scale of electrode thickness (micrometer), and
- 2) diffusion into the catalyst particle through an ionomer film at the length scale of agglomerate radius (nanometer).

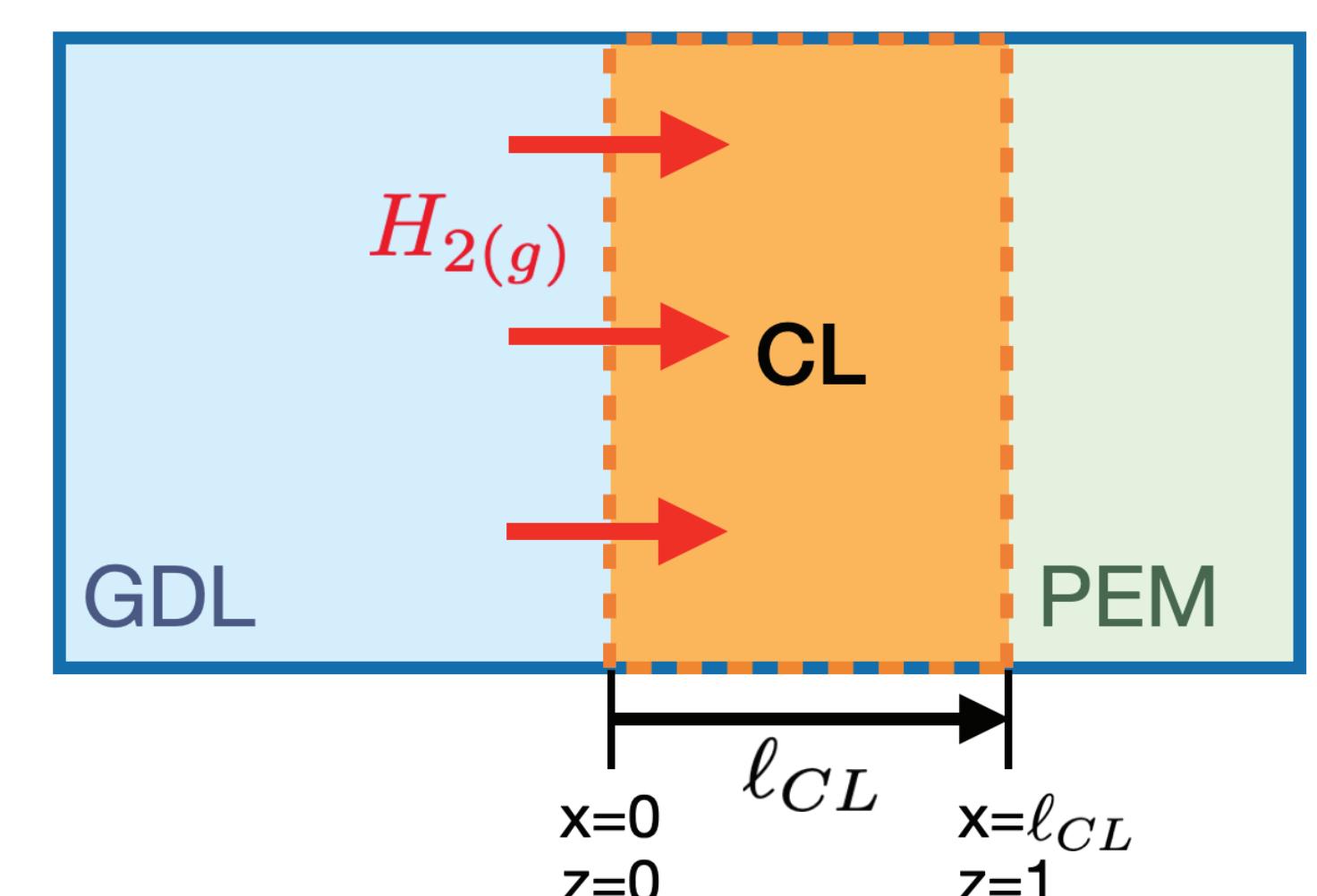


Figure 1. Diagram of 1-D micrometer-scale model of H<sub>2</sub> transport from the gas diffusion layer (GDL) through the porous electrode catalyst layer (CL), and onto the proton exchange membrane (PEM).

