Modeling quasi-steady-state phase change transport in polymer electrolyte membrane fuel cells: *Effect of surface crack density*

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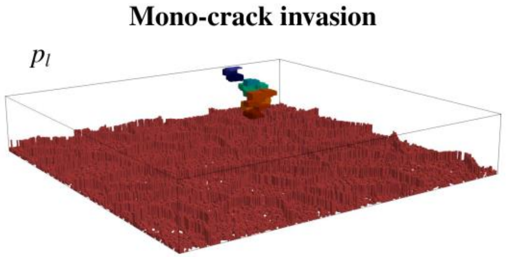
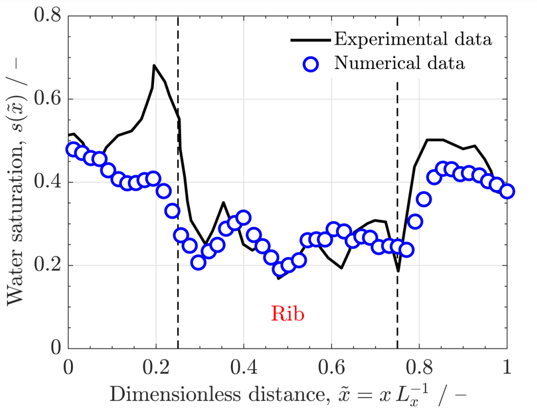
uc3m *Fluid* Mechanics

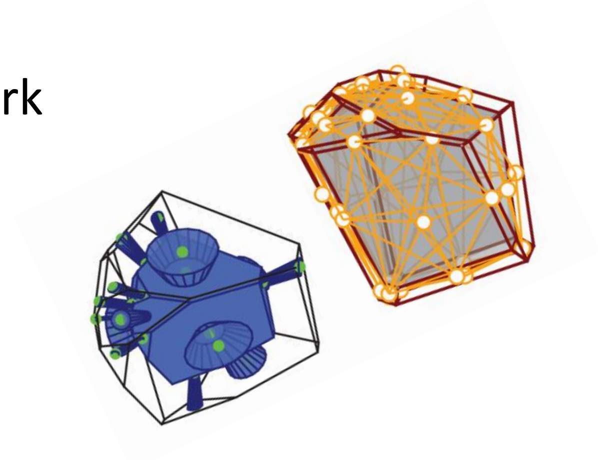
MS 19

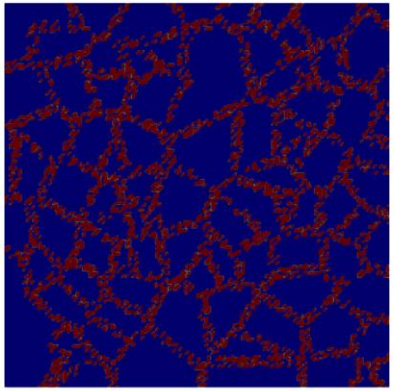
Outline

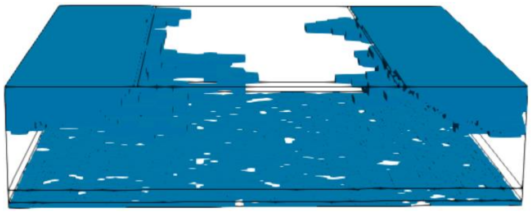
- Motivation
- Ex-situ invasion
- Quasi-steady-state pase change
- First insight on cracks
- Conclusions & future work

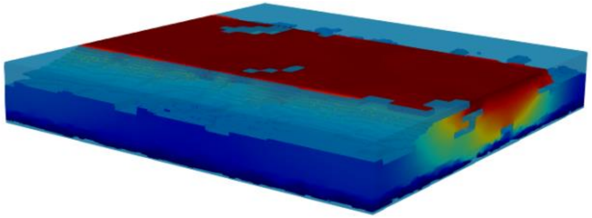


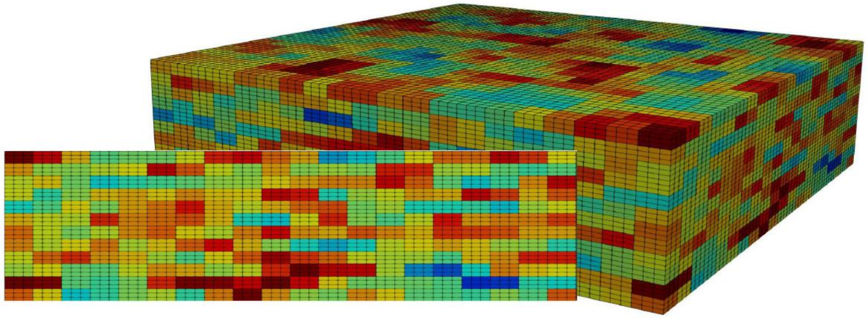






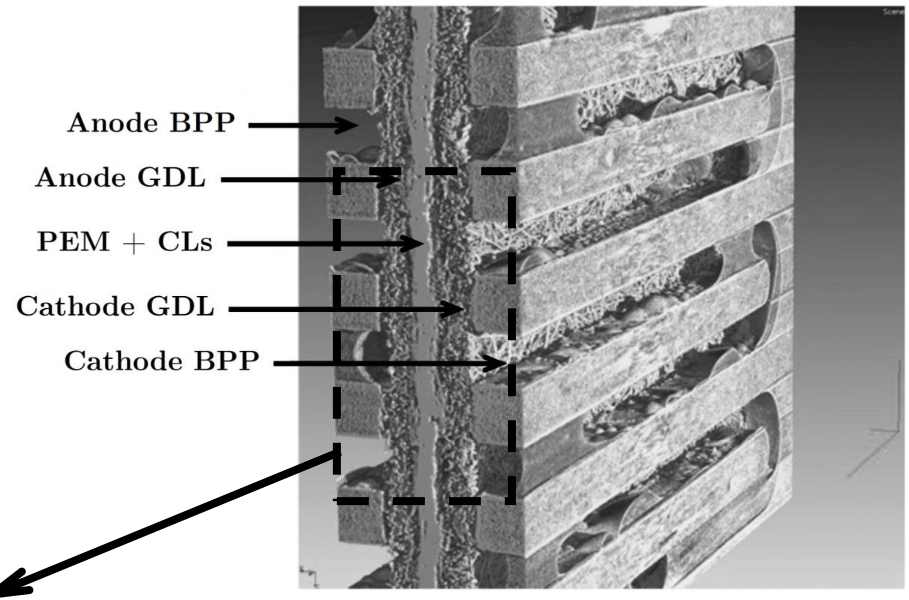




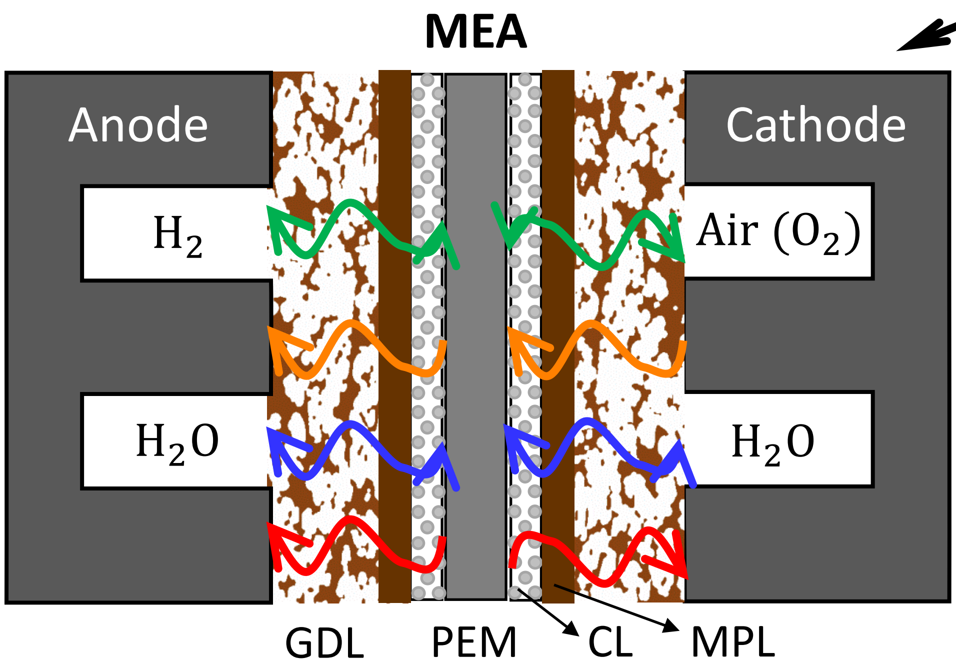


Motivation I

- **Layered Porous Media Assembly:** Understanding & Optimization
- **Multifunctional:** Coupled Phenomena



$\delta_{\mathrm{MEA}} \approx 150 - 450\ \mu\mathrm{m}$



1) Gas species transport
2) Liquid water transport
3) Electron transport
4) Heat transport

