Journal of The Electrochemical Society, 2025 **172** 074504

Simulating Morphology and Degradation of PEMFC Cathode Catalyst Layers with Porous Carbon Supports: Part I. Effect of Relative Humidity on Catalyst Utilization

Anne-Christine Scherzer,[1,z] Patrick Schneider,[1] Matthias Klingele,[2] Nada Zamel,[1] and Dietmar Gerteisen[1]

[1] *Fraunhofer Institute for Solar Energy Systems ISE, 79110 Freiburg, Germany*
[2] *Hochschule für angewandte Wissenschaften Kempten, 87435 Kempten, Germany*

We present a physical model of the cathode catalyst layer morphology which simulates the electrochemically active catalyst surface area at varying degrees of humidification. The model considers pore, particle and ionomer distributions and resulting interfaces on the nanoscale to create a unique mathematical representation of each material. Specifically, the model discriminates between catalyst particles on the support surface and inside primary pores of the support and their respective connection to the proton-conducting phase. Catalyst particles may be protonically activated by coverage with ionomer or water or be protonically inaccessible. The exact configuration depends on the particle size and location as well as the cell operating conditions, sensitizing the simulated catalyst utilization to these properties. Model results are compared against data for five samples with different support materials and ionomer loadings manufactured in-house. Further, trends in catalyst utilization which were observed in recent literature are reproduced with the model. This work provides a comprehensive analysis of material configurations and simulations at begin of test. In Part II, the presented model is integrated into a degradation model to predict the evolution of the electrode morphology and catalyst utilization during ageing.

© 2025 The Author(s). Published on behalf of The Electrochemical Society by IOP Publishing Limited. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, https://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/1945-7111/adc8d9]

Manuscript submitted December 19, 2024; revised manuscript received March 22, 2025. Published July 4, 2025.

Supplementary material for this article is available online

List of Symbols

Subscripts

activatable	Accessible for protonic activation by condensed water or ionomer
cat	Referring to catalyst powder (Pt and C)
ccl	Referring to entire CCL
char	Characterization
cond	Condensation of water vapor
cut	Cut-off, referring to critical pore size for ionomer penetration
eff	Effective
inner	Inside support primary particle nanopores, referring to entire CCL
io	Ionomer
io/C	Ionomer/carbon interface
io/Pt	Ionomer/Pt interface
mean	Mean
outer	On support primary particle surface, referring to entire CCL
p	Referring to primary pore
secondary	Secondary pores, referring to entire CCL
std	Standard deviation
total	Referring to entire CCL
water	Referring to condensed water
water/C	Condensed water/carbon interface
AST	Accelerated stress test
C	Carbon support
Pt	Platinum catalyst
Pt/C	After loading the support with Pt
Pt/Clio	After loading the support with Pt and ionomer

Parameters

γ	Surface tension, N m^{-1}
ε	Volume fraction
μ	Parameter for lognormal distribution
ρ	Material density, kg m^{-3}
σ	Parameter for lognormal distribution
Θ	Fractional coverage referring to available interfacial surface
d	Layer thickness, m
l	Length, m
m	Mass, kg
n'	Particle or pore number distribution, m^{-1}
n''	Distribution of particles in pores, m^{-1}m^{-1}
r	Particle or pore radius, m
v'	Pore volume distribution, m^{3}m^{-1}
wt	Mass fraction
x	Fraction or partition
A	Area, m^2
L	Catalyst loading, kg m^{-2}
N	Total number of particles or pores
T	Temperature, K
RH	Relative humidity
V	Volume, m^3

The nanomorphology of the cathode catalyst layer (CCL) in PEM fuel cells plays a crucial role for cell performance and degradation. A robust and performant CCL must meet various, sometimes conflicting requirements. Optimization in manufacturing methods and material combinations is typically targeted toward achieving a high electrochemically active surface area (ECSA) and good protonic accessibility of the catalyst while maintaining sufficient open pore volume to avoid oxygen mass transport limitations. In this context, high surface area carbon supports (HSA) constitute an important toolbox due to their capacity to host catalyst particles and proton conducting materials both on the outer support surface and within support pores, with different effects on the associated transport processes in each domain.[1] Investigating the relations between material combination, synthesis method and resultant CCL nanomorphology in HSA carbons has hence gathered much research

[z]E-mail: anne-christine.scherzer@ise.fraunhofer.de

Fraunhofer ISE

Welcome!

Fuel Cell Scientific Insights Series

We present our latest research findings to industry professionals, academics, and funding partners interested in fuel cells.

Upcoming Webinar

Next Generation Catalysts

Kläre Christmann & Prof. Anna Fischer

February 18, 2026



Information and registration

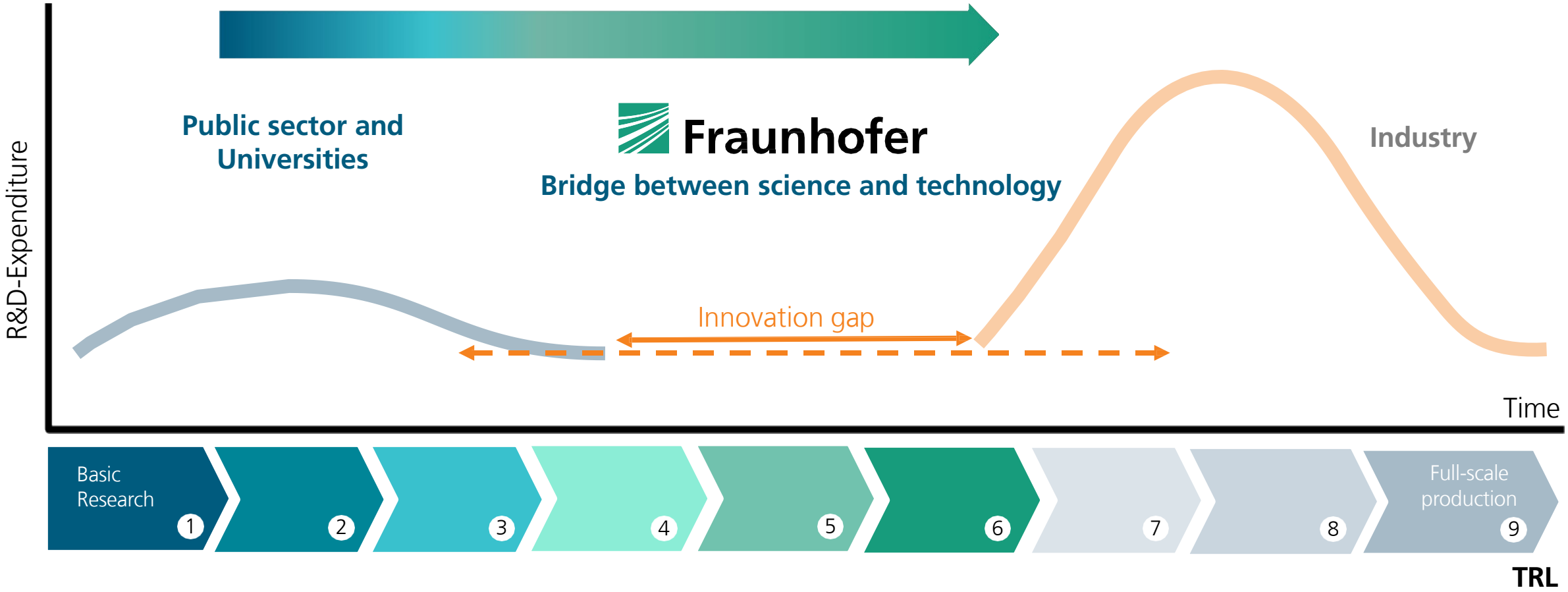
Modeling the Morphology of Porous Carbon Supports of PEMFC

Speaker: Anne-Christine Scherzer
Co-authors: Patrick Schneider, Matthias Klingele, Nada Zamel, Dietmar Gerteisen
Fuel Cell Scientific Insights Series
Freiburg, Germany, 10.12.2025
www.ise.fraunhofer.de

Fraunhofer-Gesellschaft – Leading Applied Research Organization

76 Institutes – 30.000 Staff – € 3 Billion Revenue

Bridging the gap between conceptual research to commercialization along the innovation value chain.



©Fraunhofer ISE
public

Fraunhofer ISE

Our Mission in Our Department Fuel Cell

Assisting Global Industry with Scientifically Sound Services

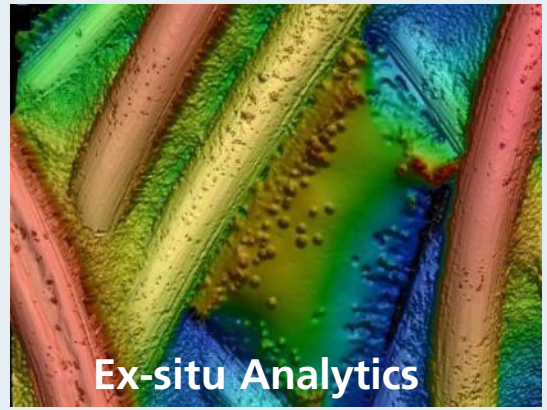
Understanding Fuel Cell Membrane Electrode Assemblies (MEAs)

Key Performance Indicators 2024:

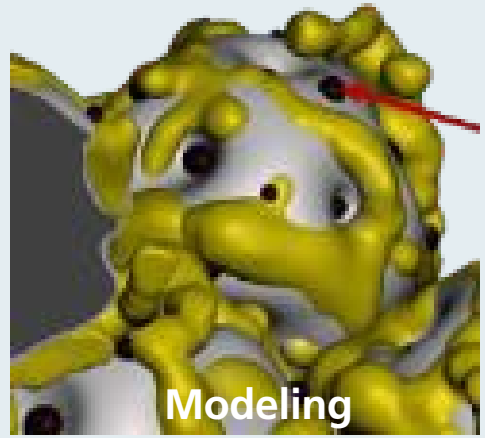
- 45 researchers plus students
- 9.2 Mio. € annual budget (w/o investments)
- 33% direct revenue by industry contract research
- > 500 m² laboratory area with 13 single cell test stations, 5 short stack test stations including temperature chamber (all fully automated for 24/7 operation)
- Focus on transport application

Enjoy our virtual lab tour









© Fraunhofer ISE

©Fraunhofer ISE
public

Fraunhofer ISE

Group Fuel Cell Modeling
Main Fields of Interest


Y. HOU


A. SCHERZER

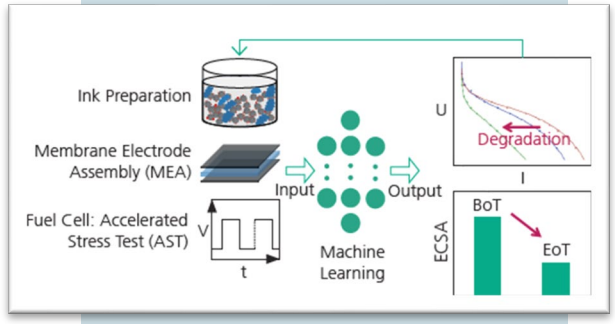

D. GERTEISEN


N. RAUE


T. KURZ

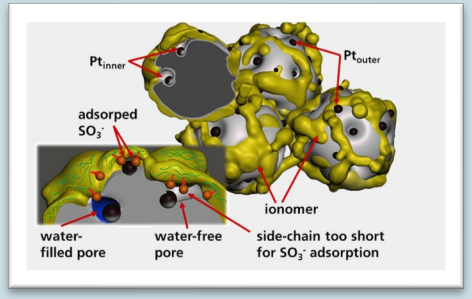
AI / Machine Learning

- CCM production
- Novel catalyst materials



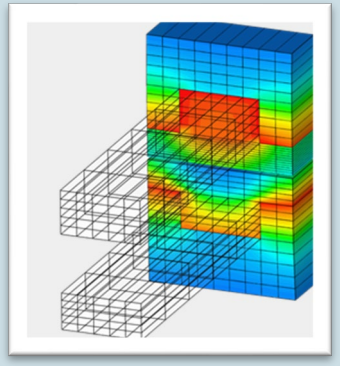
Electrode level

- In-house developed code (Python)
- Structure, performance, degradation, transport processes



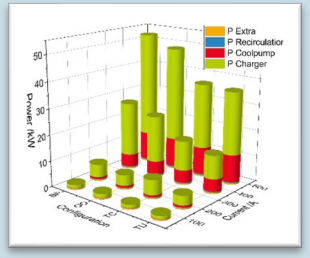
Cell level

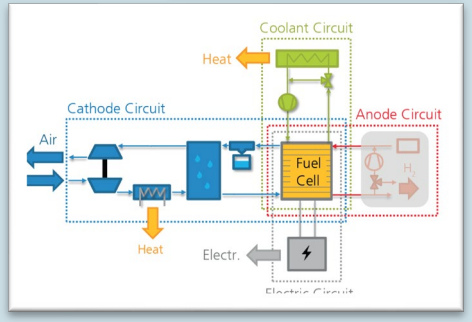
- In-house developed code (Python)
- Commercial CFD code (AVL FireM)
- Local effects