Herein, we present an analytical model for of H<sub>2</sub> transport through porous anode catalyst layer (CL):

- **multi-scale:** 1+1D (along electrode thickness and catalyst particle radius)
- **multi-phase:** porous carbon agglomerate with Pt particles; ionomer film
- **purely analytical:** derived from spherical diffusion & Butler-Volmer kinetics

## Multi-Scale Model: Derivation

### I. Agglomerate

$$\frac{1}{z^2(R_a + \delta_f)} \frac{\partial}{\partial z} \left( \frac{z^2 D_{eff}}{R_a + \delta_f} \frac{\partial c_{H_2,agg}}{\partial z} \right) + r_{H_2} = 0$$

$$BC 1: \frac{\partial c_{H_2,agg}}{\partial z} \Big|_{z=0} = 0$$

$$BC 2: D_{eff} \frac{\partial c_{H_2,agg}}{\partial z} \Big|_{z=\frac{R_a}{R_a + \delta_f}} = 0$$

### II. Ionomer film

$$\frac{1}{z^2(R_a + \delta_f)} \frac{\partial}{\partial z} \left( \frac{z^2 D_{eff}}{R_a + \delta_f} \frac{\partial c_{H_2,film}}{\partial z} \right) = 0$$

$$BC 1: c_{H_2,film} \Big|_{z=1} = S_{bulk \rightarrow film} c_{H_2,micrometer}$$

$$BC 2: D_{eff} \frac{\partial c_{H_2,agg}}{\partial z} \Big|_{z=\frac{R_a}{R_a + \delta_f}} = D_{film} \frac{\partial c_{H_2,film}}{\partial z} \Big|_{z=\frac{R_a}{R_a + \delta_f}}$$

$$BC 3: c_{H_2,agg} \Big|_{z=\frac{R_a}{R_a + \delta_f}} = S_{film \rightarrow agg} c_{H_2,film} \Big|_{z=\frac{R_a}{R_a + \delta_f}}$$