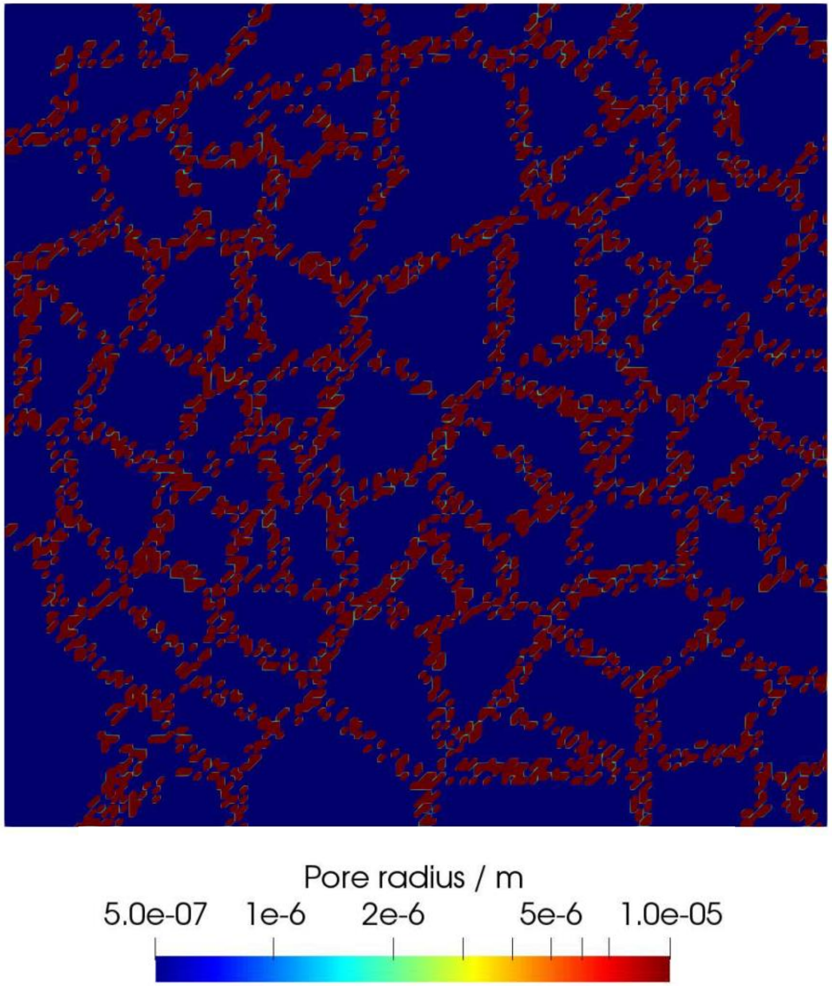
Anode: $H_2 \longrightarrow 2H^+ + 2e^- + \text{Heat}$

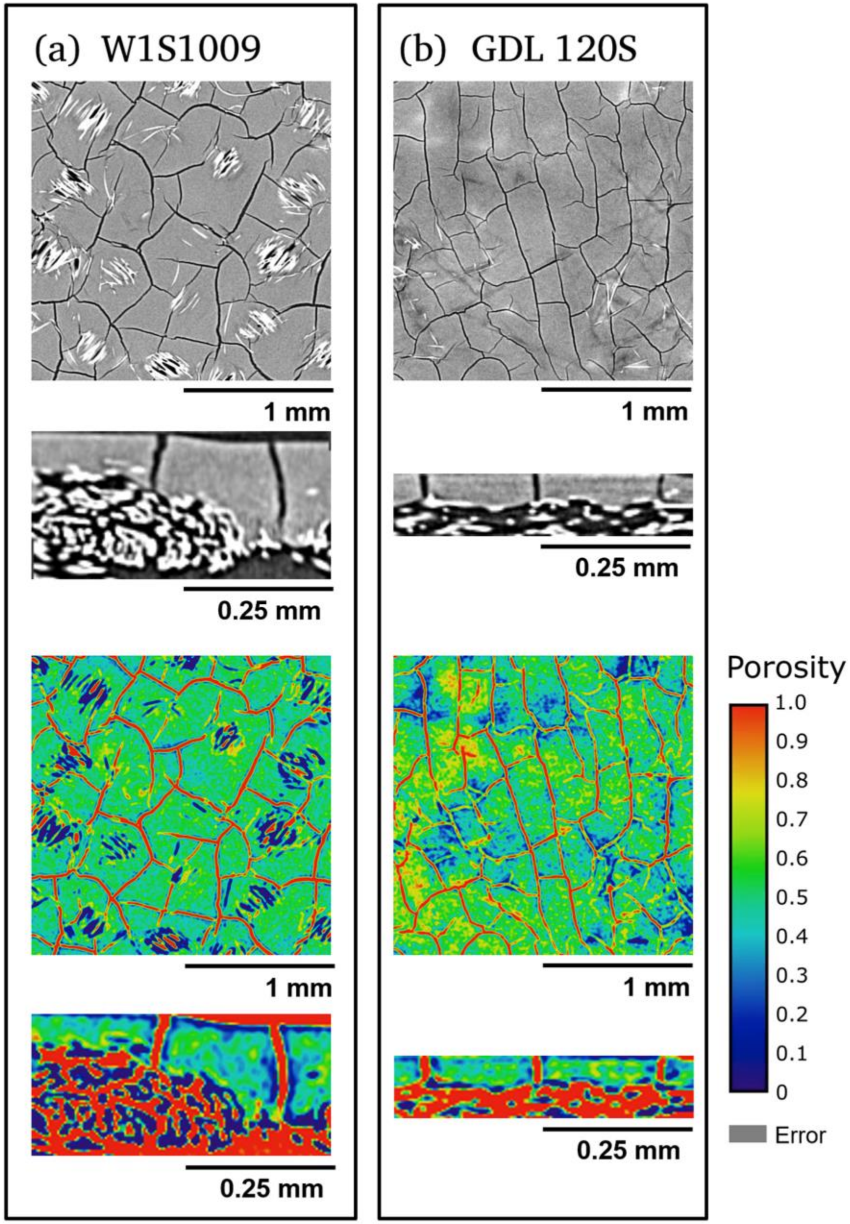
Cathode: $\frac{1}{2}O_2 + 2H^+ + 2e^- \longrightarrow H_2O + \text{Heat}$

Motivation II

Journal of Power Sources 539 **(2022)** 231612.

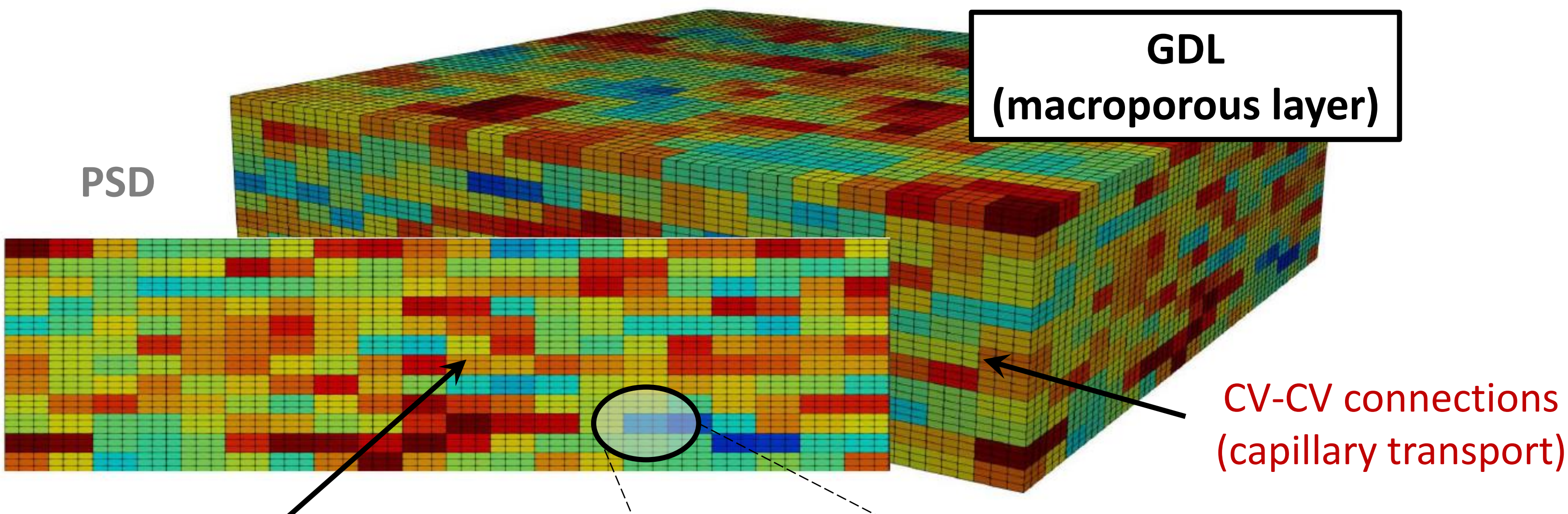
- **Cracks and defects**





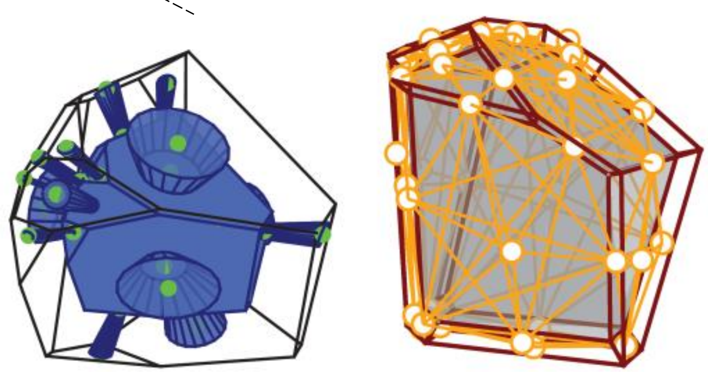
Model Formulation

- **Highly Heterogeneous Thin Porous Media**
- **Hybrid Modeling:** Continuum Formulation + Discrete Formulation (based on Pore Network Modeling) for Liquid Water Transport



Control volumes (local effective properties)

- Effective mass diffusivity tensor
- Effective thermal conductivity tensor
- Entry capillary pressure (throats)



García-Salaberri, *Int J. Heat Mass Trans.* 167 **(2021)** 120824.
García-Salaberri, *J. Power Sources* **(2023)**, in preparation.

