



PEMFC Performance Modeling Framework: Analyzing Pt Particle Size Distribution and Carbon Support Structure Impact

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A cathode catalyst layer model framework that accounts for the position of the platinum particles on the carbon support structure is proposed. Combining a discrete platinum particle size distribution (PSD) with the binary classification of whether the platinum particle is decorated on the support surface (Pt_{outer}) or buried inside the pore structure (Pt_{inner}) allows the differentiation of distinct loss mechanisms. Additional mass transport and proton accessibility issues are modelled for Pt_{inner} due to the extended diffusion path and worsened proton conduction inside the ionomer-free primary pores of the carbon support. Pt_{inner} particles suffer from the adsorption of sulphonic acid groups (ionomer poisoning) and the densification of ionomer thin film that builds a compact layer above the outer Pt particle. The influence of carbon support type such as high and low surface area carbon on the cell performance is simulated and discussed for different scenarios. A parameter study is conducted that gives insight into the complex interaction between the contribution of current generation obtained from Pt_{inner} and those from Pt_{outer} . The impact on mass activity and mass transport resistance is analyzed as well. The effect of PSD evolution on the cell performance is discussed.

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Polymer electrolyte membrane fuel cells (PEMFC) are promising candidates for generating clean power in stationary and mobile applications. Despite over three decades of intensive research aimed at enhancing their performance and durability while reducing costs, the market introduction phase proceeds slowly. One significant challenge, aside from hydrogen availability, lies in the membrane electrode assembly (MEA), the core component of the fuel cell. Specifically, the cathode catalyst layer (CL) experiences high polarization losses under load, even with substantial platinum (Pt) loading, particularly after long-term operation due to CL degradation.

Efforts to optimize CL structure focus on its components: state-of-the-art electrodes typically consist of Pt or Pt-alloy catalysts, carbon support, and ionomer. A wide range of combinations regarding type, quantity, proportion, synthesis route, and fabrication process has been explored. Key factors include the Pt-to-carbon weight ratio (Pt/C wt%),¹ ionomer-to-carbon ratio (I/C),² Pt loading, Pt particle size distribution and location,³ support type^{3–5} and ionomer type categorized by equivalent weight (EW) and side-chain length.⁶ Most studies showed that it is not expedient to focus on improving the properties of the sole ingredients itself but on their mutual complex interaction and long-term stability. For instance, a highly active catalyst characterized by rotating disc electrode measurements does not necessarily translate to improved oxygen reduction reaction (ORR) kinetics in a high-performing MEA.^{7,8} Furthermore, the dispersion and deposition of catalyst particles on the carbon support within the CL are critical.^{4,9–11} A well-conducting ionomer network is essential for delivering protons to Pt sites for ORR, and the wetting properties of the ink formulation are crucial for establishing a large electrochemically active surface area (ECSA) while ensuring thin layers of ionomer above the catalyst particles. The optimal ionomer dispersion might occur when all Pt particles are covered and directly connected to the proton conduction network. This coverage should be achieved with a thin ionomer film to minimize the oxygen diffusion barrier and also to avoid excess ionomer loading which might contribute to premature degradation of the CL.^{12,13} However, recent studies indicate that direct contact between Pt and ionomer can lead to catalyst poisoning due to the adsorption of sulfonic acid groups,¹⁴ reducing area-specific activity to as low as 22% of a non-poisoned Pt in contact with water.¹⁵ The use of high surface area carbon (HSAC), such as Ketjenblack,

provides a rough surface with tiny nanopores for Pt deposition. This buried Pt appears to be protected from SO_3^- poisoning due to the ionomer's structure and stiffness, which hinders the penetration of these pores.^{4,16,17} Park et al.⁴ reported more than a threefold increase in mass activity for Pt on HSAC compared to low surface area carbon (LSAC). Ramaswamy et al.⁵ observed similar increases in activity (2.5–3.9 times, from 175 A g_{Pt}⁻¹ for Vulcan to 440–680 A g_{Pt}⁻¹ for Ketjenblack). These findings suggest that buried Pt particles remain electrochemically accessible as long as the fuel cell operates under sufficiently humidified conditions, due to finite proton conduction over a few nanometers into primary pores via complex transport processes on the pore wall or liquid water occupancy.^{18,19} In addition to poisoning effects, simulations reveal a strong oxygen diffusion barrier in the ionomer thin film near Pt, attributed to densification of the ionomer layer due to attractive forces between the Pt surface and ionomer molecules.^{20–22} Both poisoning and ionomer restructuring appear to be dependent on relative humidity (RH).^{22,23} Molecular dynamics simulations of highly oxygen-permeable ionomers (HOPIs) indicate that both high permeation and mitigation of poisoning are due to the suppression of densely layered folding of polymer backbones near catalyst surfaces by the incorporated ring-structured matrix.²⁴ The interdependence of these properties and processes within the CL complicates the interpretation of performance data, as optimizing one property may lead to a decrease in another. To address these complexities, a performance model should incorporate through-plane transport of protons and oxygen in the CL via the ionomer and secondary pore network on a macroscopic scale.^{25–27} These processes must be coupled with micro- and mesoscale phenomena, including the adsorption of oxygen at the ionomer surface, oxygen diffusion, and proton migration within the ionomer thin film.²⁸ This includes considering the ionomer-free, open or water-occupied substructure of the carbon support and the unique properties of thin films, which differ significantly from bulk materials, as well as their interactions with Pt nearby.^{29,30}

The accessibility of oxygen at the reaction sites is critical and has been modeled at various levels of detail. Mashio et al.³¹ developed a mathematical model for local gas transport in a single carbon primary particle by merging the classical agglomerate model with local gas transport near a Pt particle, introducing two processes: gas transport through an ionomer thin film on the carbon particle's surface and through water inside the particle. To match experimentally measured gas transport resistances, they set gas permeability through the ionomer thin film to 10%–20% of that through the bulk



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Speaker: Dietmar Gerteisen

Co-authors: Patrick Schneider, Anne-Christine Scherzer

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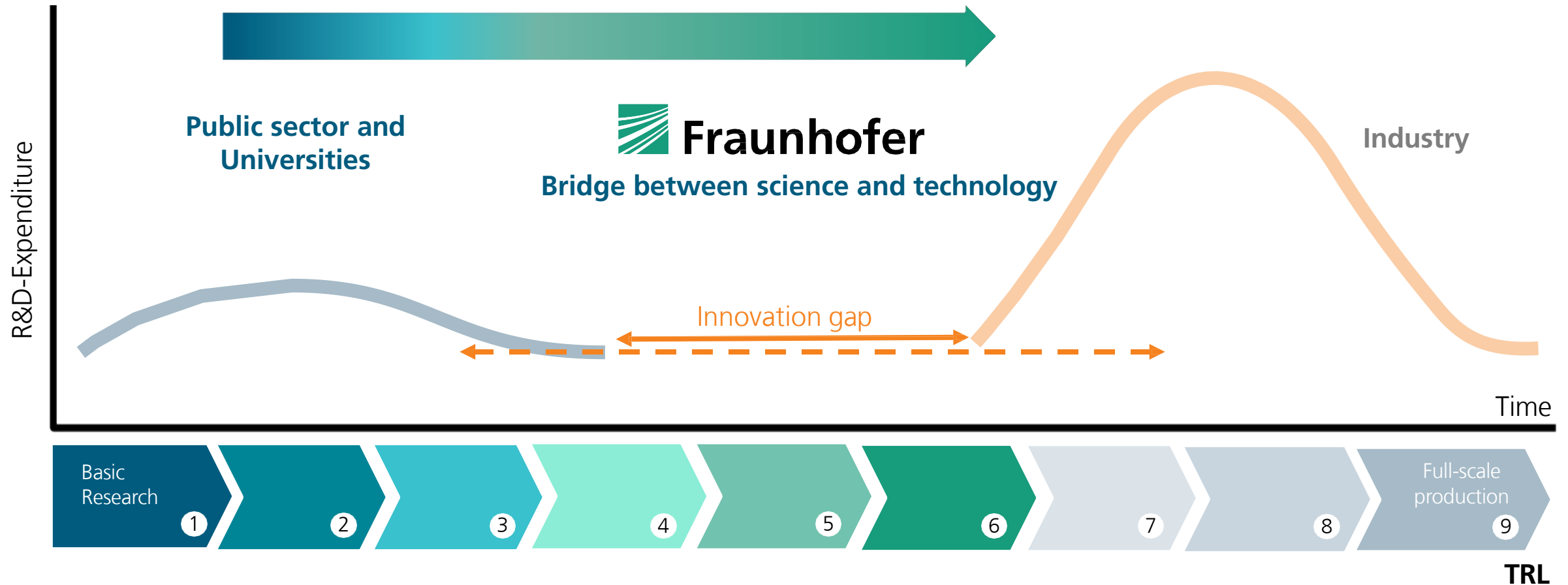
Freiburg, Germany, 20.05.2026