### III. Electrode thickness

$$D_{bulk} \frac{\partial^2 c_{H_2}}{\partial x^2} + r_{H_2} = 0$$

$$BC 1: c_{H_2}(x=0) = c_{feed}$$

$$BC 2: \frac{\partial c_{H_2}}{\partial x} \Big|_{x=L} = 0$$

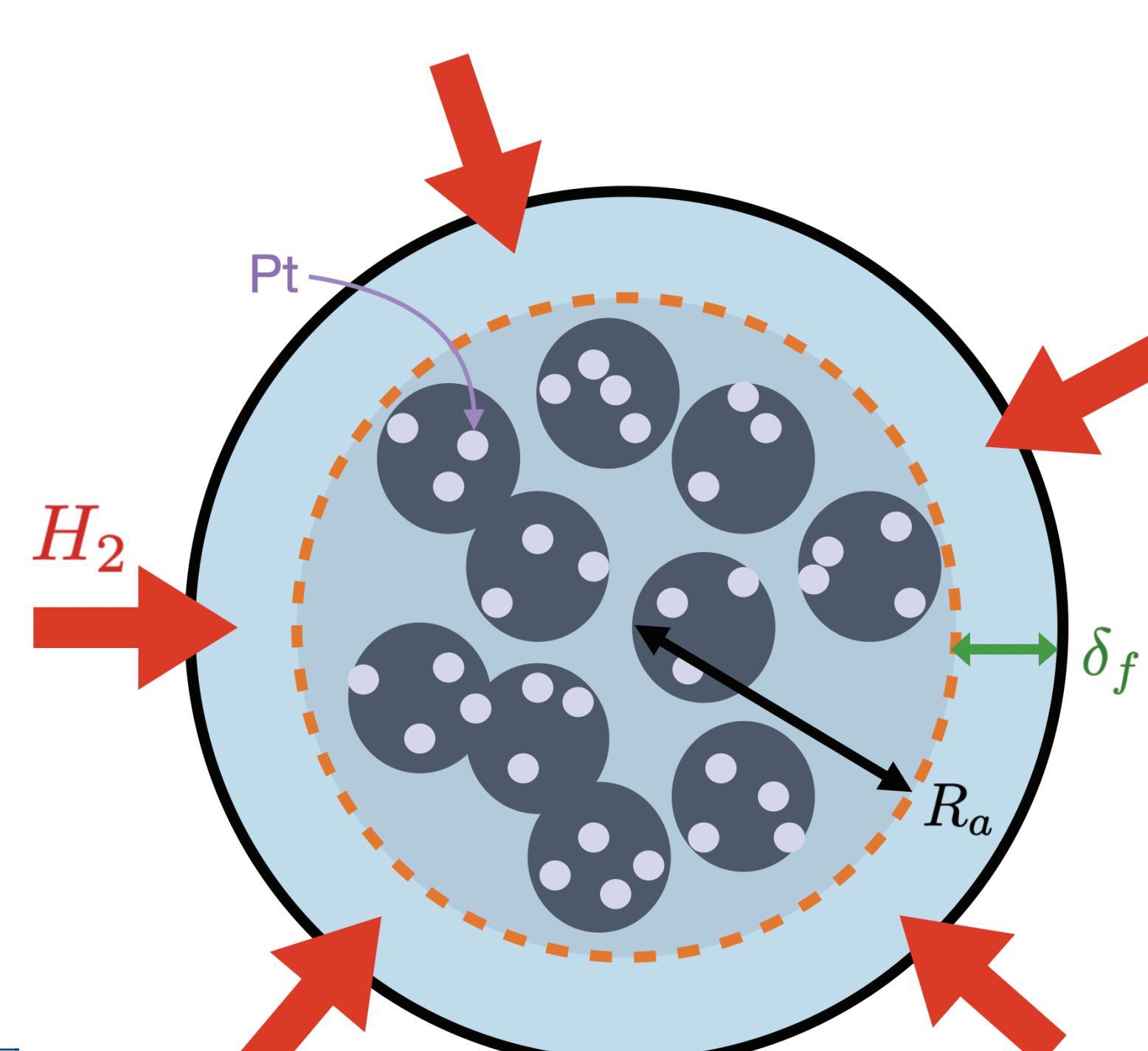


Figure 2. Diagram of radial H<sub>2</sub> transport into the catalyst particle through the ionomer film layer ( $\delta_f$ ) and into the agglomerate ( $R_a$ ).

## Derived analytical expressions

$$c_{H_2,agg} = \frac{c_{CL} S_{film \rightarrow agg} S_{CL \rightarrow film}}{\frac{R_a + \delta_f}{R_a} \frac{1}{\gamma} \frac{D_{film}}{D_{eff}} \sinh \left( \frac{\kappa R_a}{R_a + \delta_f} \right) + S_{film \rightarrow agg} \left( \frac{\delta_f}{R_a} \right)} \frac{1}{\gamma} \frac{D_{film}}{D_{eff}} \sinh(\kappa z) \frac{1}{z}$$

$$c_{H_2,film} = c_{CL} S_{CL \rightarrow film} + \frac{c_{CL} S_{film \rightarrow agg} S_{CL \rightarrow film}}{\frac{R_a + \delta_f}{R_a} \frac{1}{\gamma} \frac{D_{film}}{D_{eff}} \sinh \left( \frac{\kappa R_a}{R_a + \delta_f} \right) + S_{film \rightarrow agg} \left( \frac{\delta_f}{R_a} \right)} \left( 1 - \frac{1}{z} \right)$$

$$c_{H_2,micrometer} = c_{feed} \left( \cosh(\sqrt{\nu}x) - \tanh(\sqrt{\nu}L) \sinh(\sqrt{\nu}x) \right)$$

## Effectiveness Factor

Effectiveness factor ( $E_R$ ) is calculated as the ratio of real versus ideal flux in the agglomerate radius.

$$E_R = \frac{W_{AR}}{W_{AR,0}} = \frac{\text{actual rxn rate in catalyst particle}}{\text{rxn rate using surface concentration}}$$

$$= \frac{D_{film} \frac{S_{film \rightarrow agg} S_{CL \rightarrow film}}{\frac{R_a + \delta_f}{R_a} \frac{1}{\gamma} \frac{D_{film}}{D_{eff}} \sinh \left( \frac{\kappa R_a}{R_a + \delta_f} \right) + S_{film \rightarrow agg} \left( \frac{\delta_f}{R_a} \right)}}{\frac{1}{3} (R_a + \delta_f)^2 \left( \frac{a_v i_0}{2F} \right) \frac{1}{c_{ref}} \exp \left( \frac{\alpha_a F}{RT} (E - E_0) \right)}$$