Local Entry Capillary Pressure

MPL & CL (Cylindrical Pore)

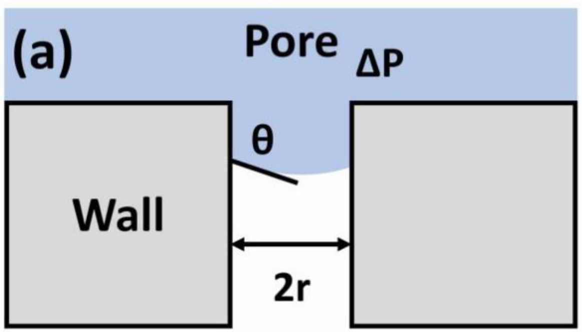
$$p_c^{th} = \frac{-2\sigma}{r}\cos\theta$$

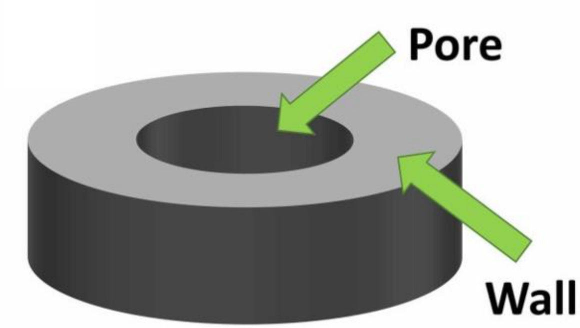
GDL (Toroidal Pore)

$$p_c^{th} = \frac{-2\sigma}{r_i}\frac{\cos(\theta-\alpha)}{1+\frac{f_d}{2\,r}(1-cos\alpha)}$$

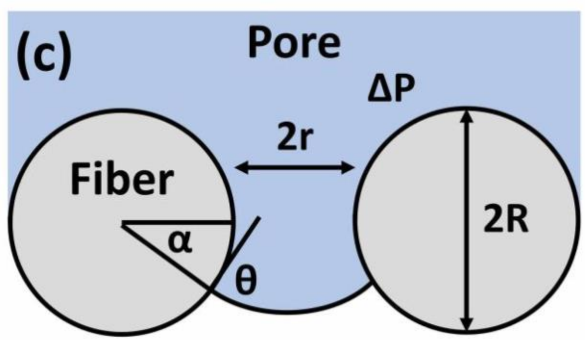
$$\alpha = \theta - \pi + \arcsin\left(\frac{\sin\theta}{1+\frac{2r}{f_d}}\right)$$

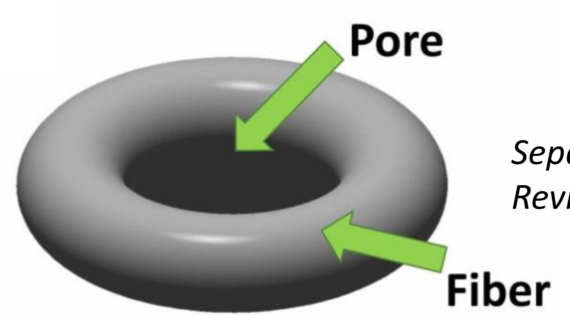
Washburn





Purcell

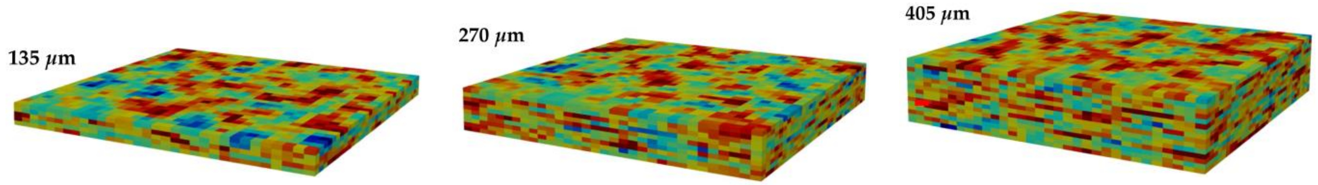




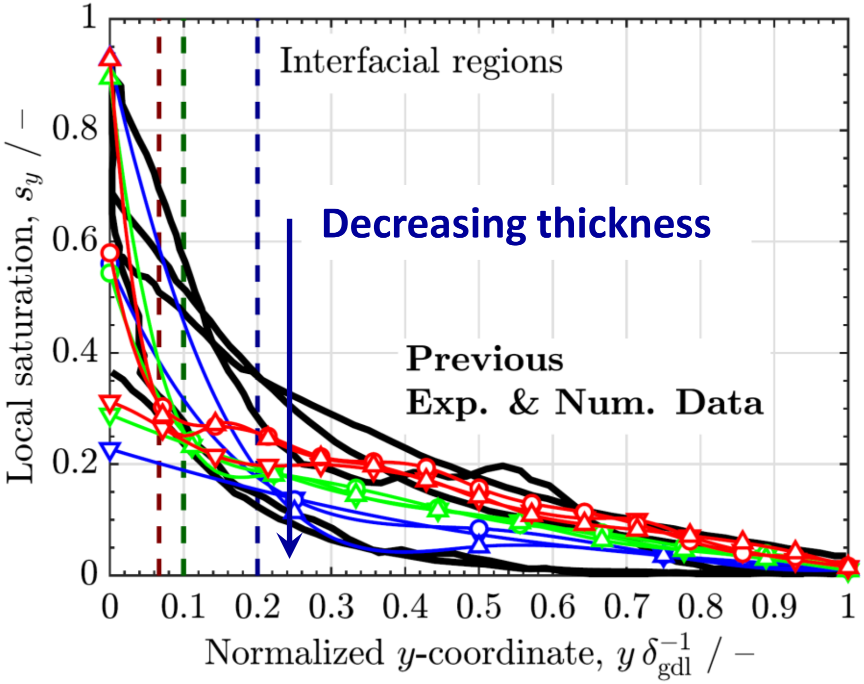
Separation & Purification Reviews 49 **(2020)** 317-356.

Ex-situ Water Invasion: Thickness

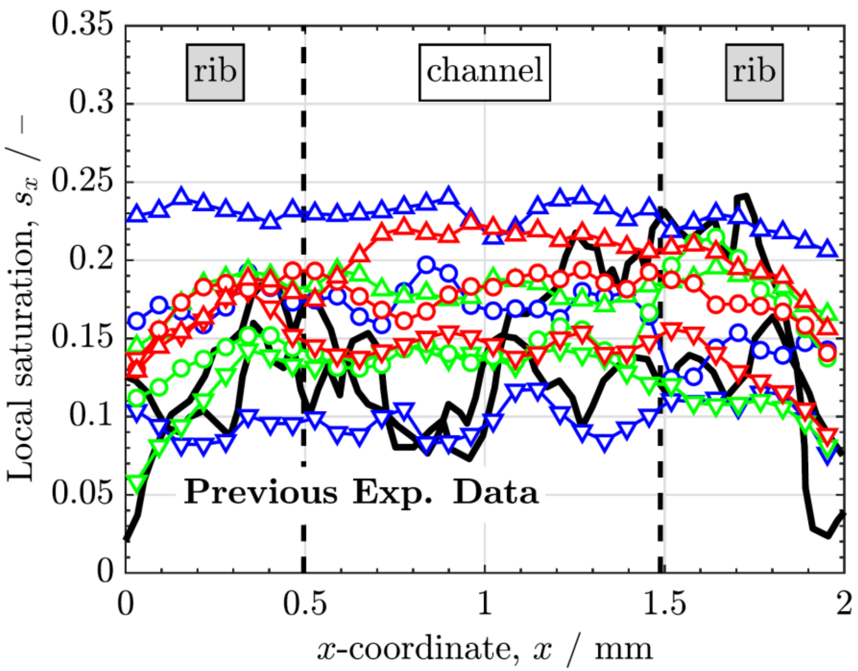
- **Invasion-Percolation (no trapping): Ca<<1**