System level

- Design and optimization



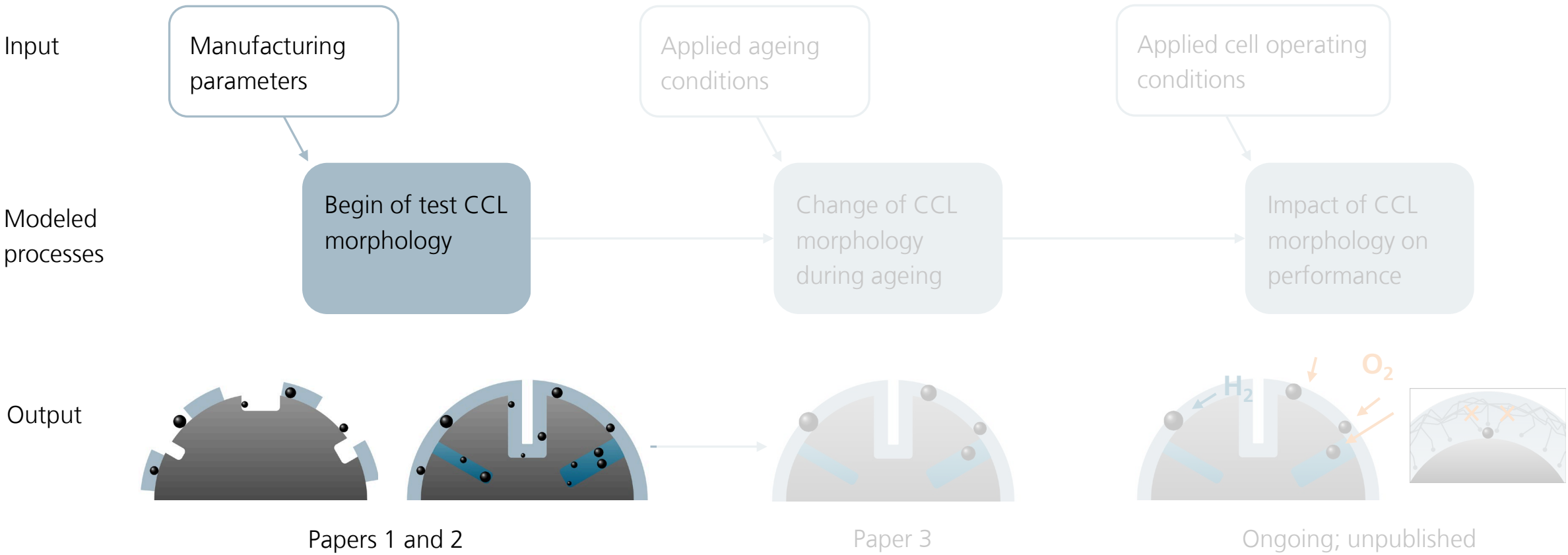


©Fraunhofer ISE
public

Fraunhofer ISE

Model Structure

Coupled Models for Morphology + Degradation + Performance

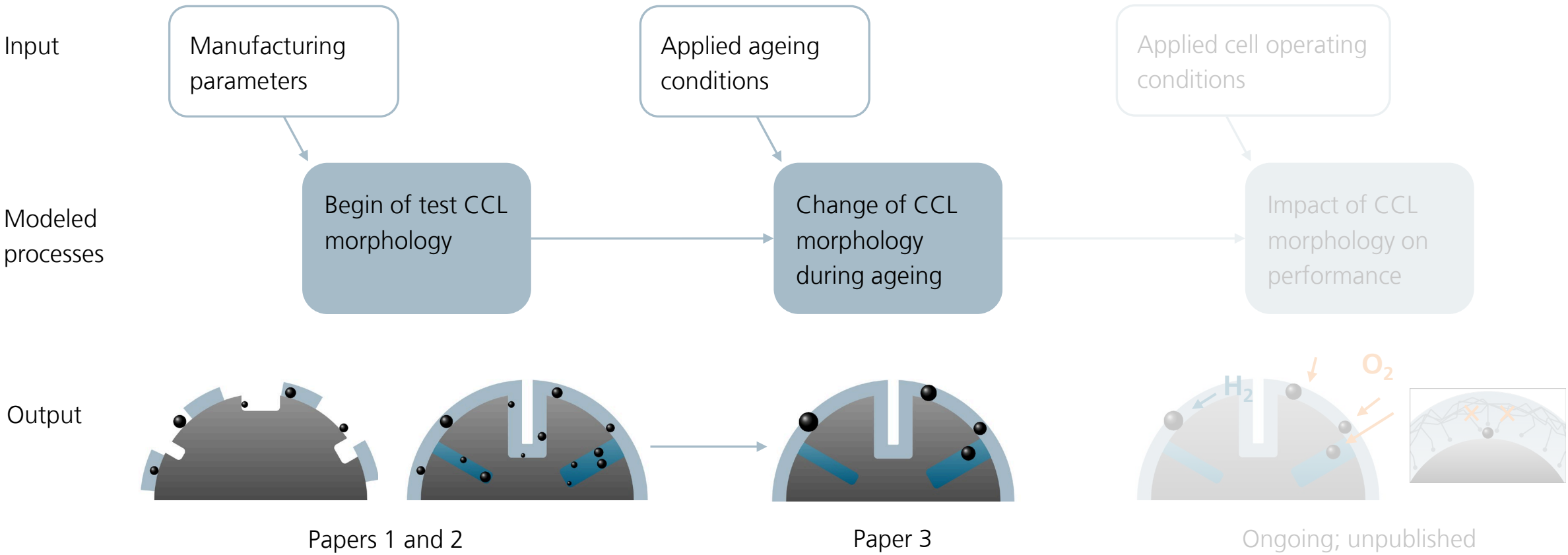


©Fraunhofer ISE
public

Fraunhofer ISE

Model Structure

Coupled Models for Morphology + Degradation + Performance

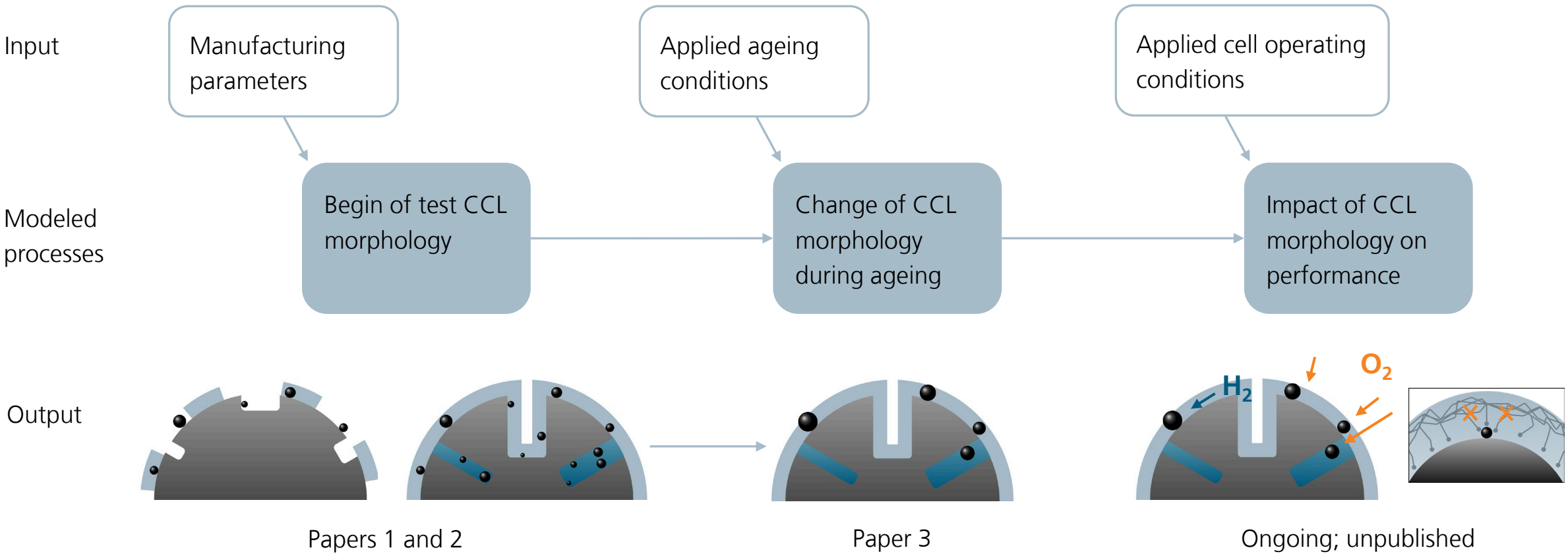


©Fraunhofer ISE
public

Fraunhofer ISE

Model Structure

Coupled Models for Morphology + Degradation + Performance

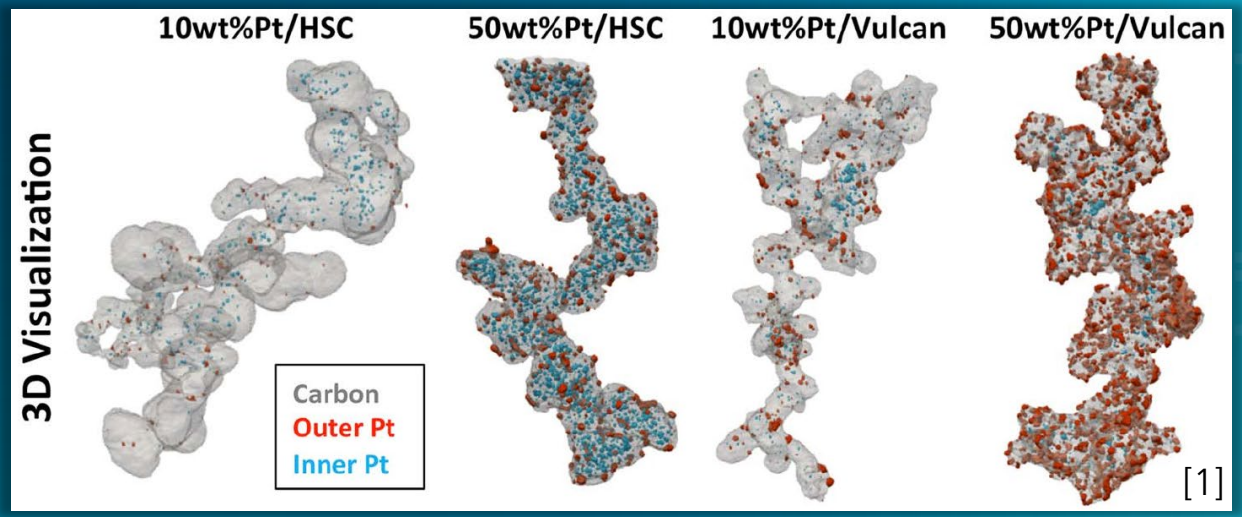


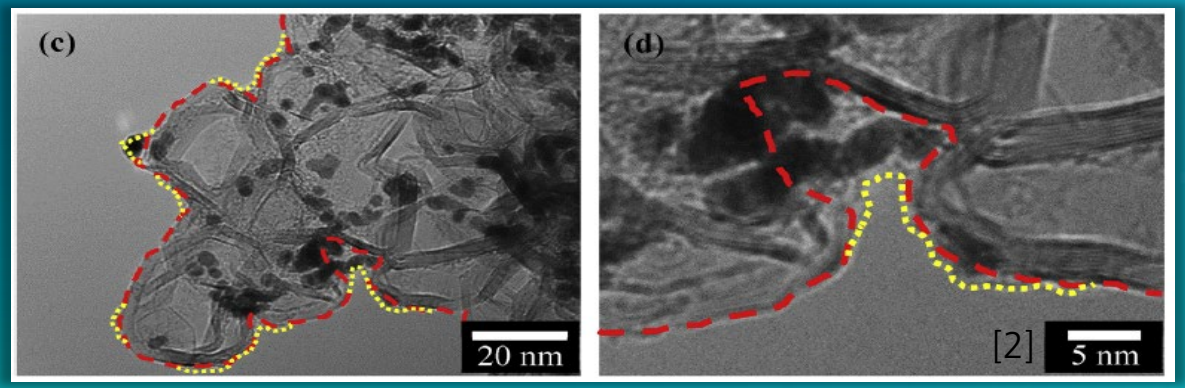
©Fraunhofer ISE
public

Fraunhofer ISE

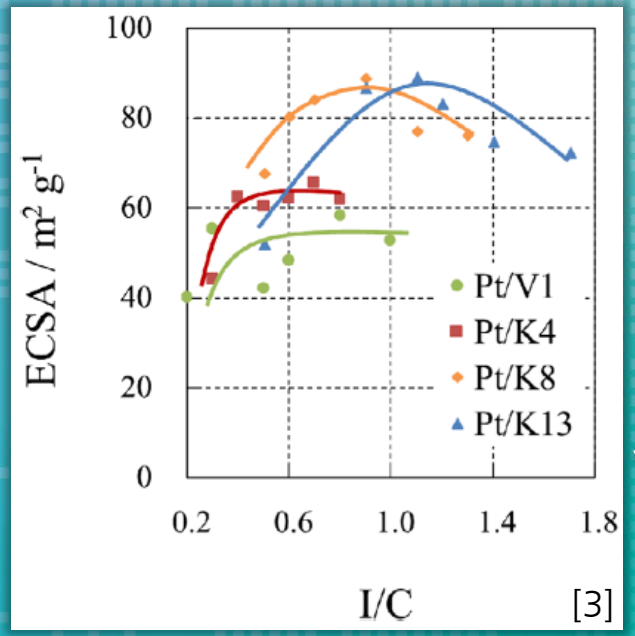
Morphology Model

Motivation: Nanomorphology of each Pt/C/ionomer system is individual and affects global behavior of CCL





Carbon surface
Ionomer surface



Increasing support porosity

[1] Padgett et al., 2018, DOI 10.1149/2.0541803jes
[2] Park et al., 2016, DOI 10.1016/j.jpowsour.2016.02.091
[3] Kobayashi et al., 2021, DOI 10.1021/acsaem.0c02841

©Fraunhofer ISE
public

Fraunhofer ISE

Morphology Model: Implementation
Distribution-Based Approach

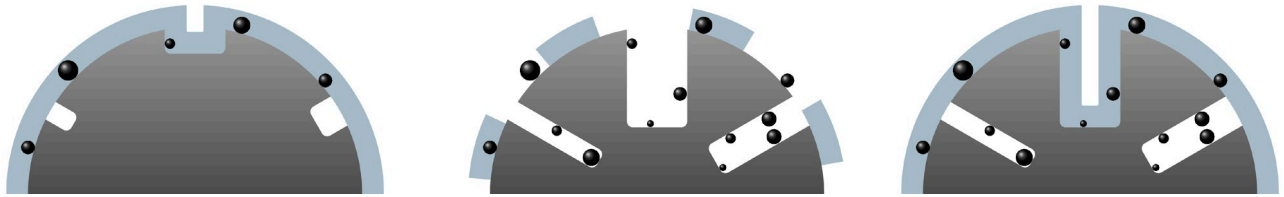
Input

Manufacturing parameters

Carbon loading, pore volume distribution
Catalyst loading, particle size distributions on support surface / in primary pores
Ionomer loading and distribution properties

Model

Distribution-based 0D representation of CCL nanomorphology



Output

Global parameters at BoT for validation against experiment

Pore volume distributions of C, Pt/C, Pt/C/io
ECSA
Ionomer coverage on catalyst
...

©Fraunhofer ISE
public

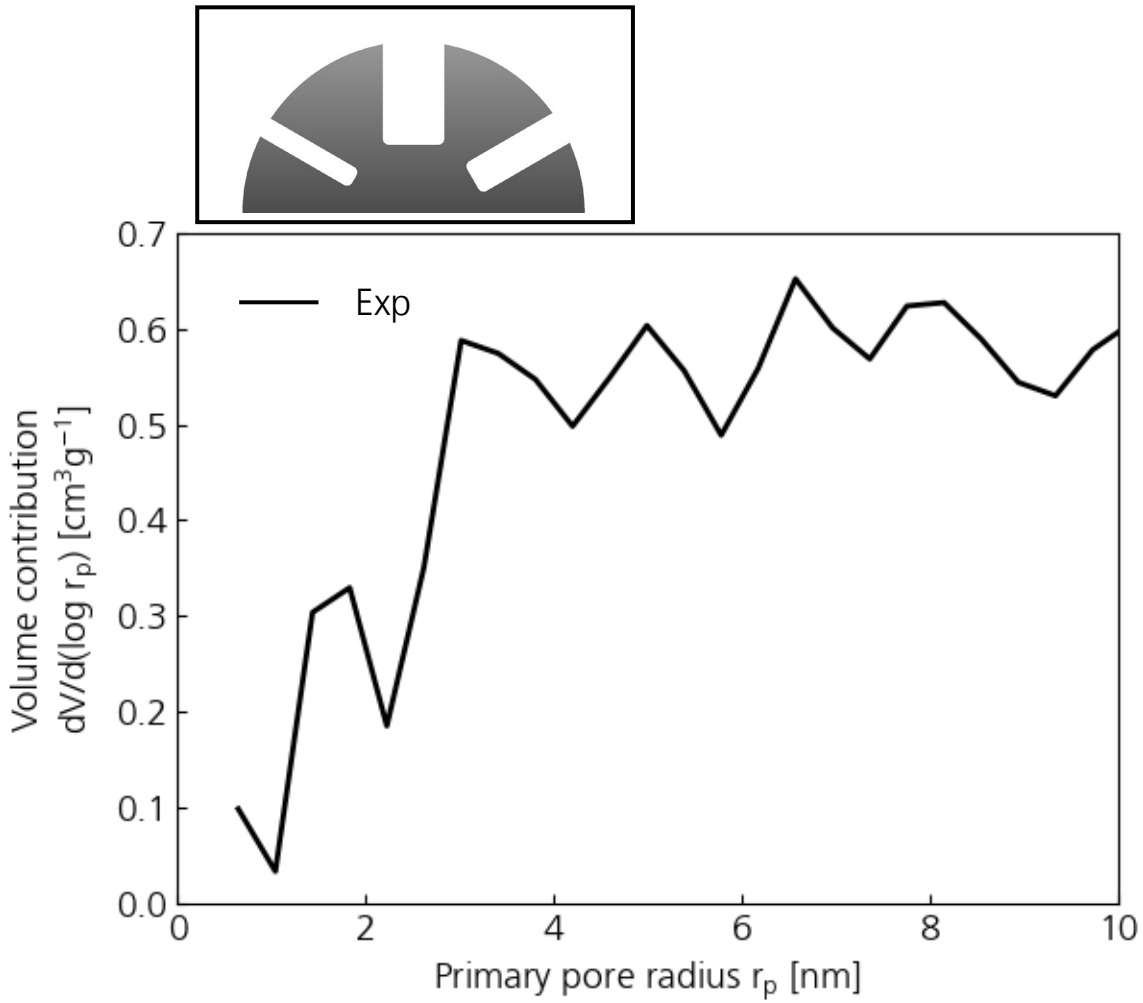
Fraunhofer ISE

Morphology Model: Implementation

Mathematical Description of the CCL Structure

Porous carbon support characterized by

- Carbon mass and material properties
- Pore size distribution



©Fraunhofer ISE
public

Fraunhofer ISE

Morphology Model: Implementation

Mathematical Description of the CCL Structure

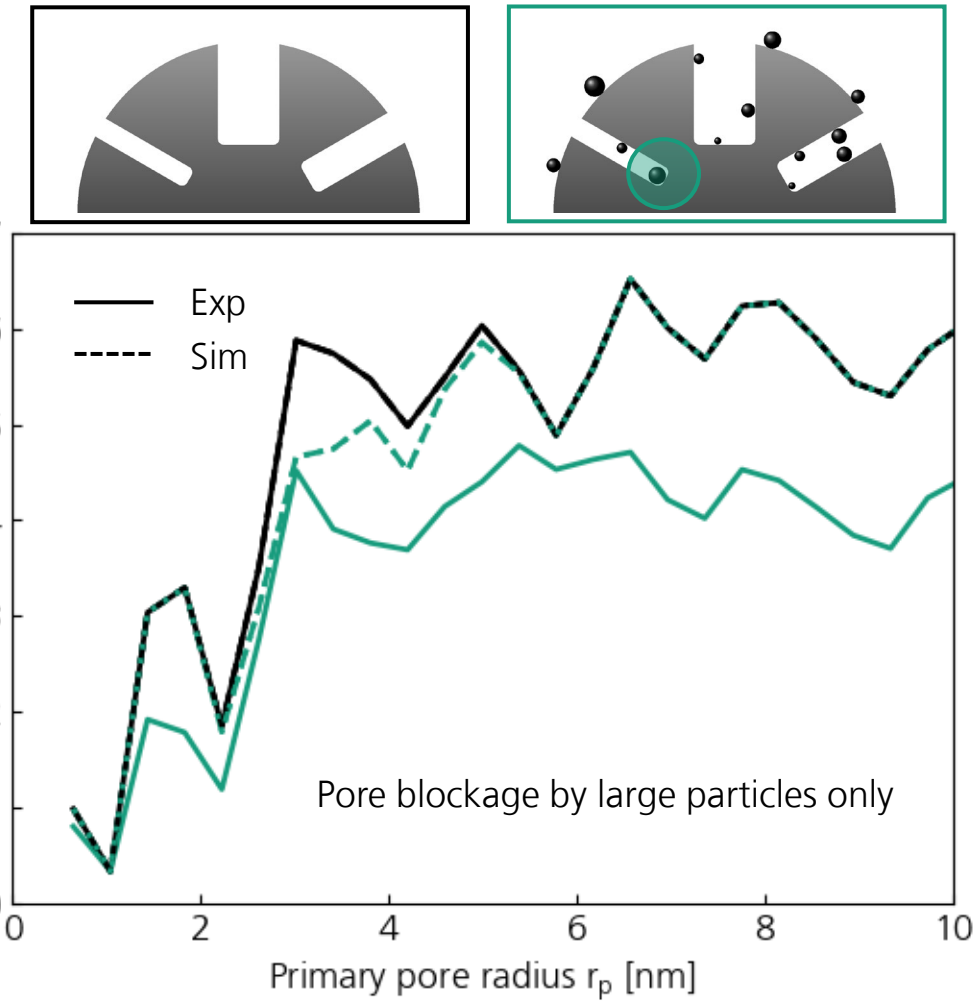
Porous carbon support characterized by
- Carbon mass and material properties
- Pore size distribution

Pt distribution on support characterized by
- Particle size distribution on support surface
- Particle size distribution in carbon primary pores
- Model representation of Pt deposition method

$$x_{p,Pt/C,blocked}(r_p) = \frac{\int_{0.6r_p}^{r_p} n''_{Pt,p}(\hat{r}_{Pt}, r_p)\mathrm{d}\hat{r}_{Pt}}{n'_{p,C}(r_p)}$$

$$x_{p,Pt/C,blocked}(r_p) = \frac{2\int_0^{\infty} \pi\hat{r}_{Pt}^2 n''(\hat{r}_{Pt}, r_p)\mathrm{d}\hat{r}_{Pt}}{A_{p,opening}(r_p)n'_{p,C}(r_p)}$$

[1]



