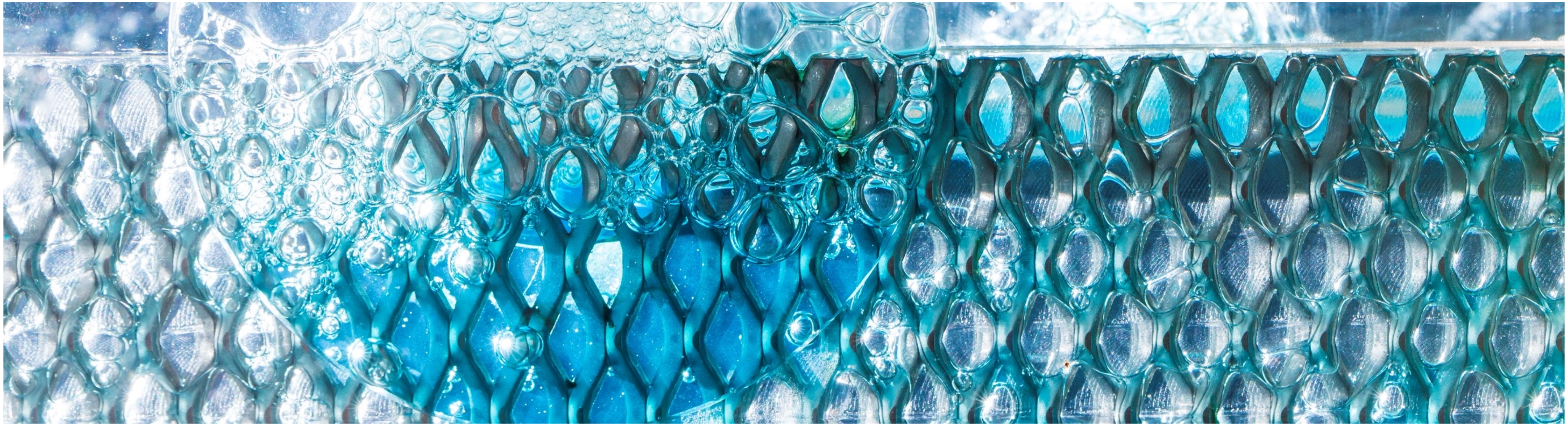

CATALYST LAYER MODELING: THE NEXT GENERATION

Further FC Workshop, DLR Stuttgart, July 6, 2022

Michael Eikerling, Institute of Energy and Climate Research, IEK-13

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WHAT CAN BE LEARNED FROM EXISTING MODELS?

LOW PT LOADING: WHAT IS TIPPING THE BALANCE?

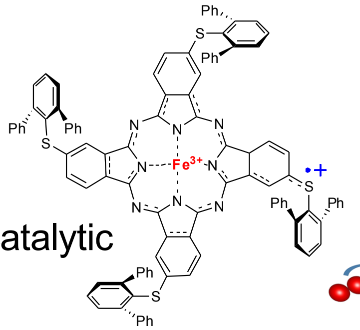
RATIONALIZE WETTING BEHAVIOUR IN CCL

IMPORTANCE OF CROSS-COMPONENT COUPLING

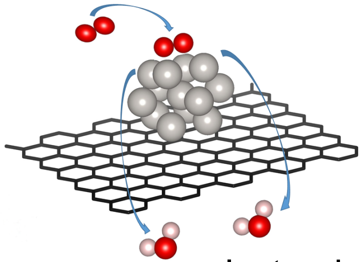
SFU
HELMHOLTZ RESEARCH FOR GRAND CHALLENGES
BOSCH
JÜLICH Forschungszentrum
Funded by
Federal Ministry of Education and Research
RWTH AACHEN UNIVERSITY

WHY THEORY AND COMPUTATION?

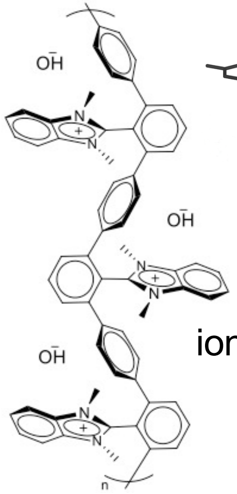
Molecular & atomistic design → **Structured materials & interfaces** → **Composites & porous media** →



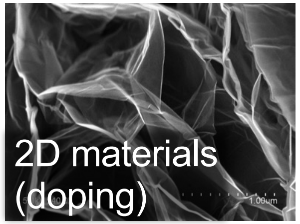
catalytic



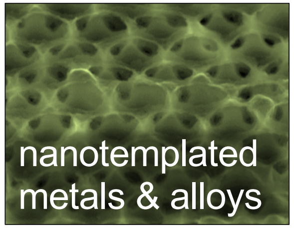
electronic



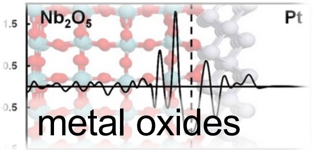
ionic



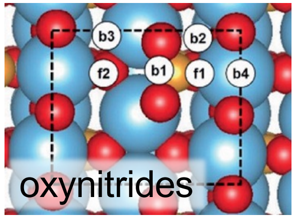
2D materials (doping)



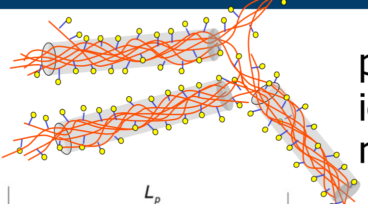
nanotemplated metals & alloys



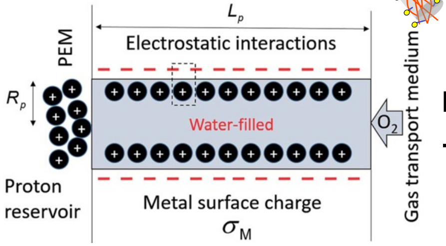
metal oxides



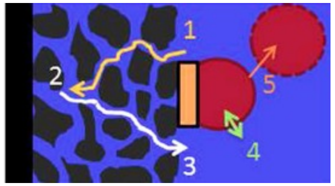
oxynitrides



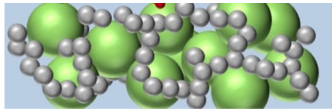
polymer/ ionomer networks



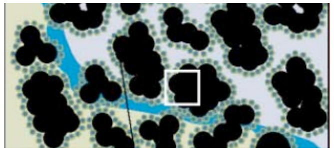
nanoprotonics/ -ionics



transport media



mixed conductors



multiphase composites

BATTERY ENERGY STORAGE

HYDROGEN FOR MOBILITY

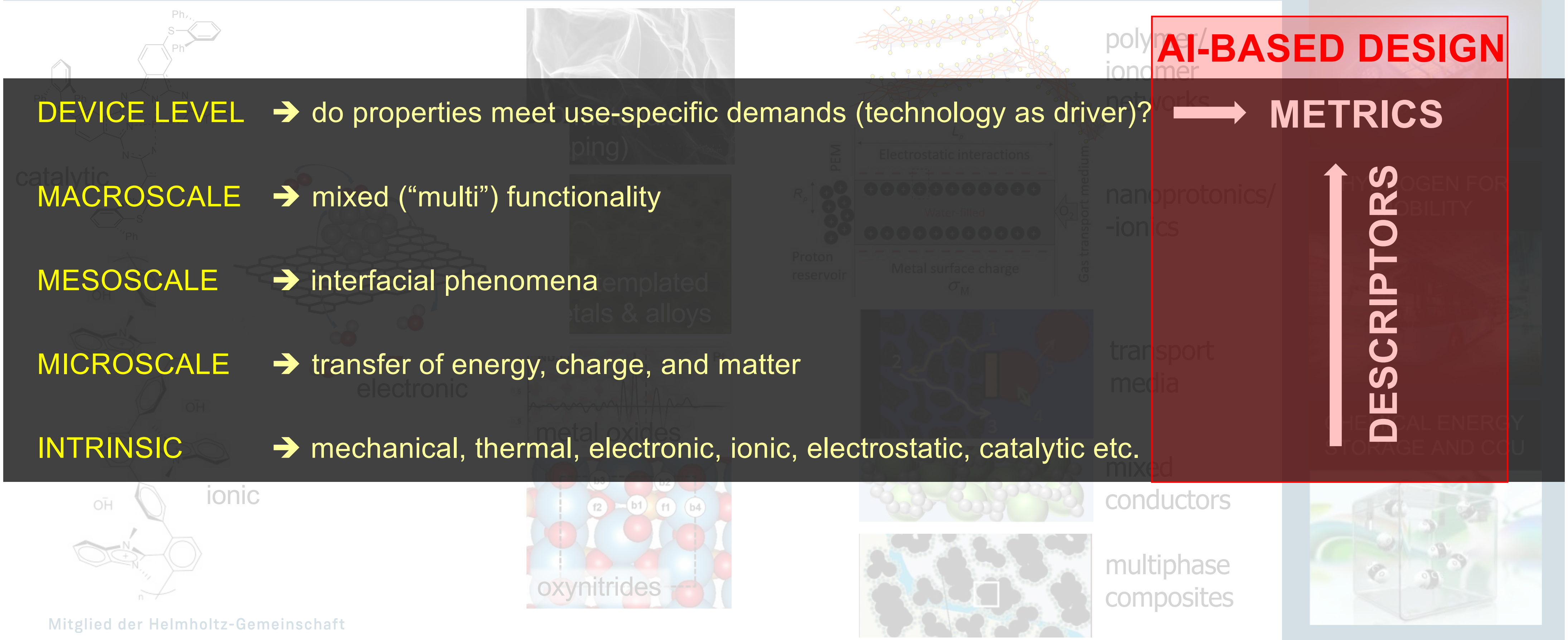
CHEMICAL ENERGY STORAGE AND CCU

m.eikerling@fz-juelich.de

WHY THEORY AND COMPUTATION?

Molecular & atomistic design → Structured materials & interfaces → Composites & porous media →

BATTERY ENERGY STORAGE



DEVICE LEVEL → do properties meet use-specific demands (technology as driver)?

MACROSCALE → mixed ("multi") functionality

MESOSCALE → interfacial phenomena

MICROSCALE → transfer of energy, charge, and matter

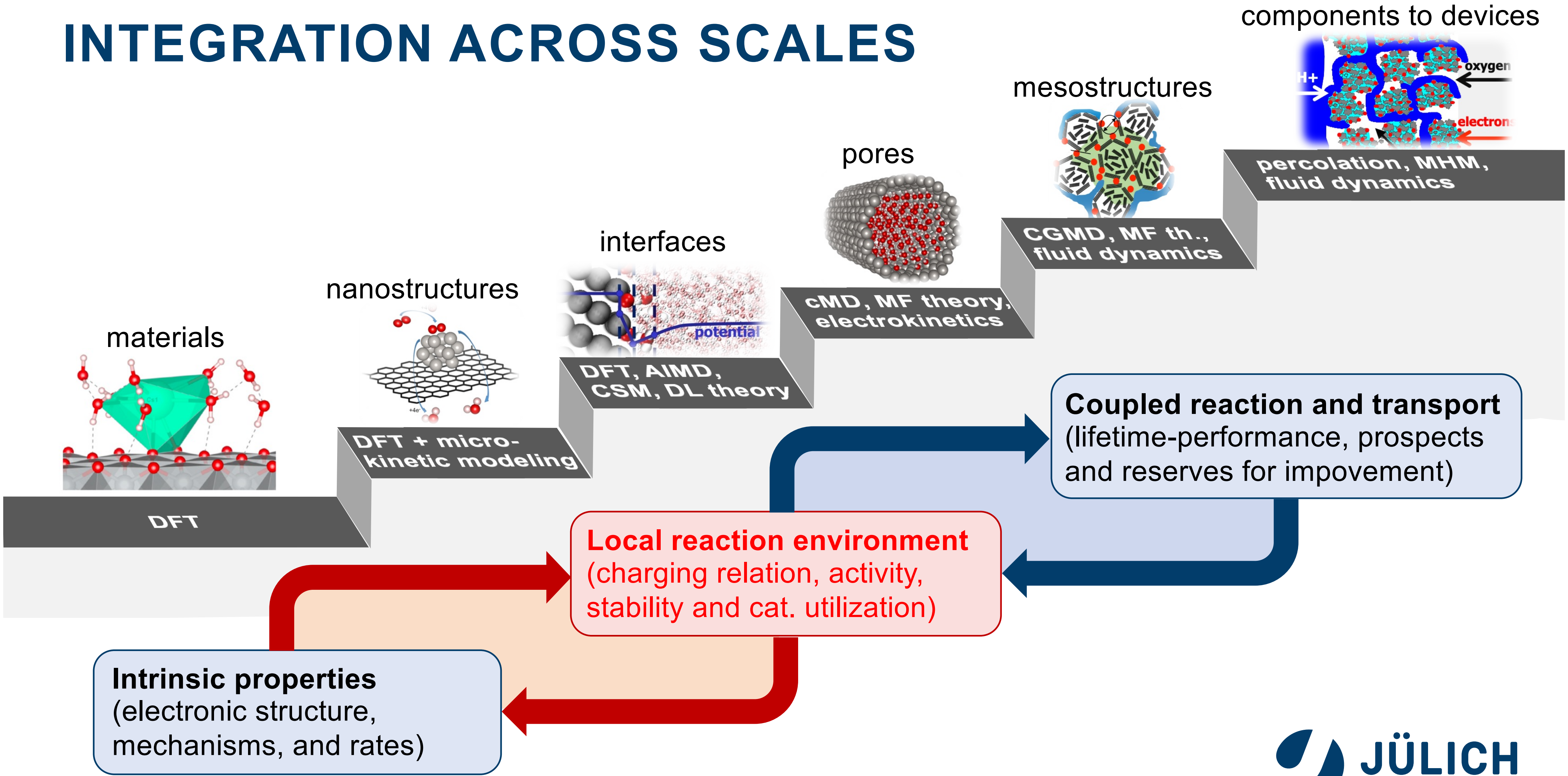
INTRINSIC → mechanical, thermal, electronic, ionic, electrostatic, catalytic etc.

AI-BASED DESIGN

→ **METRICS**

↑ **DESCRIPTORS**

INTEGRATION ACROSS SCALES



materials

DFT

nanostructures

DFT + micro-kinetic modeling

interfaces

DFT, AIMD, CSM, DL theory

pores

cMD, MF theory, electrokinetics

mesostructures

CGMD, MF th., fluid dynamics

components to devices

percolation, MHM, fluid dynamics

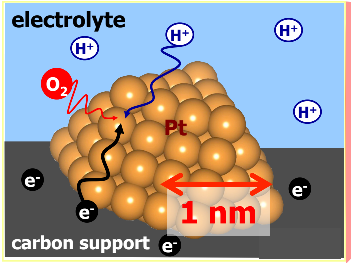
Coupled reaction and transport
(lifetime-performance, prospects and reserves for impovement)

Local reaction environment
(charging relation, activity, stability and cat. utilization)

Intrinsic properties
(electronic structure, mechanisms, and rates)

LOCAL REACTION ENVIRONMENT: COUPLING

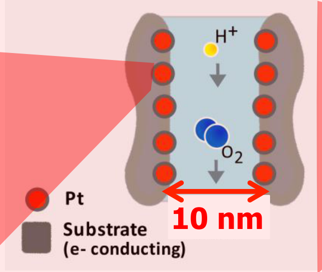
Electrocatalysis



- ☐ mechanisms
- ☐ eff. parameters

➔ DFT, AIMD
➔ thermochem. mod.
➔ kinetic modeling

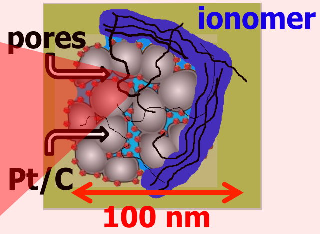
Nanopore



- ☐ electrostatic effects
- ☐ effectiveness factor

➔ PNP theory
➔ nanoprotonics
➔ classical MD

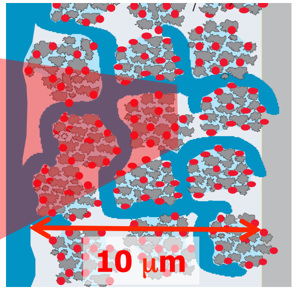
Agglomerate



- ☐ self-organization
- ☐ ionomer, water
- ☐ effectiveness factor

➔ coarse-grained MD
➔ PNP model

Composite CL



- ☐ regimes of operation
- ☐ water balance
- ☐ total effectiveness

➔ transport & reaction
➔ hierarchical model

- ☐ mechanistic understanding
- ☐ material selection & design
- ☐ key electrode parameters

local reaction environment

transport

nonuniformity

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STRUCTURE-BASED MODELING OF CATHODE CATALYST LAYERS IN PEM FUEL CELLS