Through-Plane

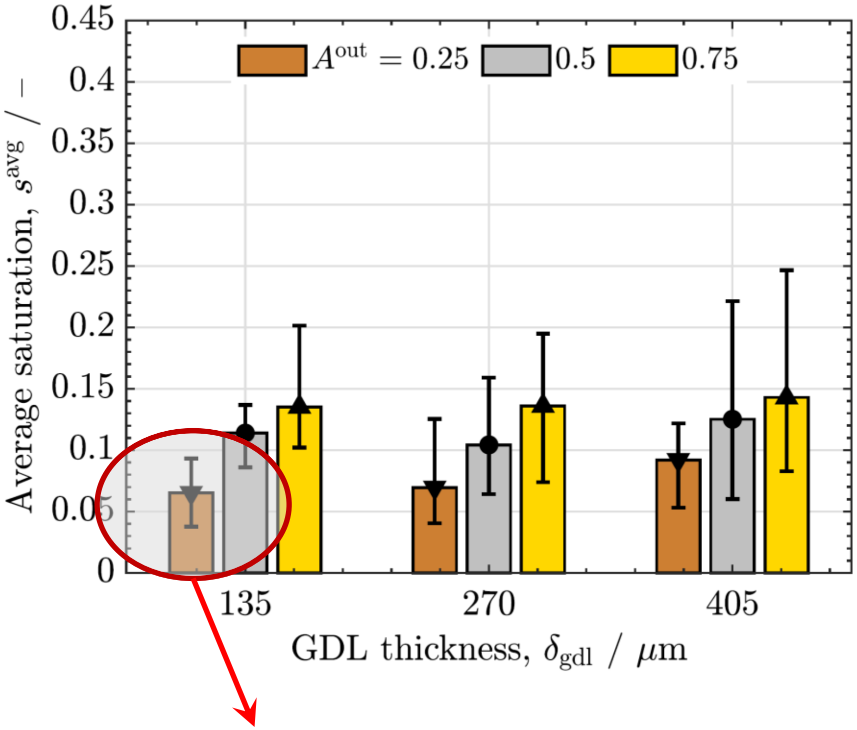


In-Plane

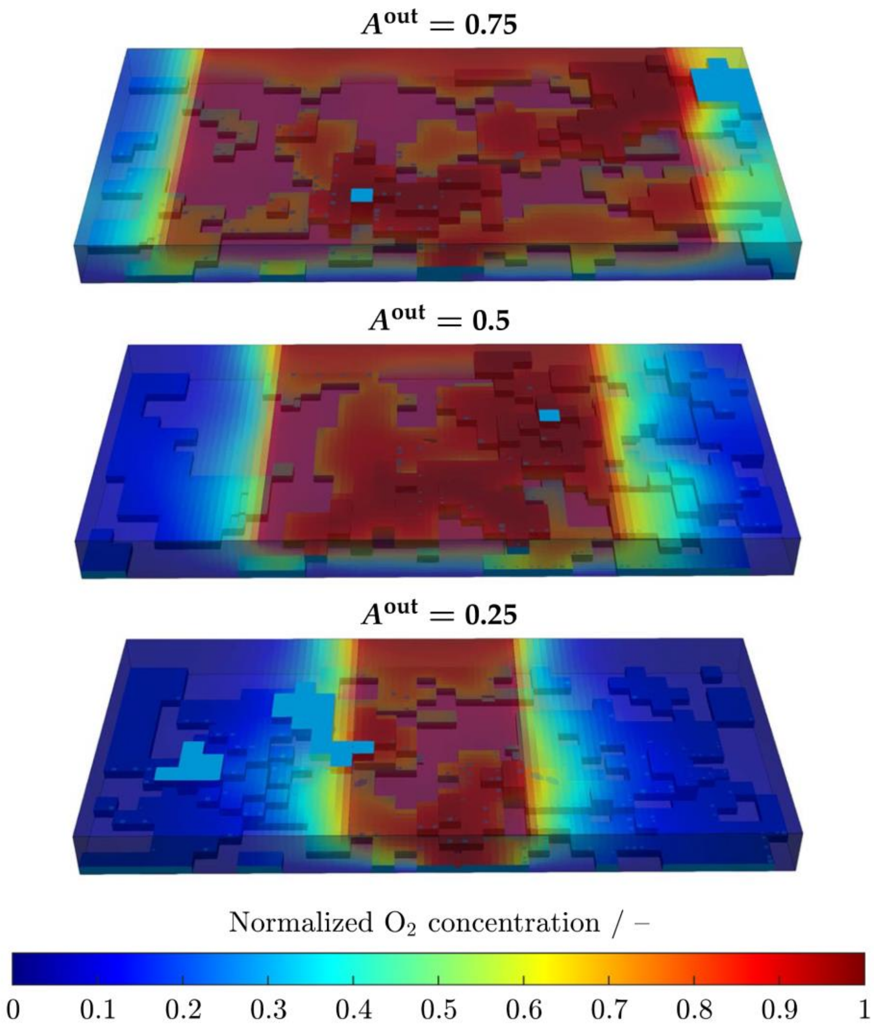


Ex-situ Water Invasion: Outlet Area Fraction (OAF)

- Increasing outlet area fraction
- Decreasing thickness
- Facilitated water capillary transport

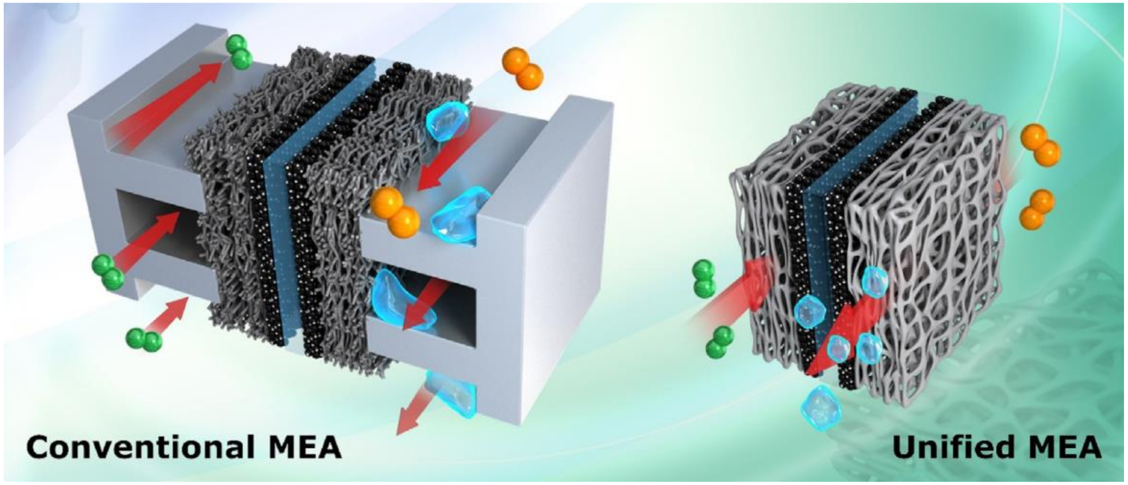


Small thickness, High OAF
Reduced O_2 transport resistance



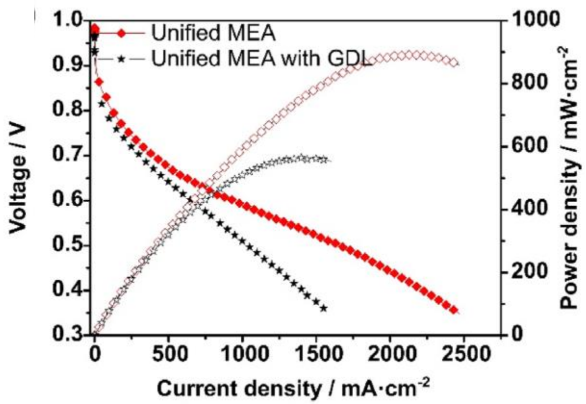
Ex-situ Water Invasion: Porous Distributors

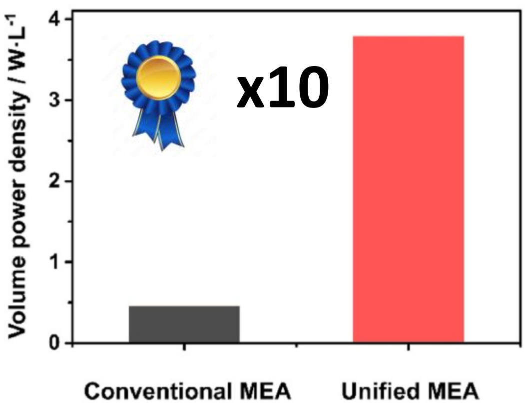
- **Unified MEA/Flow distributor: Break-through volume power**



Electrochimica Acta 323 **(2019)** 134808.