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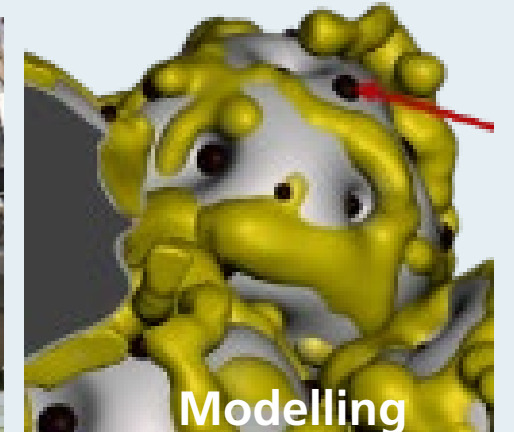
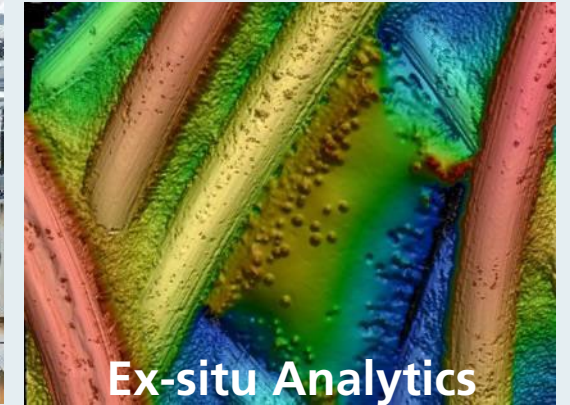
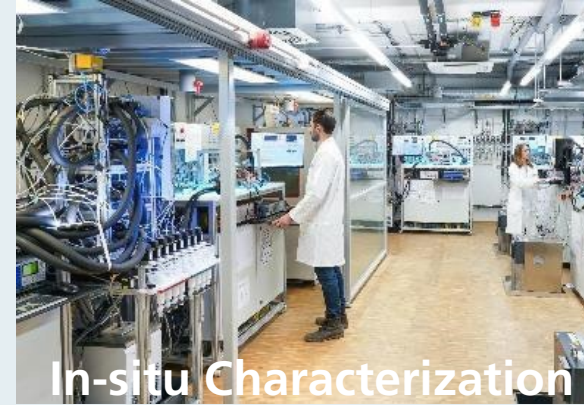
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- 45 researchers plus students
- 9.4 Mio. € annual budget (w/o investments)
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- Focus on transport application

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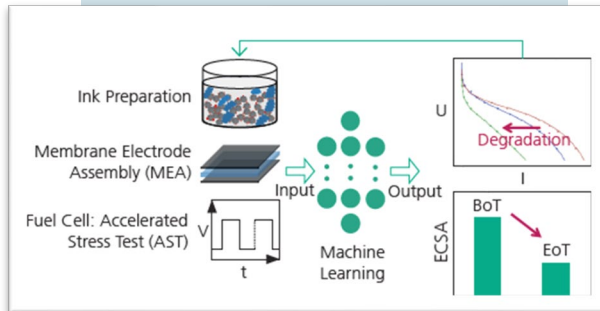
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Fuel Cell Modeling Team

Main Topics

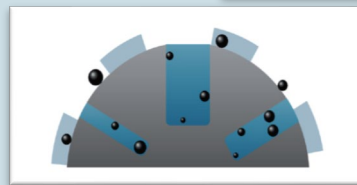
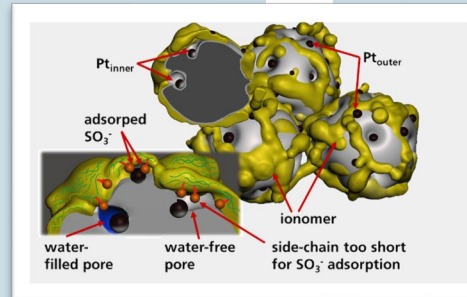
AI / Machine Learning

- CCM production



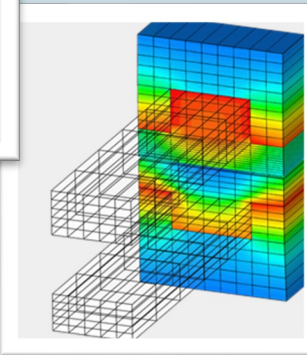
Electrode level

- Self developed codes, focus: Python
- Structure, performance degradation, transport processes



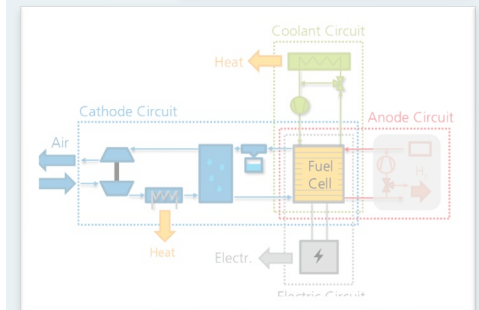
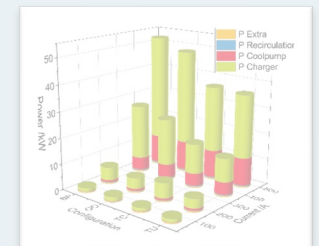
Cell level

- Self developed codes (Python)
- Commercial CFD code (FireM)
- Local effects



System level

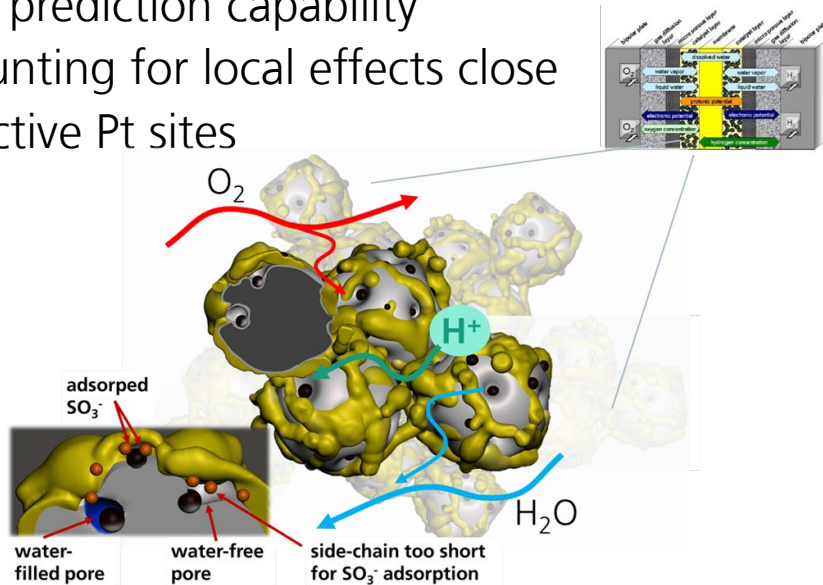
- Design and optimization



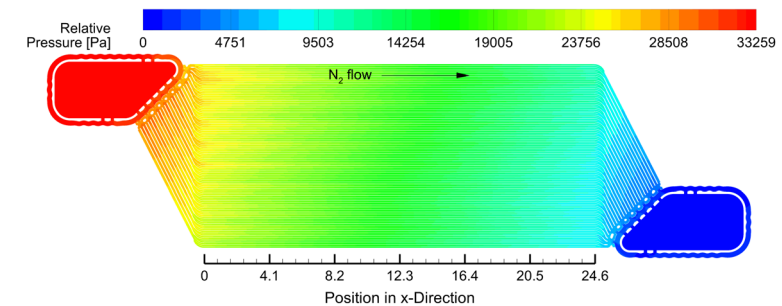
Motivation

Aim of the model framework

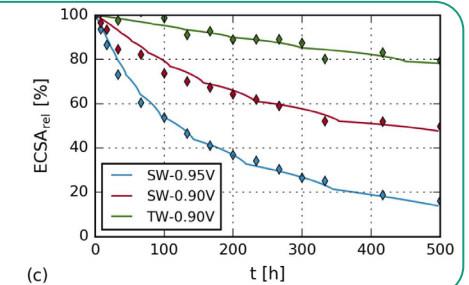
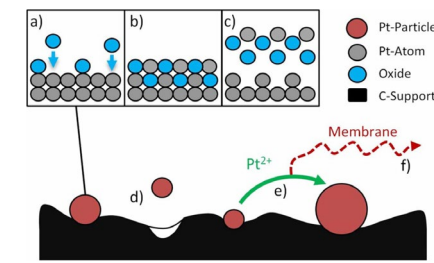
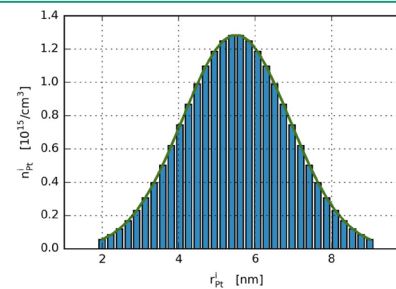
- Improving prediction capability
 - by accounting for local effects close to the active Pt sites



- BUT
 - without increasing too much computational efforts
 - Integration into 3D-CFD code is essential



- Besides performance, degradation modeling is of interest
 - Adaption on existing degradation model based on particle size distribution (PSD)



And its associated limiting processes in the electrode

- Platinum supported on carbon particles
- Ionomer covers Pt particles
- Secondary pores between agglomerates