[1] Scherzer et al., 2022, DOI 10.1149/1945-7111/ac58c2

©Fraunhofer ISE
public

Fraunhofer ISE

Morphology Model: Implementation

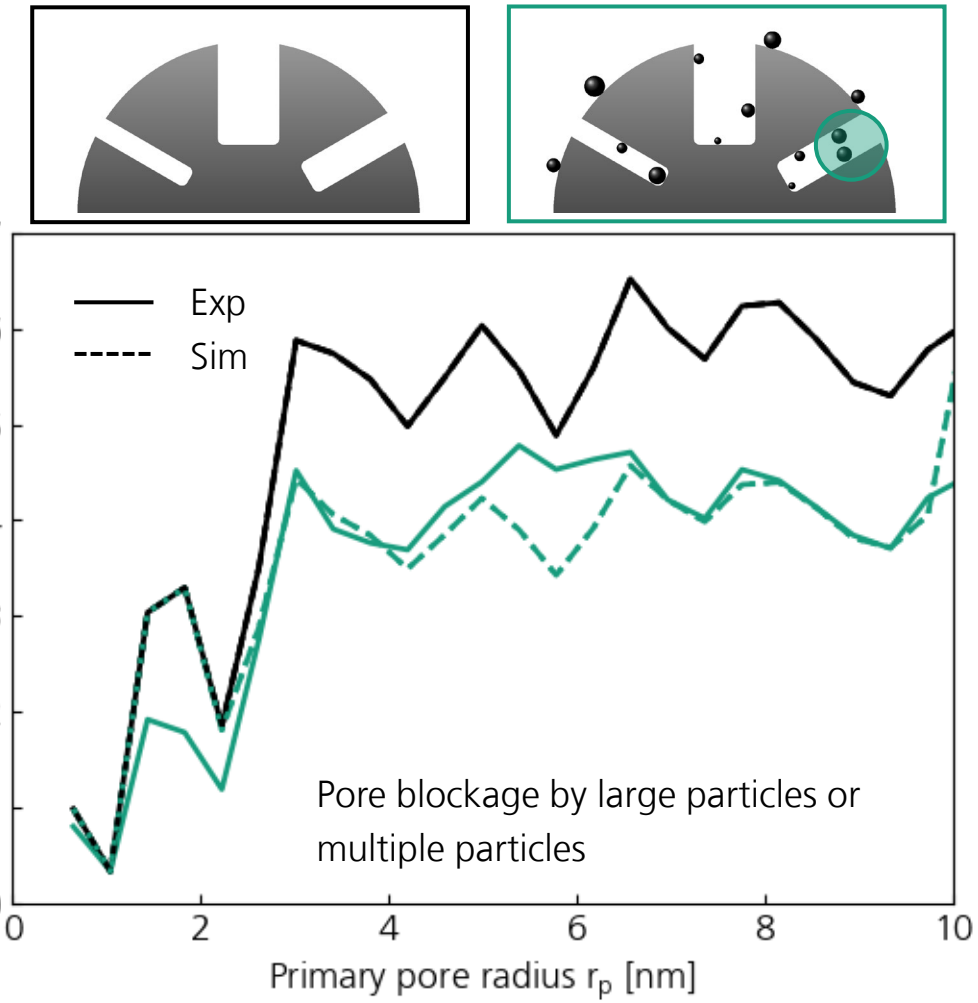
Mathematical Description of the CCL Structure

Porous carbon support characterized by
- Carbon mass and material properties
- Pore size distribution

Pt distribution on support characterized by
- Particle size distribution on support surface
- Particle size distribution in carbon primary pores
- Model representation of Pt deposition method

$$x_{p,Pt/C,blocked}(r_p) = \frac{\int_{0.6r_p}^{r_p} n''_{Pt,p}(\hat{r}_{Pt}, r_p)\mathrm{d}\hat{r}_{Pt}}{n'_{p,C}(r_p)}$$

$$x_{p,Pt/C,blocked}(r_p) = \frac{2\int_0^{\infty} \pi \hat{r}_{Pt}^2 n''(\hat{r}_{Pt}, r_p)\mathrm{d}\hat{r}_{Pt}}{A_{p,opening}(r_p) n'_{p,C}(r_p)} \quad [1]$$



[1] Scherzer et al., 2022, DOI 10.1149/1945-7111/ac58c2

©Fraunhofer ISE
public

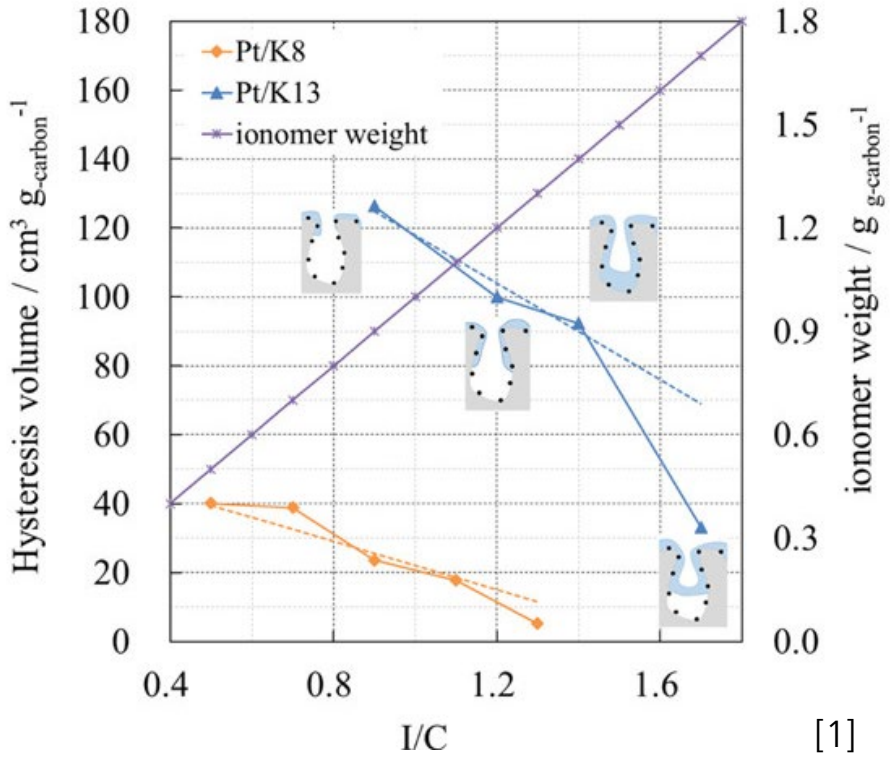
Morphology Model: Implementation

Mathematical Description of the CCL Structure

Porous carbon support characterized by
- Carbon mass and material properties
- Pore size distribution

Pt distribution on support characterized by
- Particle size distribution on support surface
- Particle size distribution in carbon primary pores
- Model representation of Pt deposition method

Ionomer distribution characterized by
- I/C ratio
- Minimum thickness of formed ionomer film
- Model representation of ionomer deposition method



[1]

[1] Kobayashi et al., 2021, DOI 10.1021/acsaem.0c02841

©Fraunhofer ISE
public

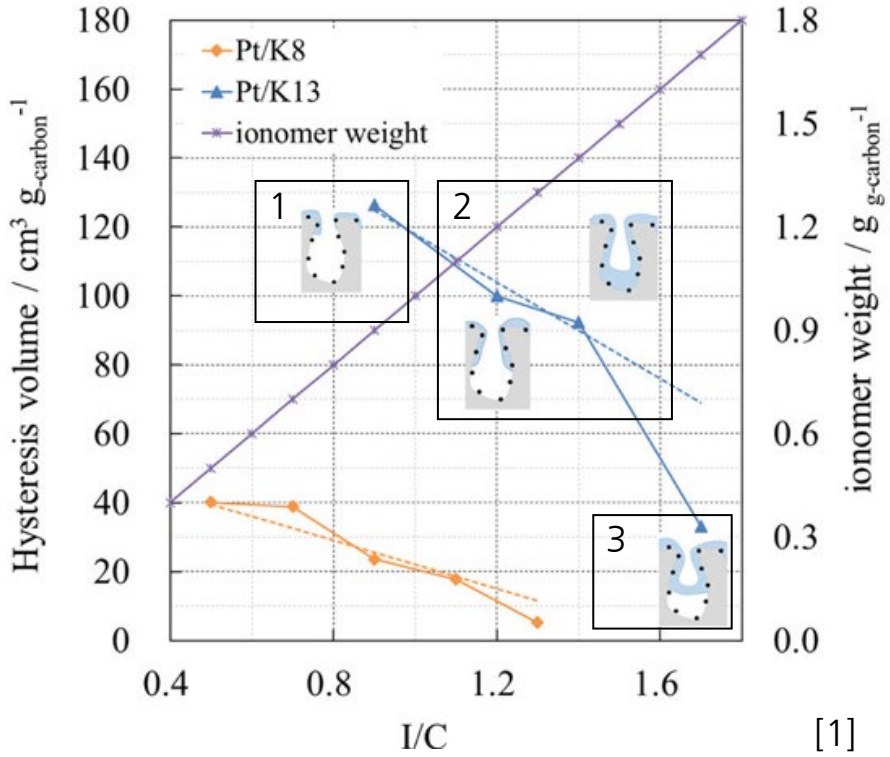
Morphology Model: Implementation

Mathematical Description of the CCL Structure

Porous carbon support characterized by
- Carbon mass and material properties
- Pore size distribution

Pt distribution on support characterized by
- Particle size distribution on support surface
- Particle size distribution in carbon primary pores
- Model representation of Pt deposition method

Ionomer distribution characterized by
- I/C ratio
- Minimum thickness of formed ionomer film
- Model representation of ionomer deposition method



[1]

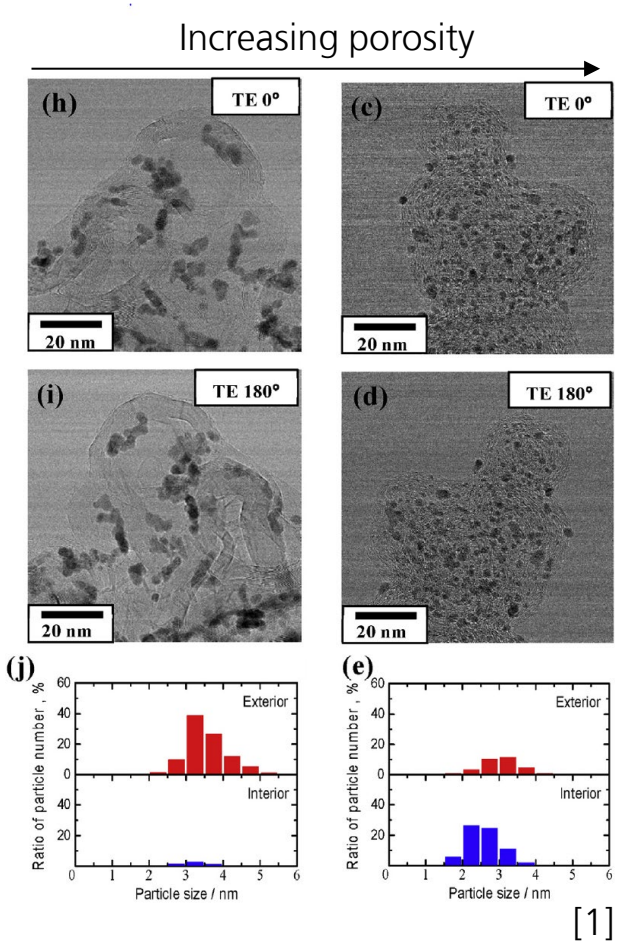
[1] Kobayashi et al., 2021, DOI 10.1021/acsaem.0c02841

©Fraunhofer ISE
public

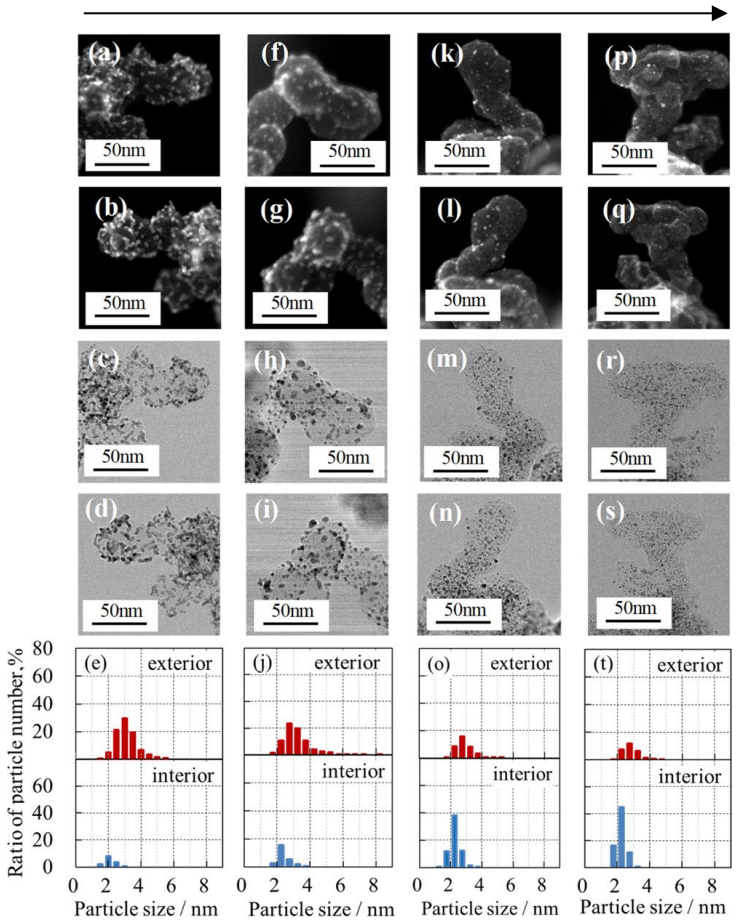
Morphology Model: Validation

Variation of Carbon Support Surface Area

- Six different catalyst supports with surface area between 141 m^2/g_C and 1335 m^2/g_C
- Pore and Pt particle size distributions from literature as direct input to model



[1]



[2]

©Fraunhofer ISE
public

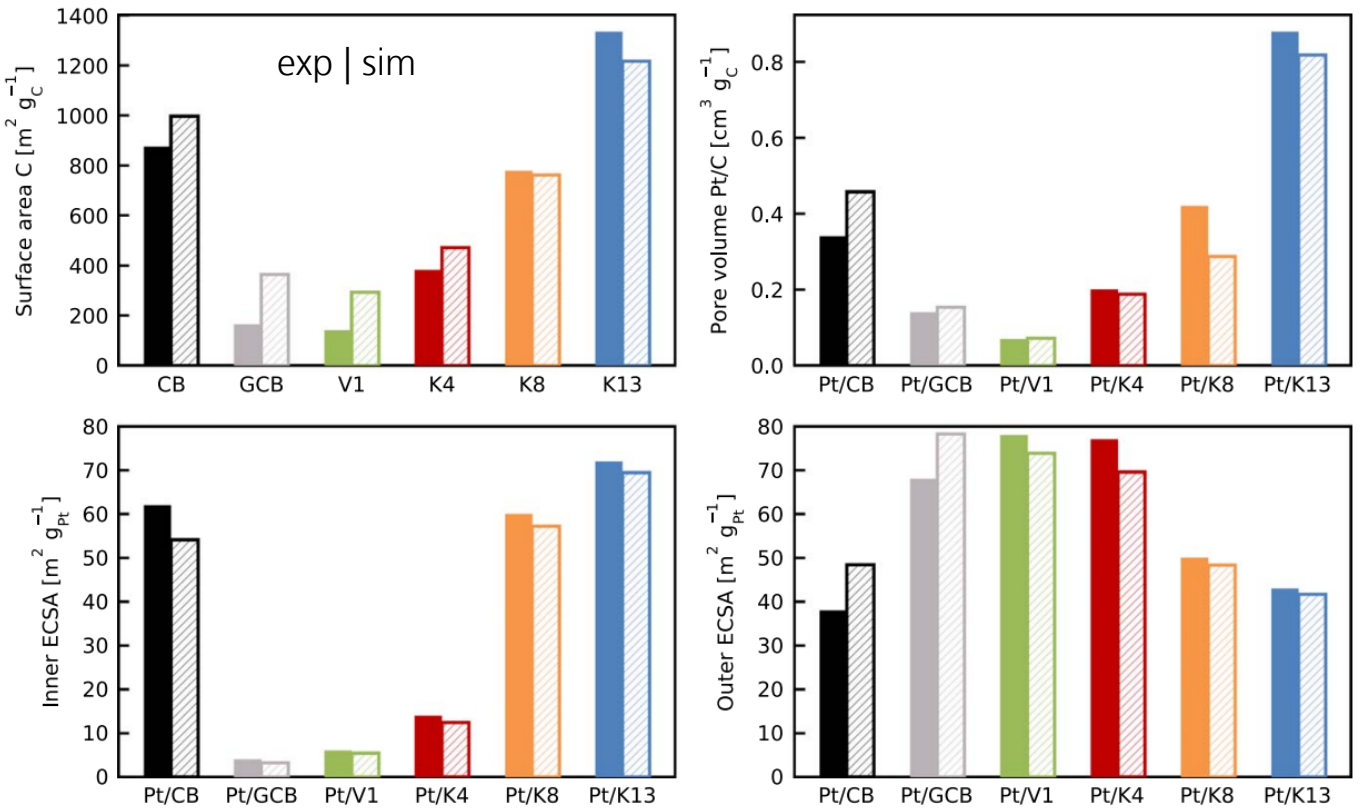
[1] Park et al., 2016, DOI 10.1016/j.jpowsour.2016.02.091
[2] Kobayashi et al., 2021, DOI 10.1021/acsaem.0c02841

Fraunhofer ISE

Morphology Model: Validation

Variation of Carbon Support Surface Area

- Six different catalyst supports with surface area between 141 m^2/g_C and 1335 m^2/g_C
- Pore and Pt particle size distributions from literature as direct input to model
- Validation on global CCL properties
- Validation on pore volume distributions after Pt/ionomer deposition



[1]

[1] Scherzer et al., 2022, DOI 10.1149/1945-7111/ac58c2

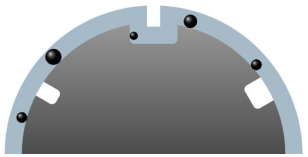
©Fraunhofer ISE
public

Fraunhofer ISE

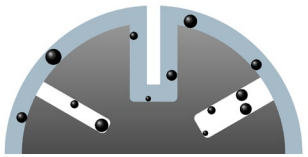
Morphology Model: Validation

Variation of Carbon Support Surface Area and Ionomer Content

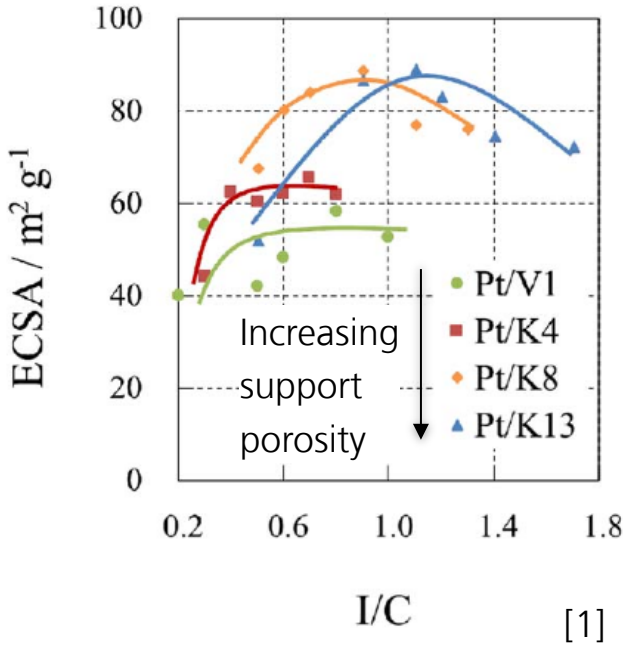
- Six different catalyst supports with surface area between 141 m^2/g_C and 1335 m^2/g_C
- Pore and Pt particle size distributions from literature as direct input to model
- Validation on global CCL properties
- Validation on pore volume distributions after Pt/ionomer deposition