FROM COMPOSITION TO EFFECTIVE PROPERTIES

Primary parameters

- ☐ component densities: $\rho_{Pt},\ \rho_C,\ \rho_{el}$
- ☐ weight fractions: $Y_{Pt},\ Y_{el}$
- ☐ Pt mass loading: m_{Pt}

  per geometric surface area
- ☐ layer thickness: l_{CL}

Volumetric composition

$$X_{Pt} = \frac{m_{Pt}}{l_{CL}}\frac{1}{\rho_{Pt}},$$

$$X_C = \frac{m_{Pt}}{l_{CL}}\frac{1-Y_{Pt}}{Y_{Pt}\rho_C},$$

$$X_{el} = \frac{m_{Pt}}{l_{CL}}\frac{Y_{el}}{(1-Y_{el})\,Y_{Pt}\rho_{el}}$$

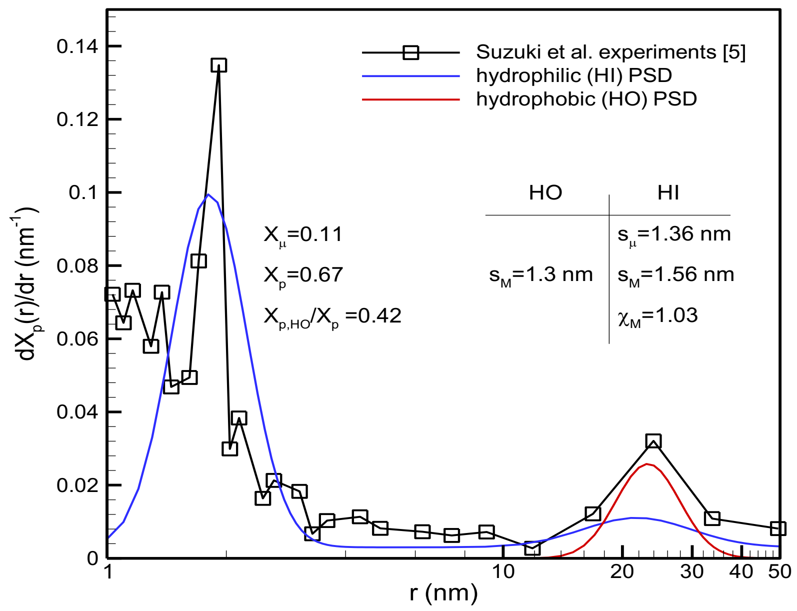
Effective properties from percolation theory

$$\sigma_{el} = \sigma_0\left(\frac{X_{el}-X_c}{1-X_c}\right)^{\mu}\Theta(X_{el}-X_c)$$

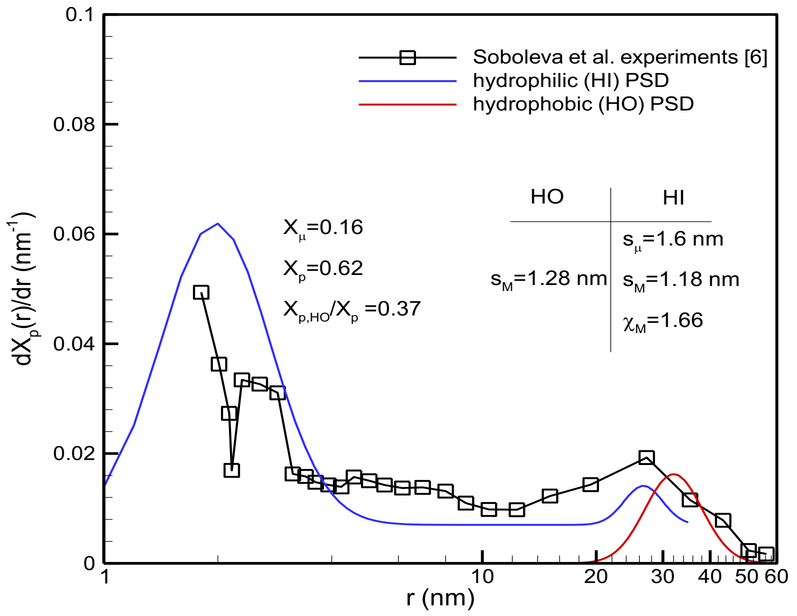
$$D^{o,v,r}(S_r) = D_0^{o,v,r}\frac{(X_P-X_\mu-X_c)^{2.4}}{(1-X_c)^2\,(X_P-X_c)^{0.4}}\left\{\left[\frac{(1-S_r)\,X_P-X_c}{X_P-X_\mu-X_c}\right]^{2.4}\Theta\left(S_r-\frac{X_\mu}{X_P}\right)+\Theta\left(\frac{X_\mu}{X_P}-S_r\right)\right\}+D^{res}\ ,\qquad D_0^{o,v} = \sqrt{\frac{2RT}{\pi M^{o,v}}}\,\frac{4}{3}\,r_{crit}$$

$$j^0 = j_*^0\frac{m_{Pt}N_A}{M_{Pt}\nu_{Pt}}\Gamma_{np}\Gamma_{stat}\ ,\quad \Gamma_{stat} = g(S_r)\frac{f(X_{PtC},X_{el})}{X_{PtC}}$$

EXPERIMENTAL PORE SIZE DISTRIBUTIONS



T. Suzuki *et al.*, Int. J. Hydrogen Energy, 36, 12361 (2011).



T. Soboleva *et al.*, ACS AMI, 2, 375 (2010).

- bimodal pores size distribution (➔ agglomeration)
- hydrophobic and hydrophilic pores

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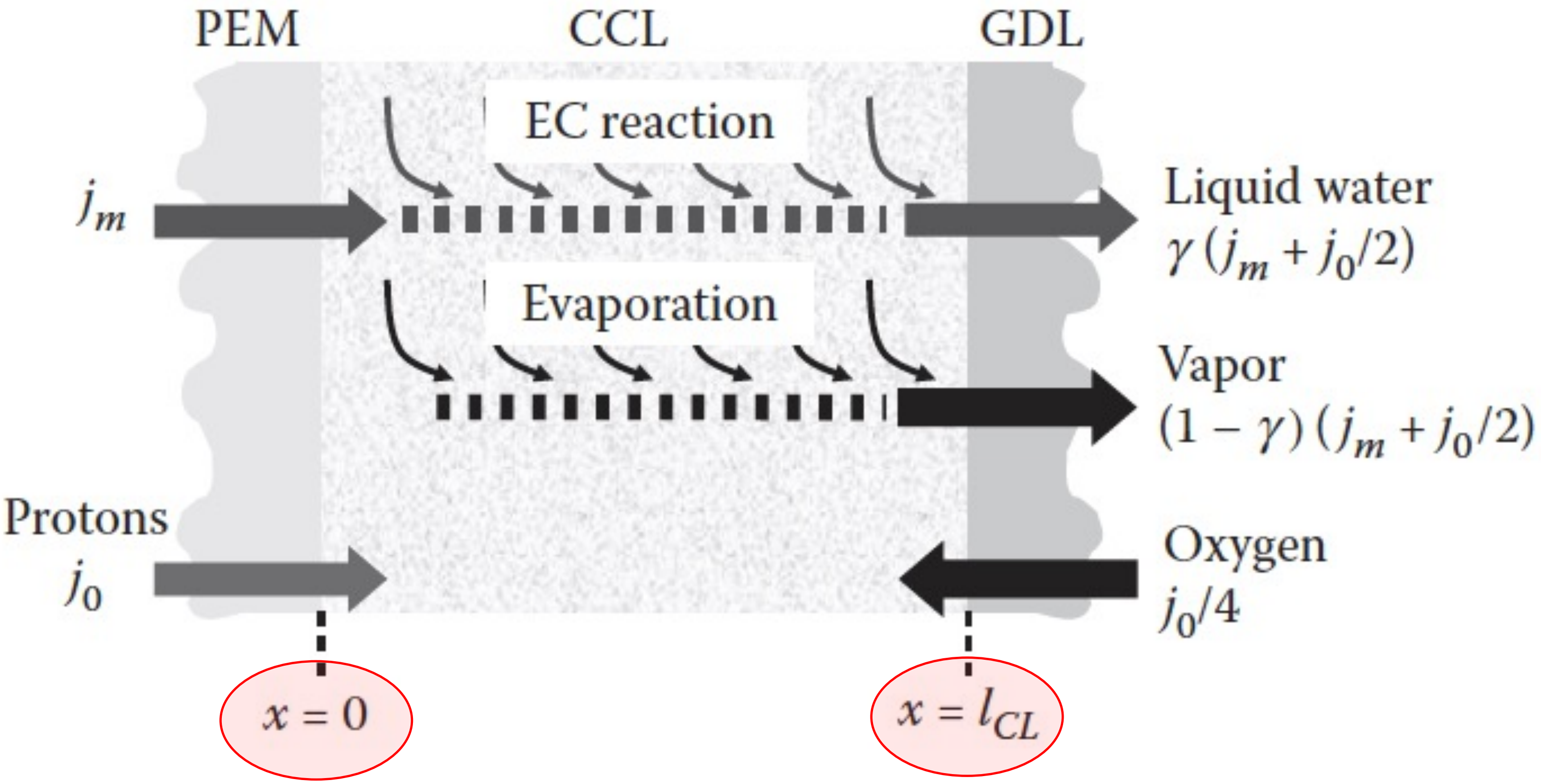
COUPLED SPECIES FLUXES IN CCLS



MHM: COUPLING

Part A: Governing equations for electrochemical processes

Proton transport
$$\frac{\mathrm{d}\eta}{\mathrm{d}x}=\frac{j_{\mathrm{p}}(x)}{\sigma_{\mathrm{el}}(S(x))}$$

Interfacial reaction
$$\frac{\mathrm{d}j_{\mathrm{p}}}{\mathrm{d}x}=-Q^{\mathrm{ec}}(x)$$

Oxygen diffusion
$$\frac{\mathrm{d}p}{\mathrm{d}x}=\frac{j_0-j_{\mathrm{p}}(x)}{4fD^{o}(S(x))}$$

explicit coupling

Part B: Governing equations for water fluxes

Water formation and vaporization
$$\frac{\mathrm{d}j^{\mathrm{l}}}{\mathrm{d}x}=\frac{1}{2}Q^{\mathrm{ec}}(x)-Q^{\mathrm{lv}}(x)$$

Liquid transport
$$\frac{\mathrm{d}p^{\mathrm{l}}}{\mathrm{d}x}=\frac{1}{B_0fK^{\mathrm{l}}(S(x))}\left[\left(n+\frac{1}{2}\right)\left(j_{\mathrm{p}}(x)-j_0\right)+j^{\mathrm{v}}(x)+nj_0-j_{\mathrm{m}}\right]$$

Vaporization exchange
$$\frac{\mathrm{d}j^{\mathrm{v}}}{\mathrm{d}x}=Q^{\mathrm{lv}}(x)$$

Vapour diffusion
$$\frac{\mathrm{d}q}{\mathrm{d}x}=-\frac{j^{\mathrm{v}}(x)}{fD^{\mathrm{v}}(S(x))}$$

Problem: implicit coupling – dependence of solution on $S(x)$

Polymer Electrolyte Fuel Cells – Physical Principles of Materials and Operation, M. Eikerling and A.A. Kulikovsky, CRC Press, 2014.

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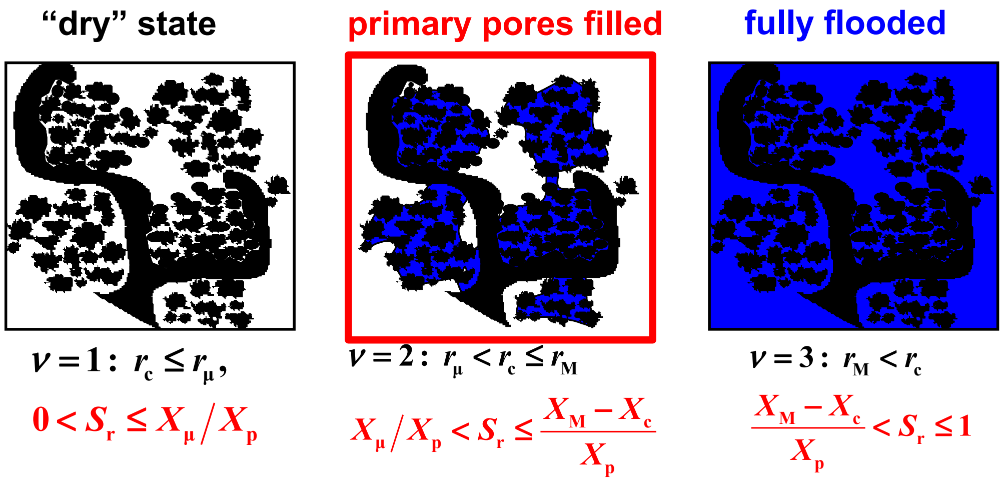
WHAT HARM CAN A FLOODED CCL POSSIBLY DO?



$\nu = 1: \; r_c \le r_\mu,$

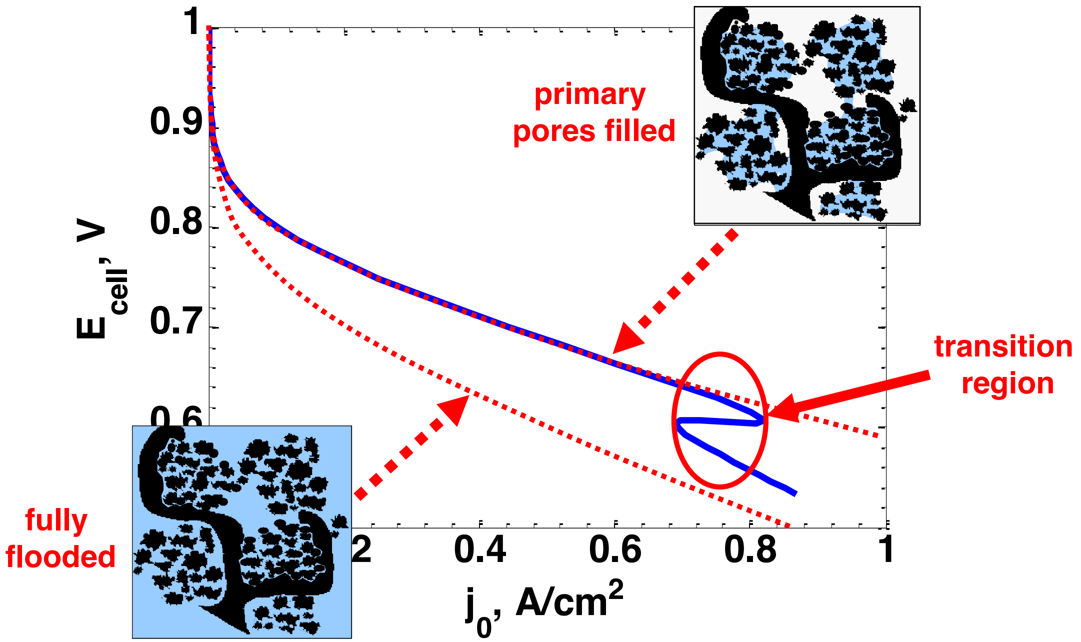
$0 < S_r \le X_\mu / X_p$

$\nu = 2: \; r_\mu < r_c \le r_M$

$X_\mu / X_p < S_r \le \dfrac{X_M - X_c}{X_p}$

$\nu = 3: \; r_M < r_c$

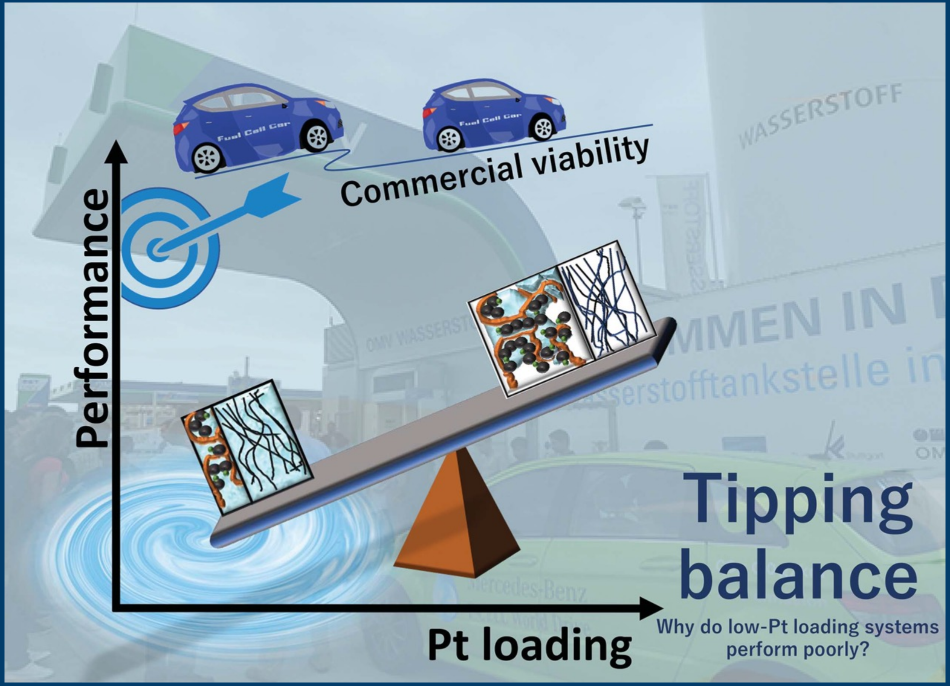
$\dfrac{X_M - X_c}{X_p} < S_r \le 1$



- ❑ important impact: thickness, composition, pore size distribution, wettability
- ❑ **assumption of constant composition sufficient below transition region**

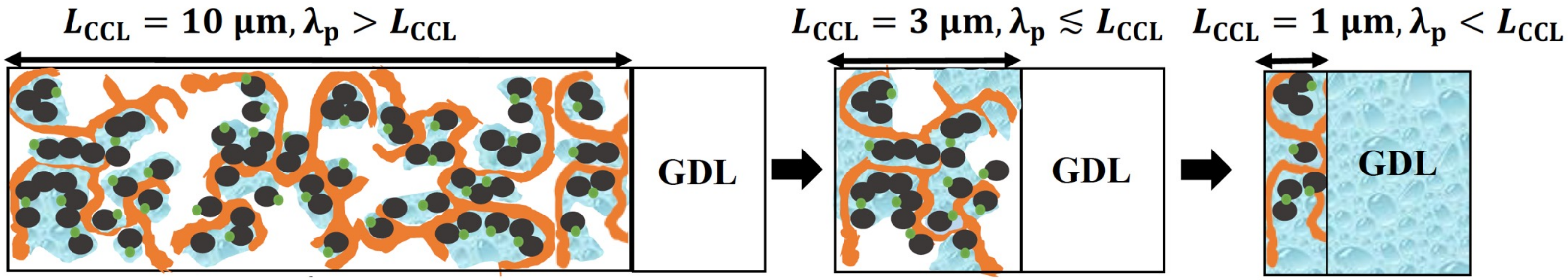
CCL flooding: important, but not critical! A flooded electrode could still perform well.