Structure of the catalyst layer

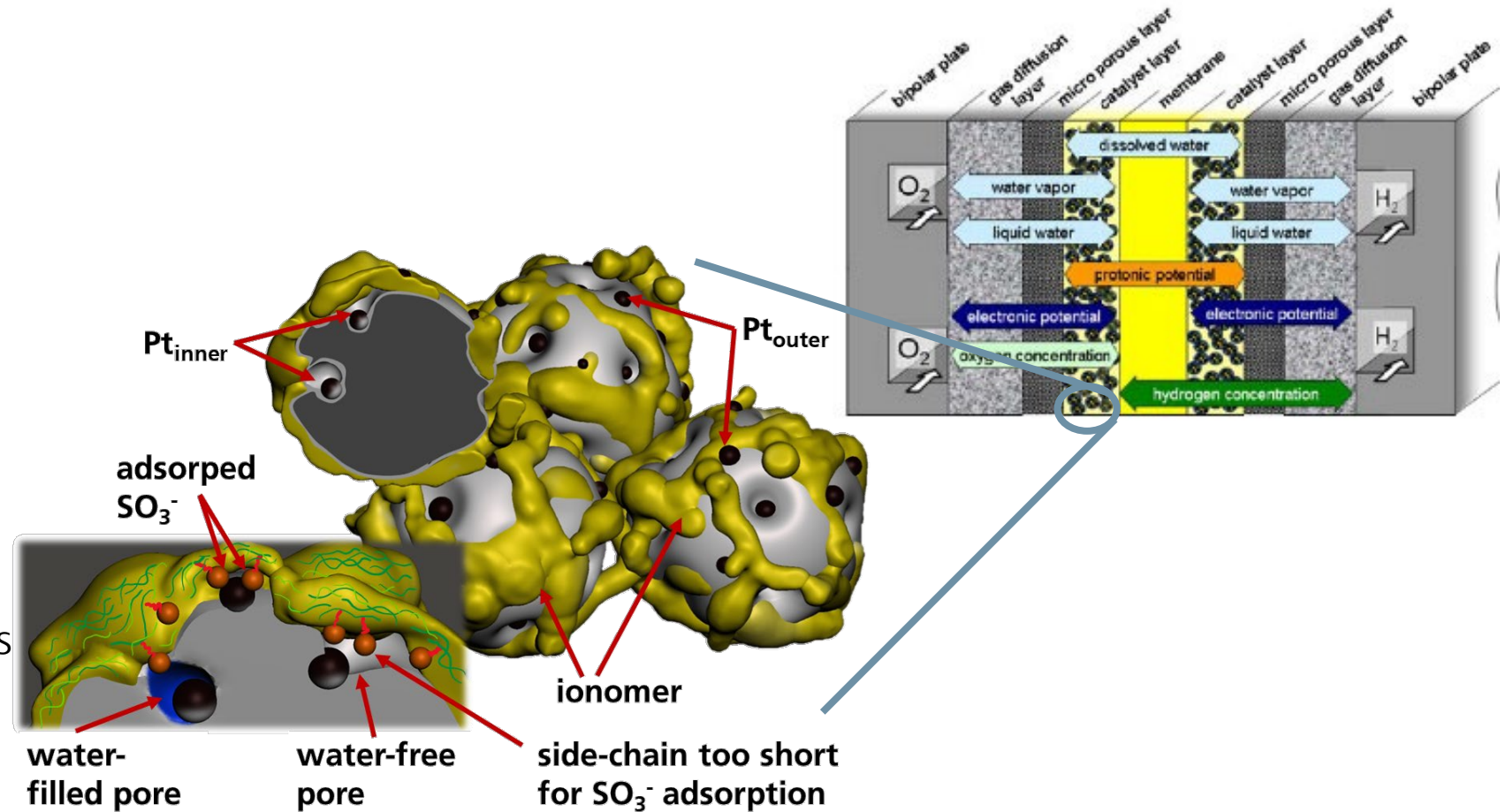
And its associated limiting processes in the electrode

Matrix of Pt/C/ionomer

- Platinum supported on carbon particles
- Ionomer covers Pt particles
- Secondary pores between agglomerates

Limiting processes

- Low ORR kinetics
- High mass transport limitations
- High humidity-dependence of proton conductivity and Pt accessibility

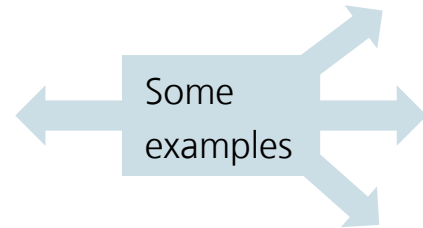


Structure of the catalyst layer

And its associated limiting processes in the electrode

Findings from the literature

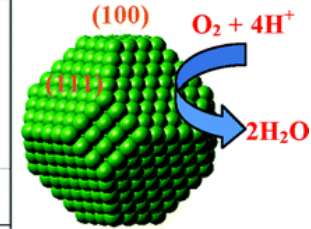
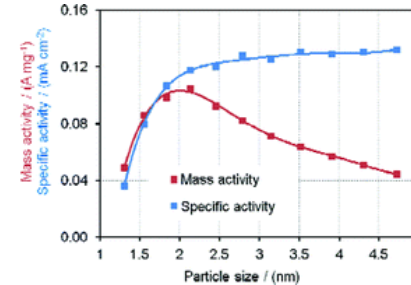
- Kinetics is Pt particle-size dependent
 - ORR activity
 - Oxide formation
 - Pt dissolution



Needs for 'realistic' CL model

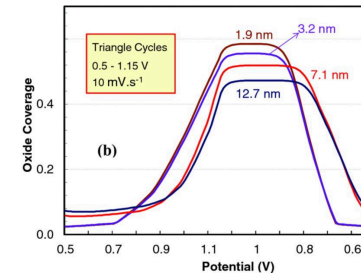
- Distinguish between Pt particle sizes → PSD (particle size distribution)

Pt-size dependent activity



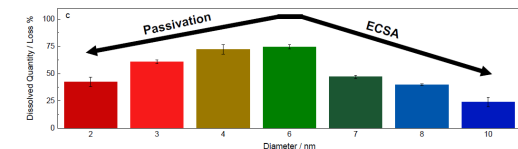
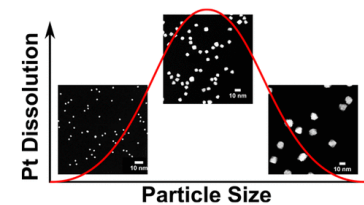
Shao et al., Nano Letters, 11, 3714-3719, (2011)

Pt-size dependent oxide formation



Ahluwalia et al., JES, 160 (4) F447-F455 (2013)

Pt-size dependent degradation



Sandbeck et al., ACS Catal., 10, 11, 6281-6290, (2020)

Structure of the catalyst layer

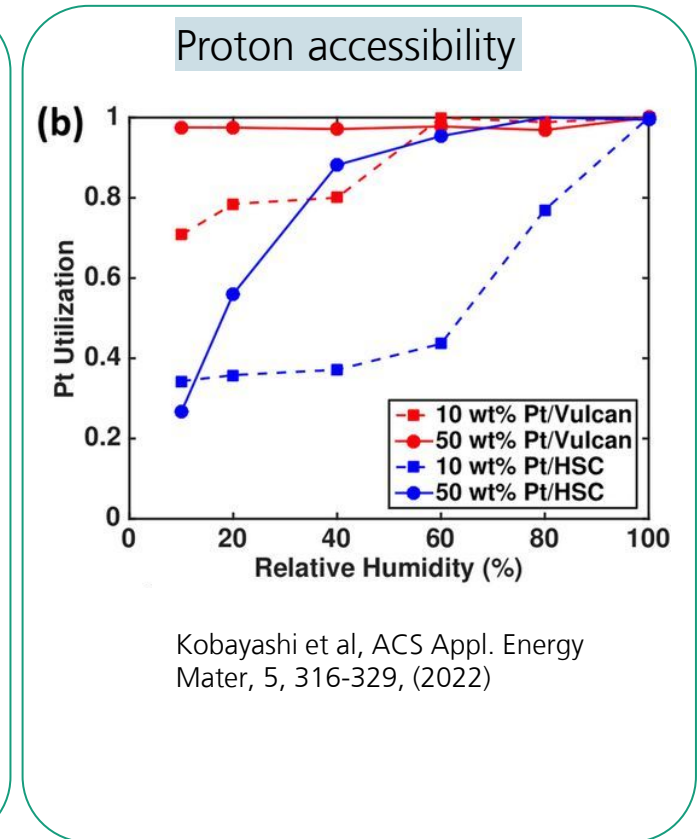
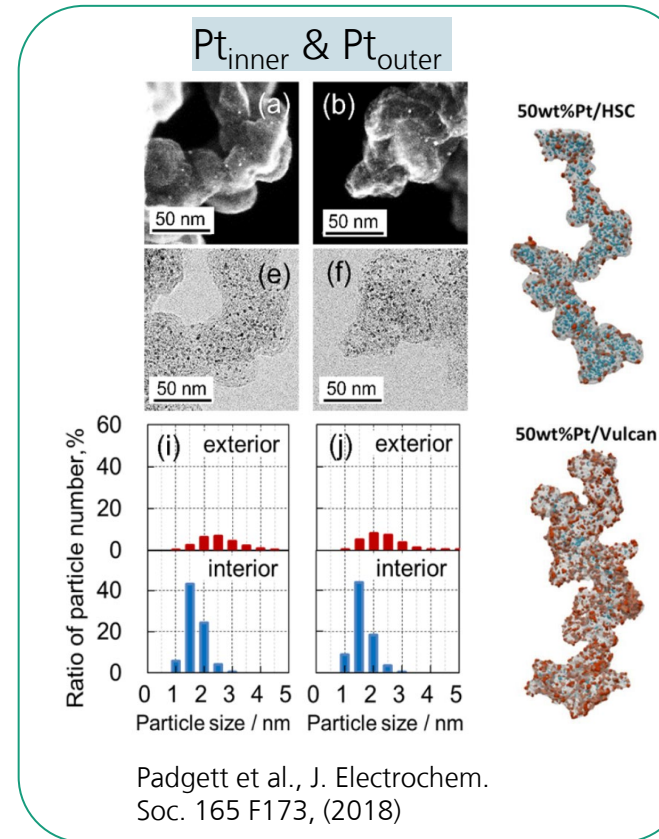
And its associated limiting processes in the electrode