Small thickness, High OAF
+
Small rib width (fiber diameter)

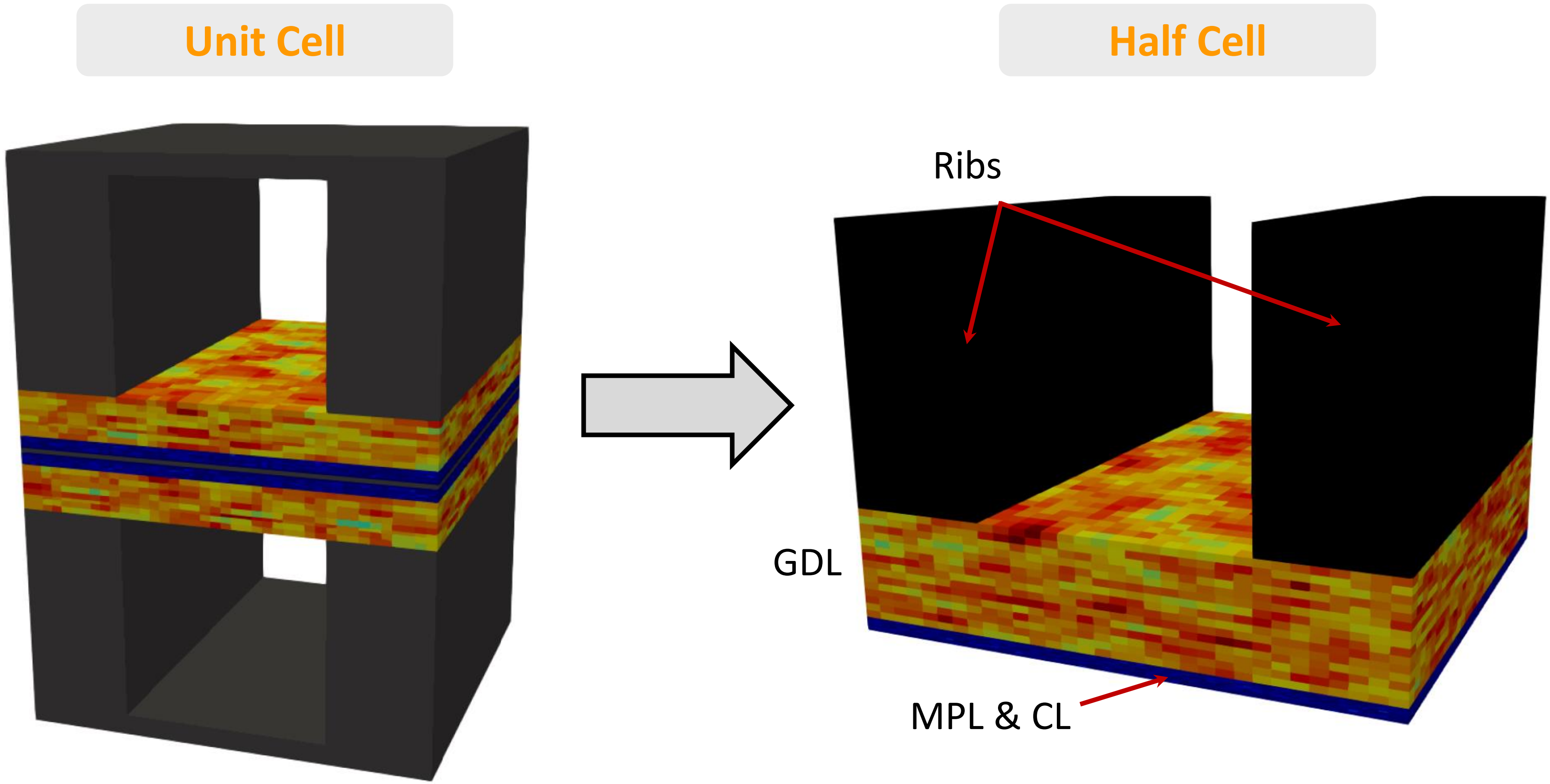




Unified Porous Assembly

But…What about phase change of water?
And cracks?

Phase Change of Water: Still No Electrochemistry



Multiscale PSD

CL (0.001-0.1 μm), MPL (0.1-1 μm) & GDL (1-10 μm)

Quasi-Steady-State Assumption

Nucleation + Growth Algorithm (Transport-Dominated Phase Change)

- Evaporation/Condensation interfacial kinetics is much faster than vapor diffusion & liquid-phase viscous capillary transport ($t_{vl} \ll t_d \sim t_c$)
- In agreement with previous experimental data & DNS

Hertz–Knudsen Mass Transfer

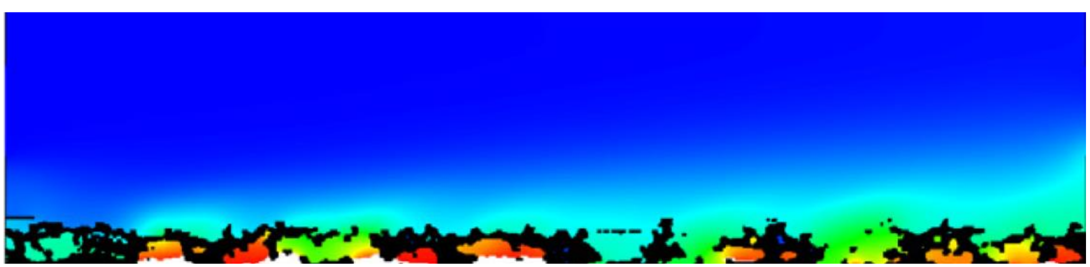
$$t_{vl} \sim k_{vl}^{-1} \sim 10^{-7} - 10^{-6}\ \mathrm{s}$$

$$k_{vl} = A_{lv}\xi_{vl};\ A_{vl} \sim 10^{7}\ \mathrm{m}^{-1}, \xi_{vl} \sim 10^{-1} - 1\ \mathrm{m\ s}^{-1}$$

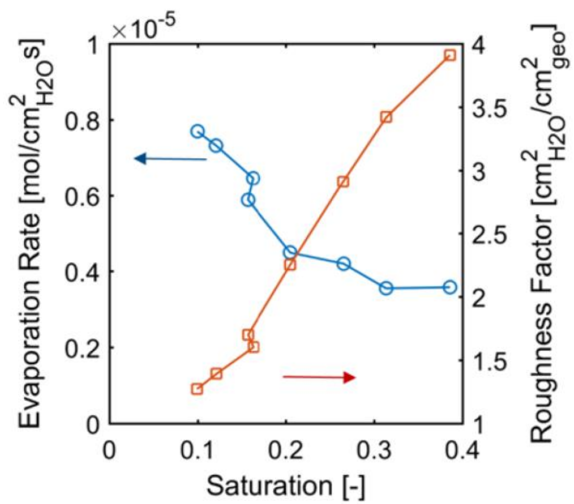
Gas Diffusion & Capillary Transport

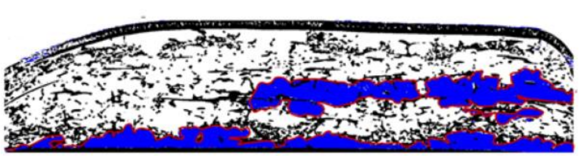
$$t_d \sim \frac{r_p^2}{D_{wv}^{eff}} \sim t_{cap} \sim \frac{\mu_w r_p^2}{K p_c^{th}} \sim 10^{-5}\ \mathrm{s}$$

Int. J. Heat Mass Trans. 129 **(2019)** 1250-1262.



J. Phys. Chem. C 120 **(2016)** 28701–28711.





Cross-section tomograph

Hybrid Approach

Continuum Formulation

Water vapor

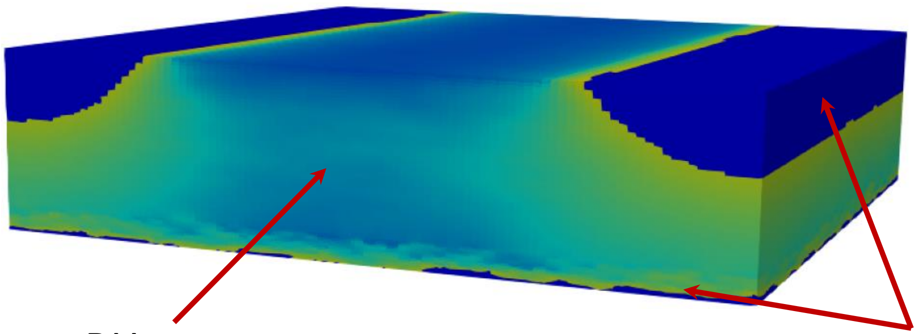
$$\nabla \cdot \left(-\overline{\overline{D}}_{wv,l}^{eff} \nabla C_{wv}\right) = S_{vl}$$

Temperature

$$\nabla \cdot \left(-\overline{\overline{k}}_{l}^{eff}(s_l) \nabla T\right) = S_T$$

Discrete Formulation

Liquid water (QSS Pore Network)