CCL WITH LOW PT LOADING: WHAT IS TIPPING THEIR PERFORMANCE?

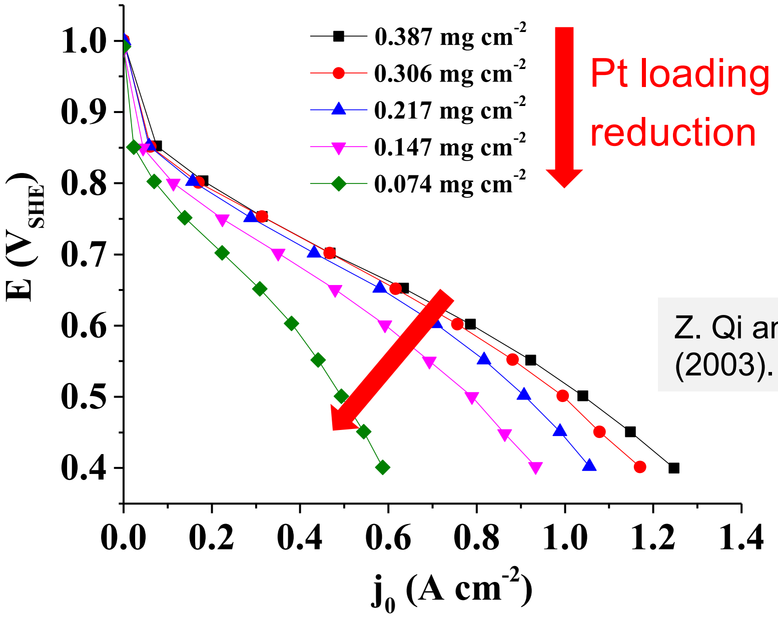


T. Muzaffar *et al*. (2018). Sustainable Energy Fuels 2, 1189-1196.

CATALYST LAYERS WITH REDUCED PT LOADING



13 studies analyzed (1992 to 2016), i.e., fitted with performance model.

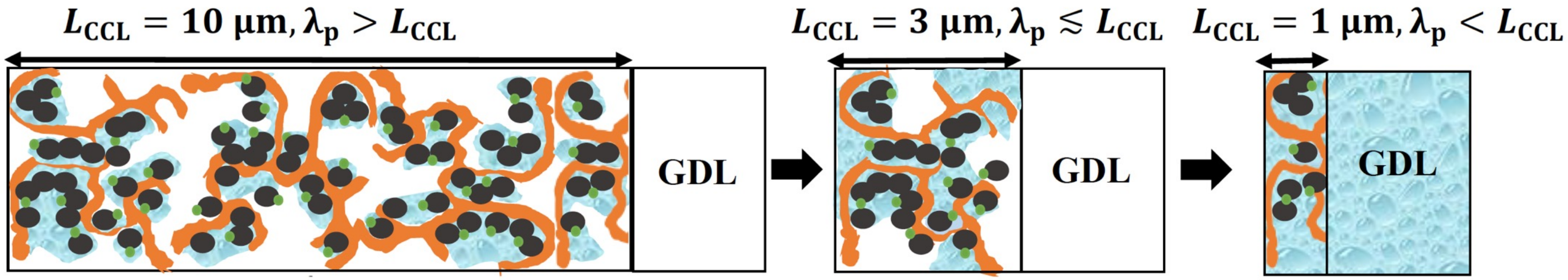


Pt loading reduction

Z. Qi and A Kaufman (2003). JPS 113, 37.

T. Muzaffar *et al*. (2018). Sustainable Energy Fuels 2, 1189-1196.

CATALYST LAYERS WITH REDUCED PT LOADING



Thickness reduction (at fixed current density)

➔ increased rate of water production per unit volume

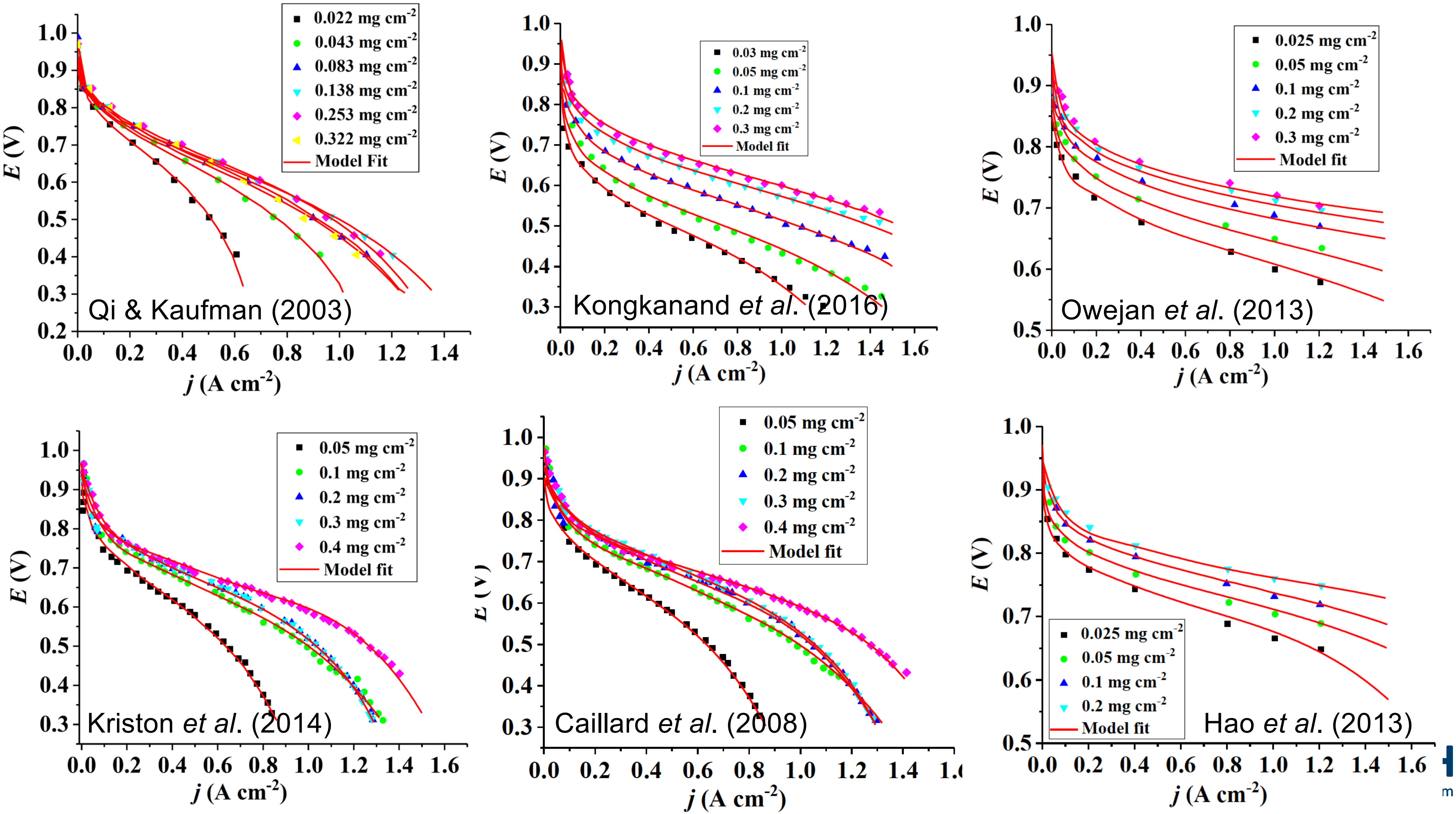
➔ loss of volumetric vaporization capability

➔ larger proportion of liquid water flux from CCL

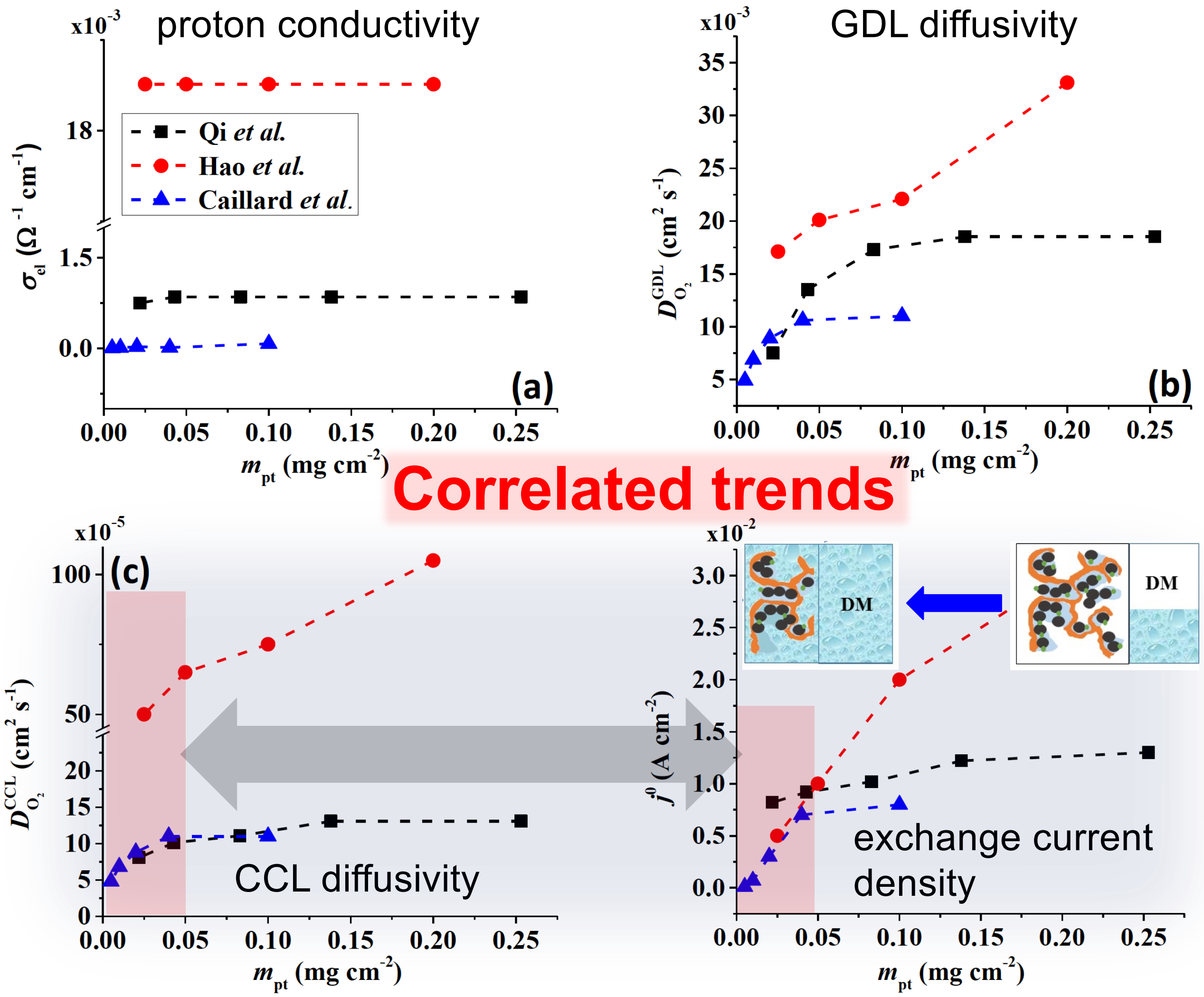
➔ **flooding of GDL**

➔ **oxygen diffusion inhibited**

T. Muzaffar *et al*. (2018). Sustainable Energy Fuels **2**, 1189-1196.


Qi & Kaufman (2003)
0.022 mg cm^{-2}
0.043 mg cm^{-2}
0.083 mg cm^{-2}
0.138 mg cm^{-2}
0.253 mg cm^{-2}
0.322 mg cm^{-2}
Model Fit
E (V)
j (A cm^{-2})
Kongkanand et al. (2016)
0.03 mg cm^{-2}
0.05 mg cm^{-2}
0.1 mg cm^{-2}
0.2 mg cm^{-2}
0.3 mg cm^{-2}
Model fit
E (V)
j (A cm^{-2})
Owejan et al. (2013)
0.025 mg cm^{-2}
0.05 mg cm^{-2}
0.1 mg cm^{-2}
0.2 mg cm^{-2}
0.3 mg cm^{-2}
Model fit
E (V)
j (A cm^{-2})
Kriston et al. (2014)
0.05 mg cm^{-2}
0.1 mg cm^{-2}
0.2 mg cm^{-2}
0.3 mg cm^{-2}
0.4 mg cm^{-2}
Model fit
E (V)
j (A cm^{-2})
Caillard et al. (2008)
0.05 mg cm^{-2}
0.1 mg cm^{-2}
0.2 mg cm^{-2}
0.3 mg cm^{-2}
0.4 mg cm^{-2}
Model fit
E (V)
j (A cm^{-2})
Hao et al. (2013)
0.025 mg cm^{-2}
0.05 mg cm^{-2}
0.1 mg cm^{-2}
0.2 mg cm^{-2}
Model fit
E (V)
j (A cm^{-2})

VARIATION OF PROPERTIES WITH PT LOADING


proton conductivity

GDL diffusivity

Correlated trends

CCL diffusivity

exchange current density

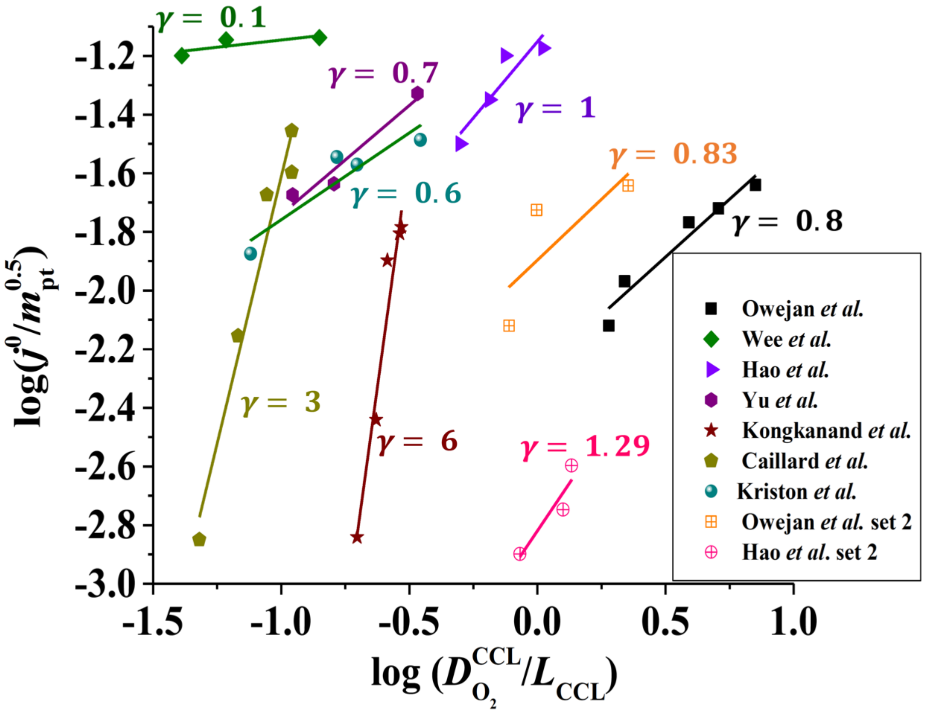
ionomer-based CCLs should not be too thin → “forbidden” thickness range