Findings from the literature

- Carbon support has high impact
 - BET, Pt dispersion, Pt location, RH-dependent Pt utilization

Needs for ‚realistic‘ CL model

- Distinguish between particle sizes
→ PSD (particle size distribution)
- Distinguish between particle location
→ Pt_{inner}/Pt_{outer}



Structure of the catalyst layer

And its associated limiting processes in the electrode

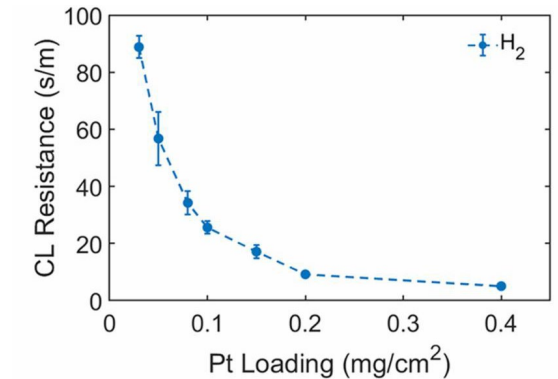
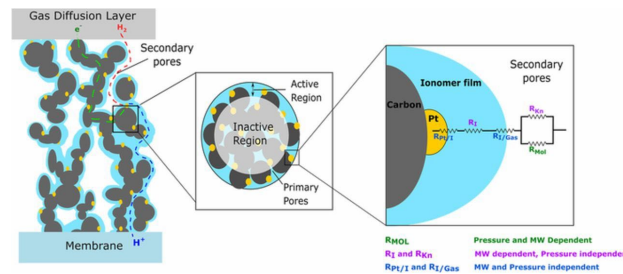
Findings from the literature

- High mass transport resistance at low Pt-loading

Needs for 'realistic' CL model

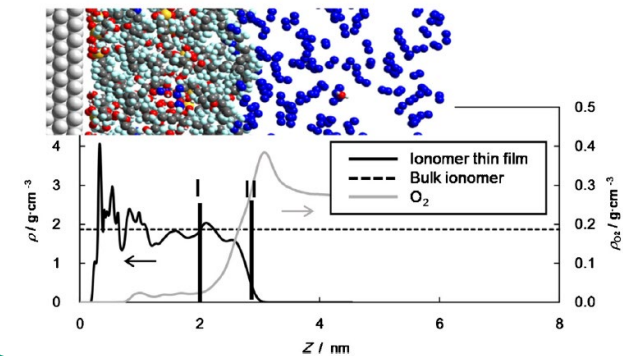
- Distinguish between particle sizes
→ PSD (particle size distribution)
- Distinguish between particle location
→ Pt_{inner}/Pt_{outer}
- Include local transport processes near Pt particle

Mass transport limitations



Schuler et al, JES, 166, F3020, (2019)

Compact ionomer layer close to Pt



molecule dynamics simulation show high compactness of ionomer thinfilm

Jinnouchi et al, Electrochimica Acta, 188, 767, (2016)

Structure of the catalyst layer

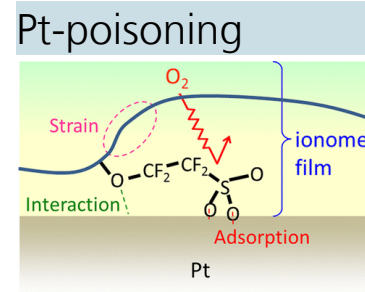
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Findings from the literature

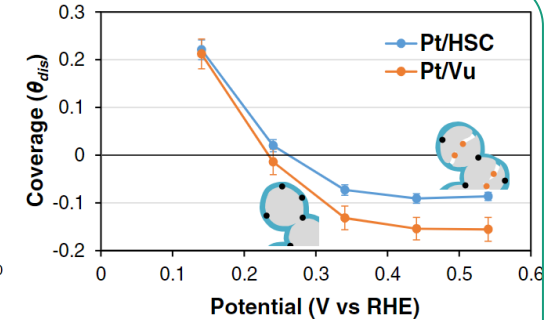
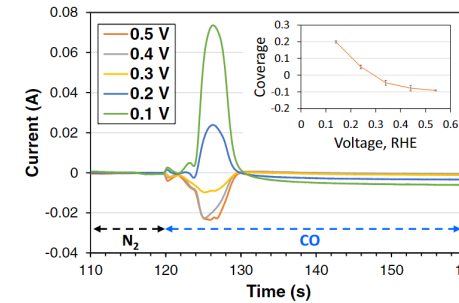
- Active sites blockage by ionomer side chains

Needs for 'realistic' CL model

- Distinguish between particle sizes
→ PSD (particle size distribution)
- Distinguish between particle location
→ Pt_{inner}/Pt_{outer}
- Include local transport processes near Pt particle
- Include Pt coverage (poisoning) by SO_3^-

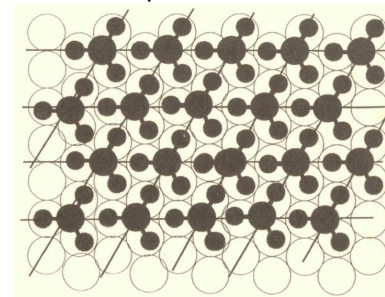


Kodama et al., ACS Catal., 8, 1, 694–700, (2018)



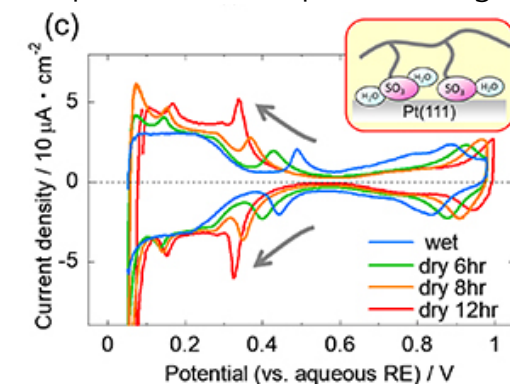
Garrick et al., JES, 164 (2), F60-F64 (2017)

Adsorption of SO_3^- groups blocks up to 3 active sites



Thomas et al 1996 J. Phys. Chem., 100, 11726-11735

RH-dependent adsorption strength



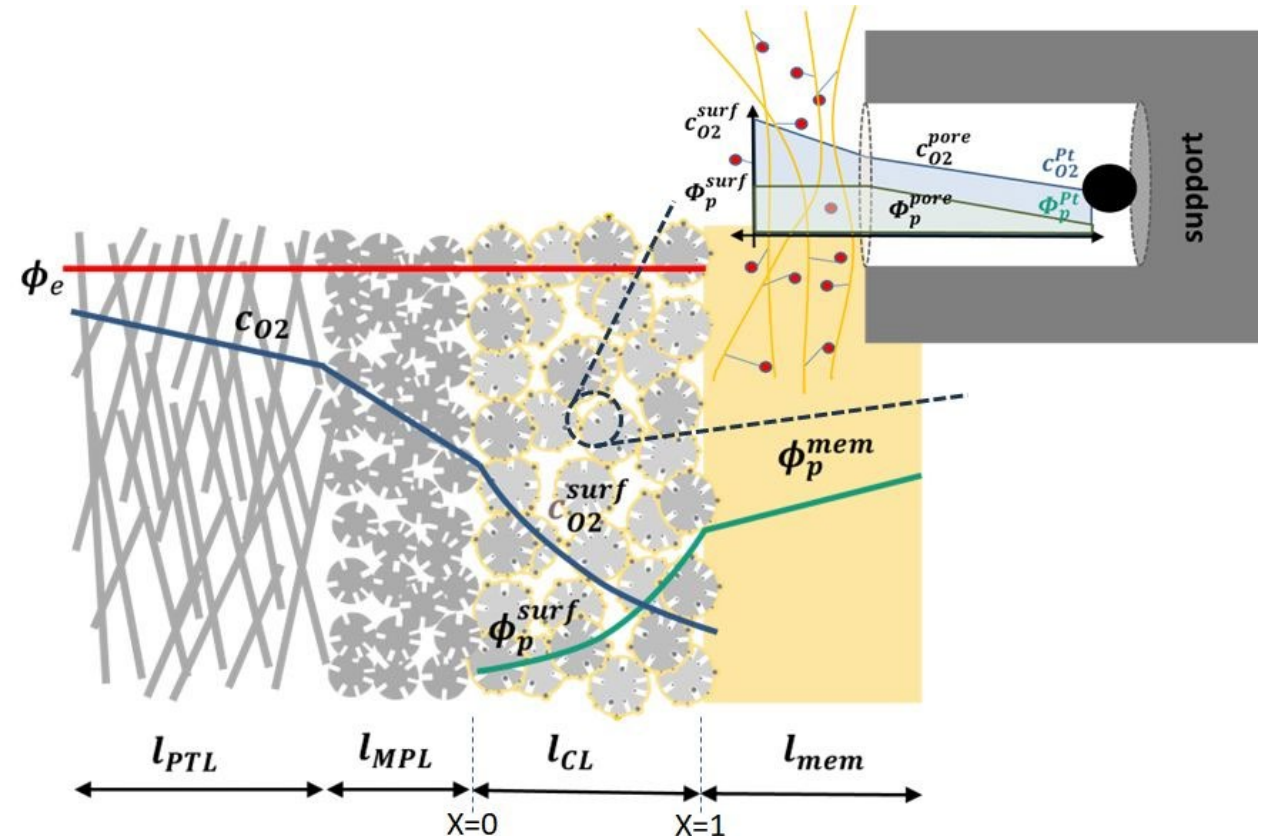
Kodama et al 2023 J. Phys. Energy 5 014018

Development of a 1D cathode catalyst layer

What is needed for a predictive cathode model?