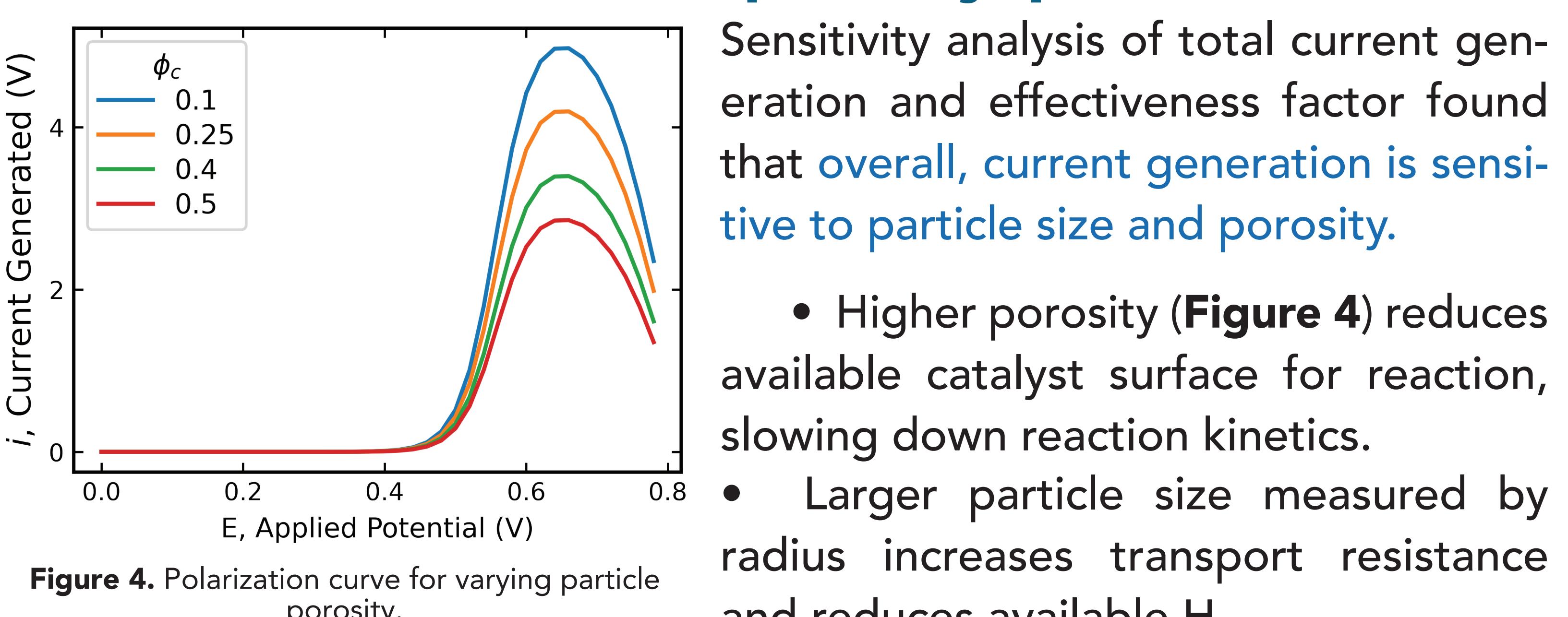
## Current Density

Total current density is solved using Butler-Volmer kinetics and integration of H<sub>2</sub> concentration across the electrode.

$$i = A \left( -\frac{3a_v i_0 (1 - \phi_c)}{c_{ref}} \right) \left( \exp \frac{\alpha_a F}{RT} (E - E_0) \right) \int_0^{CL} \left( \int_0^{\frac{R_a}{R_a + \delta_f}} c_{H_2}(z) z^2 dz \right) x dx$$

## Generation sensitive to porosity, particle size

Sensitivity analysis of total current generation and effectiveness factor found that **overall, current generation is sensitive to particle size and porosity**.