Low surface area support

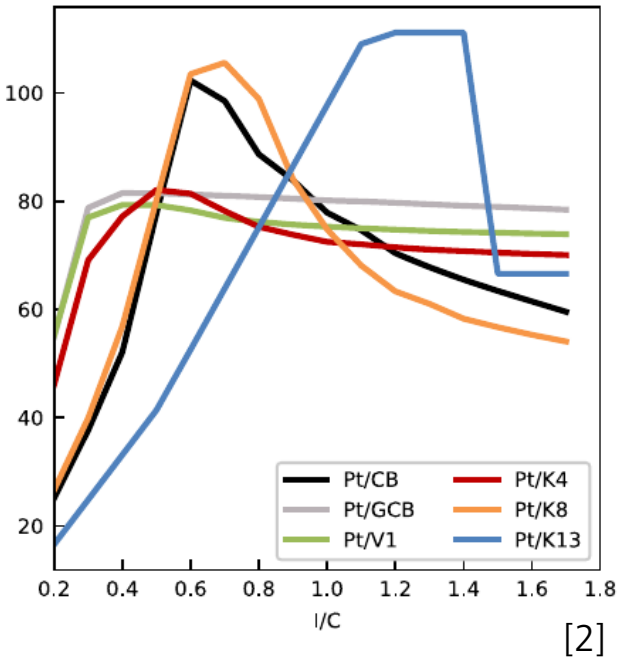


High surface area support



[1]

Measured data



[2]

Simulated data

©Fraunhofer ISE
public

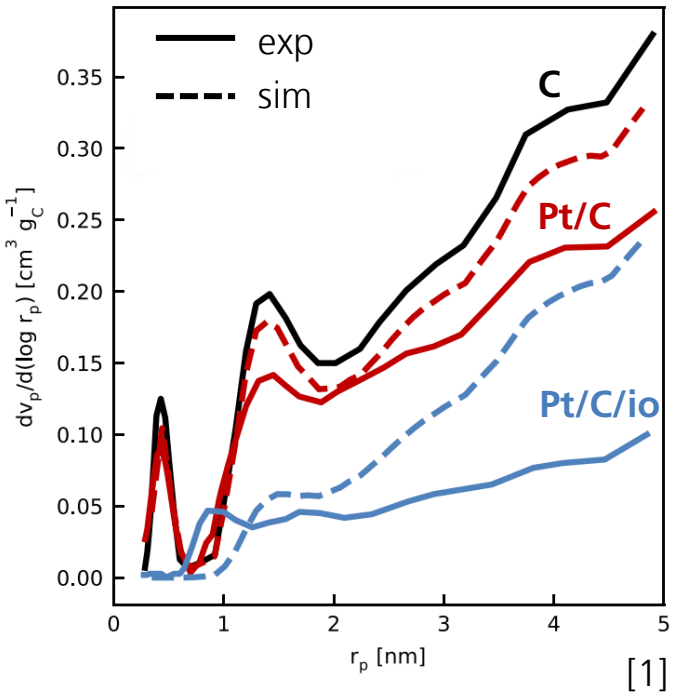
[1] Kobayashi et al., 2021, DOI 10.1021/acsaem.0c02841
[2] Scherzer et al., 2022, DOI 10.1149/1945-7111/ac58c2

Fraunhofer ISE

Morphology Model: Validation

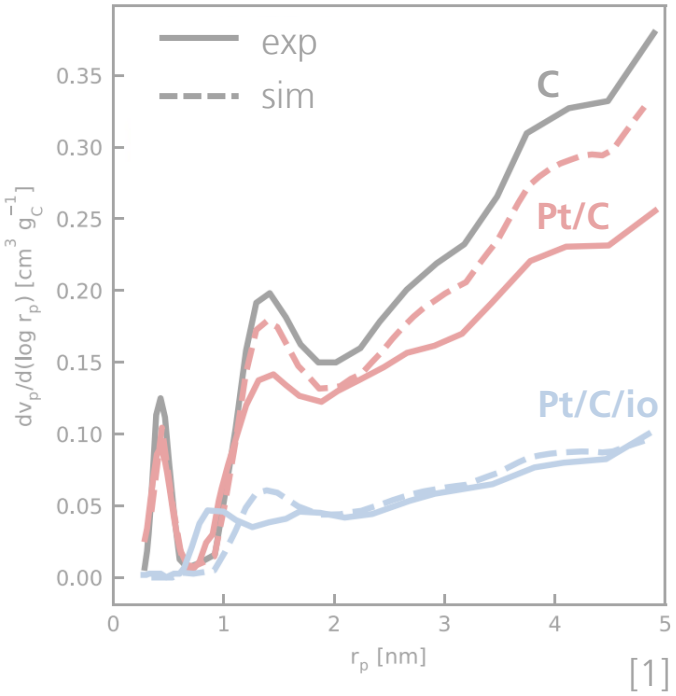
Pore Volume Distribution after Pt and Ionomer Deposition

- Six different catalyst supports with surface area between 141 m^2/g_C and 1335 m^2/g_C
- Pore and Pt particle size distributions from literature as direct input to model
- Validation on global CCL properties
- Validation on pore volume distributions after Pt/ionomer deposition



[1]

Scenario 1:
Ionomer film of homogenous thickness



[1]

Scenario 2:
Ionomer film thickness distribution

[1] Scherzer et al., 2022, DOI 10.1149/1945-7111/ac58c2

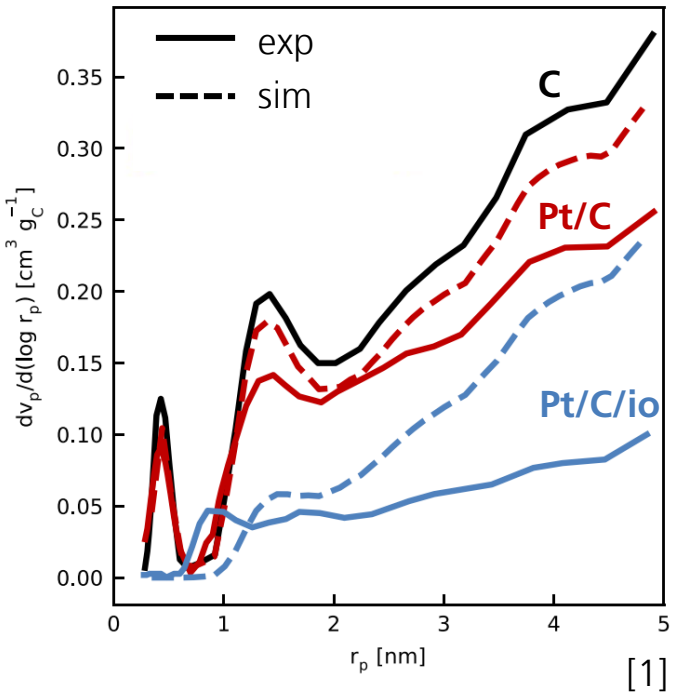
©Fraunhofer ISE
public

Fraunhofer ISE

Morphology Model: Validation

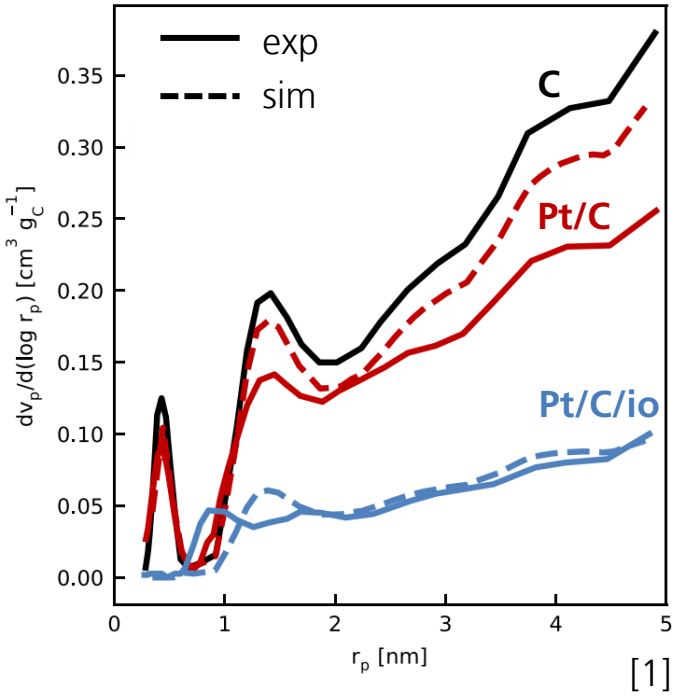
Pore Volume Distribution after Pt and Ionomer Deposition

- Six different catalyst supports with surface area between 141 m^2/g_C and 1335 m^2/g_C
- Pore and Pt particle size distributions from literature as direct input to model
- Validation on global CCL properties
- Validation on pore volume distributions after Pt/ionomer deposition



[1]

Scenario 1:
Ionomer film of homogenous thickness



[1]

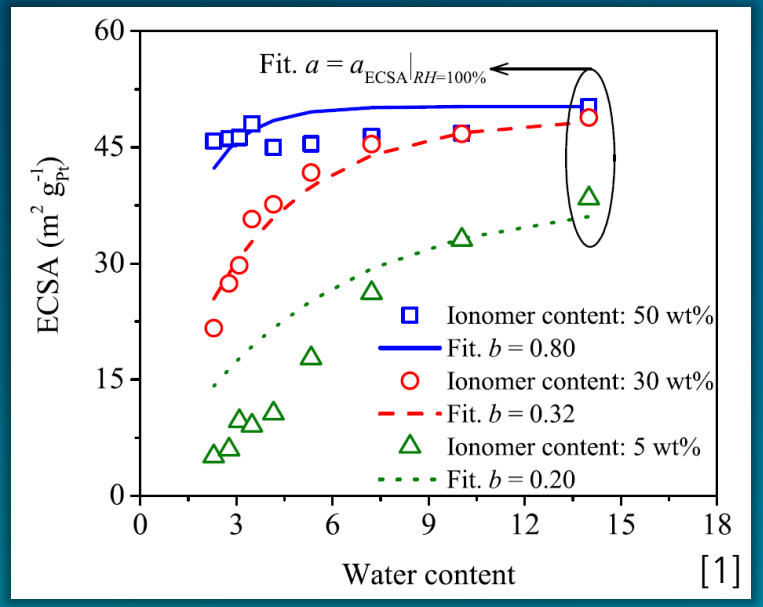
Scenario 2:
Ionomer film thickness distribution

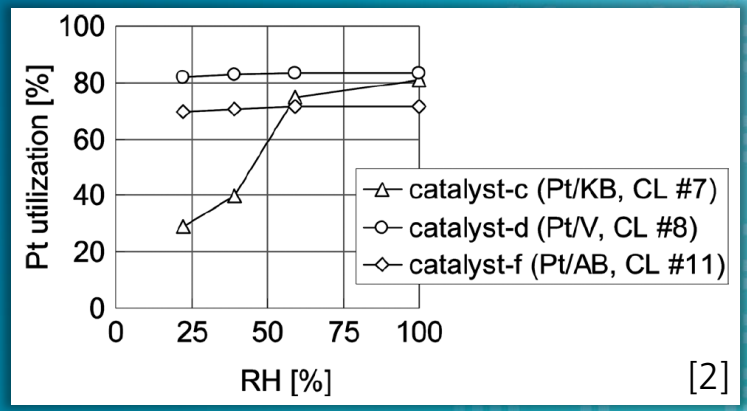
©Fraunhofer ISE
public

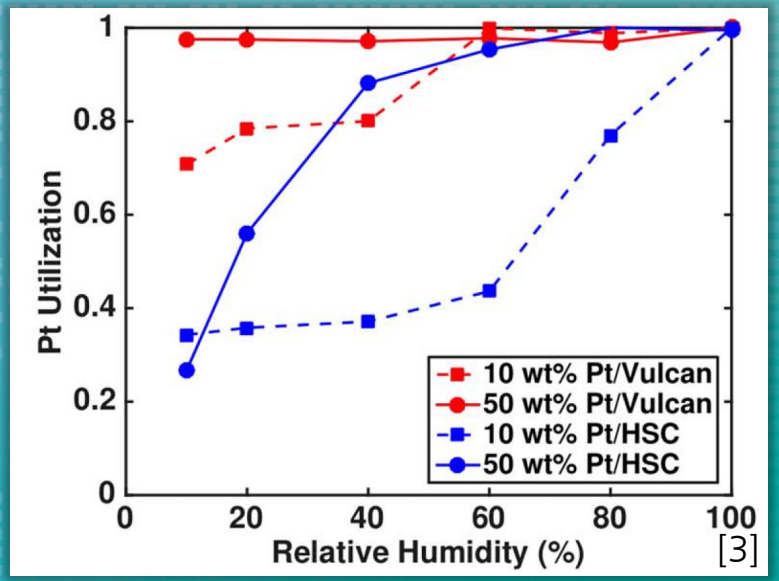
[1] Park et al., 2016, DOI 10.1016/j.jpowsour.2016.02.091
[2] Scherzer et al., 2022, DOI 10.1149/1945-7111/ac58c2

Extended Morphology Model

Motivation: Catalyst utilization versus RH exhibits strong sensitivity to CCL properties







©Fraunhofer ISE
public

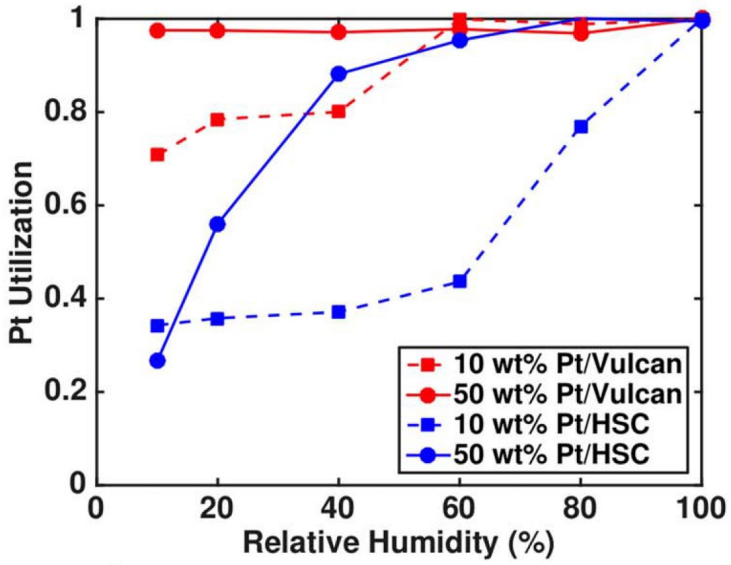
[1] Wu et al., 2022, DOI 10.1016/j.enconman.2021.114982
[2] Shinozaki et al., 2011, DOI 10.1149/1.3556906
[3] Padgett et al., 2018, DOI 10.1149/2.0541803jes

Fraunhofer ISE

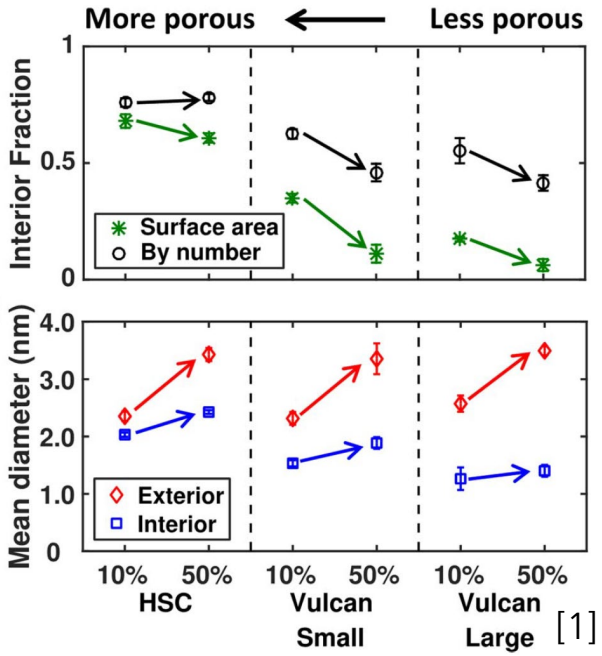
Extended Morphology Model: Implementation

Theory: Pt Inside Primary Pores Influences Pore Flooding

- Maximum catalyst utilization with respect to RH reached much earlier for higher Pt loading
- Higher Pt loading associated with fewer, but larger catalyst particles in primary pores
- Hypothesis: Pt inside pores influences capillary condensation by acting as constriction



[1]



[1]

[1] Padgett et al., 2018, DOI 10.1149/2.0541803jes

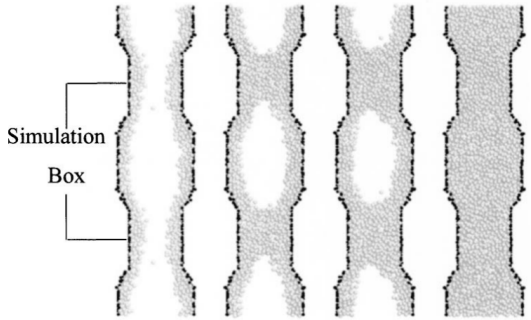
©Fraunhofer ISE
public

Fraunhofer ISE

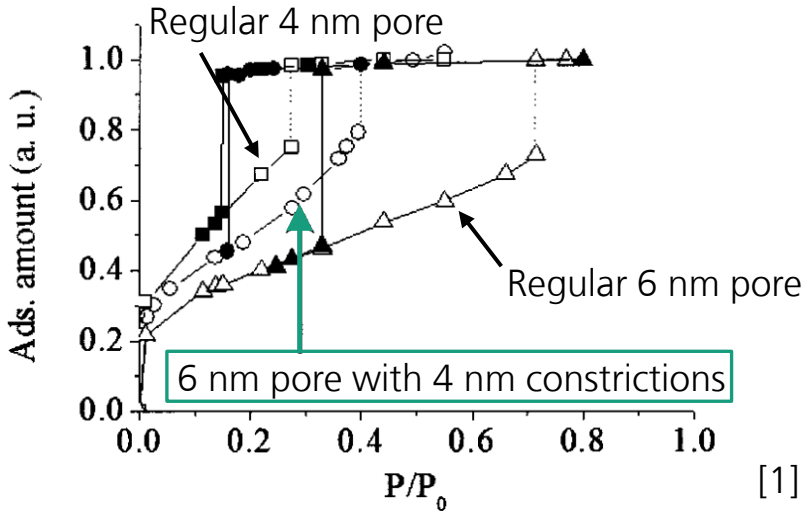
Extended Morphology Model: Implementation

Theory: Pt Inside Primary Pores Influences Pore Flooding

- Maximum catalyst utilization with respect to RH reached much earlier for higher Pt loading
- Higher Pt loading associated with fewer, but larger catalyst particles in primary pores
- Hypothesis: Pt inside pores influences capillary condensation by acting as constriction



[1]



[1]