Combine macro-homogeneous CL model with processes on the nano-structure via sink/source terms

- Besides the through-plane transport of oxygen and protons, local processes near the Pt particle need to be addressed



Development of a 1D cathode catalyst layer

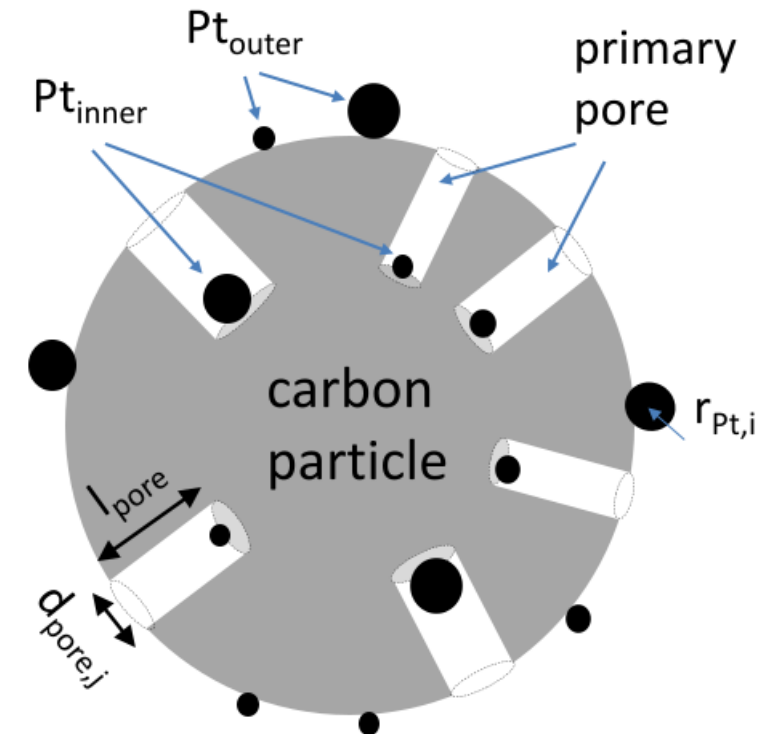
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Pt/C structure

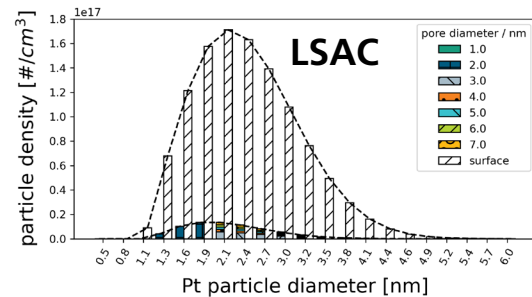
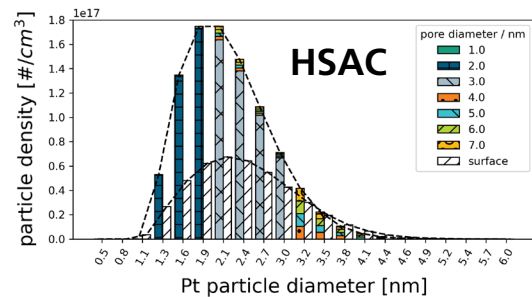
- Pt particles of different size ($r_{Pt,i}$) $\rightarrow$ discrete PSD
- Carbon particle carries Pt particles
 - on the surface: Pt_{outer}
 - in primary pores of different size ($d_{pore,j}$): Pt_{inner}
- Ionomer is not able to penetrate pores with diameter $< 8\text{nm}$



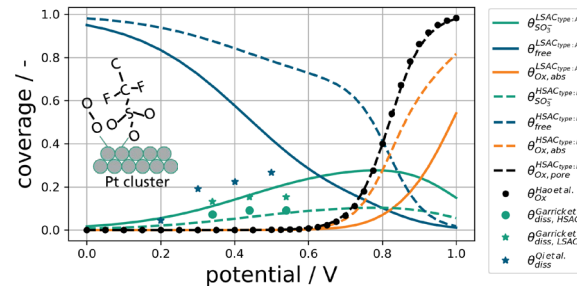
Development of a 1D cathode catalyst layer

Impact of Pt/C-Classification, Ionomer poisoning, size-dependent specific activity

- **Pt-Classification** in particle size and support position (Pt_{inner} , Pt_{outer})
- **C-Classification** in high & low surface area carbon



- **Ionomer poisoning** of Pt_{outer} which is in contact with ionomer and can be poisoned/blocked by SO_3^- group of side chain
- Simplified Langmuir competitive adsorption model is used, where one adsorbate blocks 3 Pt sites



Simulating potential dependent Pt-coverages

$$\theta_{SO_3^-} = \frac{K_{SO_3^-}^{eq}}{1 + \vartheta_b * K_{SO_3^-}^{eq} + K_{Ox}^{eq}}$$

$$\theta_{Ox} = \frac{K_{Ox}^{eq}}{1 + \vartheta_b * K_{SO_3^-}^{eq} + K_{Ox}^{eq}}$$

$$\theta_{free} = 1 - \vartheta_b * \theta_{SO_3^-} - \theta_{Ox}$$

with equilibrium constant

$$K_n^{eq} = S_n / S_{free}$$

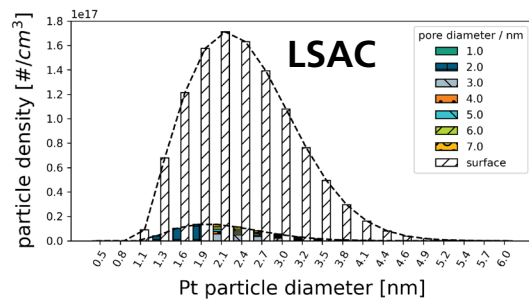
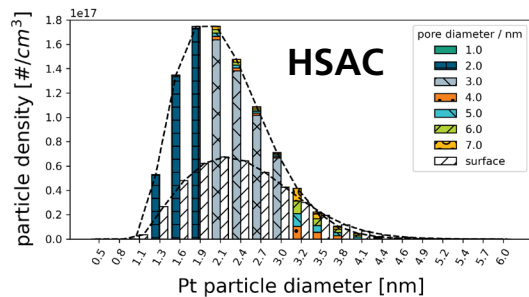
expressed as RH & potential – dependent Tafel expression

$$K_n^{eq} = \psi_n(RH) e^{\left(-\frac{\alpha_n F}{R T} (\Phi_n^0 - (\Phi_e - \Phi_p)) \right)}$$

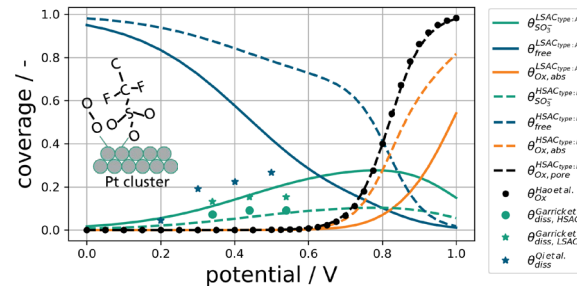
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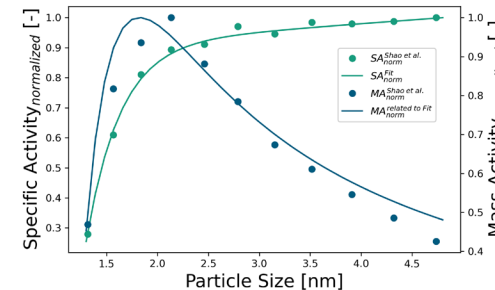
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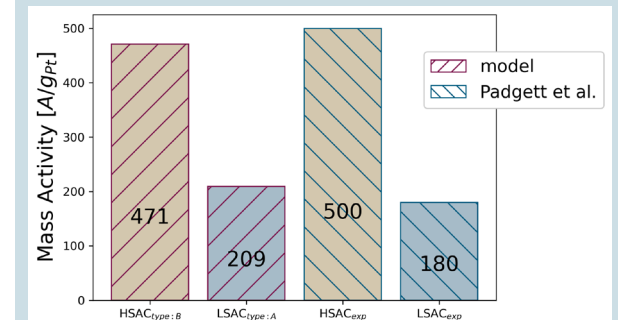


- **Pt-size dependent specific activity**
- Fitted with data from *Shao et al. (2011): Nano letters 11 (9), S. 3714–3719*
- Mass activity vs size results automatically for a fixed PSD