In Figure 5 (right), we see that:

$$as i \rightarrow i_{max}, E_R \rightarrow 0$$

This behavior is expected; as overpotential increases, reaction kinetics overtake transport and the particle becomes transport-limited.

H<sub>2</sub> concentration within the particle reduces to zero, causing:

$$\nabla c_{H_2} \rightarrow 0 \\ W_{AR} \rightarrow 0 \\ E_R \rightarrow 0$$

Figure 5. Sensitivity analysis of total current generated (top) and effectiveness factors (bottom) for varying catalyst particle radii.

## Catalyst particle is dominantly transport-limited

Notable features of concentration profile across the electrode:

- Steep gradient within the ionomer film layer surrounding the agglomerate
- At  $E \sim 1$  V, concentration of H<sub>2</sub> drops to 0 while the bulk CL concentration (not shown) outside of the particle is positive and non-zero.
- H<sub>2</sub> only declines at a small radial volume between  $0.9 \geq z \geq z|_{\text{film boundary}}$ .

These characteristics imply that:

- 1) the ionomer film poses significant transport resistance to H<sub>2</sub> transport, especially at high overpotentials.
- 2) H<sub>2</sub> transport into the catalyst particle is dominantly transport-limited.
- 3) no reaction occurs at radii less than  $z=0.9$ , and thus the catalyst sites closer to the center of the agglomerate are not being utilized.