[1] Coasne and Pellenq, 2004, DOI 10.1063/1.1772757

©Fraunhofer ISE
public

Extended Morphology Model: Implementation

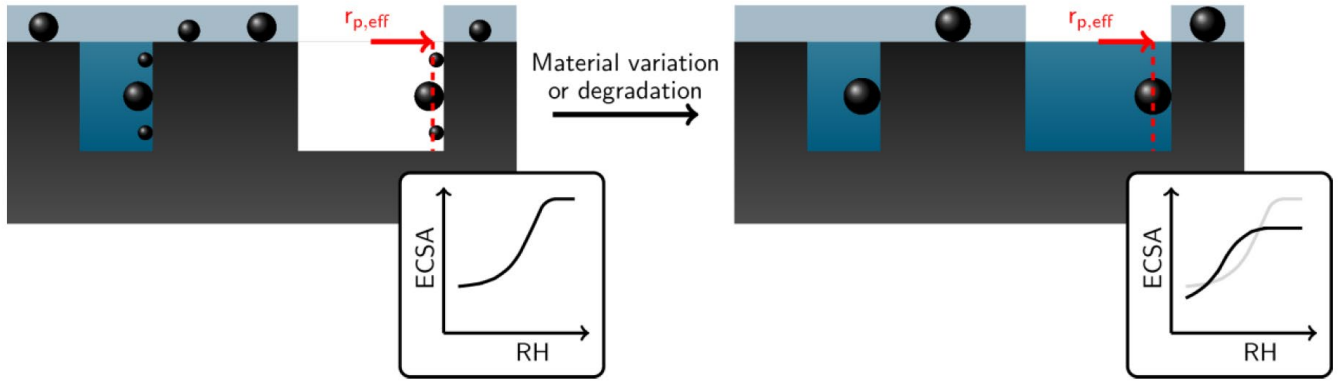
Capillary Condensation and Effective Pore Size

- Kelvin equation for capillary condensation, 'condensation radius'
- Effective Pt size in each pore size class
- Effective pore size = pore size - effective Pt size
  Pore is flooded if effective size is < condensation radius

$$r_{p,cond}(RH) = -\frac{2\gamma_{water}V_{m,water}}{RT\ln(RH)}$$

$$r_{Pt,eff}(r_p,t) = \frac{\int_0^\infty \hat{r}_{Pt} n''_{Pt,p,activatable}(\hat{r}_{Pt},r_p,t)\mathrm{d}\hat{r}_{Pt}}{\int_0^\infty n''_{Pt,p,activatable}(\hat{r}_{Pt},r_p,t)\mathrm{d}\hat{r}_{Pt}}$$

$$r_{p,eff}(r_p,t) = r_p - r_{Pt,eff}(r_p,t) \quad [1]$$



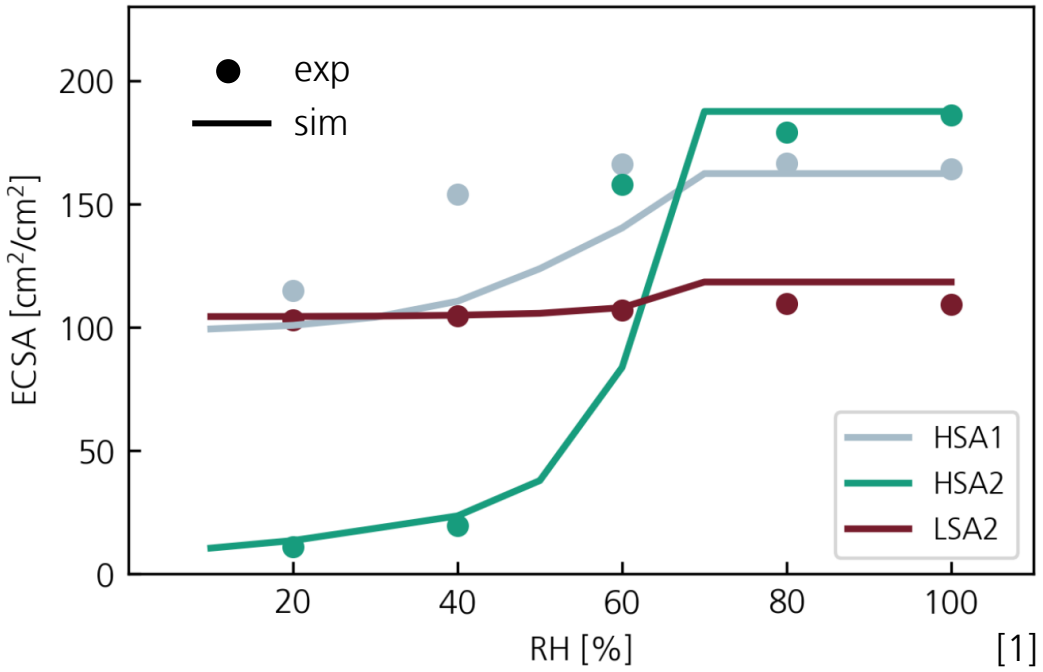
[1] Scherzer et al., 2025, DOI 10.1149/1945-7111/adc8d9

©Fraunhofer ISE
public

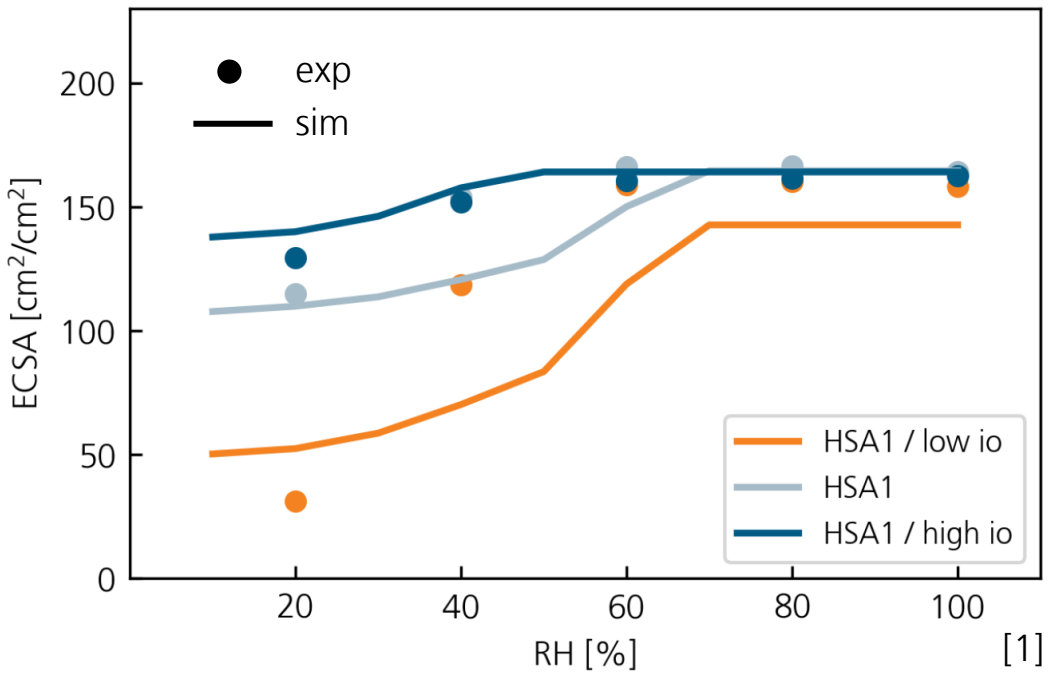
Fraunhofer ISE

Extended Morphology Model: Validation

In-House Variation of Support Type and Ionomer Loading



Support type variation @ 0.4 mg/cm² Pt, I/C = 0.8
(HSA: high surface area, LSA: low surface area carbon)



Ionomer loading variation I/C = 0.5 / 0.8 / 1.2
@ 0.4 mg/cm² Pt on HSA carbon

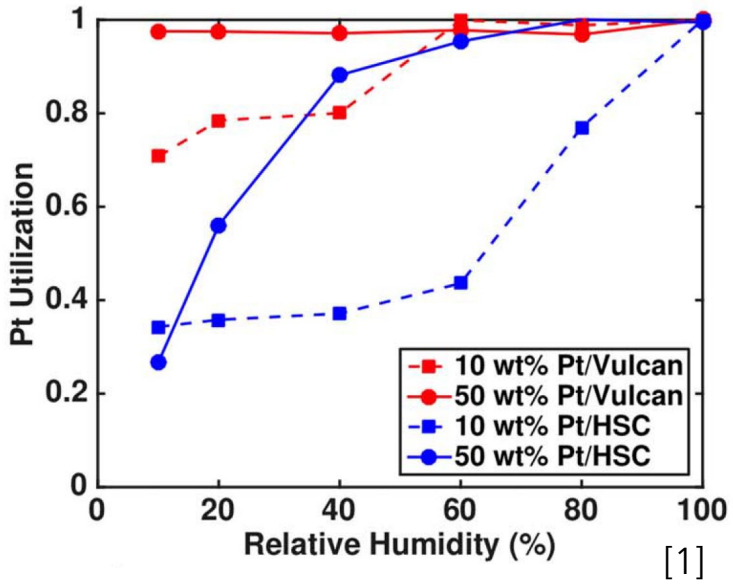
[1] Scherzer et al., 2025, DOI 10.1149/1945-7111/adc8d9

©Fraunhofer ISE
public

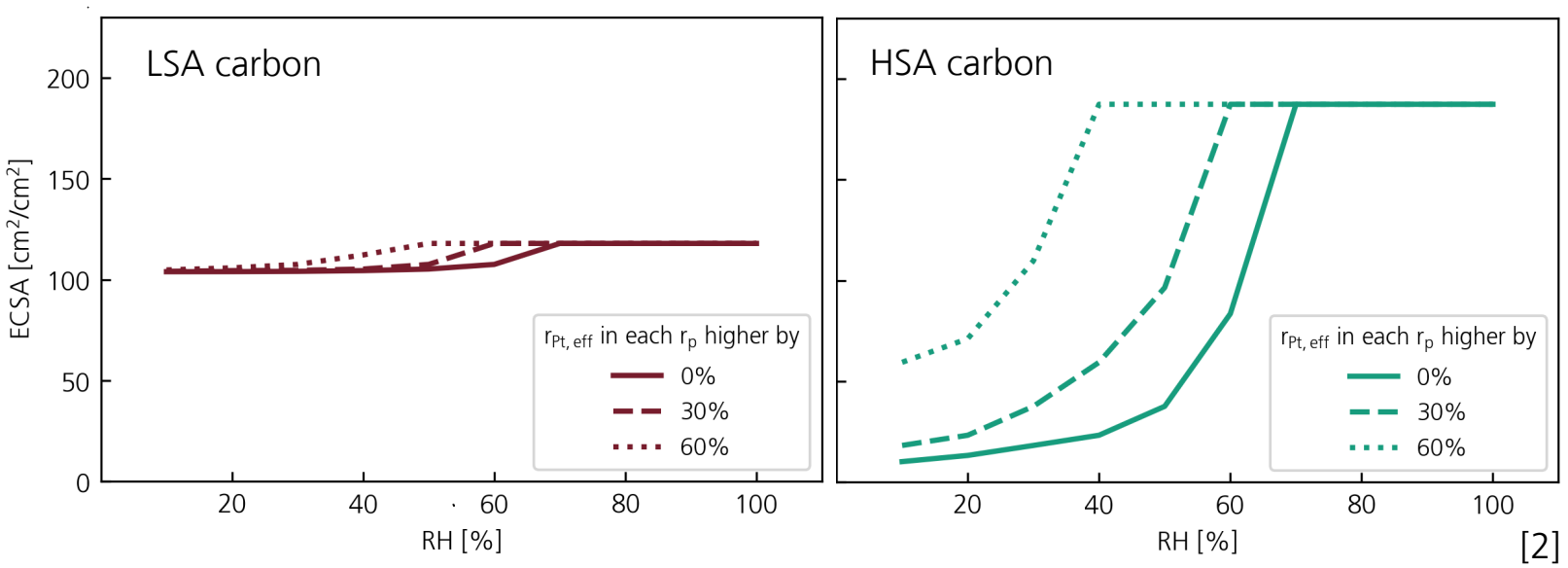
Fraunhofer ISE

Extended Morphology Model: Validation

Parameter Study for Comparison Against Literature



[1]



[2]

Simulated impact of the Pt constriction size (effective Pt size increased by 30% / 60%)

©Fraunhofer ISE
public

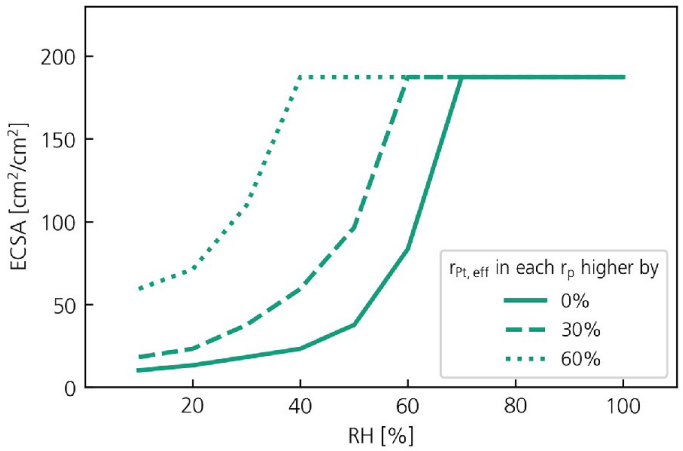
[1] Padgett et al., 2018, DOI 10.1149/2.0541803jes
[2] Scherzer et al., 2025, DOI 10.1149/1945-7111/adc8d9

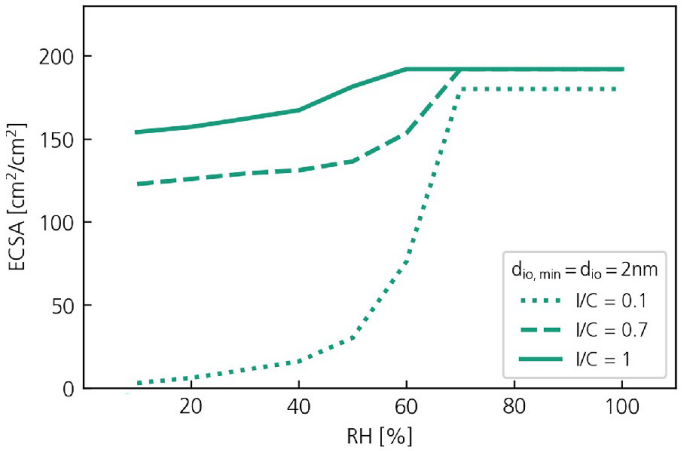
Fraunhofer ISE

Extended Morphology Model: Validation

Parameter Study for Comparison Against Literature

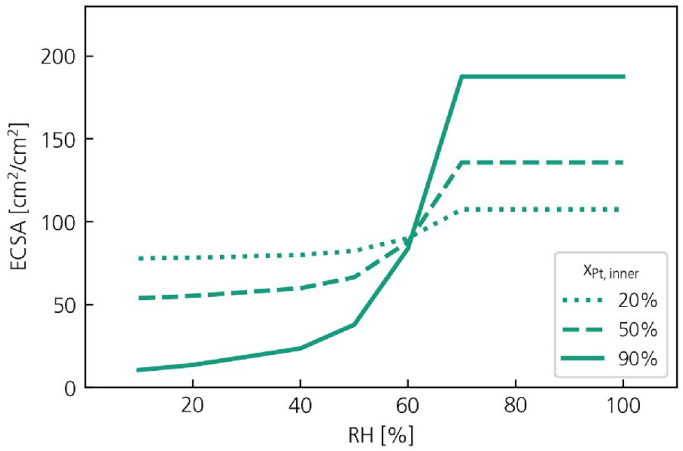
Effective Pt size in pores

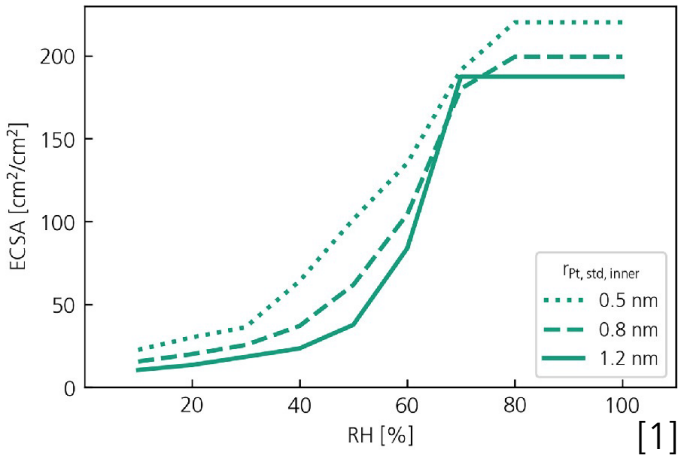




Ionomer loading

Share of Pt particles residing in pores





Width of Pt particle size distribution in pores

[1]

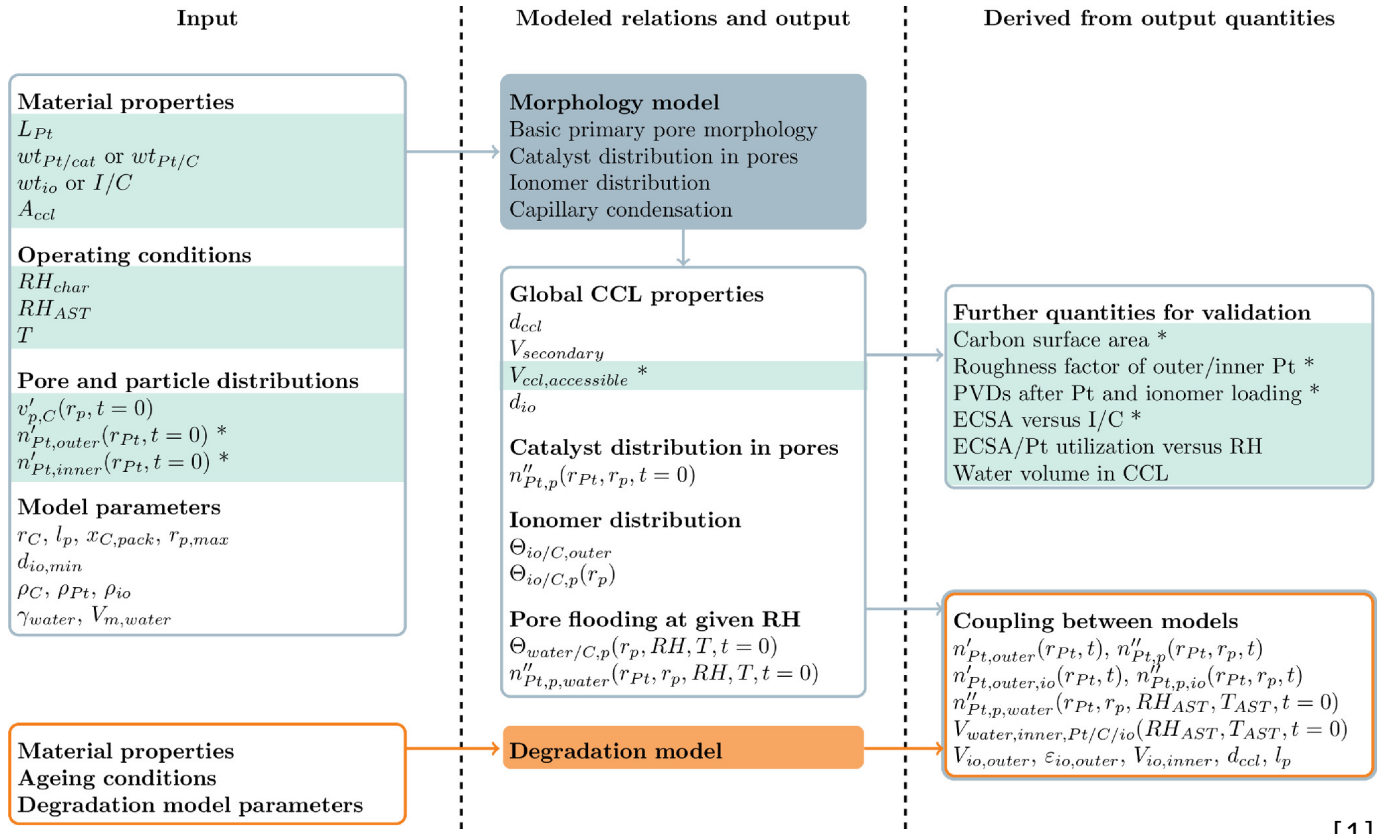
[1] Scherzer et al., 2025, DOI 10.1149/1945-7111/adc8d9