Simulation result

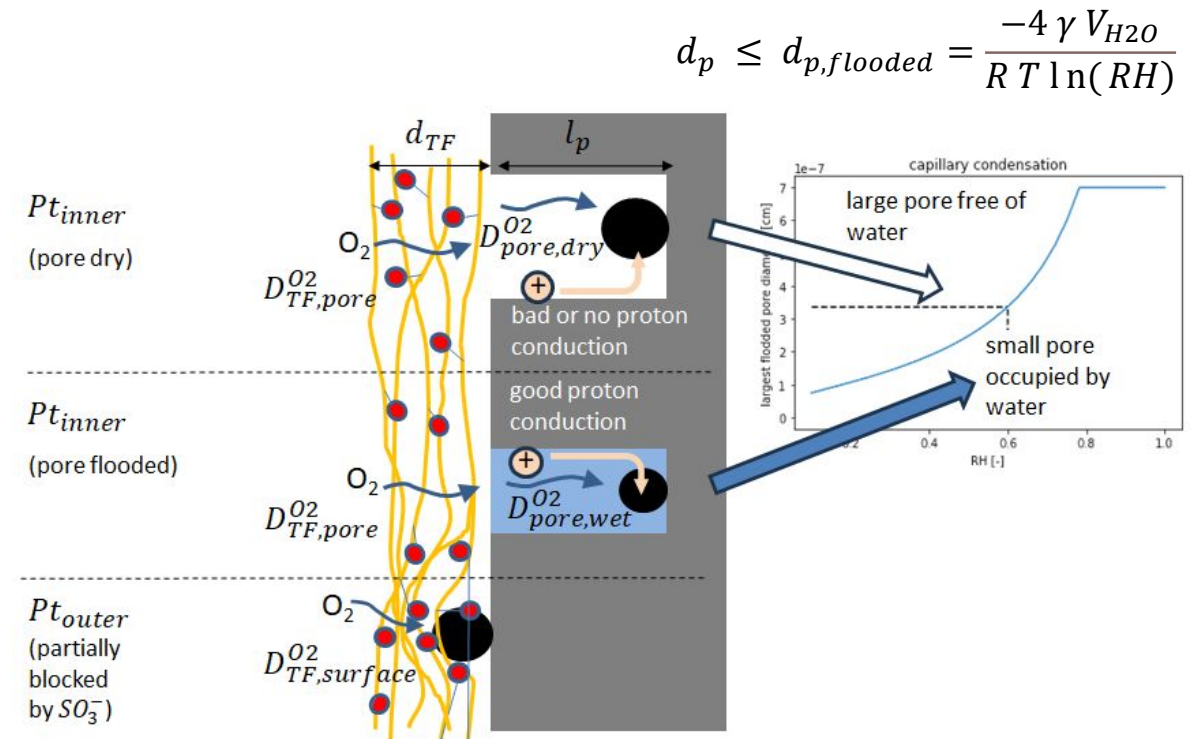
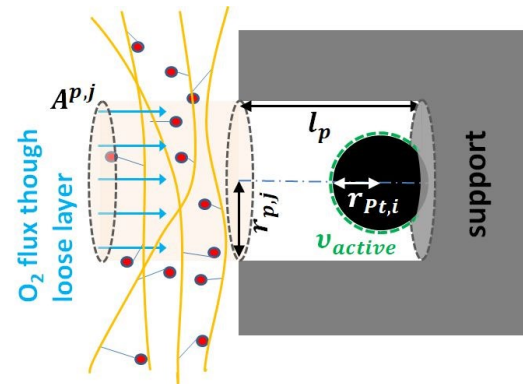
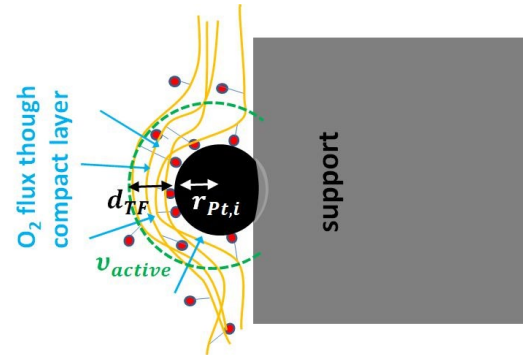
- Support-type dependent mass activity shows
 - Lower values for Vulcan due to the ionomer poisoning
 - Good agreement with measured data of Padgett et al. (2018)



Development of a 1D cathode catalyst layer

Impact of Pt/C-Classification on oxygen diffusion through ionomer thin-film and into pore

- Diffusion to Pt_{outer} is hindered by ionomer which can form a compact layer close to Pt particle
- Cross-section for diffusion: hemisphere of ionomer over Pt particle
- Diffusion to Pt_{inner} is additionally hindered by water in the pore, but water is essential to activate Pt
- Cross-section for diffusion: circle with diameter of primary pore

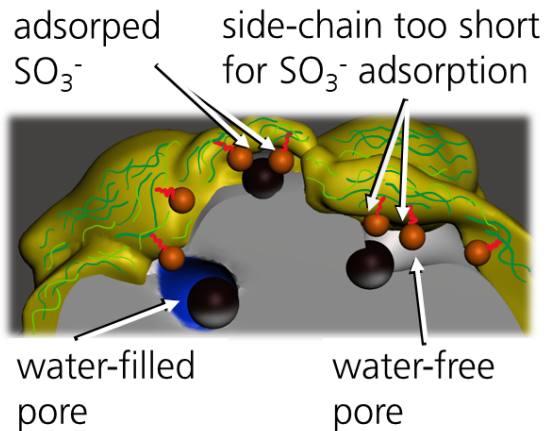


Development of a 1D cathode catalyst layer

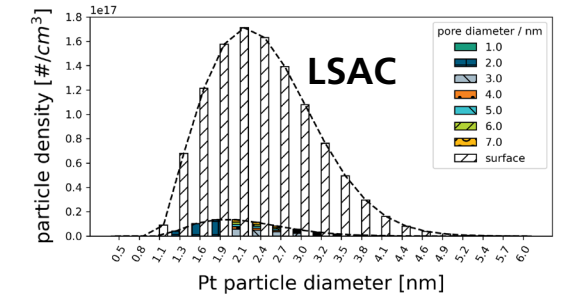
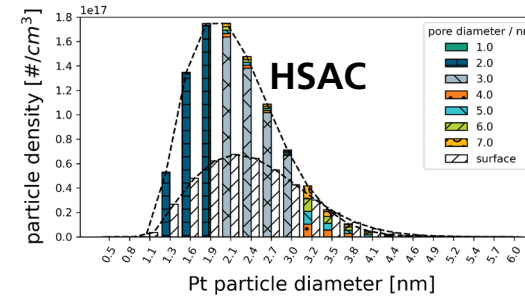
Our approach in a nutshell : Proton accessibility via ionomer and water

- Capillary condensation equation defines the pore that are flooded depending on its pore size

$$d_p \leq d_{p,flooded} = \frac{-4 \gamma V_{H_2O}}{R T \ln(RH)}$$



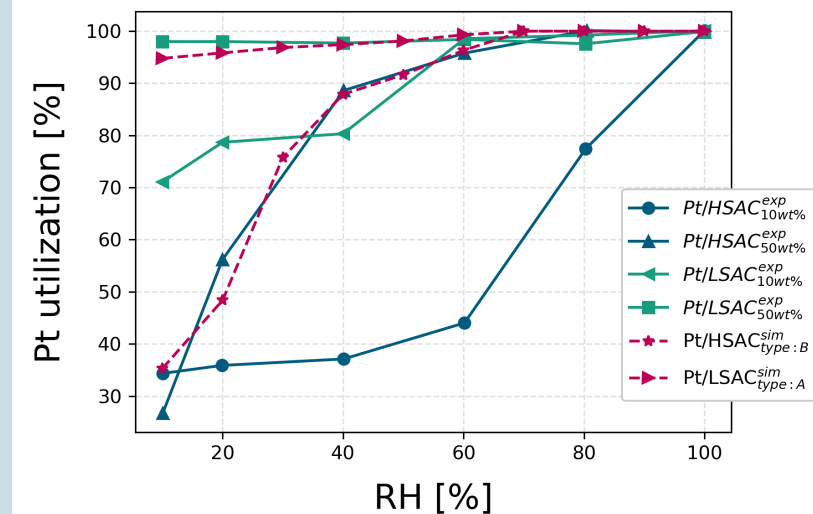
- Pt in water-free pores are inactive (not accessible by protons) or limited in activity due to high ohmic losses for the proton transport



Simulation result

- RH-dependent Pt utilization can be modelled for different C-support type

Experimental data from
Kobayashi et al 2022 ACS Appl.
Energy Mater, 5, 316-329



Validation of mass transport parameters

Fitting limiting current density measurements → extract pressure independent mass transport resistance