T. Muzaffar *et al*. (2018). Sustainable Energy Fuels **2**, 1189-1196.

VARIATION OF PROPERTIES WITH PT LOADING

Correlation analysis based on porous electrode theory

$$\boxed{j^0_{\text{eff}} = \frac{2\left(m_{\text{Pt}}\, j^0_*\, \delta\right)^{1/2}}{j_0}\left(\frac{4Fp^0_{\text{O}_2}}{RT}\right)^{\gamma}\left(\frac{D^{\text{CCL}}_{\text{O}_2}}{L_{\text{CCL}}}\right)^{\gamma}}$$



Well-designed layer:

$0 \le \gamma \le 0.5$

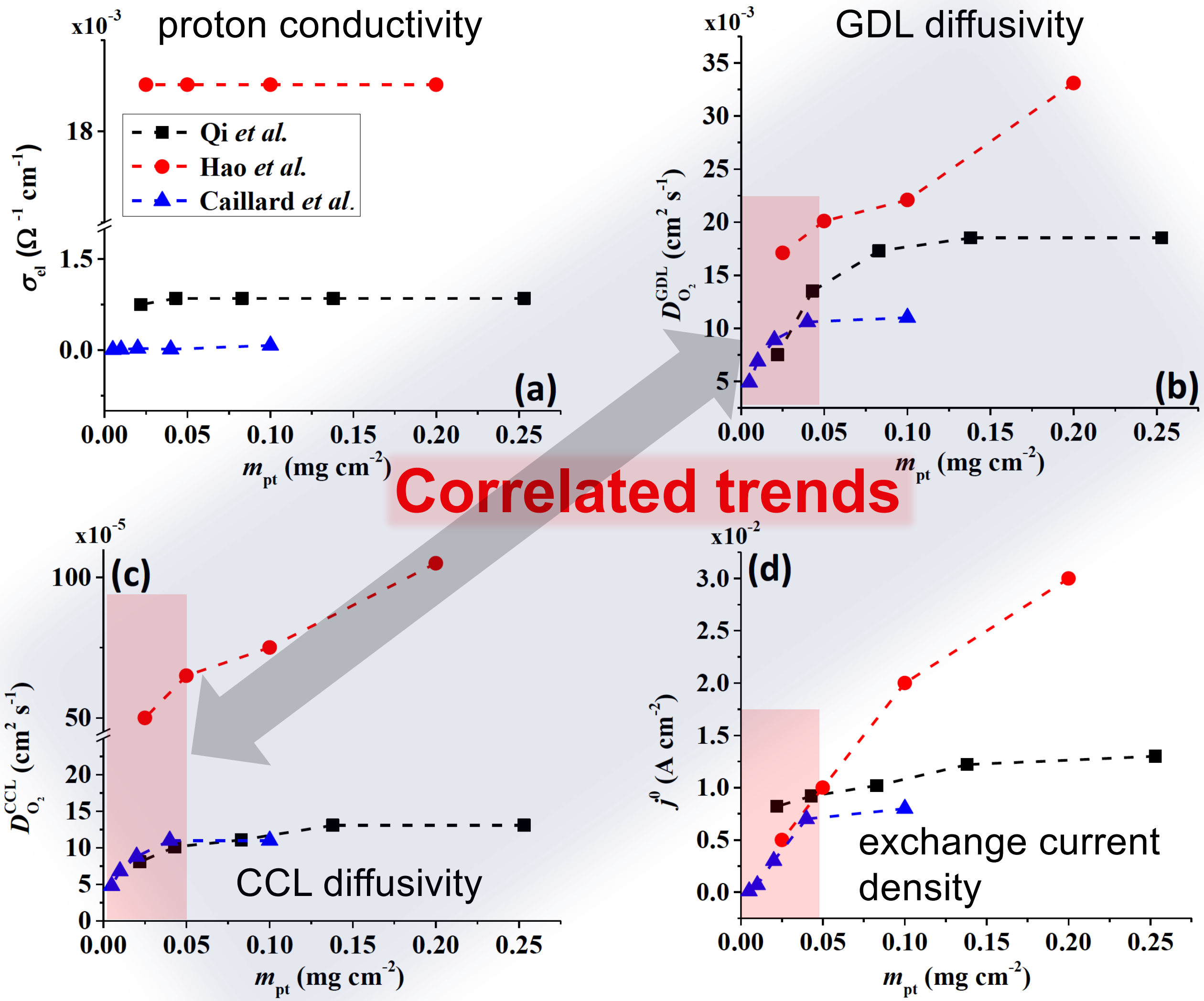
ideal utilization

power performance

T. Muzaffar *et al*. (2018). Sustainable Energy Fuels **2**, 1189-1196.

VARIATION OF PROPERTIES WITH PT LOADING

CCL flooding triggers GDL flooding → origin of dramatic decline in performance?



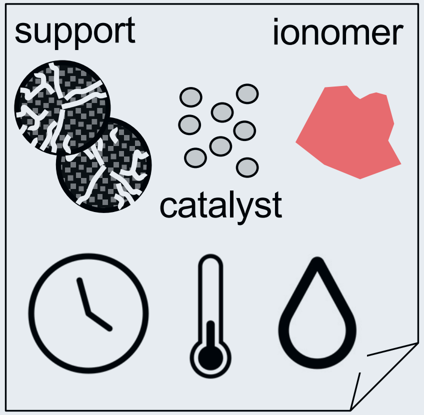
T. Muzaffar *et al*. (2018). Sustainable Energy Fuels **2**, 1189-1196.

MODELING MICROSTRUCTURE FORMATION AND WETTABILITY EFFECTS IN CCL

MODELING MICROSTRUCTURE FORMATION IN CCL

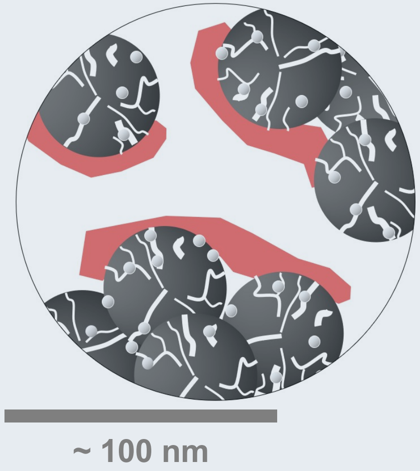
Prediction of volumetric composition and ionomer film thickness and coverage based on ink recipe

Ink recipe & fab conditions

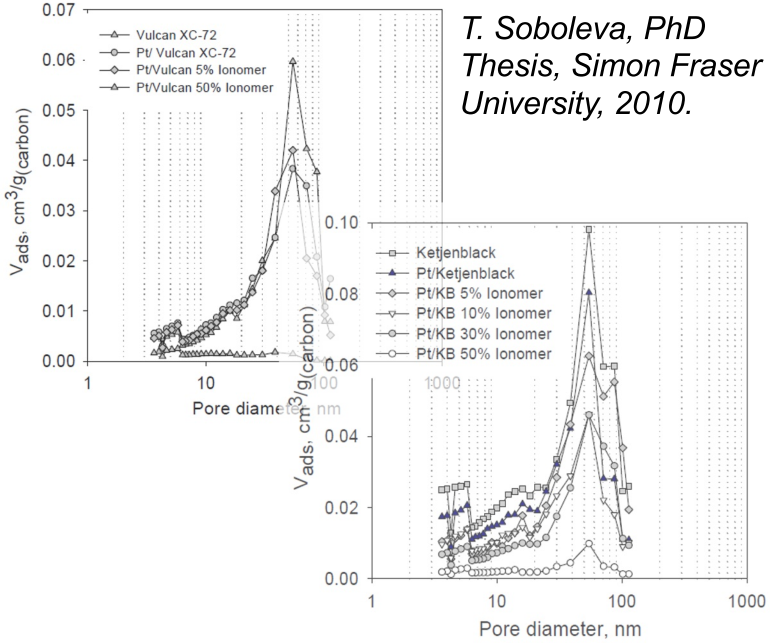


- ☐ ink composition (Pt:C, I:C)
- ☐ specific materials properties (support, catalyst, ionomer)
- ☐ dispersion medium
- ☐ fabrication conditions

CCL structure



- ☐ volume fractions (percolation)
- ☐ pore size distributions
- ☐ interface areas and properties
- ☐ wettability (distribution)
- ☐ ECSA, activity, and transport parameters



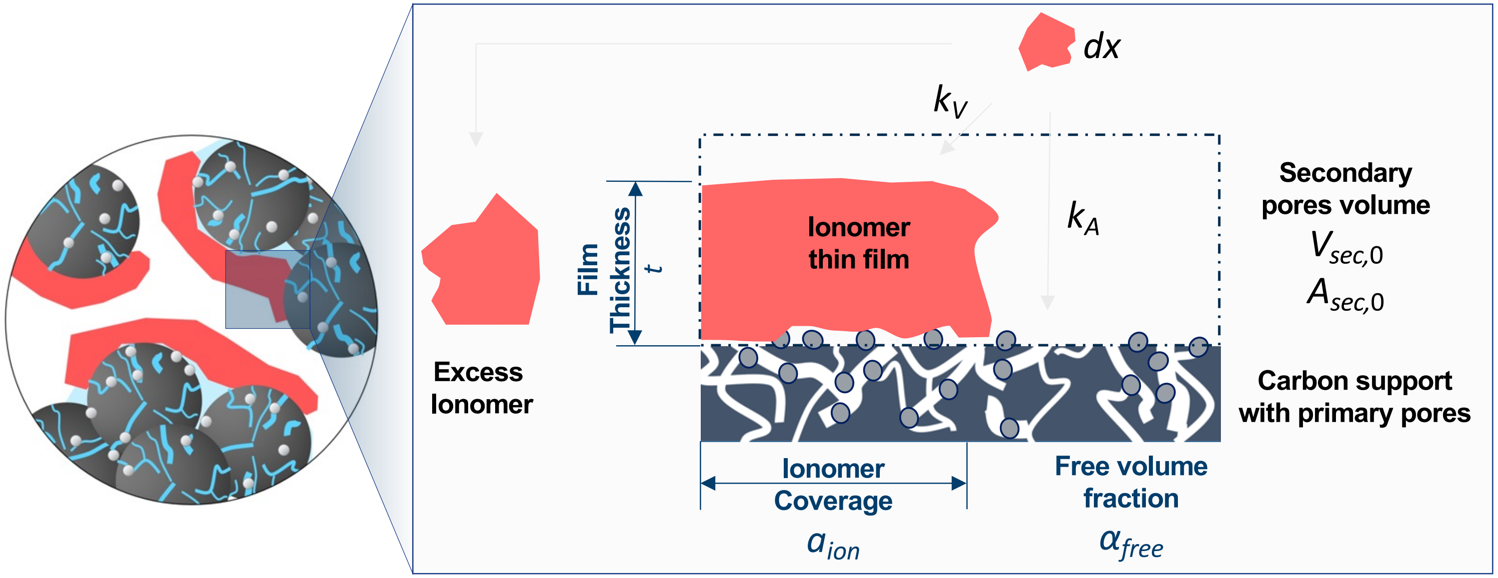
T. Soboleva, PhD Thesis, Simon Fraser University, 2010.

Example: evolution of pore size distribution and porosity

MODELING MICROSTRUCTURE FORMATION IN CCL

Prediction of volumetric composition and ionomer film thickness and coverage based on ink recipe

Model: Piecewise self-assembly of ionomer and carbon support during fabrication



$$x = \frac{V_{ion}}{V_{sec,0}}$$

$$d\alpha_{free} = -\alpha_{free} k_V dx$$

$$da_{Ion.} = (1 - a_{Ion.}) k_A dx$$

$$\alpha_{free} = \exp(-k_V x)$$

$$a_{Ion.} = 1 - \exp(-k_A x)$$

$$t = \frac{V_{sec,0}}{A_{sec,0}} \frac{1 - \exp(-k_V\, x)}{1 - \exp(-k_A\, x)}$$

$$V_{ex} = V_{sec,0}(x - \exp(-k_V x))$$

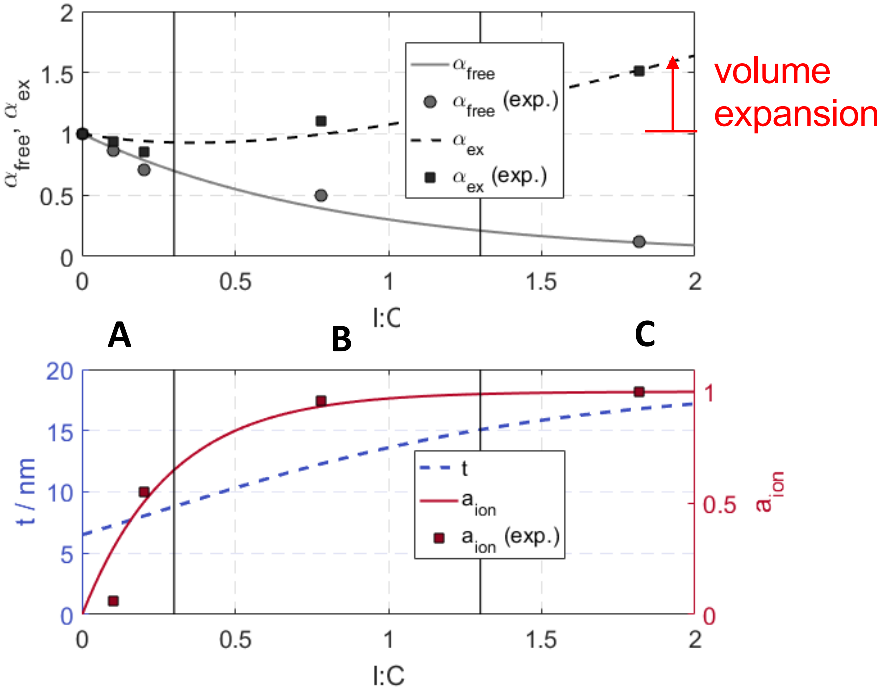
$$k_V = \frac{t_0\, A_{sec,0}}{V_{sec,0}} k_A$$

Key parameter: ionomer dispersion parameter, k_A

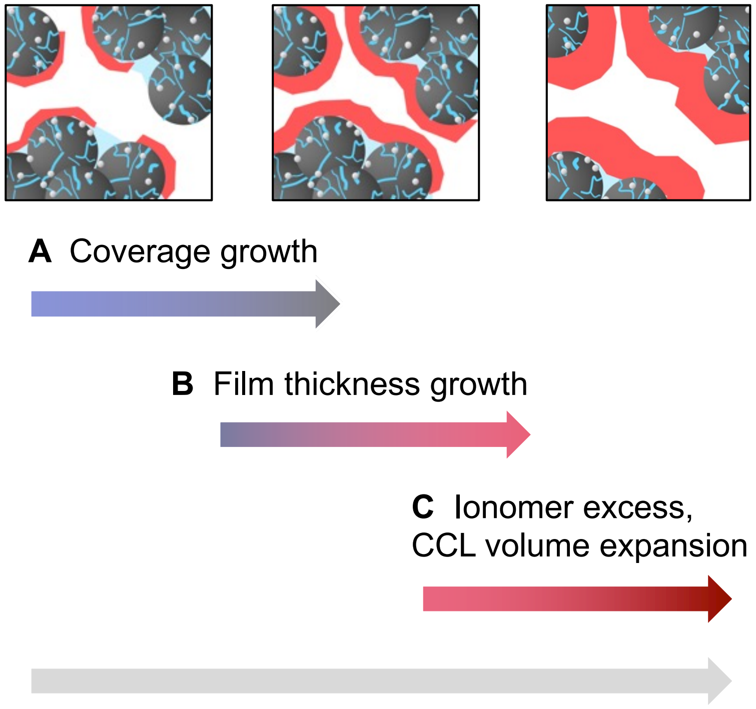
W. Olbrich *et al.*, Electrochim. Acta, under review.

MICROSTRUCTURE FORMATION MODEL: RESULTS

Basic correlations of ink parameters with CCL structure



Exp. data: T. Soboleva., PhD thesis, Simon Fraser University, 2010.