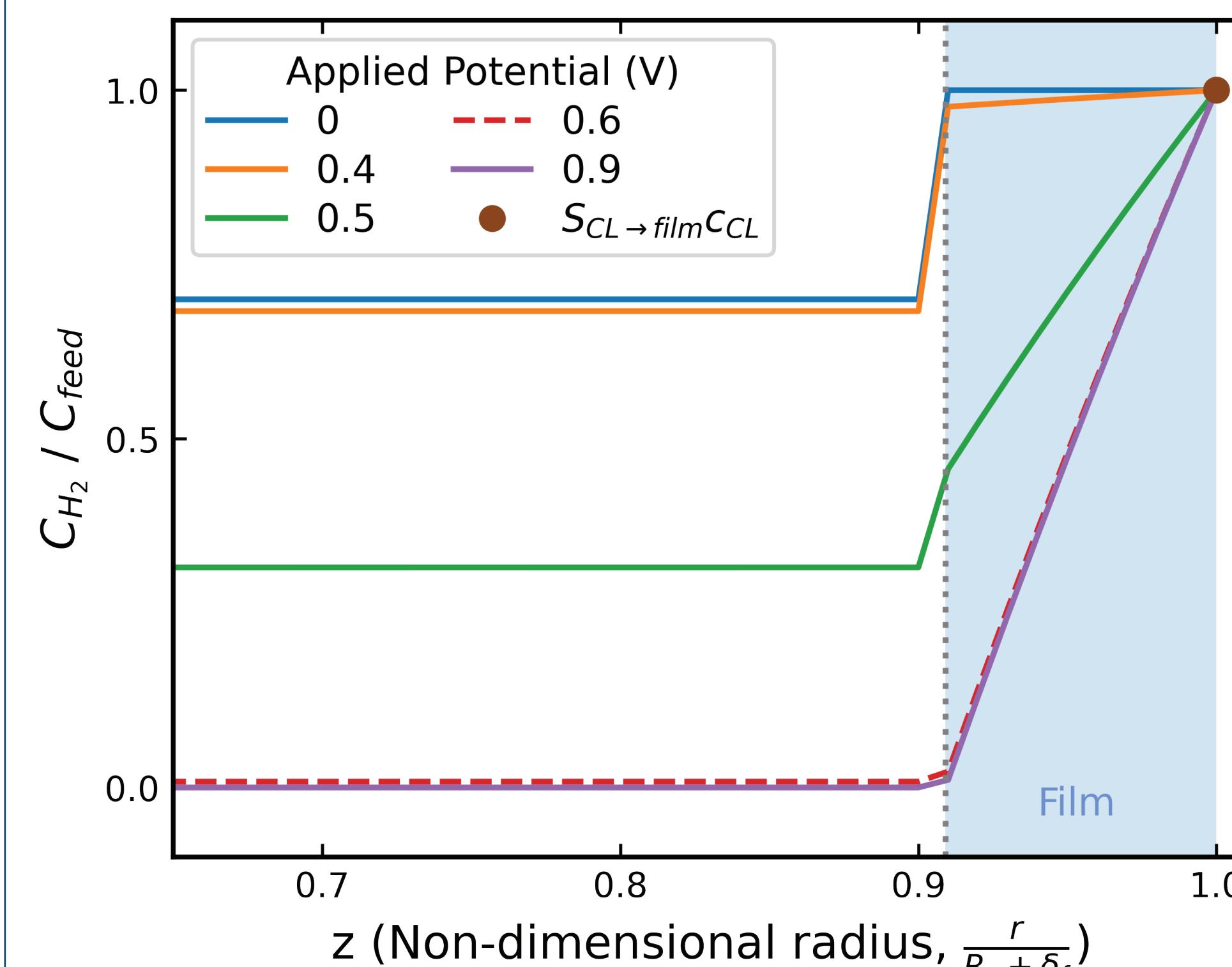


Figure 3. Diagram of H<sub>2</sub> transport through a 1-dimensional radial axis through the catalyst particle film towards the center of the carbon-Pt agglomerate, assumed as a spherical particle.