Data published in: Schneider *et al* 2023 *J. Electrochem. Soc.* **170** 024506

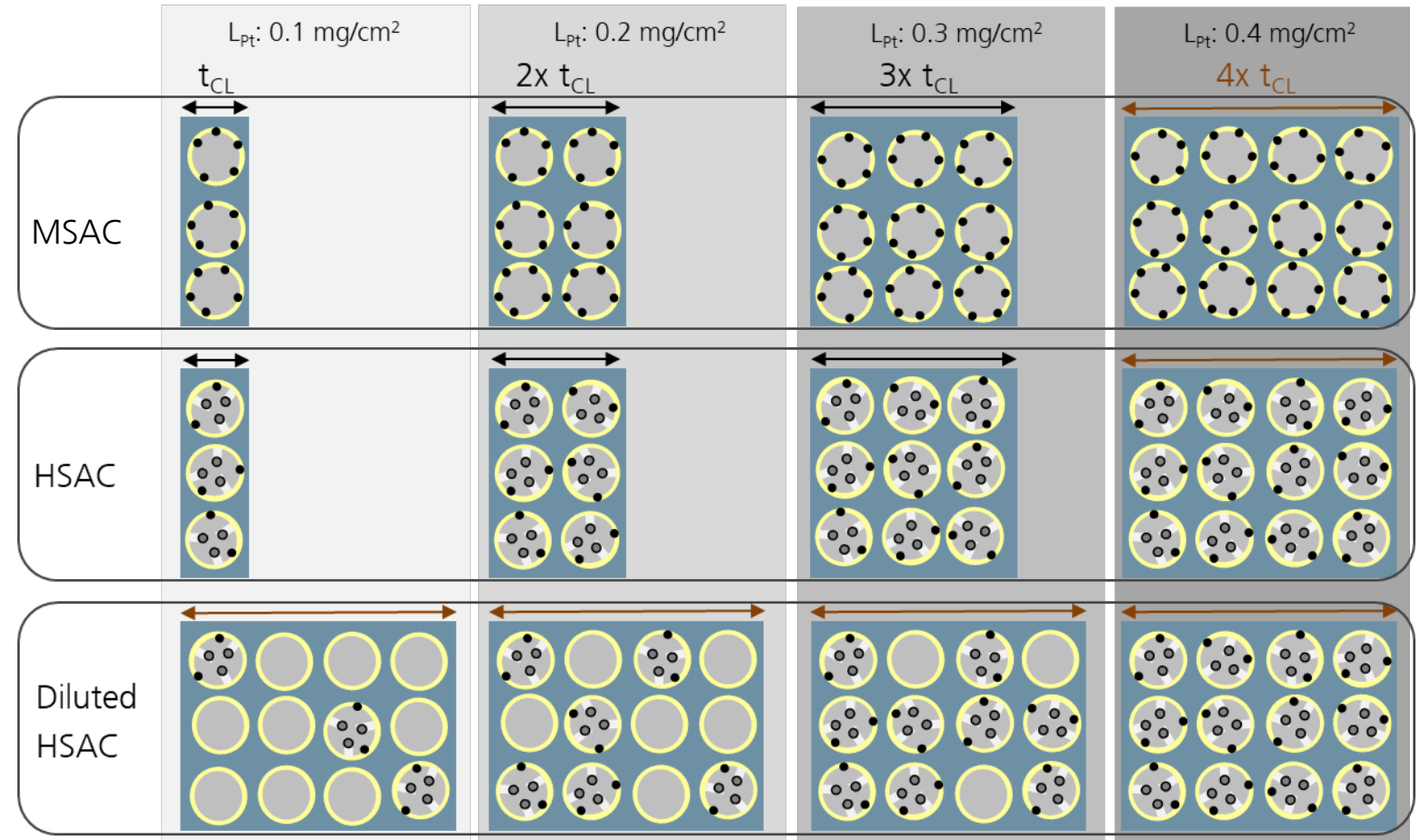
Investigation of different CCMs

- Change in Pt loading
- Change in support type (HSAC vs MSAC)
- Change in Pt loading @ constant CL thickness

Variation leads to different

- Pt area (roughness factor)
- Diffusion path (compressed thin-film vs thin-film + pore)
- Diffusion in secondary pores

Knudsen



Validation of mass transport parameters

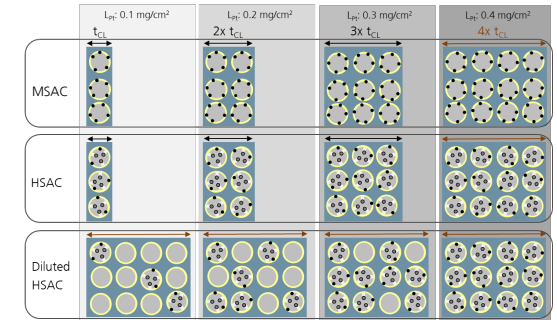
Fitting limiting current density measurements → extract pressure independent mass transport resistance

Investigation of different CCMs

- Change in Pt loading
- Change in support type (LSAC vs MSAC)
- Change in Pt loading @ constant CL thickness

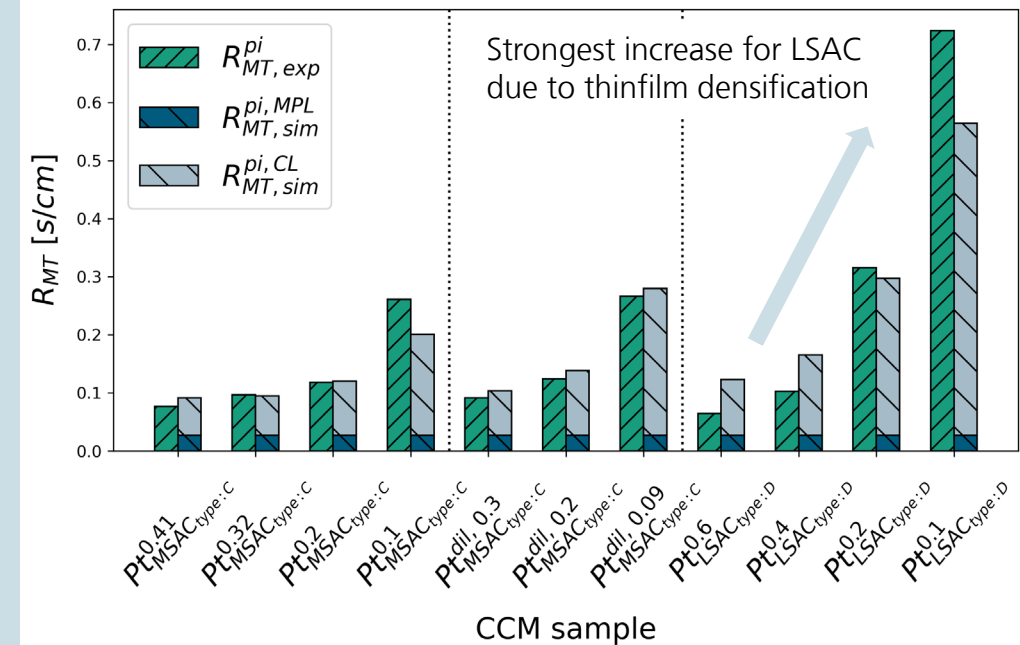
Variation leads to different

- Pt area (roughness factor)
 - Diffusion path (compressed thin-film vs thin-film + pore)
 - Diffusion in secondary pores
- Knudsen



Simulation result

- Mass transport resistance can be modelled for different C-support type, Pt/C wt% & Pt-loading



Validation of mass transport parameters

Fitting limiting current density measurements → extract pressure independent mass transport resistance

Investigation of different CCMs

- Change in Pt loading
- Change in support type (LSAC vs MSAC)
- Change in Pt loading @ constant CL thickness

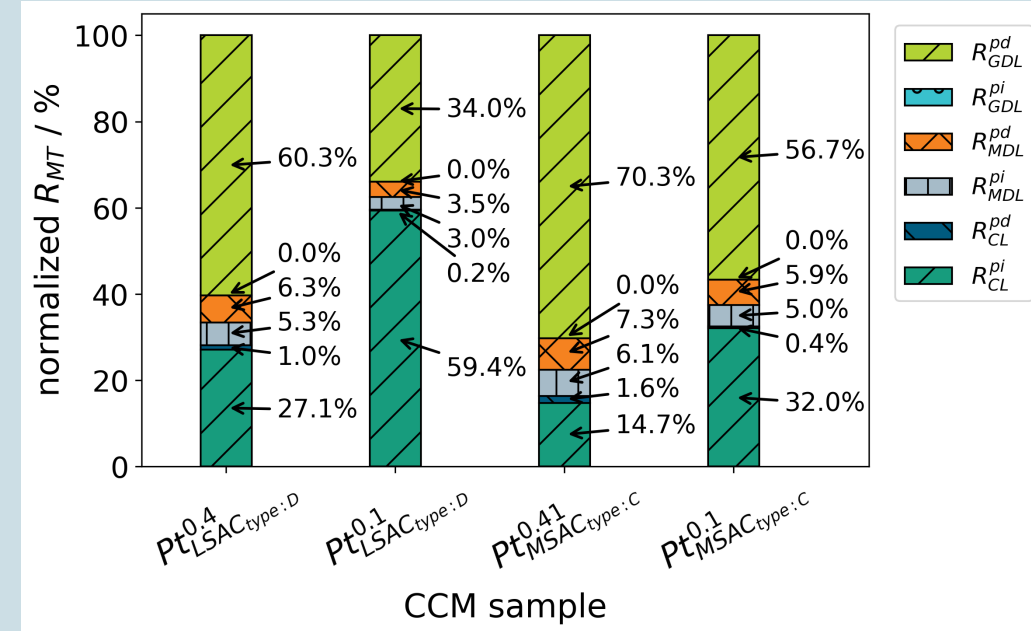
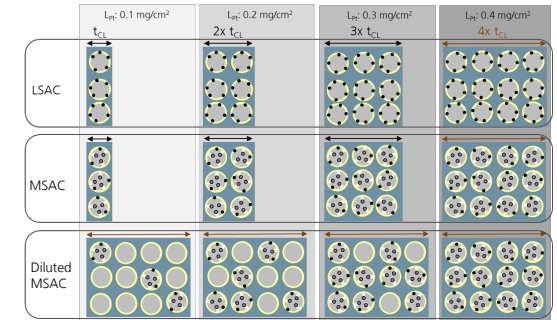
Variation leads to different

- Pt area (roughness factor)
- Diffusion path (compressed thin-film vs thin-film + pore)
- Diffusion in secondary pores