A Coverage growth

B Film thickness growth

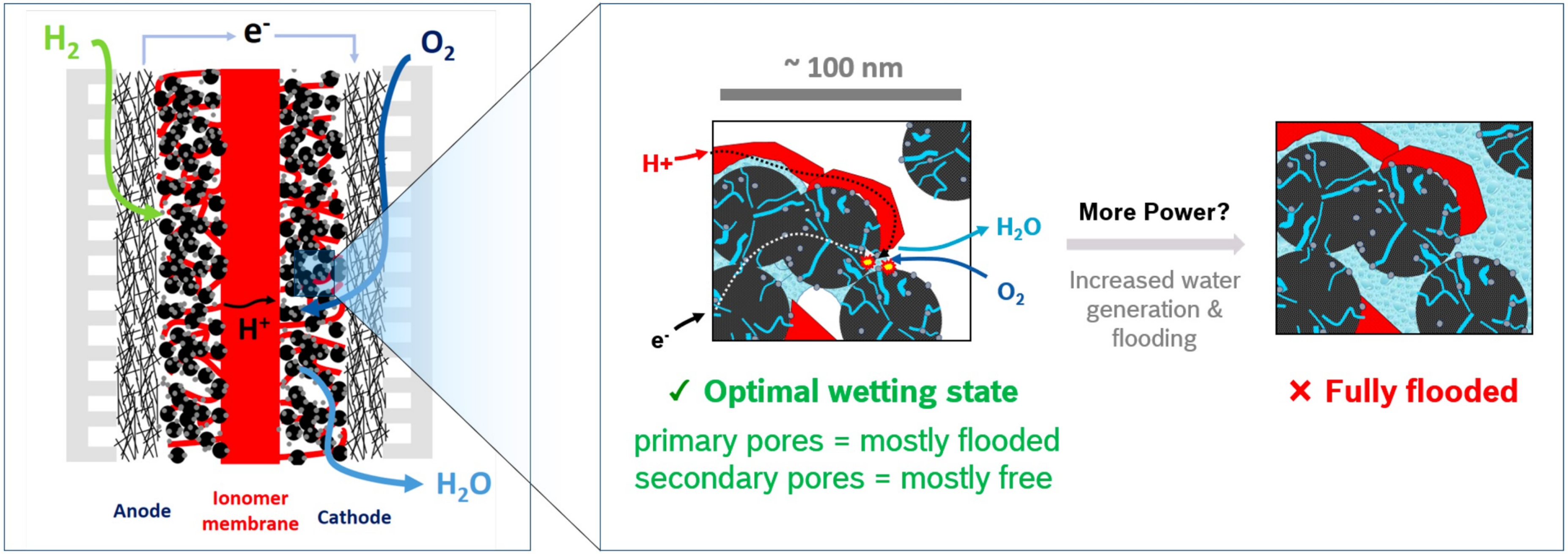
C Ionomer excess,
CCL volume expansion

I:C

W. Olbrich *et al.*, Electrochim. Acta, under review.

MODELING THE WETTABILITY DISTRIBUTION IN CCL

Water and flooding play a crucial role for CCL operation, especially at high current density



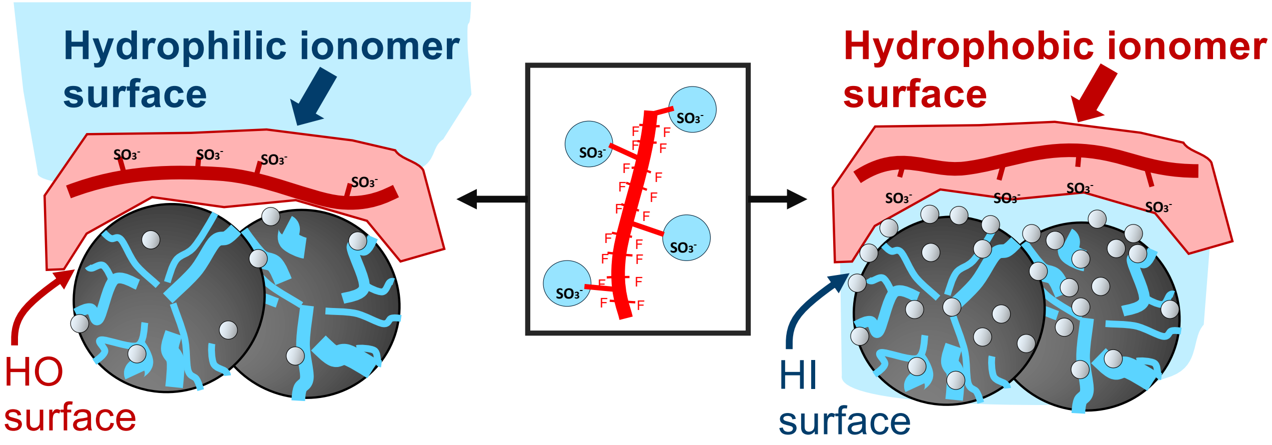
✓ **Optimal wetting state**

primary pores = mostly flooded
secondary pores = mostly free

✗ **Fully flooded**

WETTABILITY MODEL: ROLE OF IONOMER

Orientation of ionomer sidechains is the key (surface-induced ionomer inversion effect)



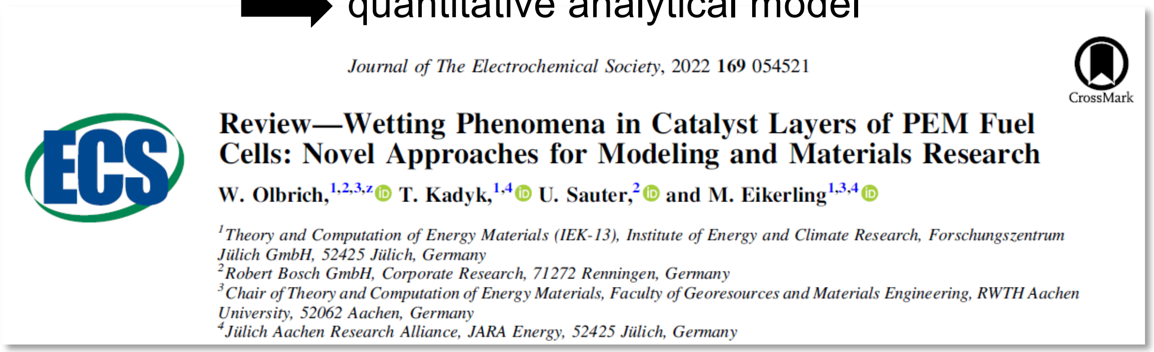
Hydrophilic ionomer surface

HO surface

Hydrophobic ionomer surface

HI surface

➡ quantitative analytical model



Journal of The Electrochemical Society, 2022 **169** 054521

CrossMark

Review—Wetting Phenomena in Catalyst Layers of PEM Fuel Cells: Novel Approaches for Modeling and Materials Research

W. Olbrich,[1,2,3,z] T. Kadyk,[1,4] U. Sauter,[2] and M. Eikerling[1,3,4]

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[3] *Chair of Theory and Computation of Energy Materials, Faculty of Georesources and Materials Engineering, RWTH Aachen University, 52062 Aachen, Germany*
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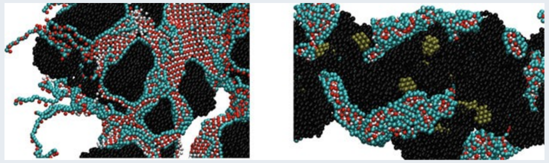
Ionomer inversion

☐ earlier MD simulations

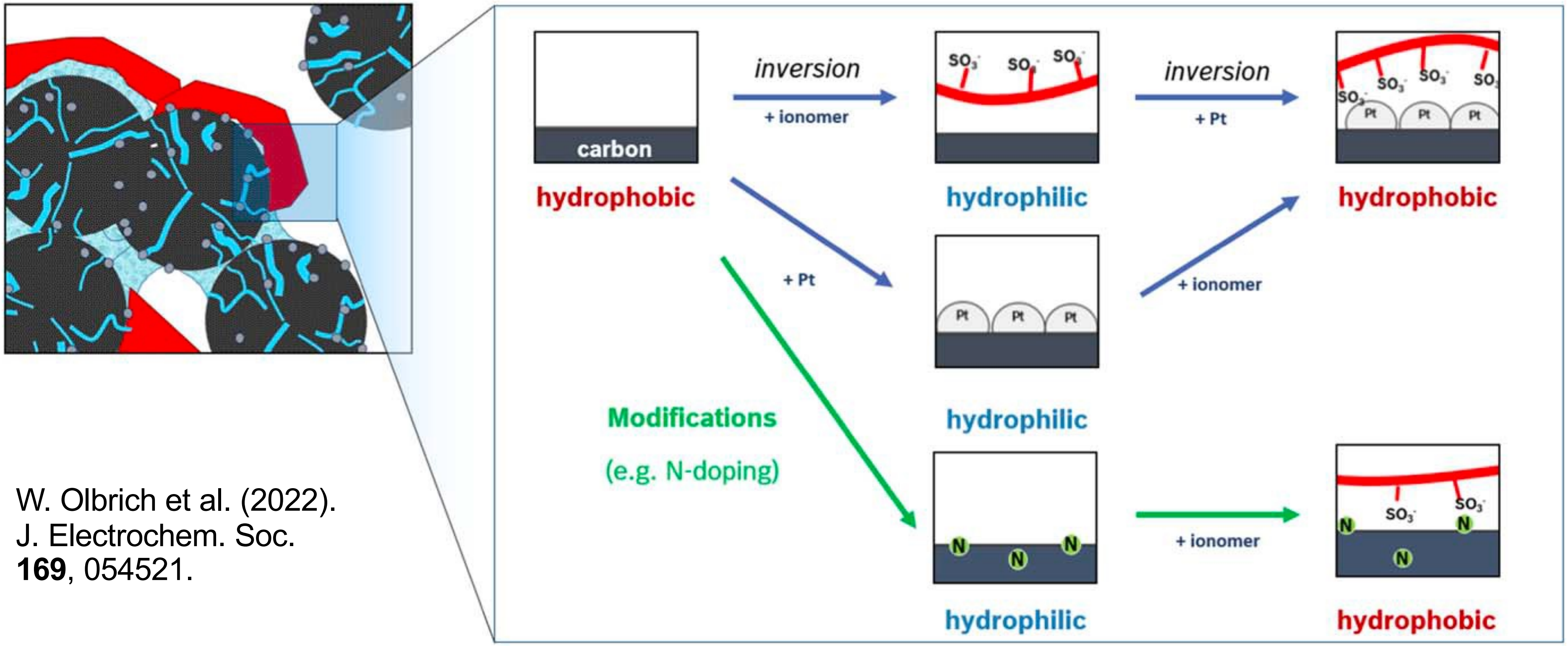


K. Malek *et al*. (2011). Electrocatalysis **2**, 141-157.

☐ experimental studies

Yu. M. Vol'fkovich *et al*. (2010). Russ. J. Electrochem. **438**, 46.

INVERSION MECHANISM BASED ON VOL’FKOVICH DATA

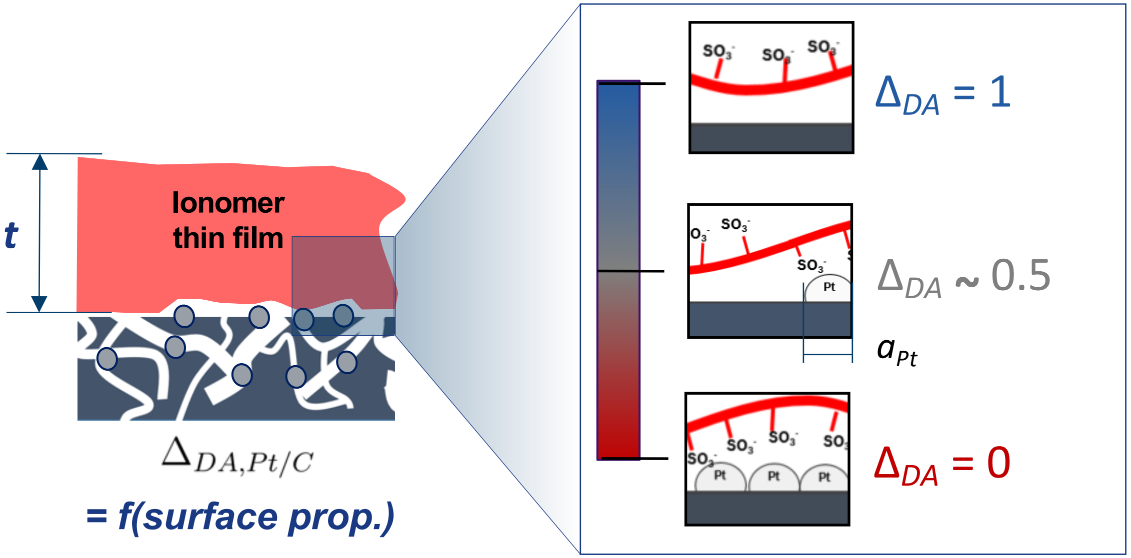


W. Olbrich et al. (2022).
J. Electrochem. Soc.
169, 054521.

WETTABILITY MODEL

Alignment of ionomer sidechains

- ☐ preferential ionomer sidechain orientation alters wettability in secondary pore space
- ☐ depends on chemical nature of surface and interaction with ionomer constituents
- ☐ Pt particles: help align sidechains towards support surface



$\Delta_{DA,Pt/C}$

= *f(surface prop.)*

Definition: degree of alignment, Δ_{DA},

$$\Delta_{DA} = 1 \Leftrightarrow \theta_{HI} = 30^\circ$$

$$\Delta_{DA} = 0 \Leftrightarrow \theta_{HO} = 120^\circ$$

$$\Delta_{DA,\infty} \sim 1/3 \Leftrightarrow \theta_\infty \sim 90^\circ$$

$$\Delta_{DA_{Pt/C}} = \Delta_{DA_C}(1 - a_{pt}) + \Delta_{DA_{Pt}} a_{pt}$$

$$\Delta_{DA}(t) = \Delta_{DA,\infty} + (\Delta_{DA,Pt/C} - \Delta_{DA,\infty}) \exp(1 - \frac{t}{t_0})$$

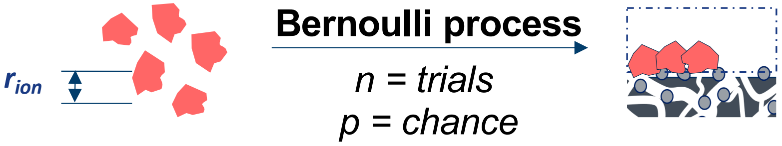
$$\cos(\theta_{ion}) = \Delta_{DA}(\cos(\theta_{HI}) - \cos(\theta_{HO})) + \cos(\theta_{HO})$$

$$\cos(\theta_{sec}) = a_{ion} \cos(\theta_{ion}) + (1 - a_{ion}) \cos(\theta_{Pt/C})$$

W. Olbrich *et al.*, Electrochim. Acta, under review.

WETTABILITY MODEL

Stochastic process to generate heterogeneously wetted surfaces



- ☐ ionomer (chunks of fixed size, $r_{ion} \sim 5$ nm) distributed randomly
- ☐ normal distributions based on mean and variance of (n,p)

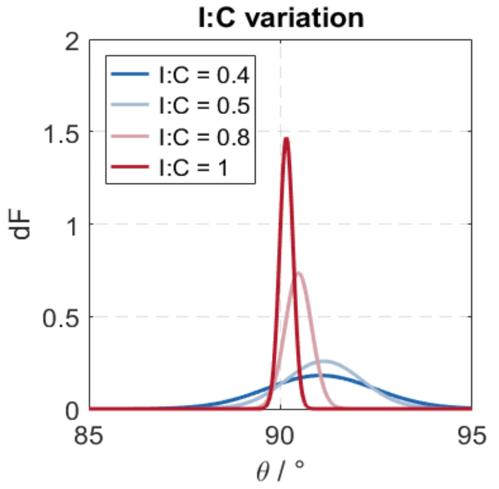
binomial process:

$$p = a_{ion}$$

$$n = k_{max} = \frac{A_{pore}}{A_{ion}} = f(r_{pore}^2)$$

$$n \gg 1$$

$$\mu_k = k_{max} a_{ion} \ , \ \sigma_k^2 = k_{max} a_{ion} (1 - a_{ion})$$



Origin of mixed wettability!