©Fraunhofer ISE
public

Fraunhofer ISE

Morphology Model
Summary

- Model sensitive to distributions of support pores, catalyst particles and ionomer
- Simulation results for different materials are a consequence of the unique morphology of each Pt/C/ionomer system
- Validation against literature and in-house data supports our distribution-based approach
- Modular implementation, can be adapted flexibly to reflect other material properties
- Simple relations → fast model, easy to be integrated into fit routines



[1]

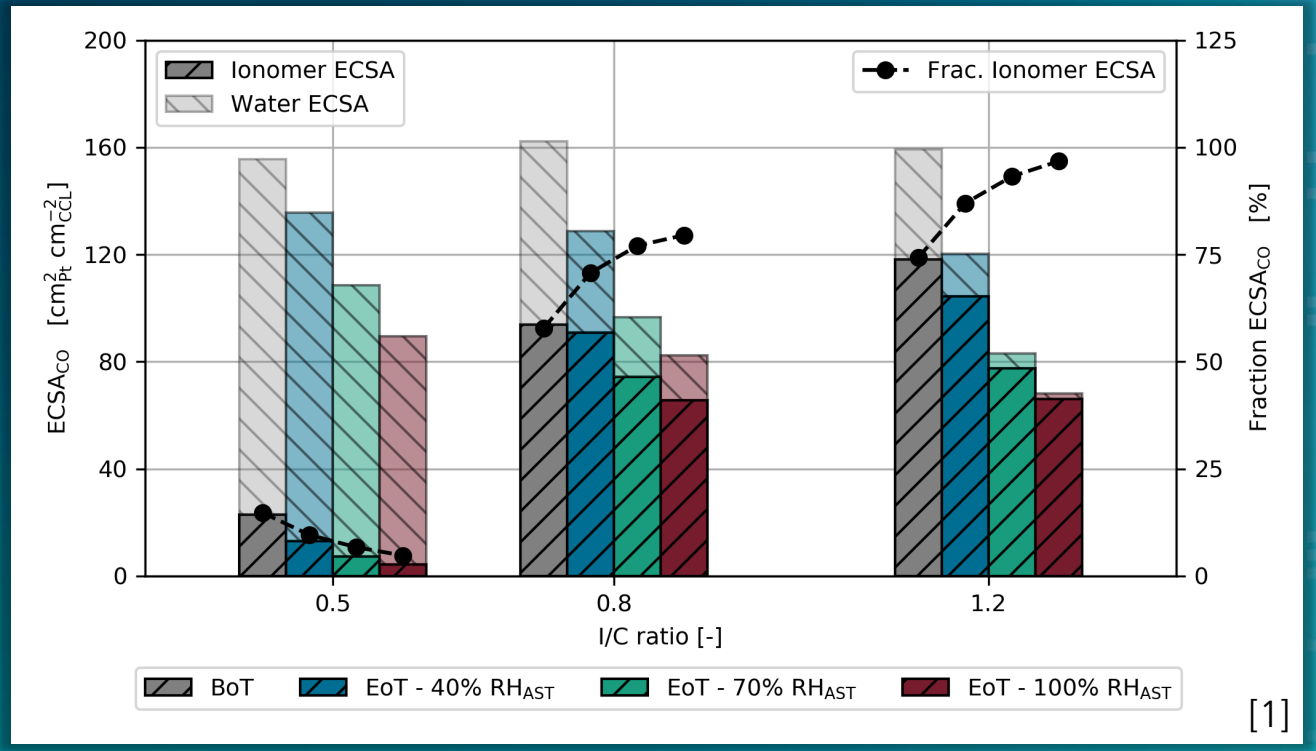
[1] Scherzer et al., 2025, DOI 10.1149/1945-7111/adc8d9

©Fraunhofer ISE
public

Fraunhofer ISE

Degradation Model

Motivation: Degradation is impacted by operating conditions as well as present CCL morphology



Data labels			Cathode properties						AST	
Material variation	AST variation	Test no.	Pt load	I/C ratio	Io. EW	Pt/C ratio	Catalyst type	Support type	UPL	RH
			mg/cm^2		g/mol	%			V	%
Ionomer to carbon ratio	UPL	1	0,3839	0,5	790	50	Pt (SUP1)	HSA	0,95	100
	0.95V	2	0,3793	0,8	790	50	Pt (SUP1)	HSA	0,95	100
	100% RH	3	0,381	1,2	790	50	Pt (SUP1)	HSA	0,95	100
	UPL	4	0,3839	0,5	790	50	Pt (SUP1)	HSA	0,95	70
	0.95V	5	0,3838	0,8	790	50	Pt (SUP1)	HSA	0,95	70
	70% RH	6	0,3827	1,2	790	50	Pt (SUP1)	HSA	0,95	70
	UPL	7	0,3863	0,5	790	50	Pt (SUP1)	HSA	0,95	40
	0.95V	8	0,381	0,8	790	50	Pt (SUP1)	HSA	0,95	40
	40% RH	9	0,3847	1,2	790	50	Pt (SUP1)	HSA	0,95	40
	UPL	10	0,3863	0,5	790	50	Pt (SUP1)	HSA	1,15	100
	1.15V	11	0,3816	0,8	790	50	Pt (SUP1)	HSA	1,15	100
	100% RH	12	0,381	1,2	790	50	Pt (SUP1)	HSA	1,15	100
Ionomer equivalent weight	UPL 0.95V 100% RH	13	0,3846	1,2	720	50	Pt (SUP1)	HSA	0,95	100
		14	0,381	1,2	790	50	Pt (SUP1)	HSA	0,95	100
		15	0,3884	1,2	830	50	Pt (SUP1)	HSA	0,95	100
		16	0,3896	1,2	980	50	Pt (SUP1)	HSA	0,95	100
	UPL 1.15V 100% RH	17	0,3862	1,2	720	50	Pt (SUP1)	HSA	1,15	100
		18	0,381	1,2	790	50	Pt (SUP1)	HSA	1,15	100
		19	0,4162	1,2	830	50	Pt (SUP1)	HSA	1,15	100
		20	0,3717	1,2	980	50	Pt (SUP1)	HSA	1,15	100
Platinum on carbon ratio	UPL 0.95V 100% RH	21	0,378	0,8	790	60	Pt (SUP2)	HSA	0,95	100
		22	0,3995	0,8	790	50	Pt (SUP2)	HSA	0,95	100
		23	0,3754	0,8	790	40	Pt (SUP2)	HSA	0,95	100
		24	0,3638	0,8	790	30	Pt (SUP2)	HSA	0,95	100
		25	0,4017	0,8	790	20	Pt (SUP2)	HSA	0,95	100
	UPL 1.15V 100% RH	26	0,3859	0,8	790	60	Pt (SUP2)	HSA	1,15	100
		27	0,4128	0,8	790	50	Pt (SUP2)	HSA	1,15	100
		28	0,3847	0,8	790	40	Pt (SUP2)	HSA	1,15	100
		29	0,3755	0,8	790	30	Pt (SUP2)	HSA	1,15	100
		30	0,4059	0,8	790	20	Pt (SUP2)	HSA	1,15	100
Platinum alloys	UPL 0.95V	31	0,3793	0,8	790	50	Pt (SUP1)	HSA	0,95	100
		32	0,3547	0,8	790	50	PtCo (SUP1)	HSA	0,95	100
	UPL 1.15V	33	0,3816	0,8	790	50	Pt (SUP1)	HSA	1,15	100
		34	0,3569	0,8	790	50	PtCo (SUP1)	HSA	1,15	100
Carbon support	UPL 0.95V	35	0,4123	0,8	790	50	Pt (SUP2)	HSA	0,95	100
		36	0,4142	0,8	790	50	Pt (SUP2)	LSA	0,95	100
	UPL 0.95V	37	0,4163	0,8	790	50	Pt (SUP2)	HSA	0,95	70
		38	0,4167	0,8	790	50	Pt (SUP2)	LSA	0,95	70
	UPL 0.95V	39	0,4181	0,8	790	50	Pt (SUP2)	HSA	0,95	40
		40	0,4059	0,8	790	50	Pt (SUP2)	LSA	0,95	40
	UPL 1.15V	41	0,4128	0,8	790	50	Pt (SUP2)	HSA	1,15	100
		42	0,4102	0,8	790	50	Pt (SUP2)	LSA	1,15	100

[2]

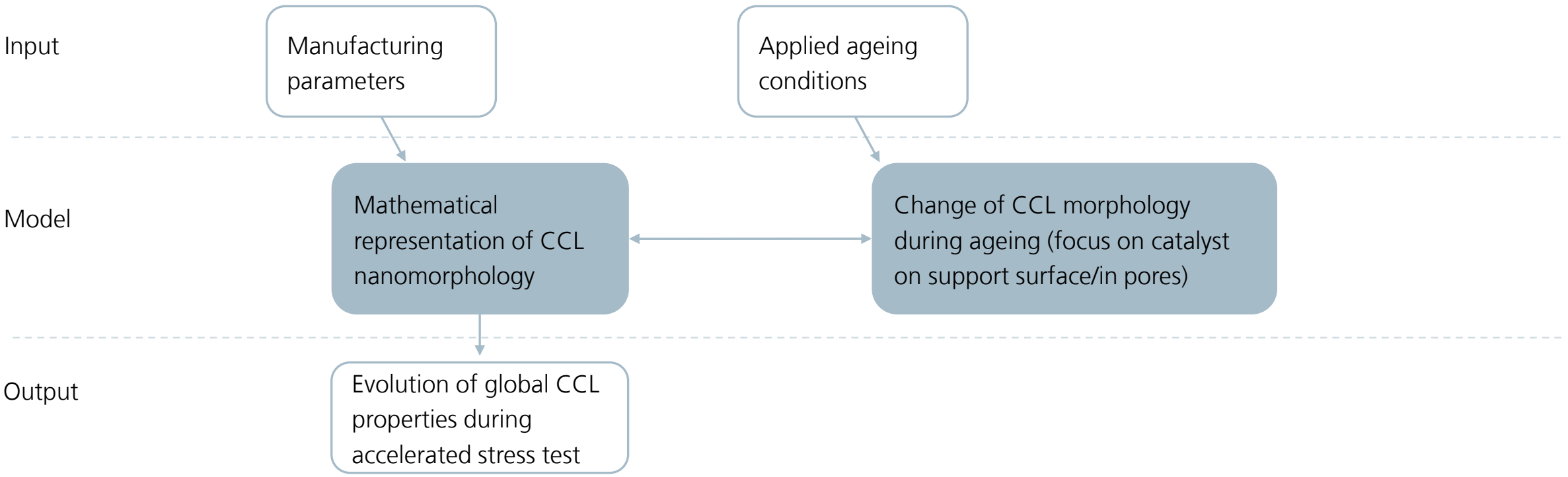
[1] Schneider et al., 2023, DOI 10.1149/1945-7111/acff1f
[2] Schneider et al., 2024, DOI 10.1038/s41597-024-03662-w

©Fraunhofer ISE
public

Fraunhofer ISE

Model Structure

Coupled Morphology + Degradation Model

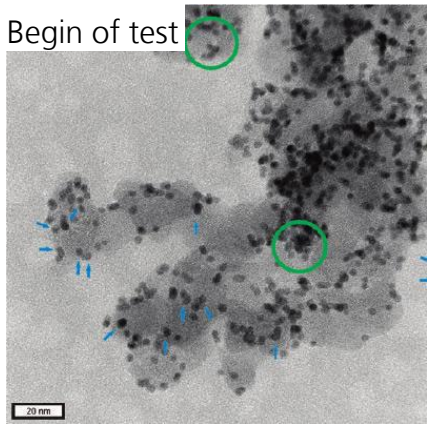


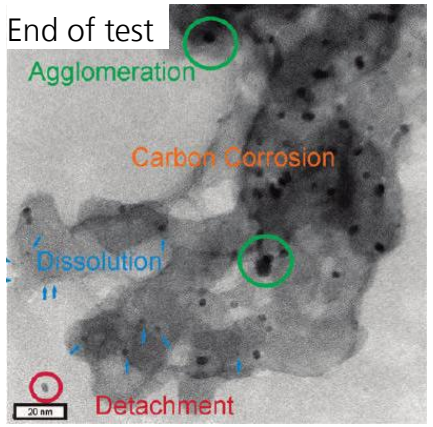
©Fraunhofer ISE
public

Fraunhofer ISE

Degradation Model: Implementation

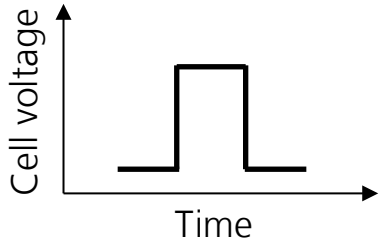
Description of Catalyst Degradation at Given Morphology and Operating Conditions

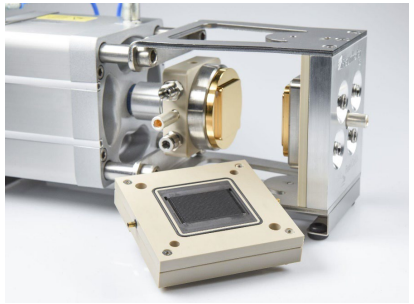




[1]

Repeated potential cycles with square wave between 0.6 V (3 s) and 0.95 V (3 s)



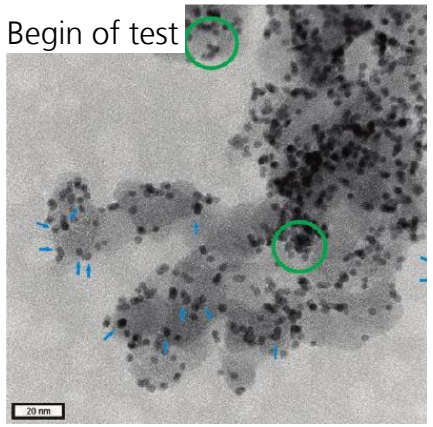


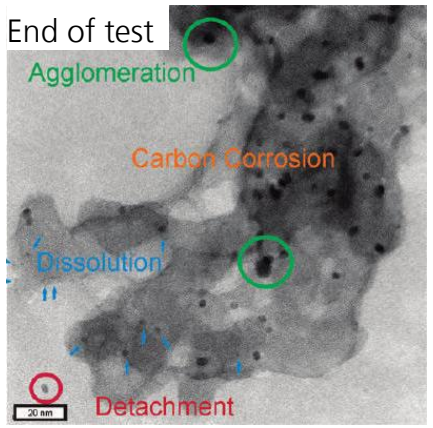
[1] Meier et al., 2012, DOI 10.1021/cs300024h

©Fraunhofer ISE
public

Degradation Model: Implementation

Description of Catalyst Degradation at Given Morphology and Operating Conditions



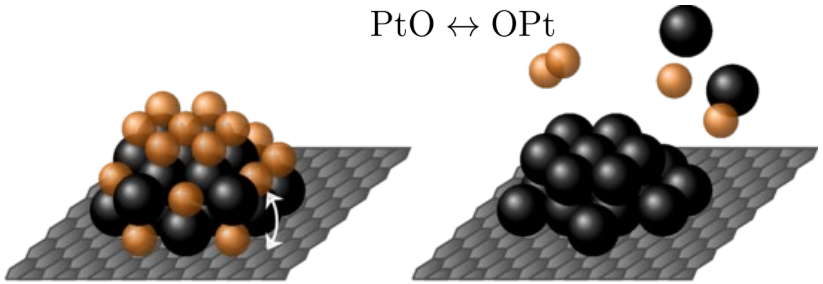


CCL potential

- Pt atoms
- Oxygen
- Protons / Ionomer / dissolved and re-deposited Pt

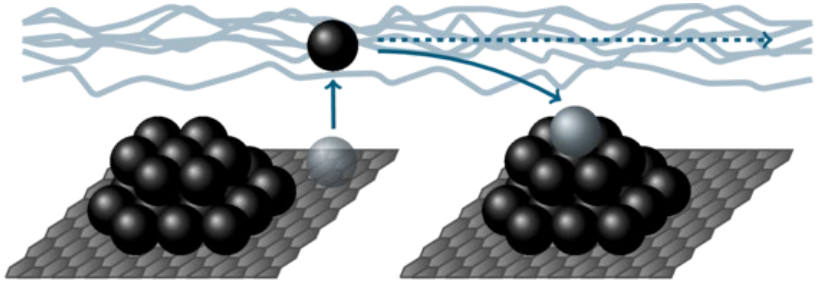
Sub-surface oxide formation (place-exchange)

$$\mathrm{PtO} \leftrightarrow \mathrm{OPt}$$



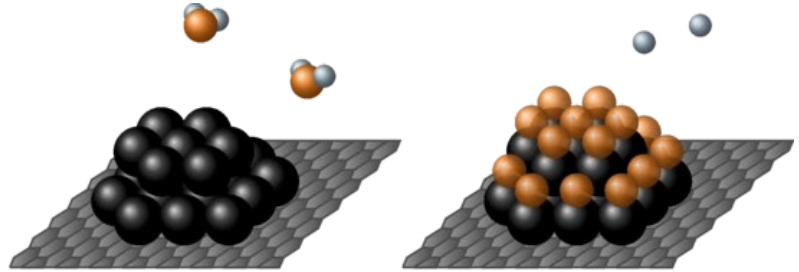
Pt dissolution/redeposition (Ostwald ripening), diffusion to membrane

$$\mathrm{Pt} \leftrightarrow \mathrm{Pt}^{2+} + 2\mathrm{e}^-$$



PtO formation and dissolution

$$\mathrm{Pt} + \mathrm{H_2O} \leftrightarrow \mathrm{PtO} + 2\mathrm{H}^+ + 2\mathrm{e}^-$$