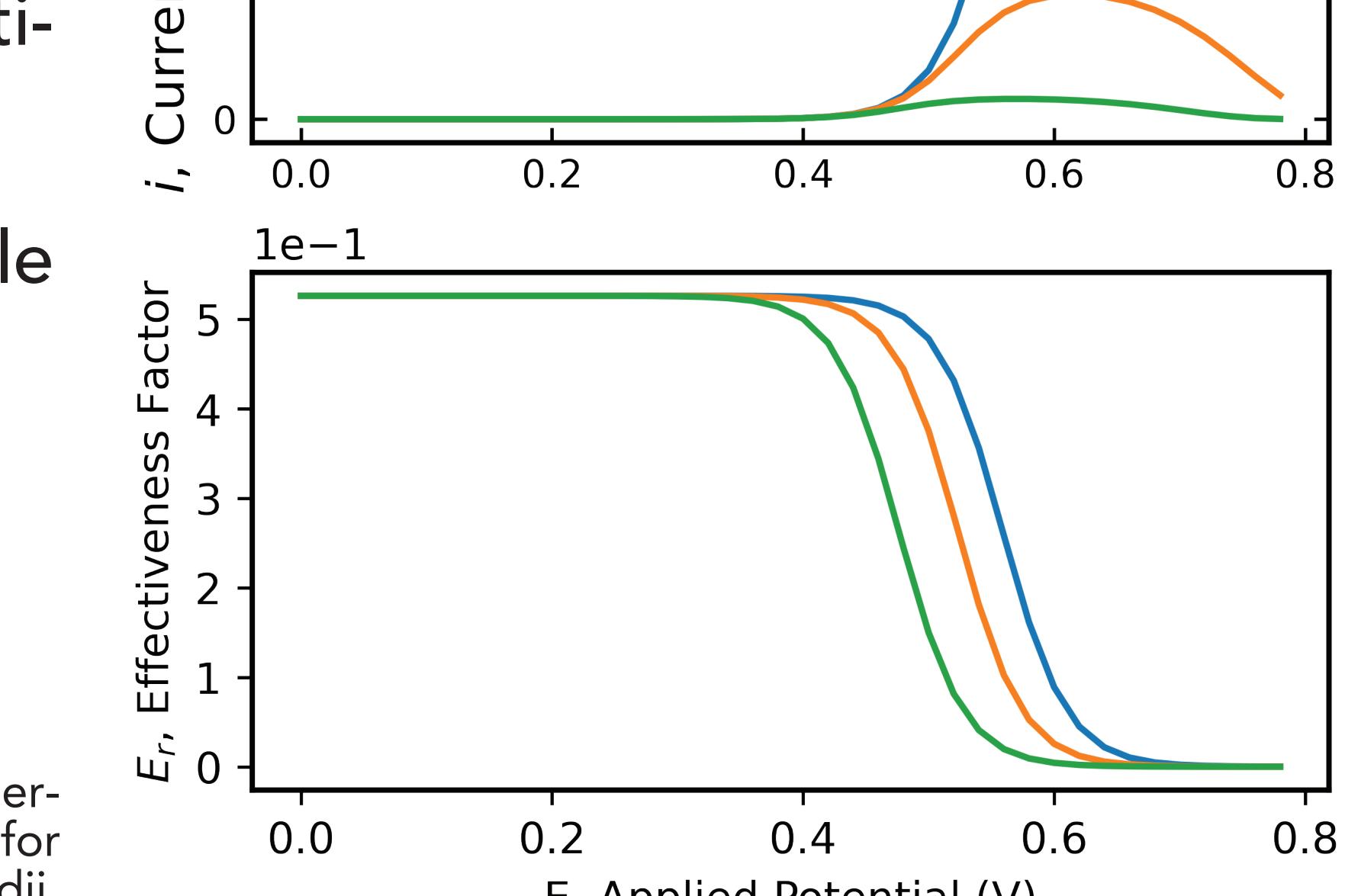
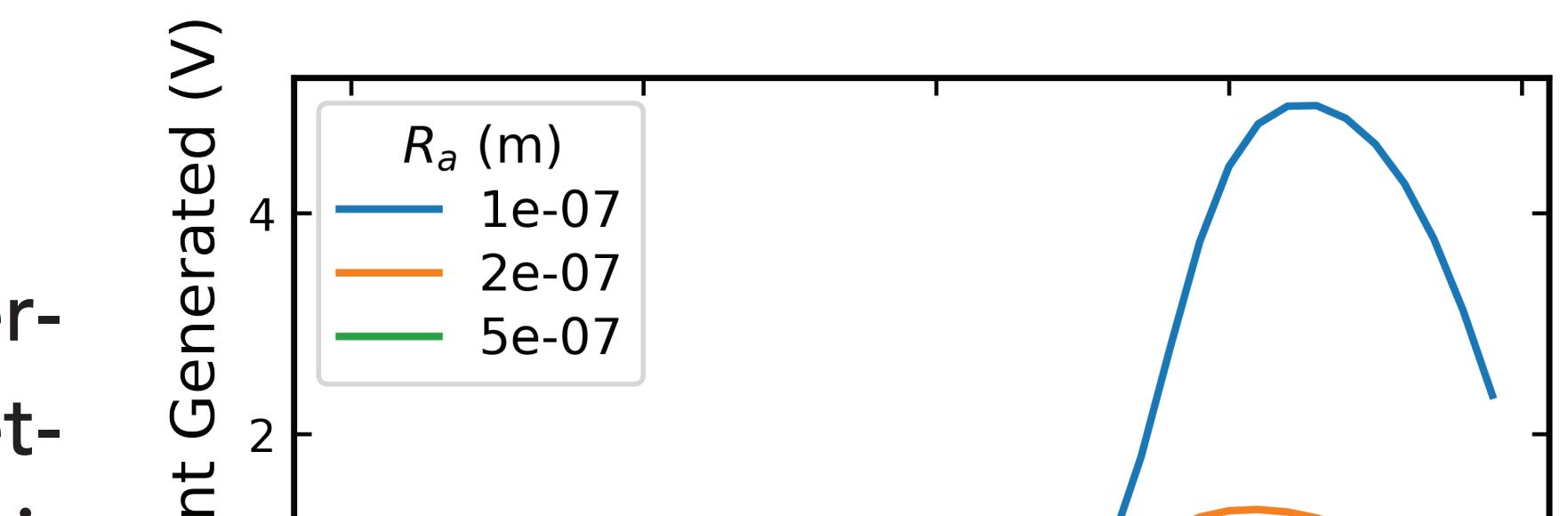
## Conclusions

### This model

- builds upon understanding of H<sub>2</sub> transport resistance within a porous electrode
- uses purely analytical operations allow for extremely fast simulations of the porous electrode set-up.

### Primary observations

- anode is dominantly transport-limited
- reaches an upper limit of catalyst volume utilization
- porosity and size (radius) of the catalyst particle strongly impacts the electrode's current generation



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