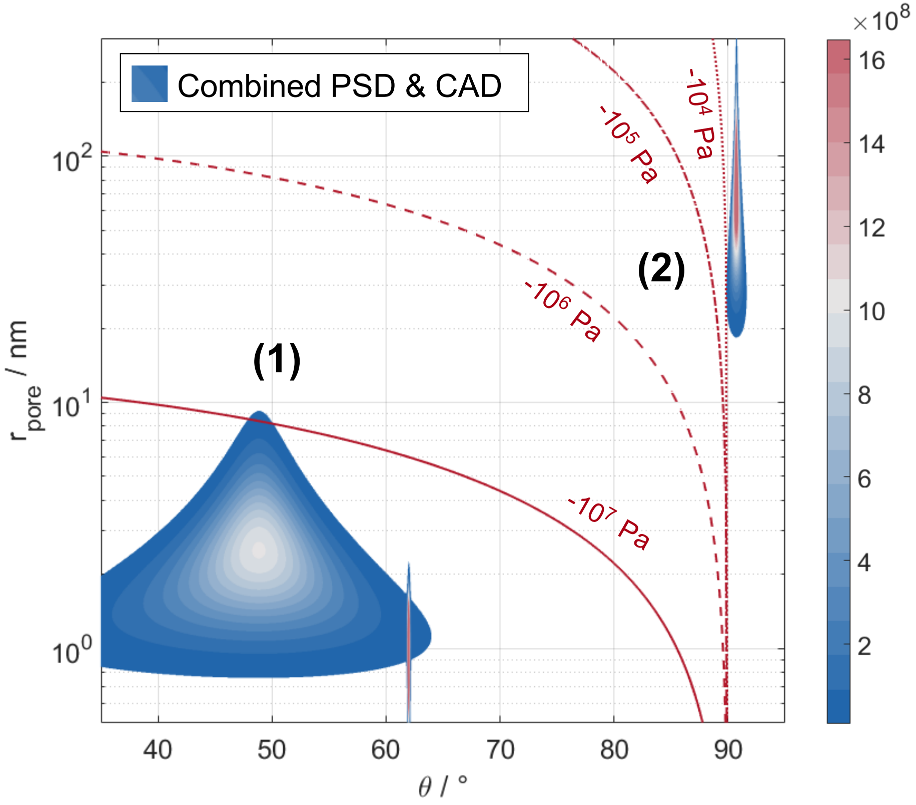
Obtain water retention curve by integration over pore size distribution (PSD), contact angle distribution (CAD) and Young-Laplace criterion (YLP):

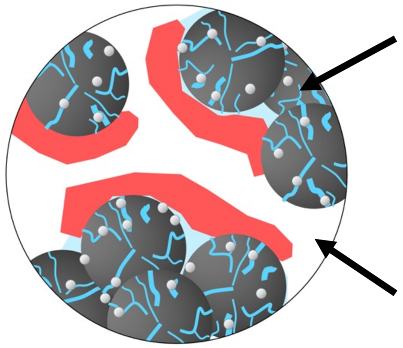
$$S(p_C) = \int_{r_{min}}^{r_{max}} \int_{-1}^{1} PSD(r) \cdot CAD(r, \cos(\theta)) \cdot YLP(r, \cos(\theta), p_C) \, d\cos(\theta) \, dr$$

W. Olbrich *et al.*, Electrochim. Acta, under review.

WETTABILITY MODEL: RESULTS

Pore size and contact angle distribution

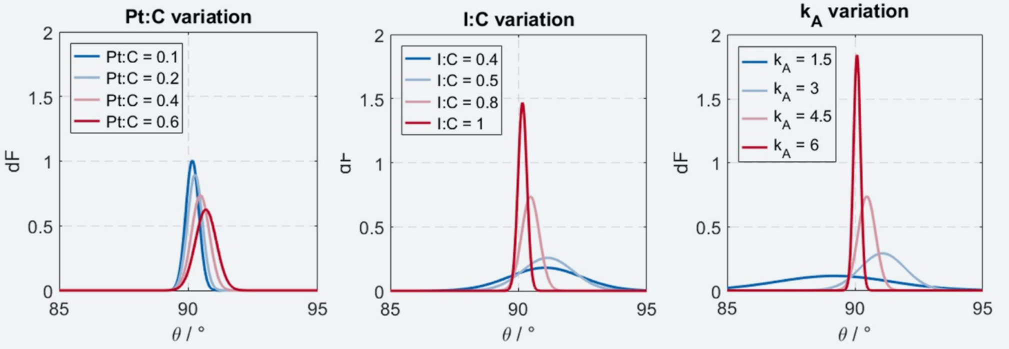




(1) Hydrophilic primary pores and Pt-free nanopores

(2) Secondary pores with mixed wettability

Contact angle distribution (secondary pores)



Pt content

ionomer content

dispersion param

W. Olbrich *et al.*, Electrochim. Acta, under review.

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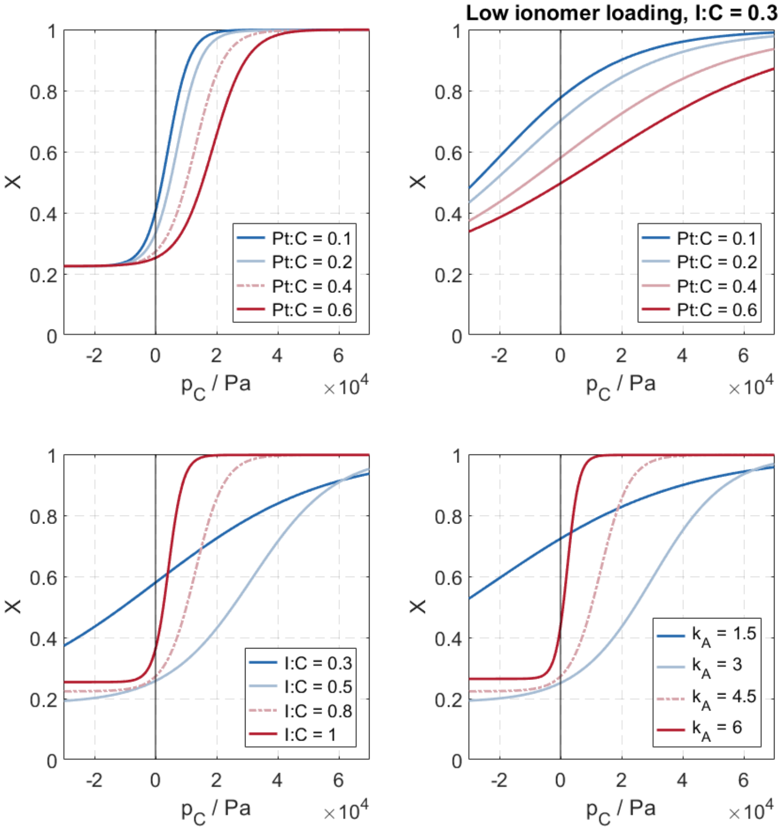
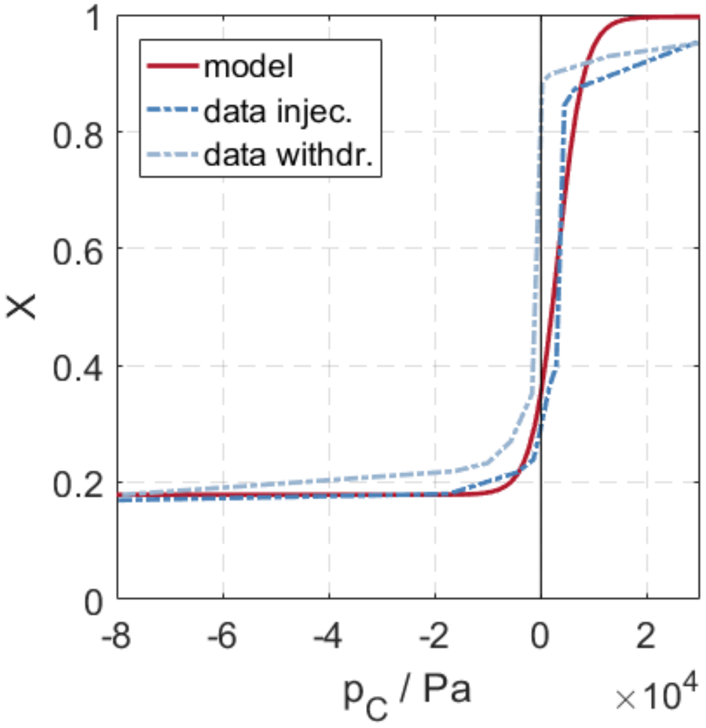
WETTABILITY MODEL: WATER RETENTION CURVES

Parametric effects



Comparison to experiment

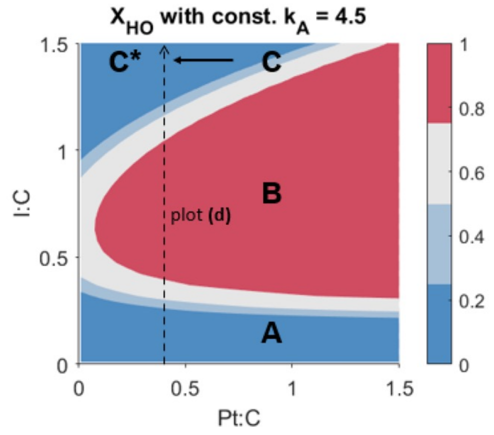


H. P. F. Gunterman, PhD thesis, UC Berkeley, 2011.

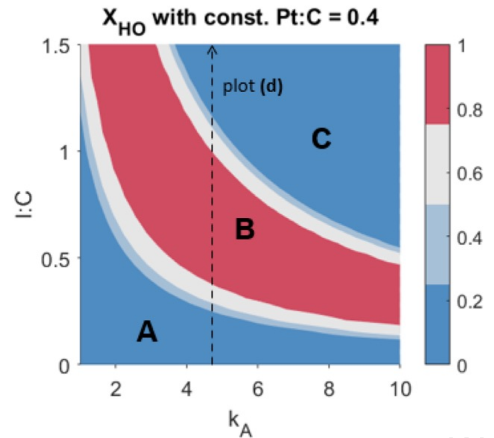
W. Olbrich *et al.*, Electrochim. Acta, under review.

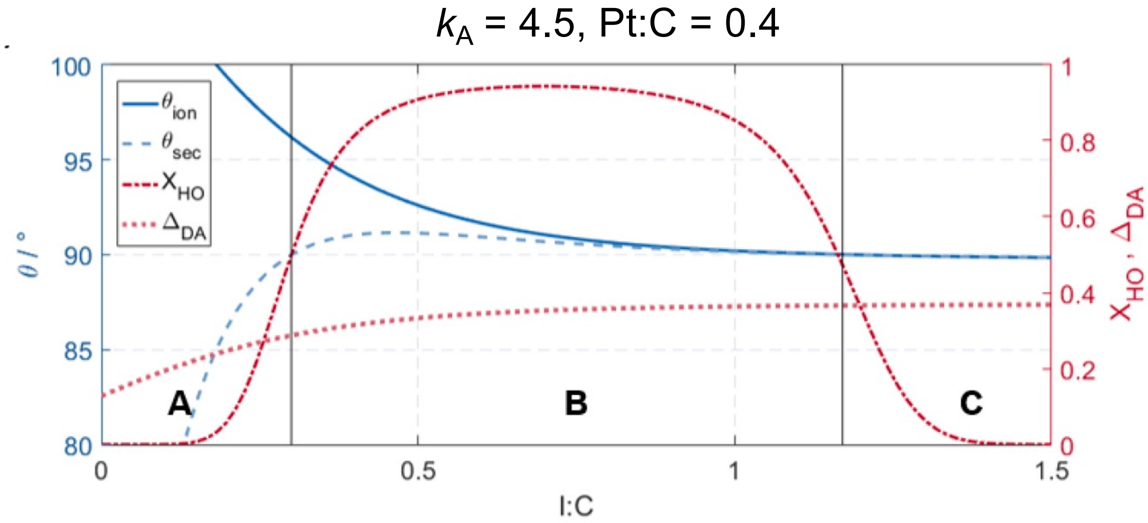
WETTABILITY MODEL: CCL OPTIMIZATION

Materials selection, modification, and design: tune parameters for optimal wettability distribution


X_{HO} with const. k_A = 4.5

fraction of hydrophobic secondary pore volume


X_{HO} with const. Pt:C = 0.4


k_A = 4.5, Pt:C = 0.4

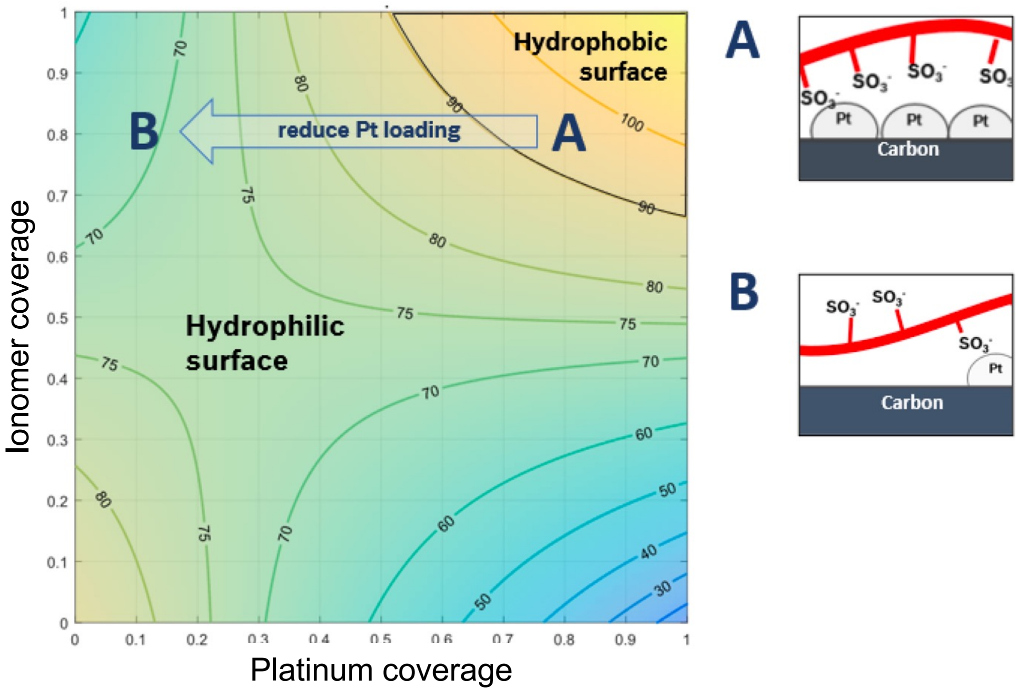
- reducing Pt loading can tip the water balance (as seen earlier)
- lower Pt loading: ionomer content must be more finely tuned
- support modification: less sensitive to Pt and ionomer loading