[1]

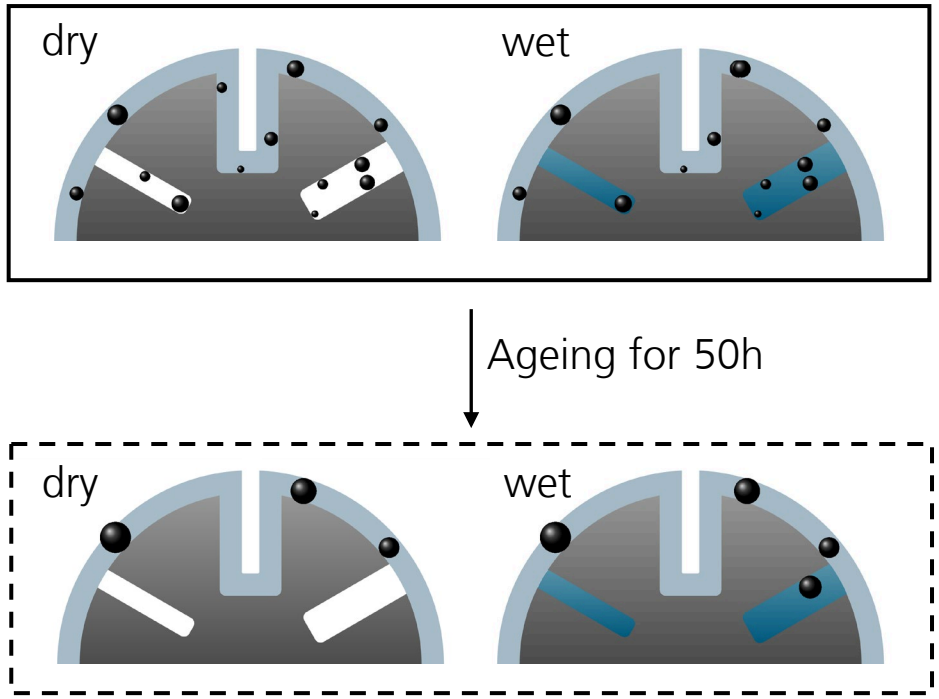
[1] Meier et al., 2012, DOI 10.1021/cs300024h

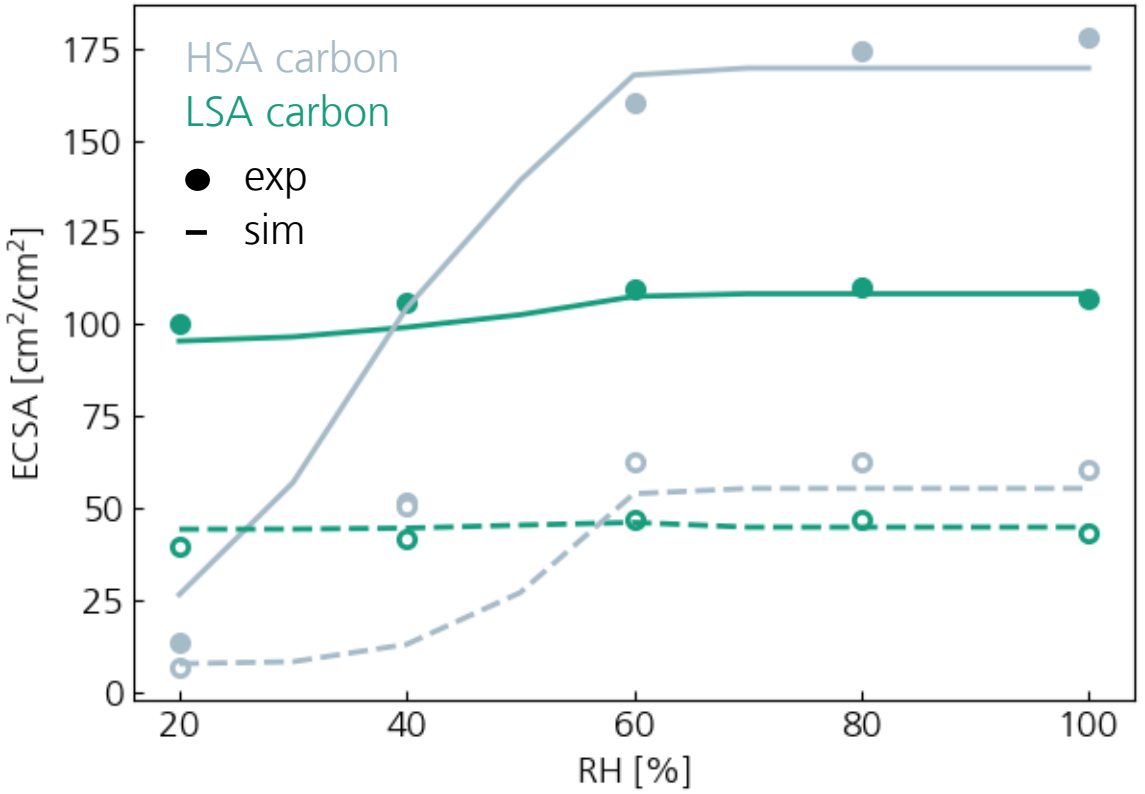
©Fraunhofer ISE
public

Fraunhofer ISE

Degradation Model: Validation

Catalyst Utilization at Begin and End of Test for Different Support Types





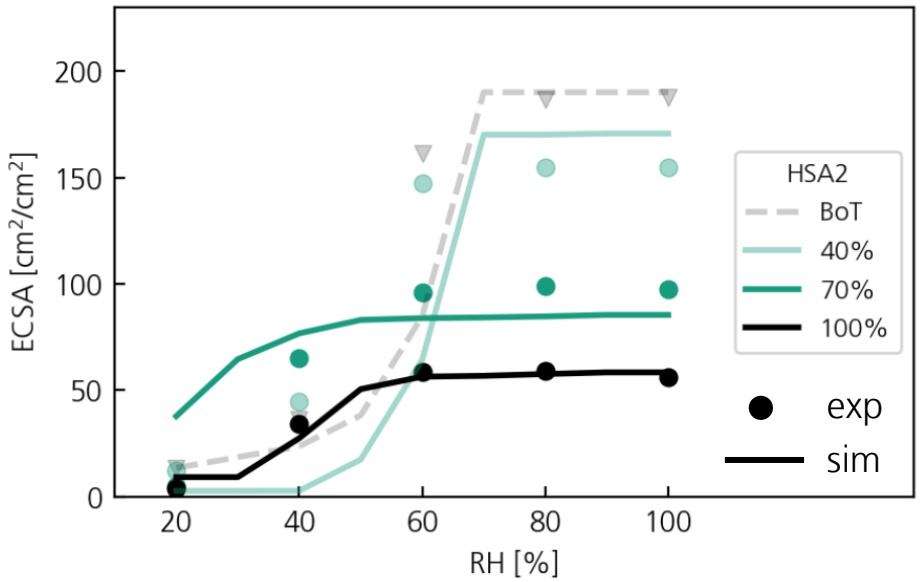
©Fraunhofer ISE
public

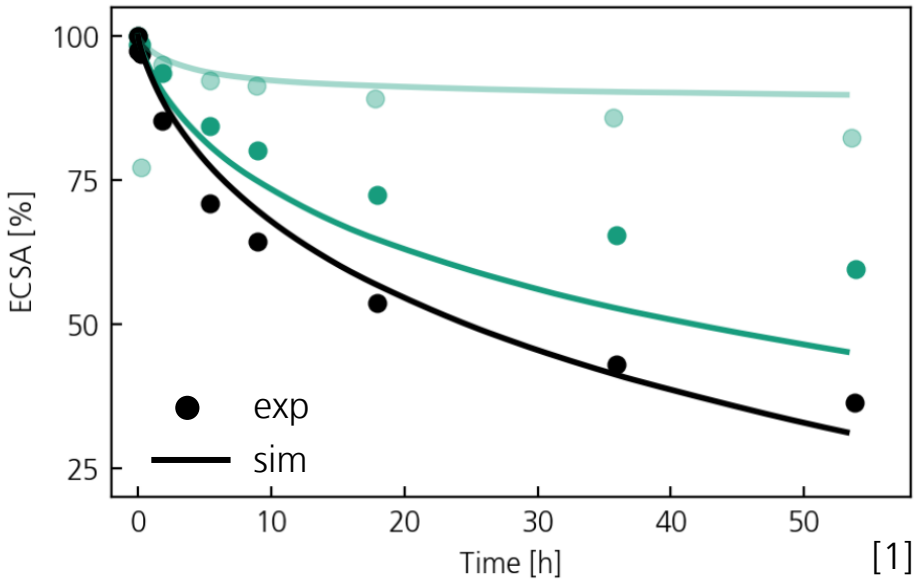
Fraunhofer ISE

Degradation Model: Validation

In-House Material Variation

- Simulations for 15 cells with varying support type, ionomer loading and RH applied during AST
- Best model results for conditions with high I/C and high RH_{AST}, weaker predictions in dry conditions and at low I/C





[1] Scherzer et al., 2025, DOI 10.1149/1945-7111/ade744

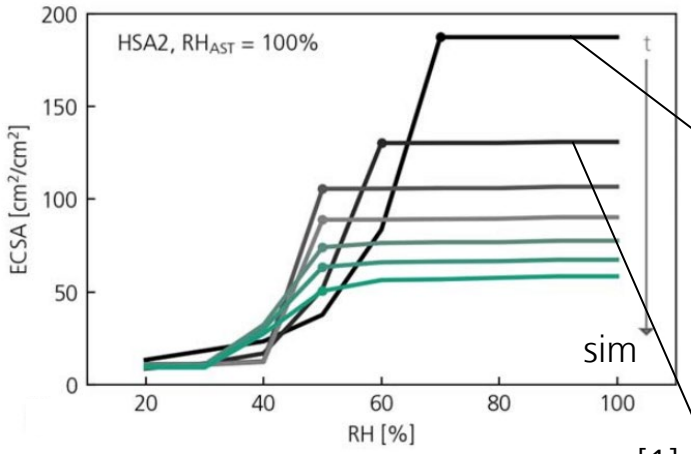
©Fraunhofer ISE
public

Fraunhofer ISE

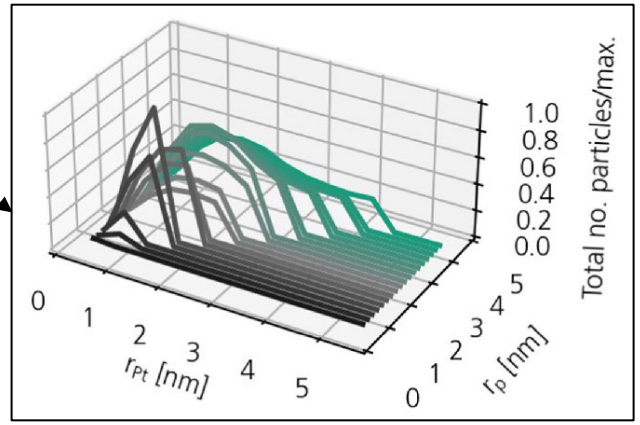
Degradation Model: Analysis of Degradation Modes

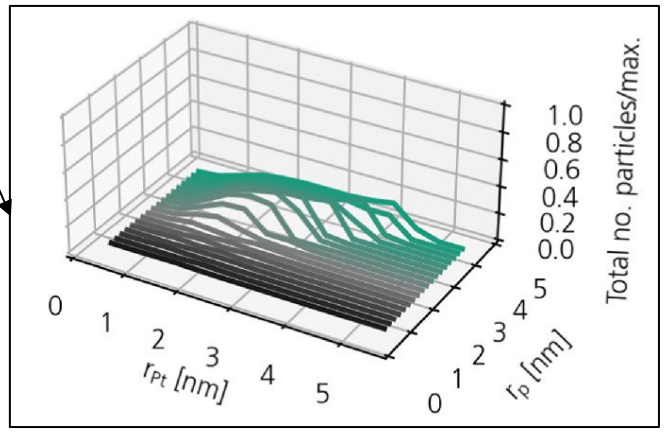
Evolution of Catalyst Utilization versus RH

- Theory: particle coarsening in pores should move the increase in catalyst utilization toward lower RH
- <u>This means catalyst utilization actually increases from BoT to EoT at certain RH!</u>
- No shift in characteristic increase expected in conditions where particles in pores should not age
- Very good agreement with measurements



[1]





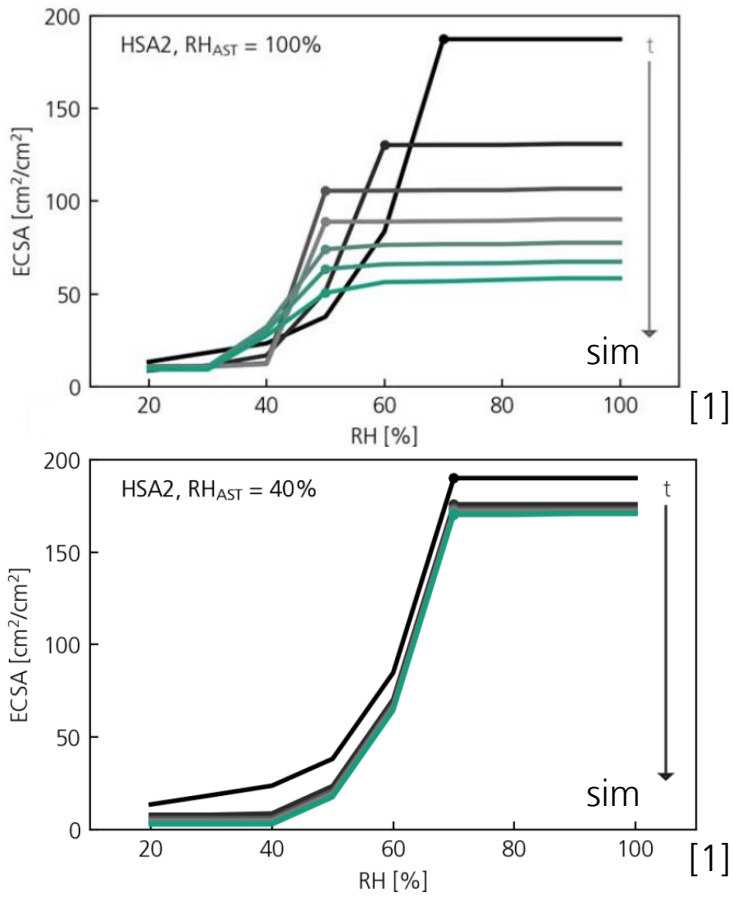
[1] Scherzer et al., 2025, DOI 10.1149/1945-7111/ade744

©Fraunhofer ISE
public

Degradation Model: Analysis of Degradation Modes

Evolution of Catalyst Utilization versus RH

- Theory: particle coarsening in pores should move the increase in catalyst utilization toward lower RH
- This means catalyst utilization actually increases from BoT to EoT at certain RH!
- No shift in characteristic increase expected in conditions where particles in pores should not age
- Very good agreement with measurements



[1]

[1]

[1] Scherzer et al., 2025, DOI 10.1149/1945-7111/ade744

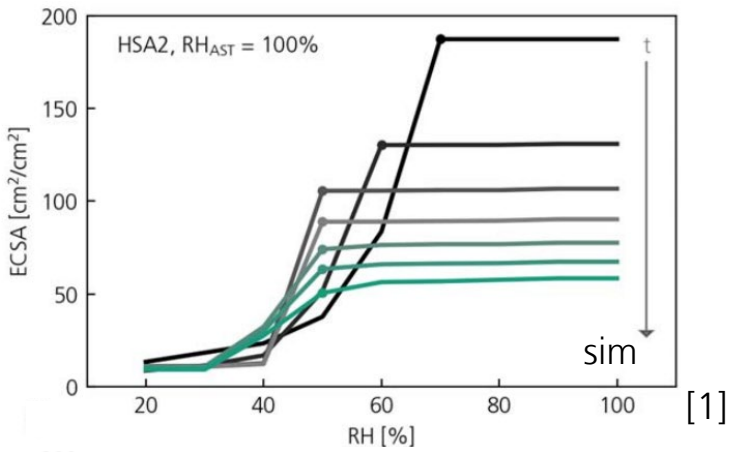
©Fraunhofer ISE
public

Fraunhofer ISE

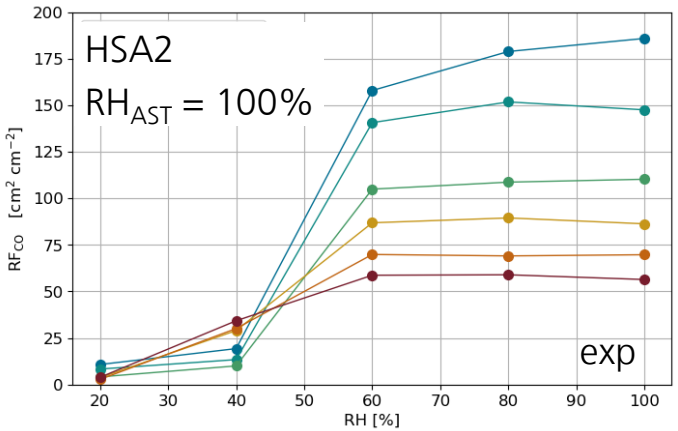
Degradation Model: Analysis of Degradation Modes

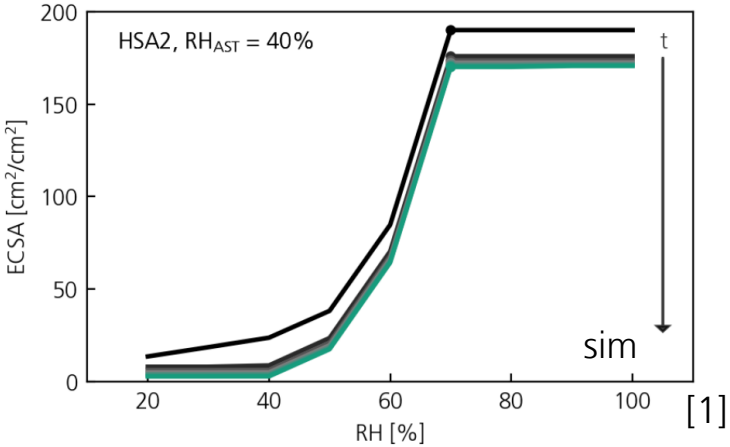
Evolution of Catalyst Utilization versus RH

- Theory: particle coarsening in pores should move the increase in catalyst utilization toward lower RH
- This means catalyst utilization actually increases from BoT to EoT at certain RH!
- No shift in characteristic increase expected in conditions where particles in pores should not age
- Very good agreement with measurements