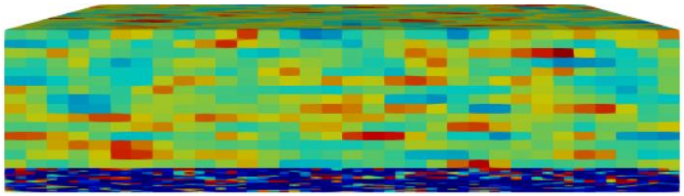


$$k_l^{eff} = k_l^{eff,dry} + (k_w - k_l^{eff,dry}) s_l$$

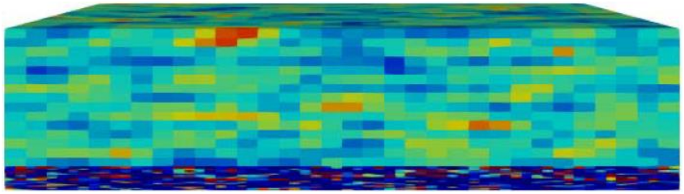
$$k_{l,\mathrm{gdl}}^{eff,dry} = \begin{cases} 0.25 \ \mathrm{W\,m^{-1}K^{-1}} \ \mathrm{TP} \\ 5 \ \mathrm{W\,m^{-1}K^{-1}} \ \mathrm{IP} \end{cases}$$

$$k_{l,\mathrm{mpl/CL}}^{eff,dry} = 0.1/0.22 \ \mathrm{W\,m^{-1}K^{-1}}$$

$D_{wv,l}^{eff}$ (IP)



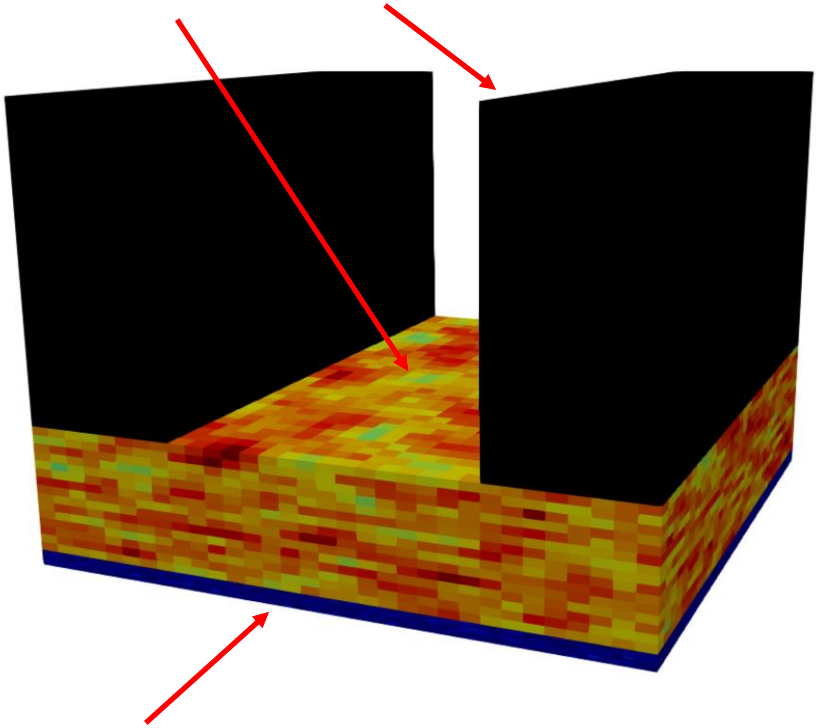
$D_{wv,l}^{eff}$ (TP)



Heterogeneous Knudsen diffusion induces water nucleation in CL

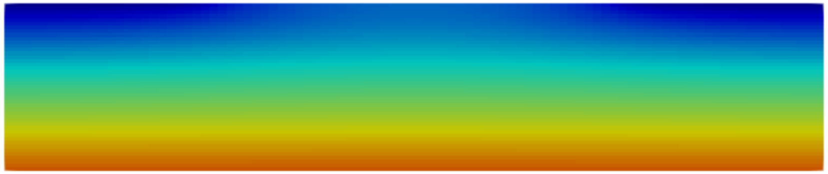
Boundary Conditions

$C_{wv} = C_{wv}^{in}, T = T^{in}$ (imposed RH & T)



RH

T



$-\overline{\overline{D}}_{wv,l}^{eff} \nabla C_{wv} \cdot \mathbf{n} = -\beta \frac{I}{2F}$ (imposed water vapor flux)

$-\overline{\overline{k}}_{l}^{eff} \nabla T \cdot \mathbf{n} = -\left(\frac{h_{lv}}{2F} - V_{cell}\right) \frac{I}{2}$ (imposed heat flux)

Water vapor and heat fluxes through CL are proportional to generated current density

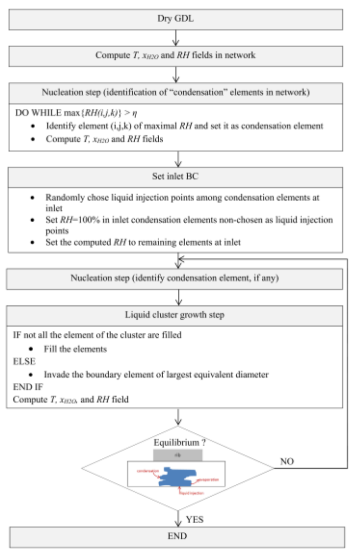
Algorithm Evolution (Continuum/Discrete Coupling)

1. Determine **steady-state solution** for **continuum variables**.
2. Label **water clusters** and determine $S_{vl,k} = \sum S_{vl}$ in each active water cluster.
3. If $S_{vl,k} > 0$, **invade** next CV with **minimum capillary resistance** in cluster k.
   If $S_{vl,k} < 0$, **remove** CV with **minimum capillary resistance** in cluster k.
4. Repeat Steps 1-3 until all water clusters either **reach the channel or show negligible mass change**, $|S_{vl,k}| \leq \mathrm{tol}, \mathrm{tol} = 10^{-16}$.

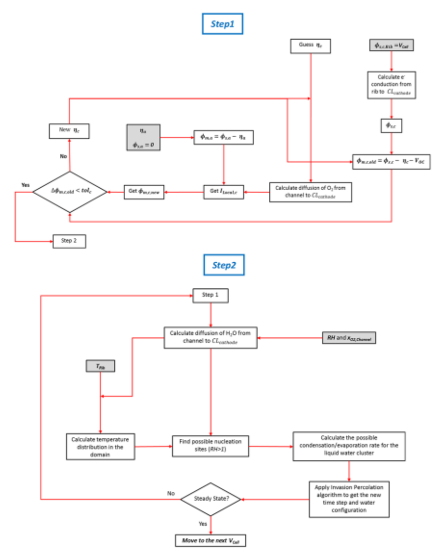
Main advantages

- Widespread availability of CFD software.
- Facilitated coupling of multiscale porous media assemblies.
- Simplified algorithm compared to previous fully PNM approaches.
- Step 1 can be easily adapted to describe transient gas transport evolution using a continuum CFD solver.

Int. J. Heat Mass Trans. 47 **(2019)** 1043–1056.



J. Appl. Electrochem. 47 **(2017)** 1323–1338.



Source Terms

computed average saturation agrees with exp. data

Phase Change Mass Transfer

If $C_{wv} > C_{wv}^{sat}$(condensation) $\Rightarrow S_{vl} = k_{vl}(C_{wv} - C_{wv}^{sat}) > 0, \boldsymbol{s} = \mathbf{1}$

If $C_{wv} \leq C_{wv}^{sat}$(evaporation) $\Rightarrow \begin{cases} s > 0 \text{ (wet)}: S_{vl} = k_{vl}(C_{wv} - C_{wv}^{sat}) < 0, \boldsymbol{s} = \mathbf{1} \\ s = 0 \text{ (dry)}: S_{vl} = 0, s = 0 \end{cases}$

Phase Change Latent Heat

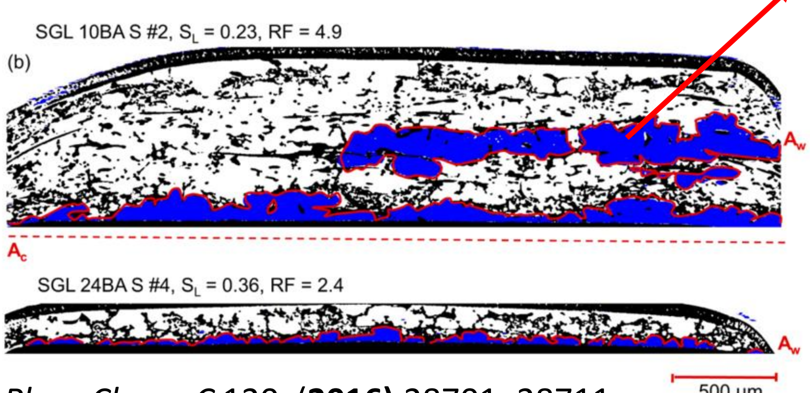
$$S_T = h_{vl}(T) S_{vl}, h_{vl}(T) = -2.44T + 3170.75 \text{ kJ kg}^{-1}$$

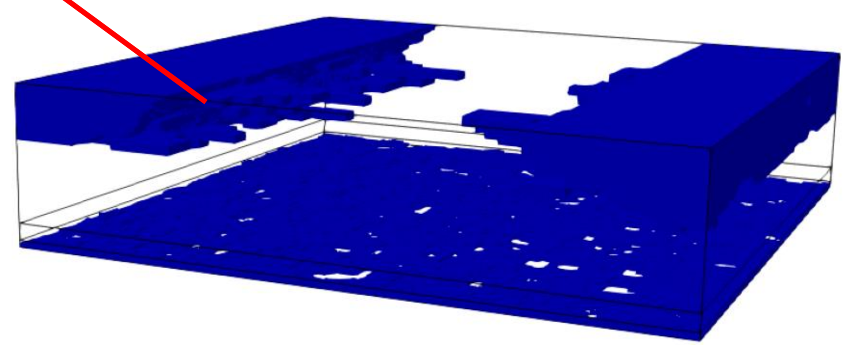
Experimental

$RH \approx 1$ (local therm. eq.)