W. Olbrich *et al.*, Electrochim. Acta, under review.

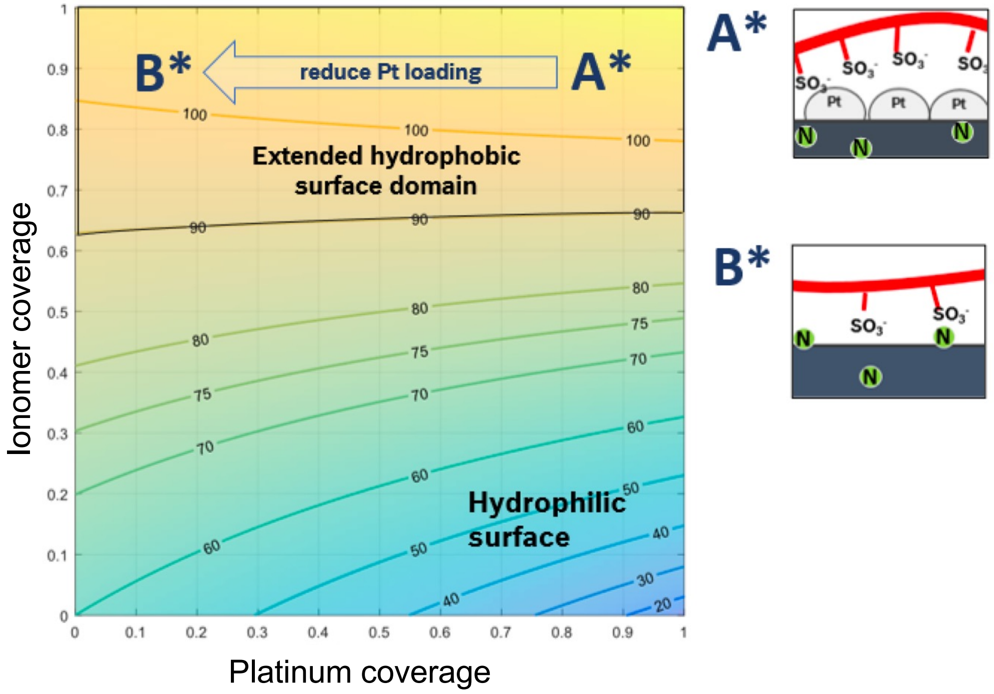
WETTABILITY MODEL: SUPPORT MODIFICATION

Effective contact angle of Pt/C/ionomer composite

conventional carbon support



functionalized carbon support

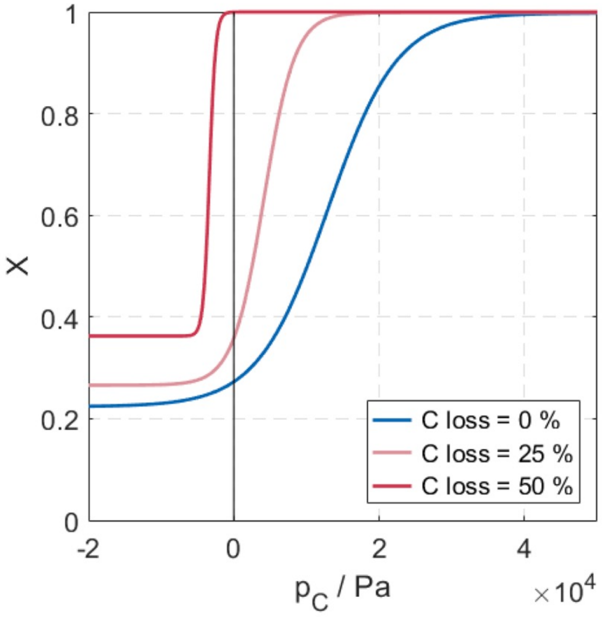


W. Olbrich et al. (2022). J. Electrochem. Soc. **169**, 054521.

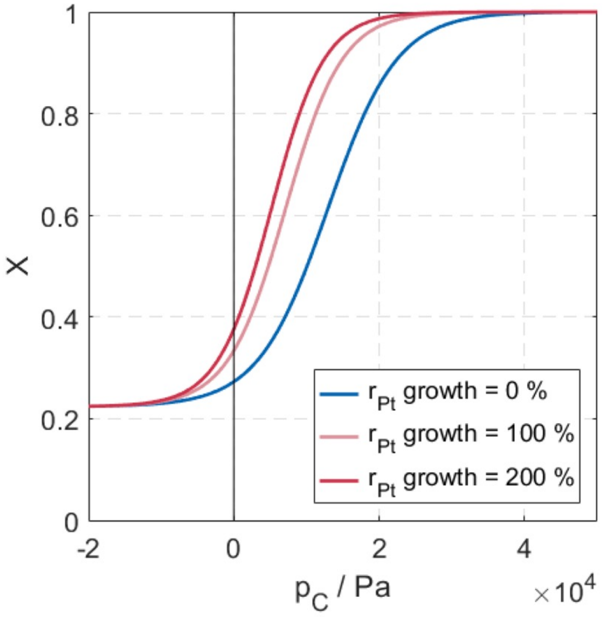
WETTABILITY MODEL: DEGRADATION EFFECTS

Changes in wettability and water retention behaviour during lifetime

carbon corrosion



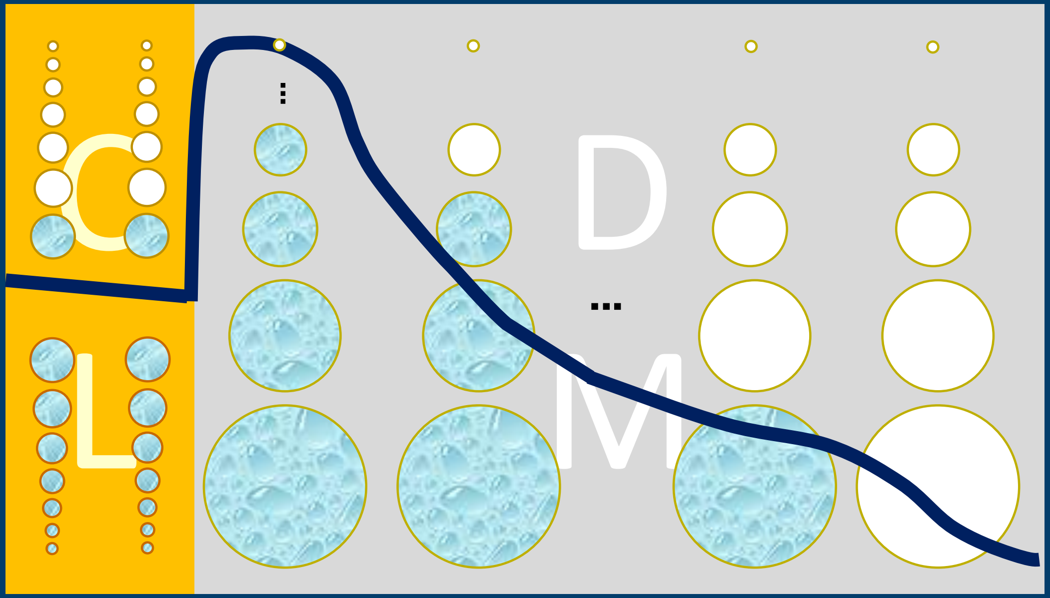
Pt particle growth



Shifting the tipping point

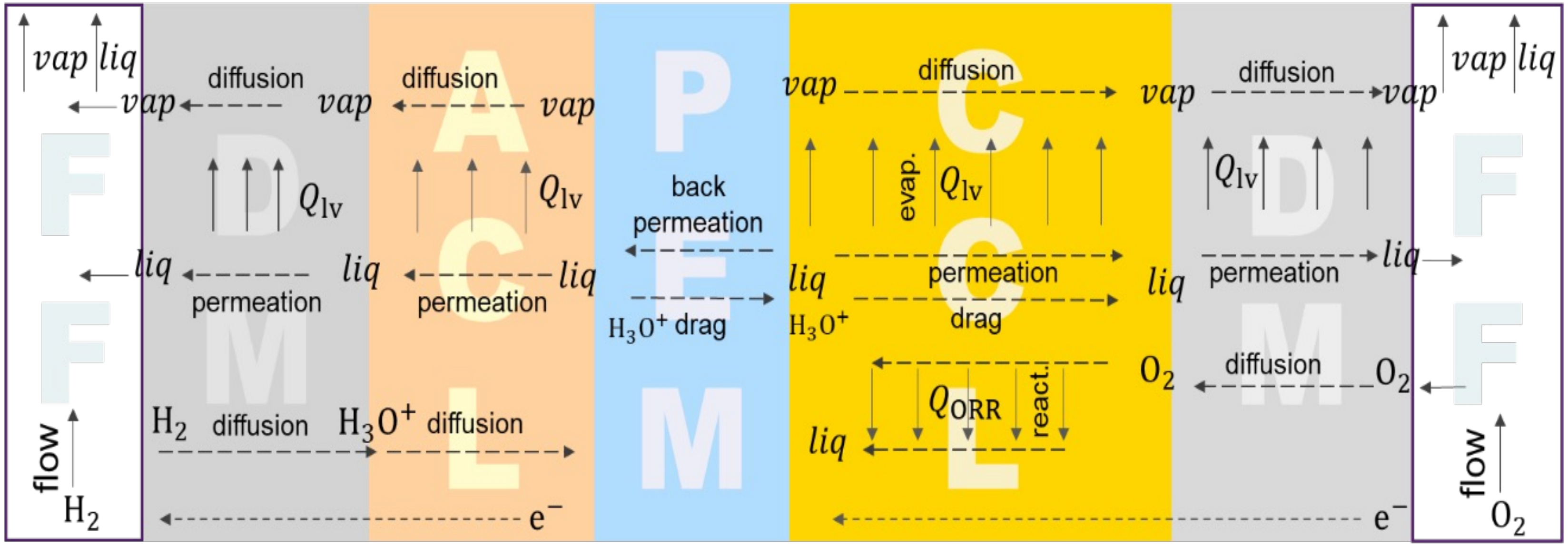
W. Olbrich *et al.*, Electrochim. Acta, under review.

DEVELOPING STORY: MODELING LIQUID WATER ACCUMULATION IN PEM FUEL CELL CATHODE



ACCOUNT FOR CROSS COMPONENT COUPLING

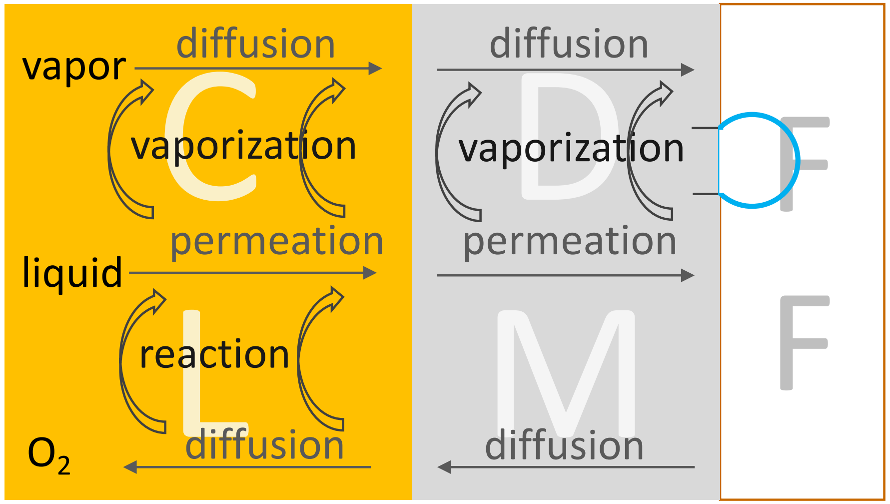
Comprehensive model for water balance in cathode CL and DM



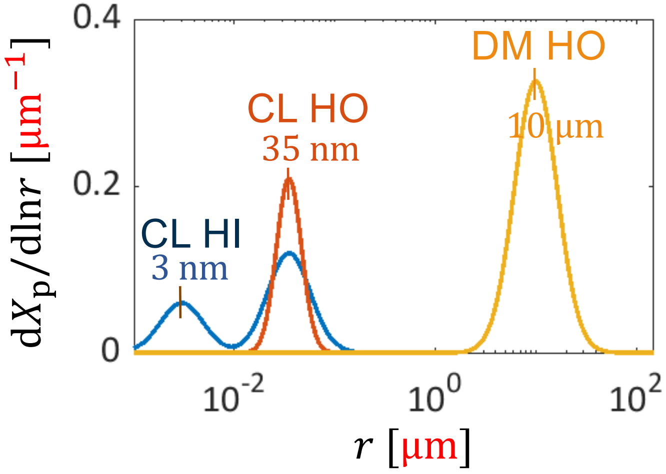
Solution space: pressure distribution → liquid saturation, fluxes

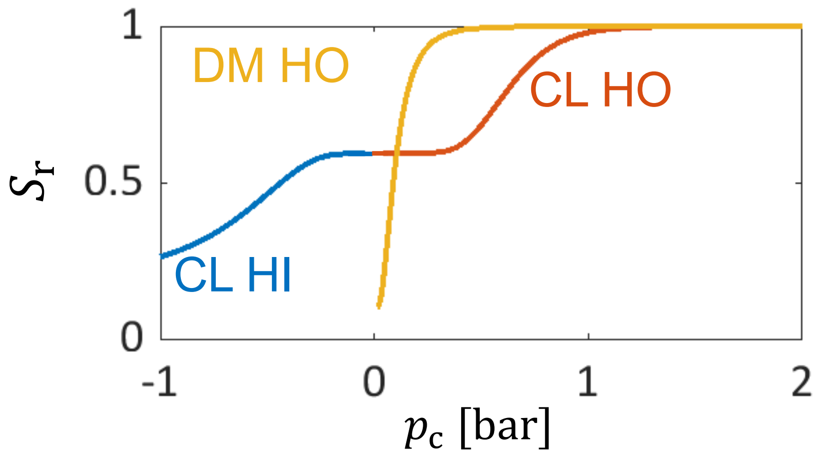
MODEL ASSUMPTIONS

- ☐ cathode side: CL & DM and DM-FF interface
- ☐ transport of oxygen (air), liquid and vapor water
- ☐ one-dimensional
- ☐ macrohomogeneous
- ☐ isothermal



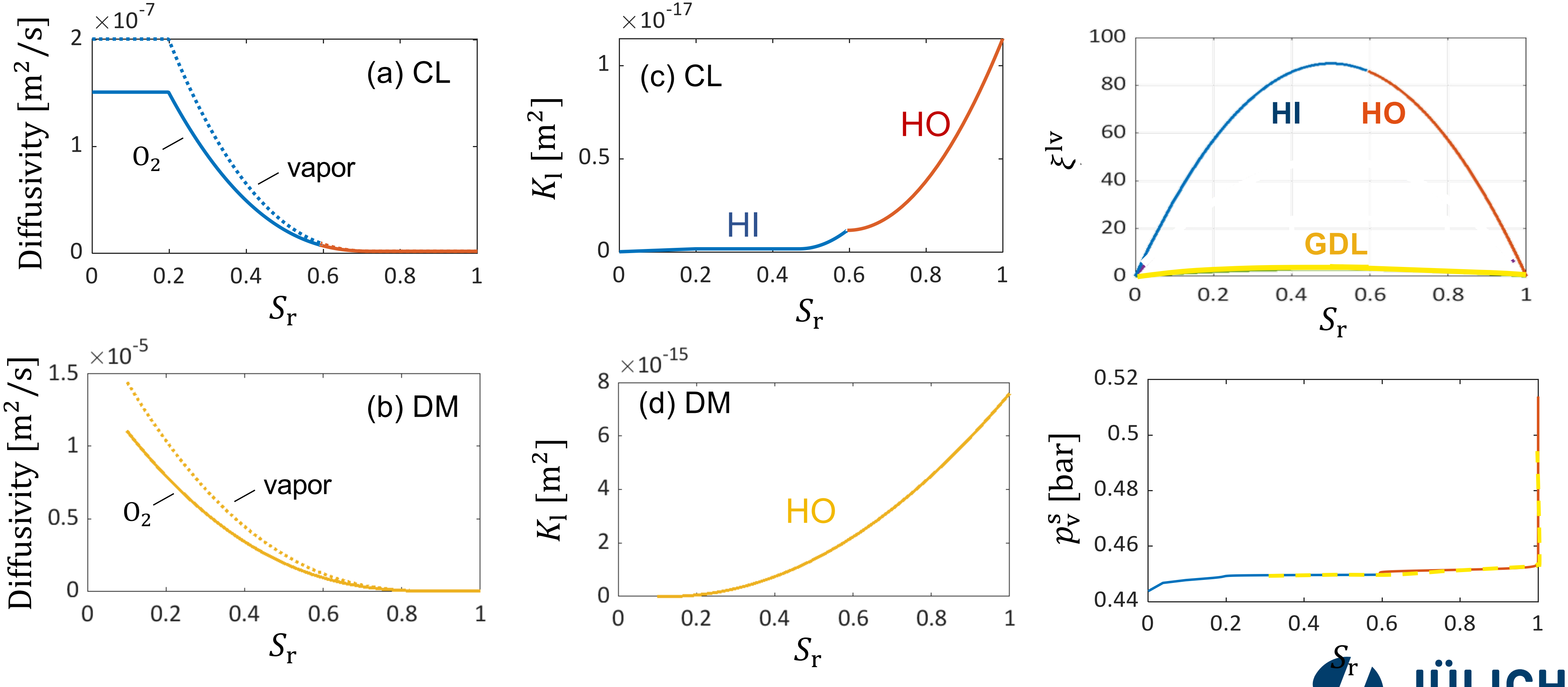
PORE SIZE DISTRIBUTIONS AND WATER RETENTION CURVES





At the same p_c, S_r in **CL** and in **DM** are different.