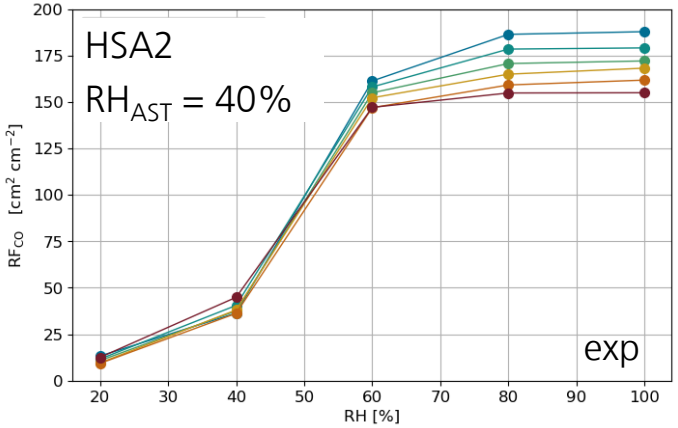


[1]





[1]



[1] Scherzer et al., 2025, DOI 10.1149/1945-7111/ade744

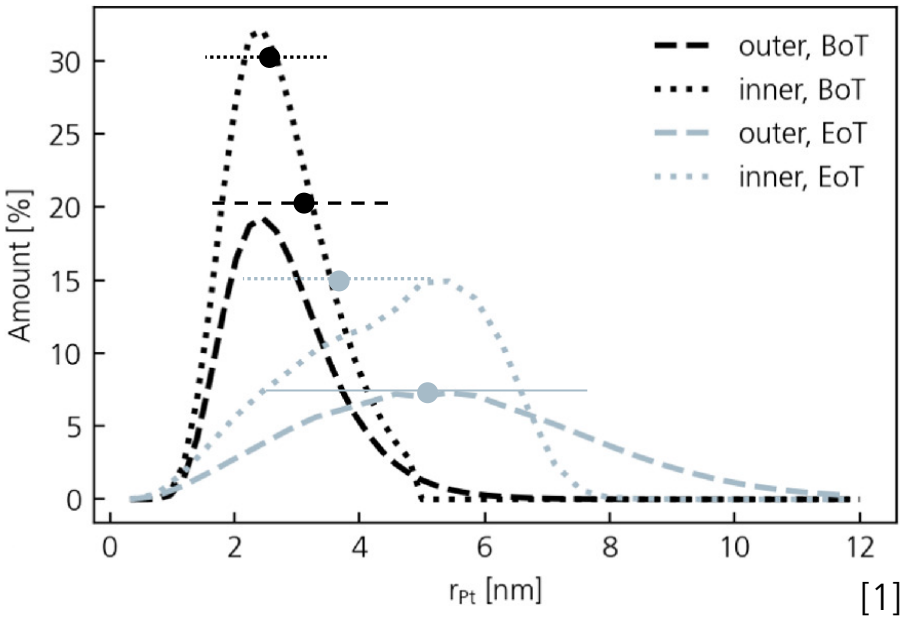
©Fraunhofer ISE
public

Fraunhofer ISE

Degradation Model: Analysis of Degradation Modes

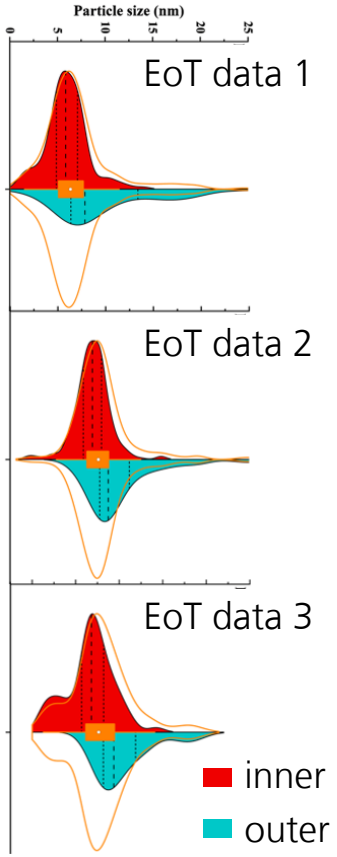
Comparison to Literature Data from Extended AST

- 150 h AST = 720,000 data points for evolution of morphology for these simulations
- Very good correspondence to literature data, specifically reported particle size distributions
- Supports our assumption that solid information on particle size distributions can be obtained by fitting morphology model to data
- Additional comprehensive data sets for model validation would be welcome



[1]

Simulated particle size distributions (lines)
Measured average size and error (points)



[2]

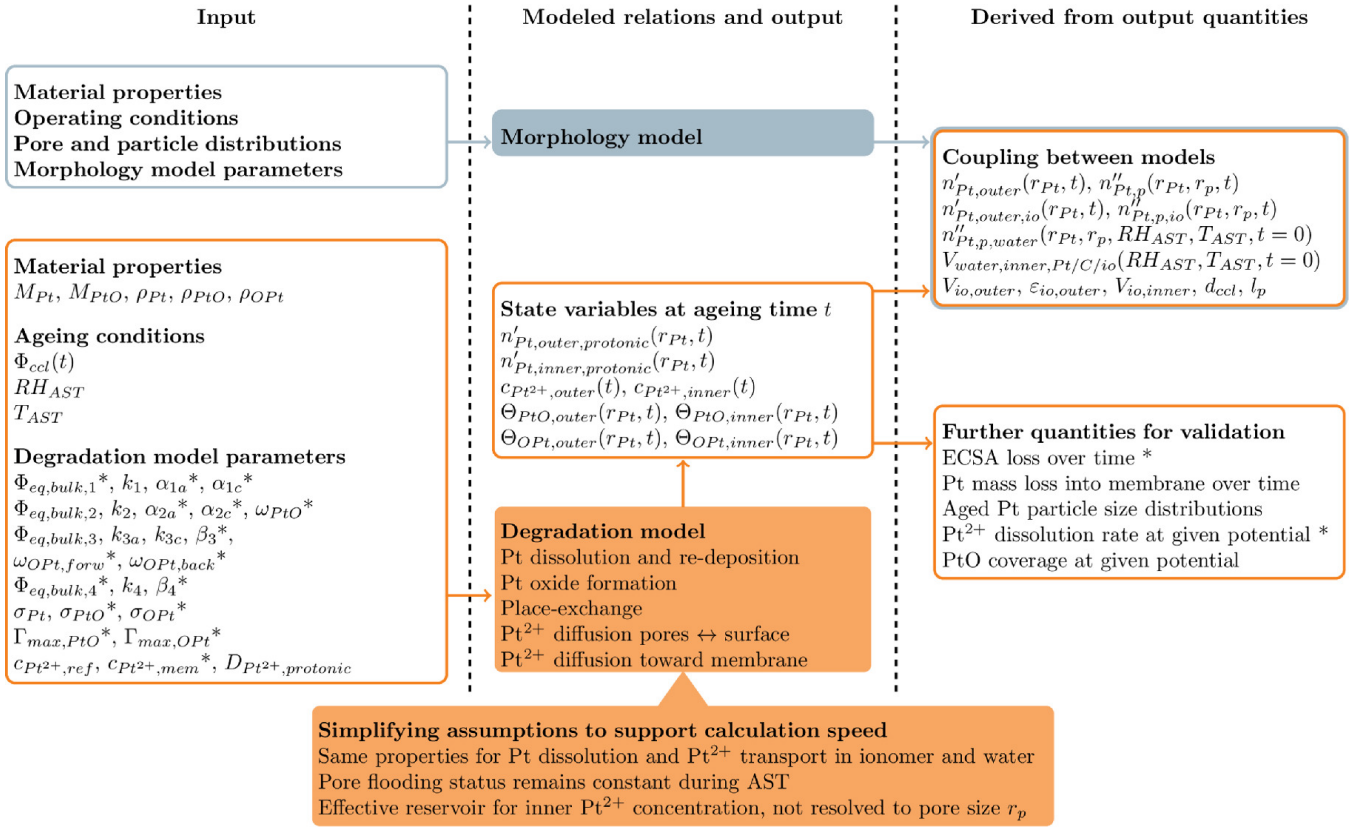
©Fraunhofer ISE
public

[1] Scherzer et al., 2025, DOI 10.1149/1945-7111/ade744
[2] Amichi et al., 2024, DOI 10.1002/aenm.202402310
(Image taken from supplementary information)

Fraunhofer ISE

Degradation Model
Summary

- Highly parametrized model, many parameters which cannot be directly measured (in-situ)
- Model tracks operating history of the electrode; ~240,000 re-calculations of morphology during an AST of 50 h → unsuitable for fit routine
- Parametrization strategy:
  - One set of parameters for all materials
  - Many parameters adapted from literature
  - Only few degradation processes dominant in given conditions
  - Solid parametrization at BoT usually leads to good results during ageing



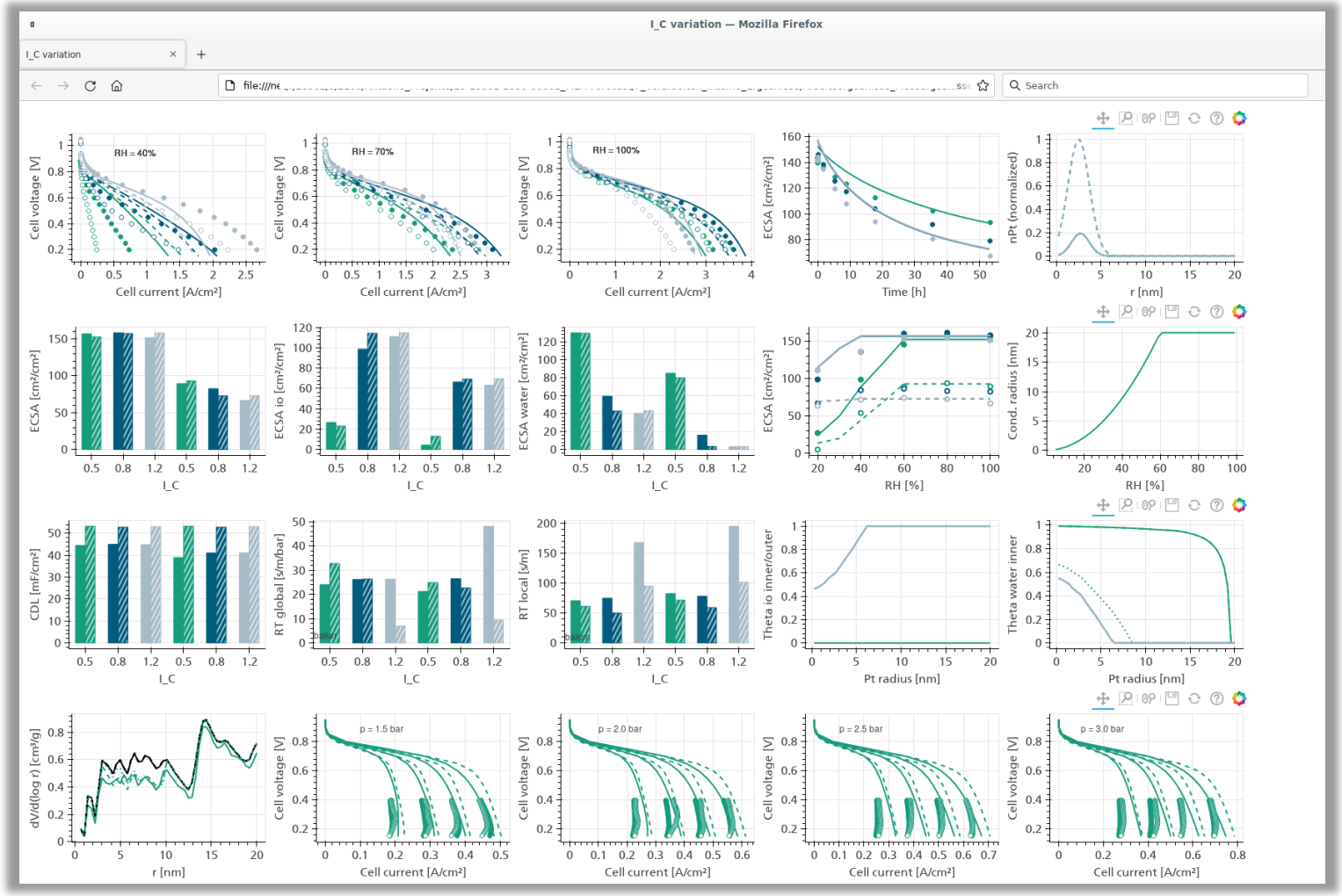
[1]

[1] Scherzer et al., 2025, DOI 10.1149/1945-7111/ade744

©Fraunhofer ISE
public

Outlook
Coupling to Performance Model

- Performance model implemented, but unpublished
- Dedicated software to compare our standard suite of in-situ data with the simulations
- Model structure allows for straightfor-ward integration of new processes and their validation



©Fraunhofer ISE
public

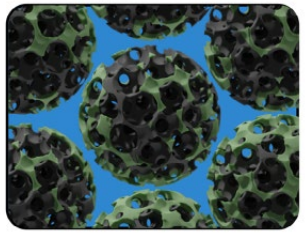
Fraunhofer ISE

Outlook
Further Planned or Possible Model Development

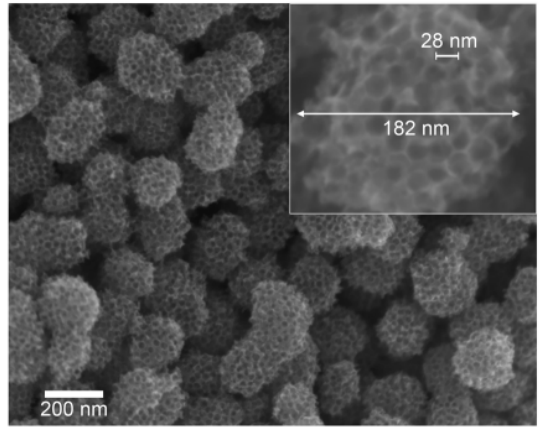
- Novel Pt/C materials (Project CORAL-HD, completed)
- Novel ionomer materials (Projects DirectStack2Scale and GIRAFFE focusing on hydrocarbon ionomers, ongoing)
- Material gradients
- Further processes, e.g.
  - ionomer degradation
  - support degradation
  - ageing under H_2/O_2 with associated inhomogeneities in reactant concentration and CCL potential
- Further cell components, e.g. impact of GDL and membrane

Gefördert durch: Bundesministerium für Verkehr
aufgrund eines Beschlusses des Deutschen Bundestages
Koordiniert durch: NOW-GMBH.DE
Projektträger: PtJ Projektträger Jülich Forschungszentrum Jülich





[1]



[1]

[1] Martin et al., 2025, 10.1002/aenm.202500954

©Fraunhofer ISE
public

Journal of The Electrochemical Society, 2025 **172** 074504

Simulating Morphology and Degradation of PEMFC Cathode Catalyst Layers with Porous Carbon Supports: Part I. Effect of Relative Humidity on Catalyst Utilization

Anne-Christine Scherzer,[1,z] Patrick Schneider,[1] Matthias Klingele,[2] Nada Zamel,[1] and Dietmar Gerteisen[1]

[1] *Fraunhofer Institute for Solar Energy Systems ISE, 79110 Freiburg, Germany*
[2] *Hochschule für angewandte Wissenschaften Kempten, 87435 Kempten, Germany*

We present a physical model of the cathode catalyst layer morphology which simulates the electrochemically active catalyst surface area at varying degrees of humidification. The model considers pore, particle and ionomer distributions and resulting interfaces on the nanoscale to create a unique mathematical representation of each material. Specifically, the model discriminates between catalyst particles on the support surface and inside primary pores of the support and their respective connection to the proton-conducting phase. Catalyst particles may be protonically activated by coverage with ionomer or water or be protonically inaccessible. The exact configuration depends on the particle size and location as well as the cell operating conditions, sensitizing the simulated catalyst utilization to these properties. Model results are compared against data for five samples with different support materials and ionomer loadings manufactured in-house. Further, trends in catalyst utilization which were observed in recent literature are reproduced with the model. This work provides a comprehensive analysis of material configurations and simulations at begin of test. In Part II, the presented model is integrated into a degradation model to predict the evolution of the electrode morphology and catalyst utilization during ageing.

© 2025 The Author(s). Published on behalf of The Electrochemical Society by IOP Publishing Limited. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, https://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/1945-7111/adc8d9]

Manuscript submitted December 19, 2024; revised manuscript received March 22, 2025. Published July 4, 2025.

Supplementary material for this article is available online

List of Symbols

Subscripts

activatable	Accessible for protonic activation by condensed water or ionomer
cat	Referring to catalyst powder (Pt and C)
ccl	Referring to entire CCL
char	Characterization
cond	Condensation of water vapor
cut	Cut-off, referring to critical pore size for ionomer penetration
eff	Effective
inner	Inside support primary particle nanopores, referring to entire CCL
io	Ionomer
io/C	Ionomer/carbon interface
io/Pt	Ionomer/Pt interface
mean	Mean
outer	On support primary particle surface, referring to entire CCL
p	Referring to primary pore
secondary	Secondary pores, referring to entire CCL
std	Standard deviation
total	Referring to entire CCL
water	Referring to condensed water
water/C	Condensed water/carbon interface
AST	Accelerated stress test
C	Carbon support
Pt	Platinum catalyst
Pt/C	After loading the support with Pt
Pt/Clio	After loading the support with Pt and ionomer

Parameters

γ	Surface tension, N m^{-1}
ε	Volume fraction
μ	Parameter for lognormal distribution
ρ	Material density, kg m^{-3}
σ	Parameter for lognormal distribution
Θ	Fractional coverage referring to available interfacial surface
d	Layer thickness, m
l	Length, m
m	Mass, kg
n'	Particle or pore number distribution, m^{-1}
n''	Distribution of particles in pores, m^{-1}m^{-1}
r	Particle or pore radius, m
v'	Pore volume distribution, m^{3}m^{-1}
wt	Mass fraction
x	Fraction or partition
A	Area, m^2
L	Catalyst loading, kg m^{-2}
N	Total number of particles or pores
T	Temperature, K
RH	Relative humidity
V	Volume, m^3

The nanomorphology of the cathode catalyst layer (CCL) in PEM fuel cells plays a crucial role for cell performance and degradation. A robust and performant CCL must meet various, sometimes conflicting requirements. Optimization in manufacturing methods and material combinations is typically targeted toward achieving a high electrochemically active surface area (ECSA) and good protonic accessibility of the catalyst while maintaining sufficient open pore volume to avoid oxygen mass transport limitations. In this context, high surface area carbon supports (HSA) constitute an important toolbox due to their capacity to host catalyst particles and proton conducting materials both on the outer support surface and within support pores, with different effects on the associated transport processes in each domain.[1] Investigating the relations between material combination, synthesis method and resultant CCL nanomorphology in HSA carbons has hence gathered much research

[z]E-mail: anne-christine.scherzer@ise.fraunhofer.de

Fraunhofer ISE

Thank You for Your Attention!

Anne-Christine Scherzer

anne-christine.scherzer@ise.fraunhofer.de