Numerical

weak spatial scale separation



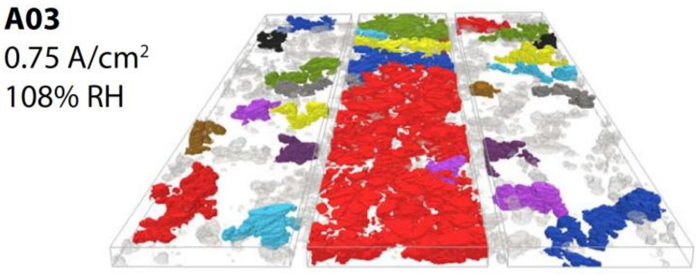


J. Phys. Chem. C 120 (**2016)** 28701–28711.

Results I

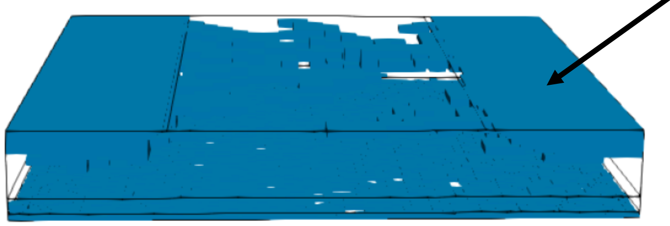
T = 80 °C, **High GDL Conductivity (e.g., Toray TGP-H-060)**

Experimental



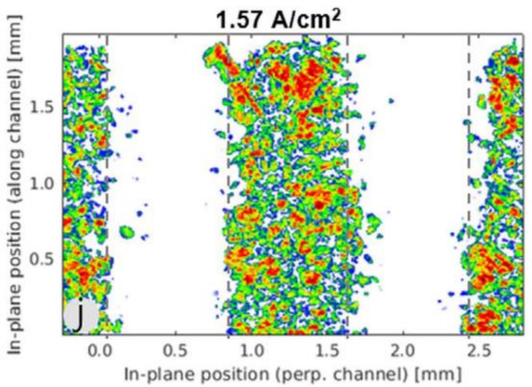
Numerical

mixed conditions



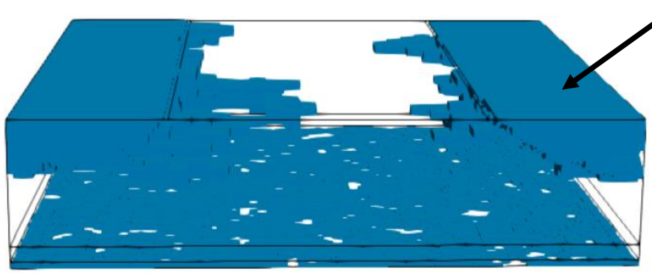
T = 80 °C, **Low GDL Conductivity (e.g., Freudenberg)**

Experimental

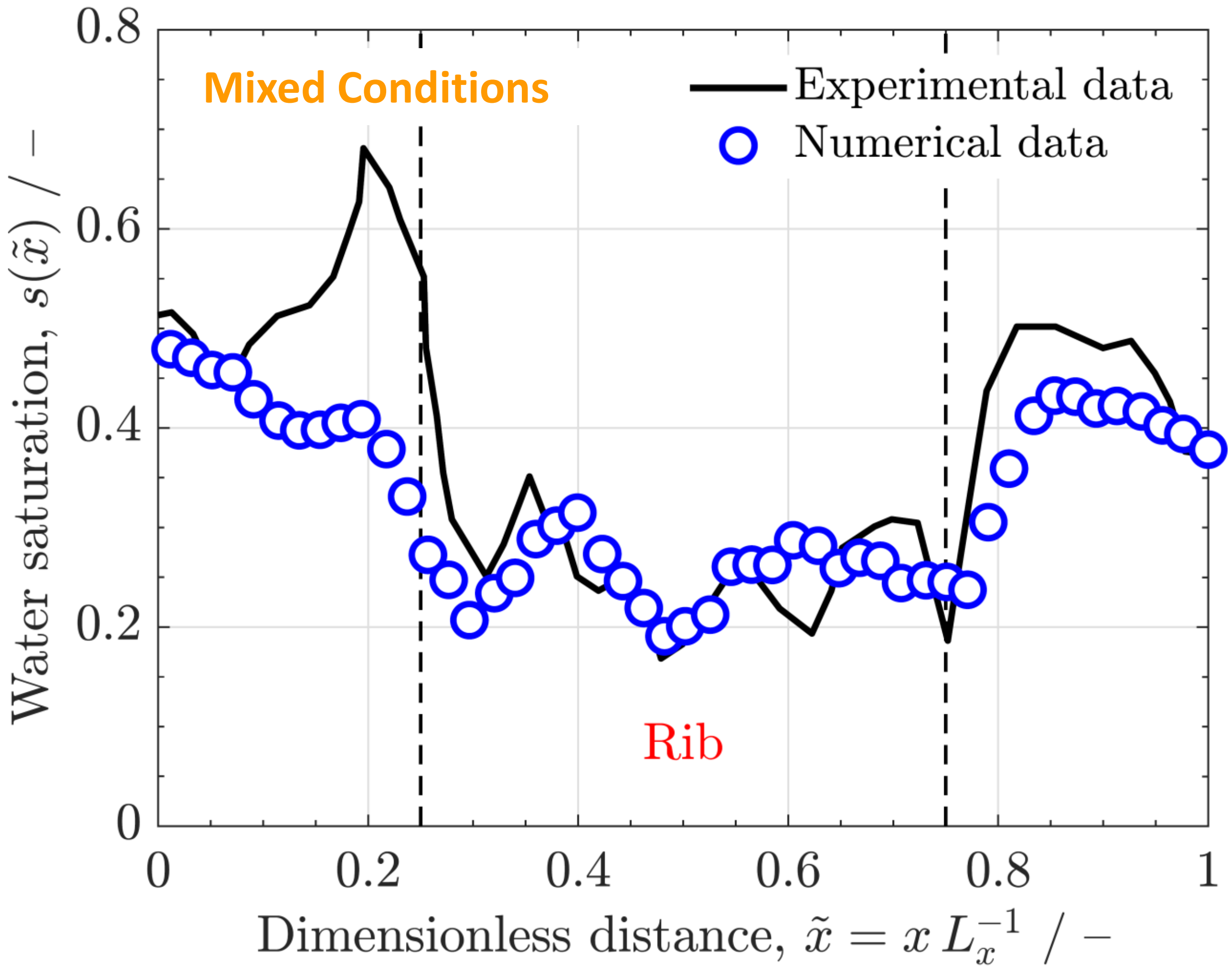


Numerical

preferential condensation under rib



Results II

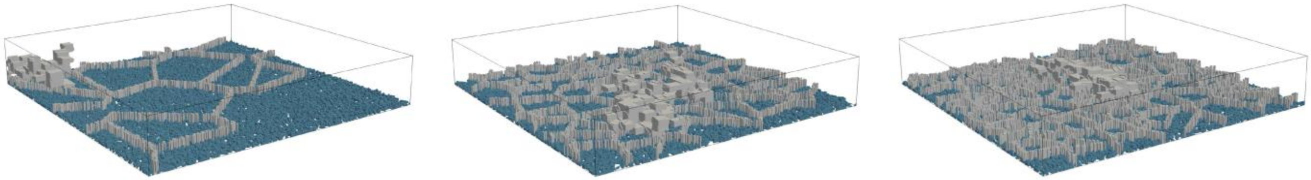


$I = 0.75\ \mathrm{A\,cm^{-2}}, \mathrm{RH}^{in} = 0.99, T^{in} = 80$ ºC, Toray TGP-H-060