EFFECTIVE PROPERTIES AS FUCNTION OF LIQUID SAT



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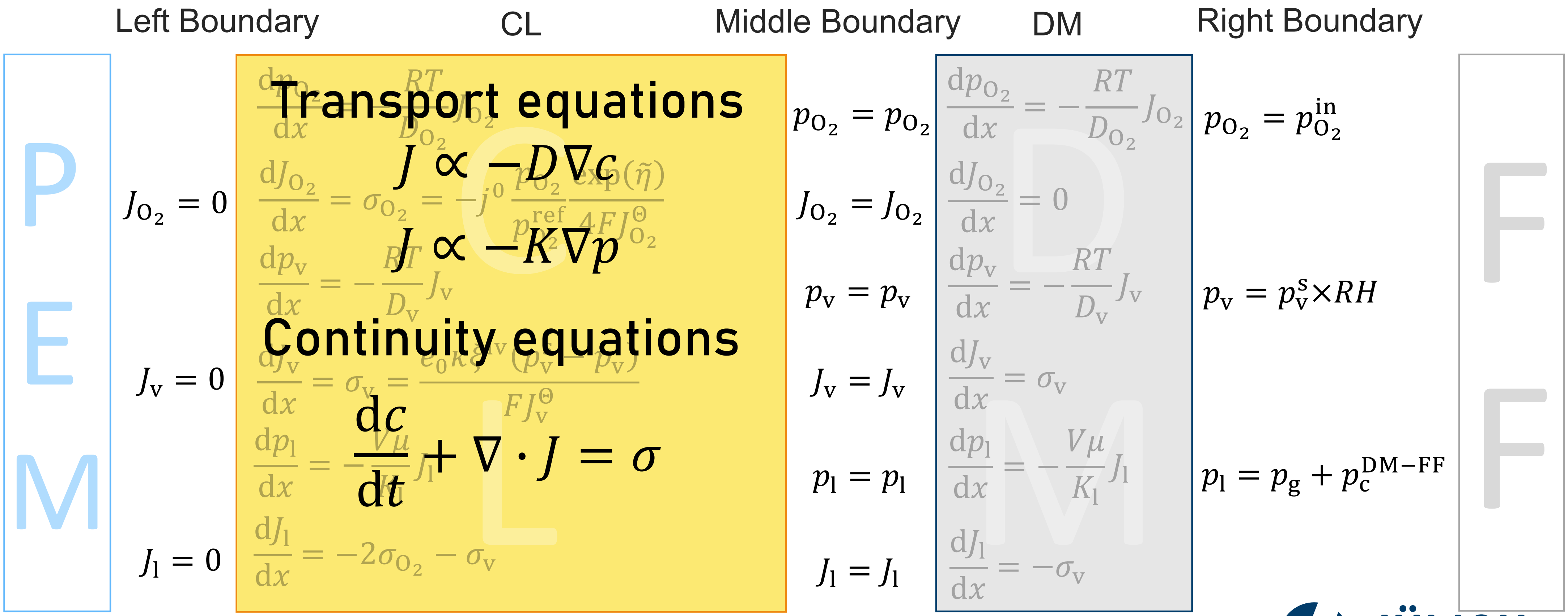
DIFFERENTIAL EQUATIONS AND BOUNDARY CONDITIONS



Left Boundary

$$J_{\mathrm{O_2}} = 0$$
$$J_\mathrm{v} = 0$$
$$J_\mathrm{l} = 0$$

CL

$$\frac{\mathrm{d}p_{\mathrm{O_2}}}{\mathrm{d}x} = -\frac{RT}{D_{\mathrm{O_2}}} J_{\mathrm{O_2}}$$
$$\frac{\mathrm{d}J_{\mathrm{O_2}}}{\mathrm{d}x} = \sigma_{\mathrm{O_2}} = -j^0 \frac{p_{\mathrm{O_2}}}{p_{\mathrm{O_2}}^{\mathrm{ref}}} \frac{\exp(\tilde{\eta})}{4FJ_{\mathrm{O_2}}^{\Theta}}$$
$$\frac{\mathrm{d}p_\mathrm{v}}{\mathrm{d}x} = -\frac{RT}{D_\mathrm{v}} J_\mathrm{v}$$
$$\frac{\mathrm{d}J_\mathrm{v}}{\mathrm{d}x} = \sigma_\mathrm{v} = \frac{e_0 k \xi^{\mathrm{av}} (p_\mathrm{v} - p_\mathrm{v})}{FJ_\mathrm{v}^{\Theta}}$$
$$\frac{\mathrm{d}p_\mathrm{l}}{\mathrm{d}x} = -\frac{V\mu}{K_\mathrm{l}} J_\mathrm{l}$$
$$\frac{\mathrm{d}J_\mathrm{l}}{\mathrm{d}x} = -2\sigma_{\mathrm{O_2}} - \sigma_\mathrm{v}$$

Transport equations

$$J \propto -D\nabla c$$
$$J \propto -K\nabla p$$

Continuity equations

$$\frac{\mathrm{d}c}{\mathrm{d}t} + \nabla \cdot J = \sigma$$

Middle Boundary

$$p_{\mathrm{O_2}} = p_{\mathrm{O_2}}$$
$$J_{\mathrm{O_2}} = J_{\mathrm{O_2}}$$
$$p_\mathrm{v} = p_\mathrm{v}$$
$$J_\mathrm{v} = J_\mathrm{v}$$
$$p_\mathrm{l} = p_\mathrm{l}$$
$$J_\mathrm{l} = J_\mathrm{l}$$

DM

$$\frac{\mathrm{d}p_{\mathrm{O_2}}}{\mathrm{d}x} = -\frac{RT}{D_{\mathrm{O_2}}} J_{\mathrm{O_2}}$$
$$\frac{\mathrm{d}J_{\mathrm{O_2}}}{\mathrm{d}x} = 0$$
$$\frac{\mathrm{d}p_\mathrm{v}}{\mathrm{d}x} = -\frac{RT}{D_\mathrm{v}} J_\mathrm{v}$$
$$\frac{\mathrm{d}J_\mathrm{v}}{\mathrm{d}x} = \sigma_\mathrm{v}$$
$$\frac{\mathrm{d}p_\mathrm{l}}{\mathrm{d}x} = -\frac{V\mu}{K_\mathrm{l}} J_\mathrm{l}$$
$$\frac{\mathrm{d}J_\mathrm{l}}{\mathrm{d}x} = -\sigma_\mathrm{v}$$

Right Boundary

$$p_{\mathrm{O_2}} = p_{\mathrm{O_2}}^{\mathrm{in}}$$
$$p_\mathrm{v} = p_\mathrm{v}^{\mathrm{s}} \times RH$$
$$p_\mathrm{l} = p_\mathrm{g} + p_\mathrm{c}^{\mathrm{DM-FF}}$$

Mitglied der Helmholtz-Gemeinschaft

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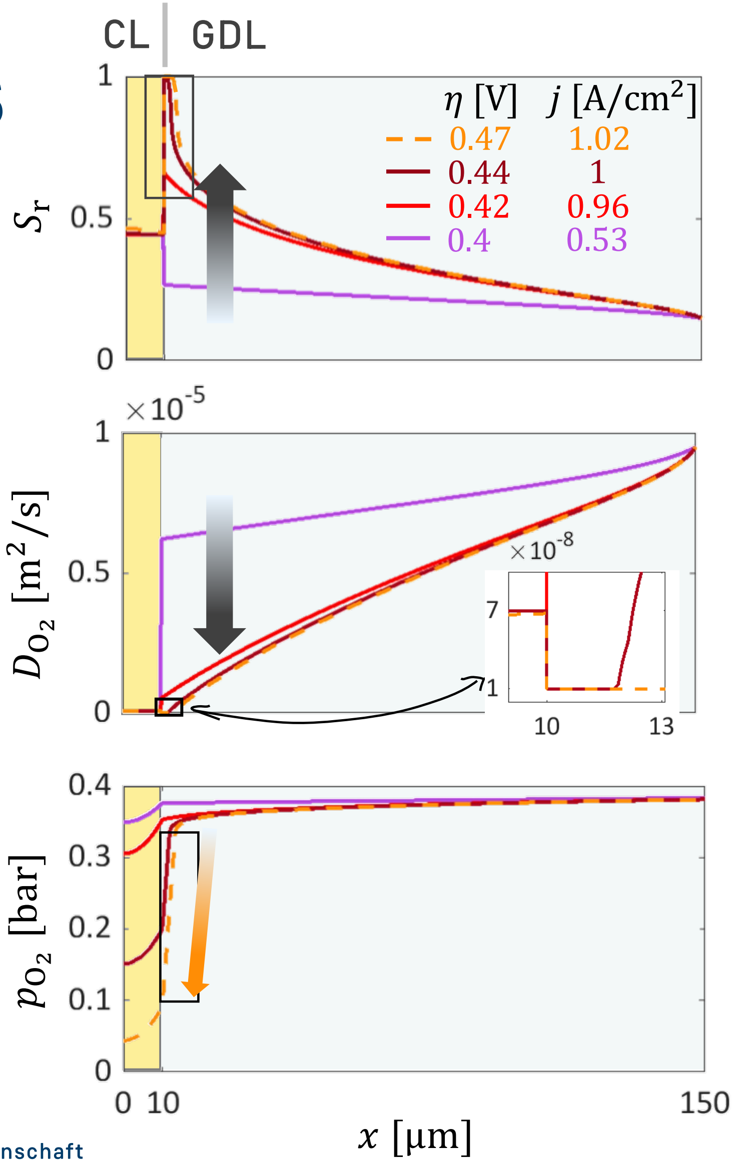
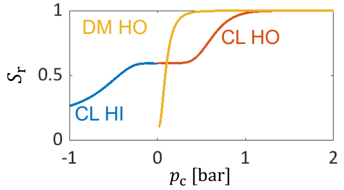
RESULTS



Liquid saturation:

- ☐ does not change much in CCL with j
- ☐ GDL: formation of water layer at CL|GDL above j_c

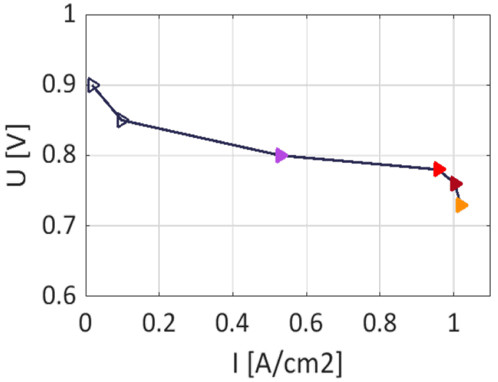


O_2 diffusivity:

- ☐ water layer causes abrupt decrease in diffusivity (to residual value)

O_2 partial pressure:

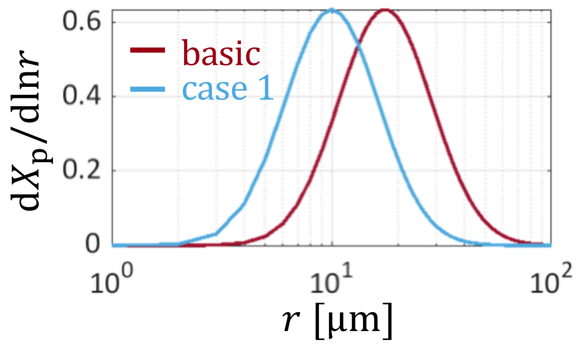
- ☐ drops drastically above j_c before even reaching the CCL

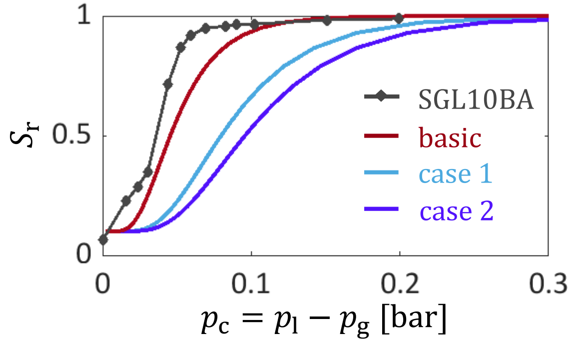


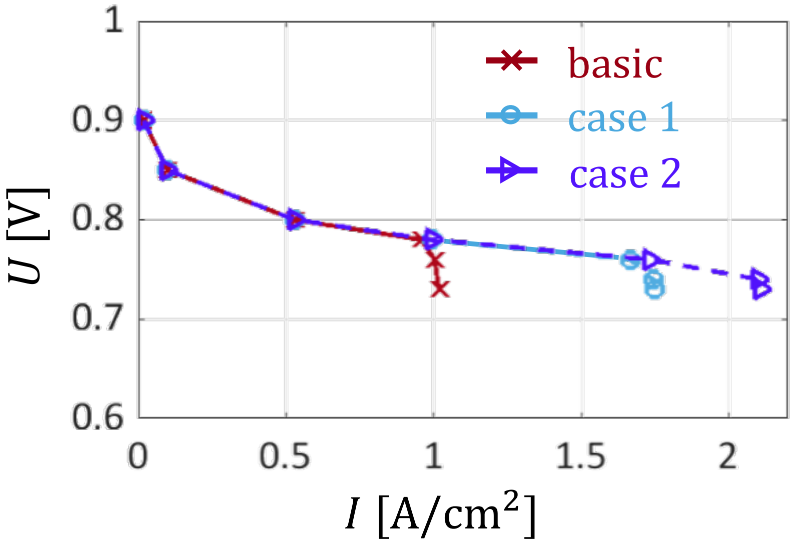
HOW TO SUPPRESS WATER LAYER FORMATION?

Tune the water retention curve: pore size distribution or contact angle

	basic	case 1	case 2
r_{GDL} [µm]	17.5	10	17.5
θ_{GDL} [°]	133	133	145







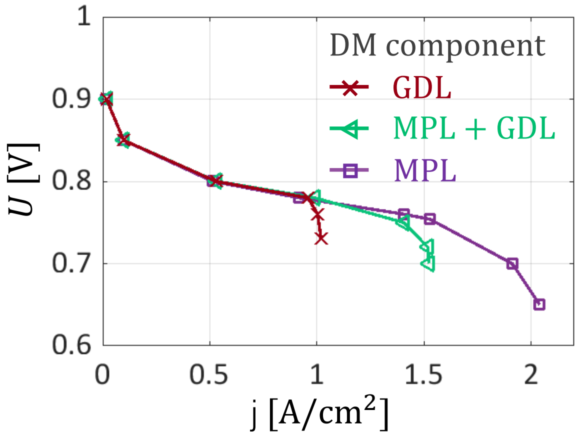
Strategies

- ☐ smaller HO pores
- ☐ larger contact angle

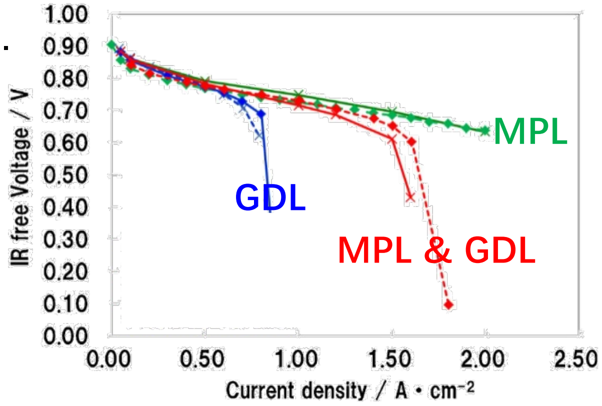
Water retention curve matters!

HOW TO SUPPRESS WATER LAYER FORMATION?

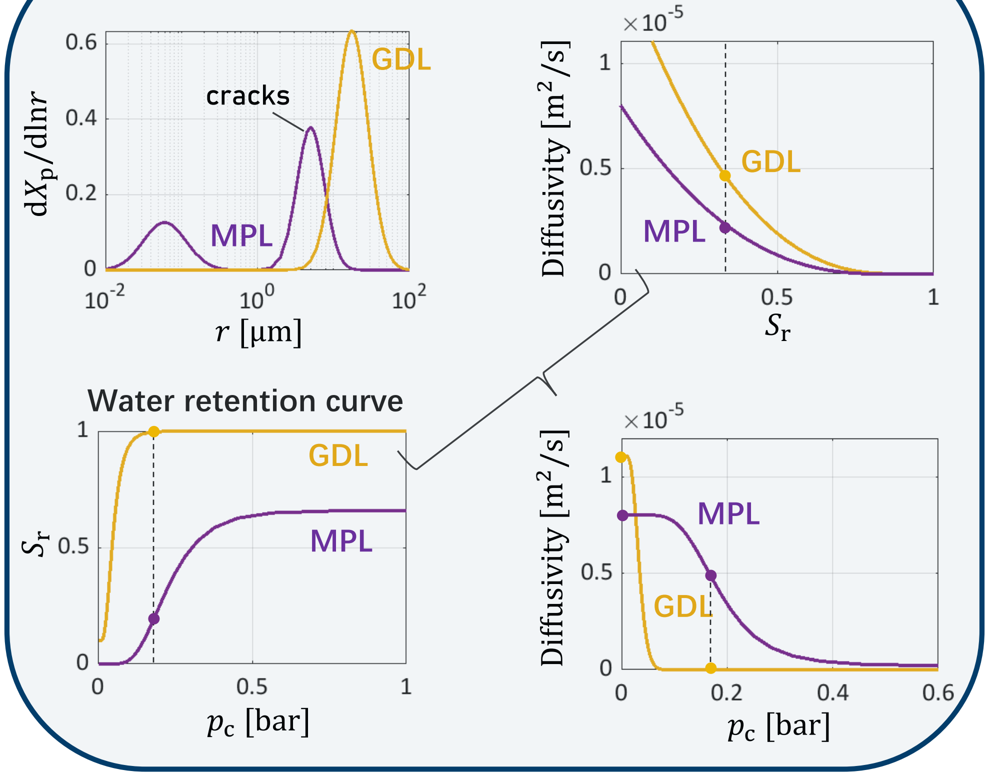
Introducing another porous layer, the MPL!



K. Totaka et al. (2014). ECS Trans. **64**, 839.



Underlying correlations



SUMMARY

- Physical modeling as starting point for correlation analysis (*j*-V data)
- Making sense of extensive performance data for Pt loading reduction
- Role of ionomer: control local pH (and conductivity) and wettability
- Model of structure formation (ionomer assembly in catalyst layer)
- Learn how to keep secondary pore space hydrophobic
- Learn how to suppress water layer formation at CL|GDL boundary