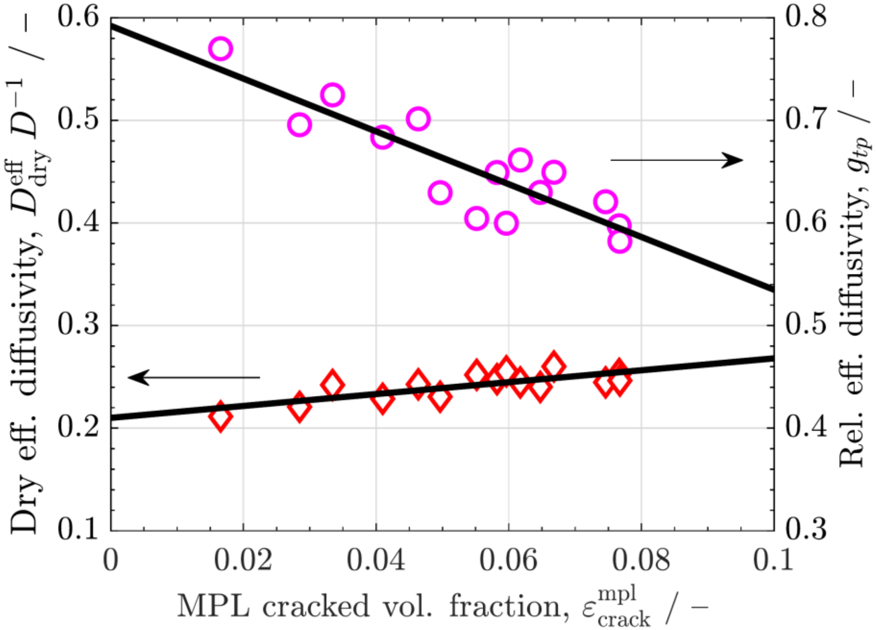
First Insight on Cracks

- **Two regimes:** **Mono- vs. Multi-crack Invasion**

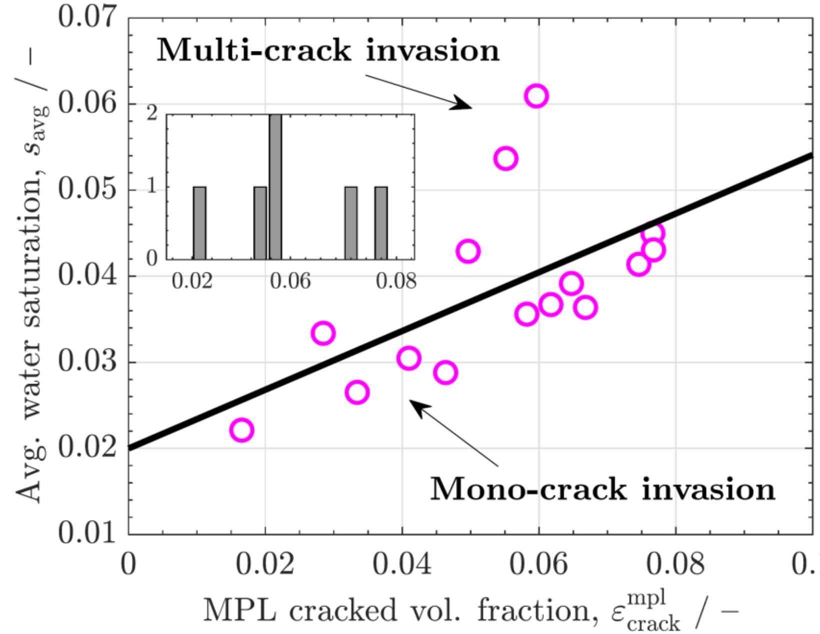
increasing crack density



Diffusivity

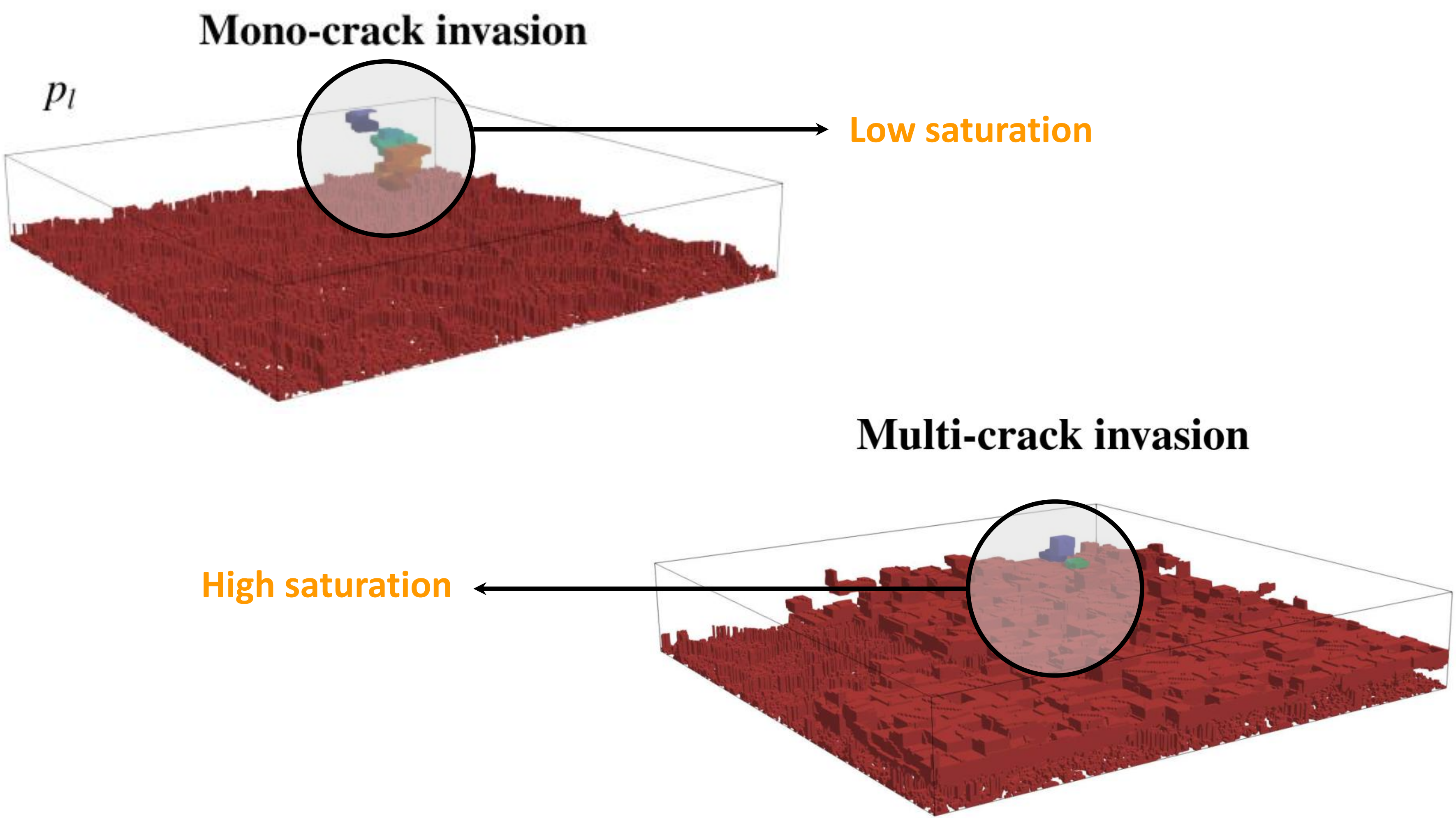


Saturation



First Insight on Cracks

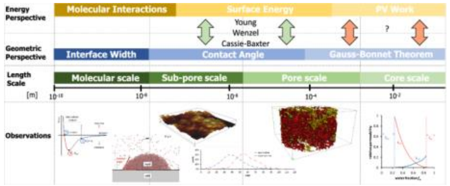
- **Two regimes:** Mono- vs. Multi-crack Invasion

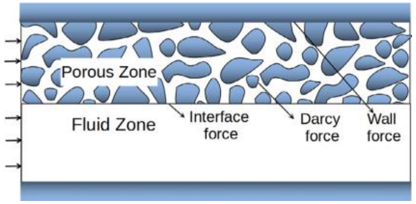


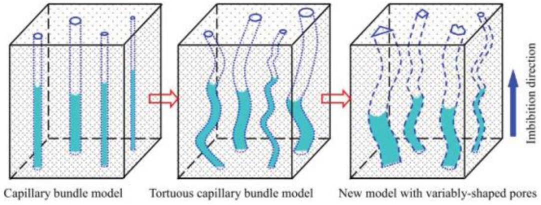
Conclusions & Future Work

- A hybrid (continuum/discrete) formulation is a convenient framework to describe heterogeneous porous media without (GDL) and with (MPL & CL) separation between pore and layer scales.
- Significantly lower characteristic time of phase change kinetics compared to gas diffusion and capillary transport allows quasi-steady-state simplification.
- Development of unitized MEAs can dramatically enhance volume power density.
- Cracks show a bifuncional behavior (mono- vs. Multi-crack invasion).

- Incorporate electrochemistry (fully coupled model).
- Analyze effect of multi-layer wetting properties.
- Include interaction w/ flow field.
- Coupling w/ multi-scale bundle of capillary tubes for CL and MPL.







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