Knudsen

Simulation result

- Mass transport resistance break down
 - GDL
 - MPL
 - CL
- Pressure in-/dependent resistance

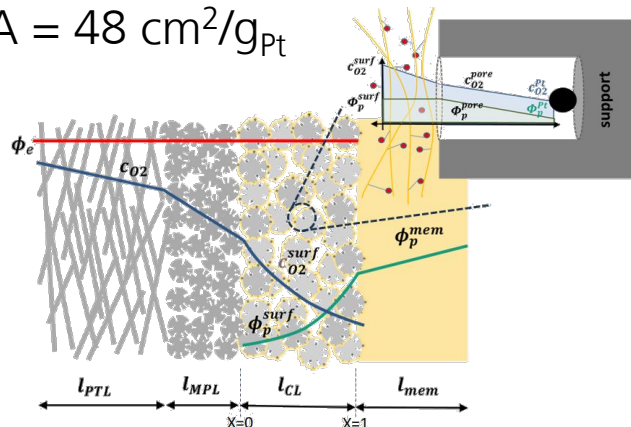


1D-Simulation of polarization curve

Example: CCM $Pt_{MSAC}^{0.41}$

MSAC catalyst with properties

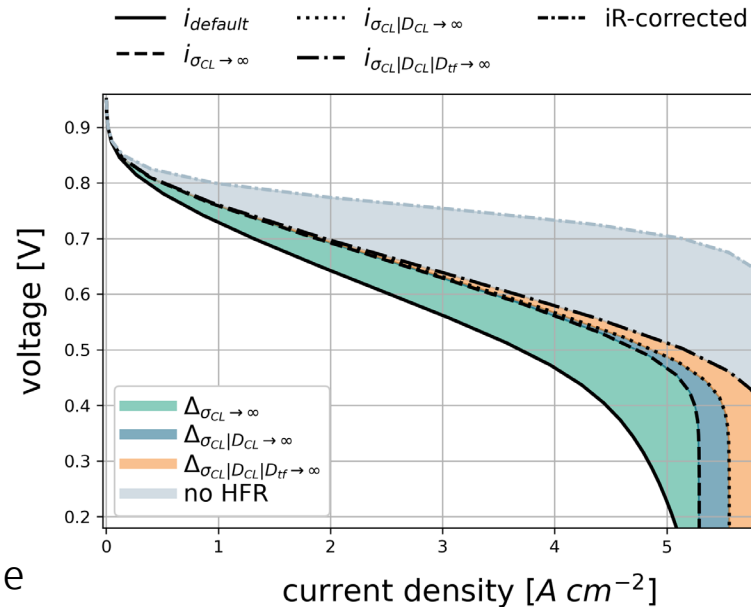
- $Pt_{inner} / Pt_{outer} = 38\% / 62\%$
- Loading = 0.41 mg/cm^2 ,
- ECSA = $48 \text{ cm}^2/\text{g}_{Pt}$



Through-plane transport of O_2 and H^+ are coupled with local processes near Pt particle

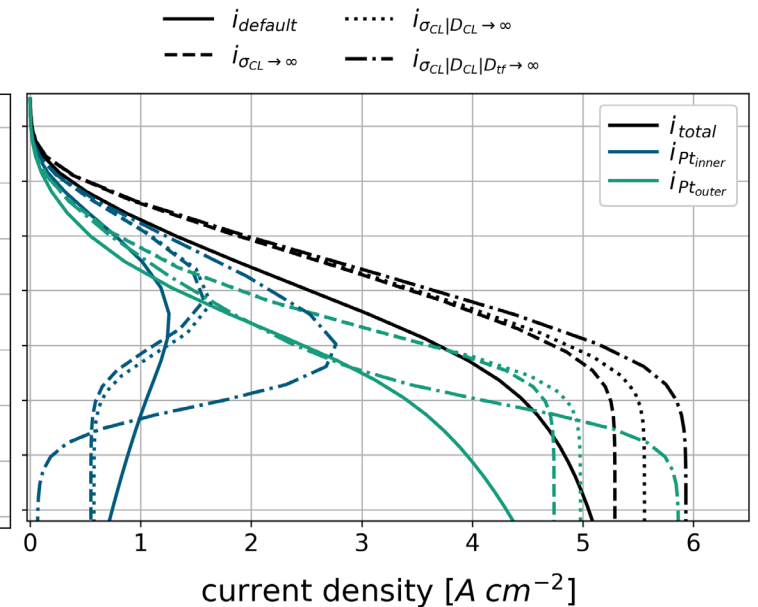
Loss breakdown

- Proton conductivity in CL
 - and HFR
- has strongest impact



Distinction between current generation of Pt_{inner} & Pt_{outer}

- Pt_{inner} bends back at lower potential $\rightarrow$ operates closer to limiting current

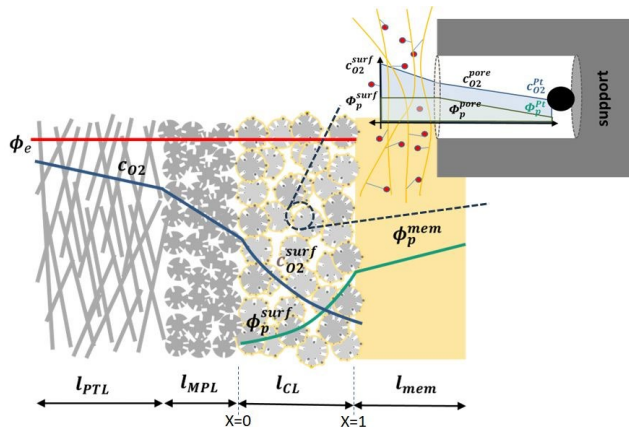


1D-Simulation of polarization curve

Example: CCM $Pt_{MSAC}^{0.41}$ & $Pt_{LSAC}^{0.1}$

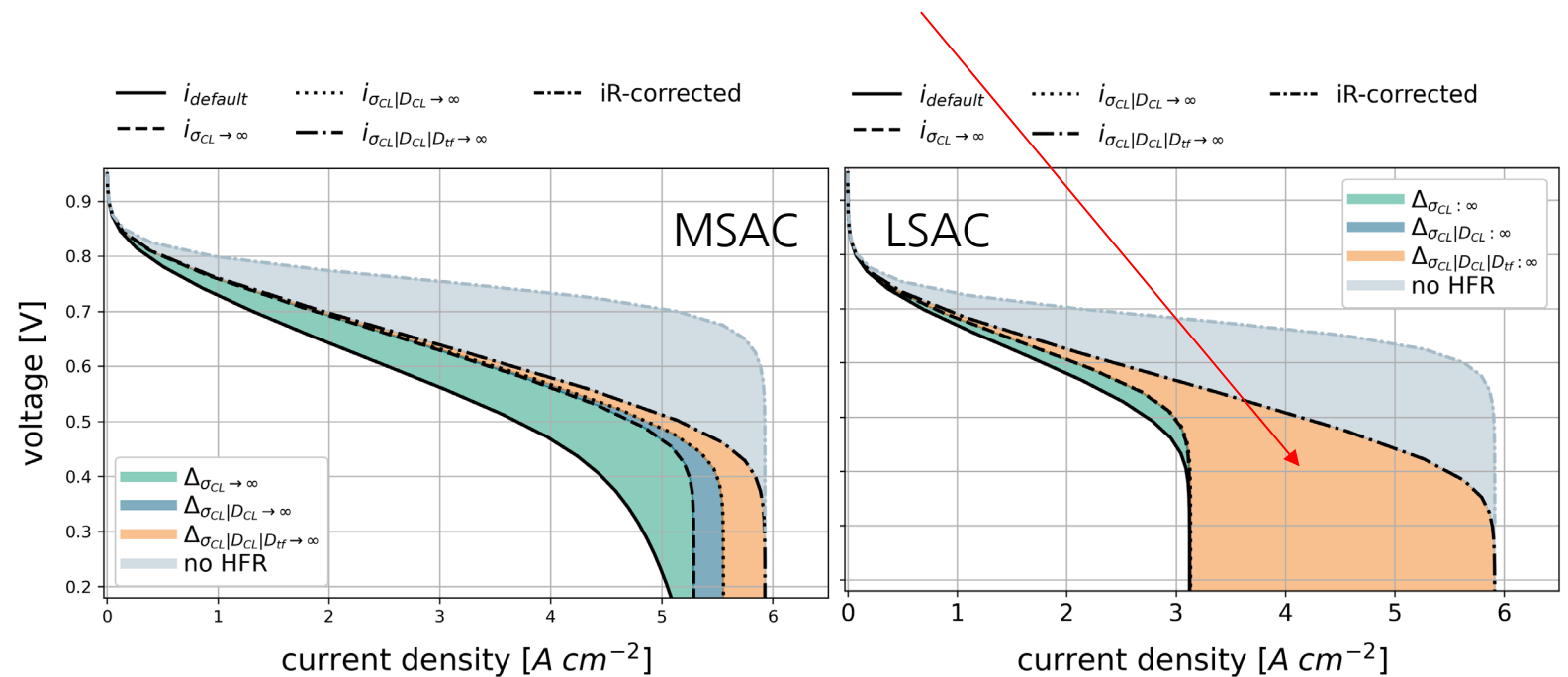
Catalyst with properties

	MSAC	LSAC
Pt _{inner} / Pt _{outer} [%]	38/62	13/87
Loading [mg/cm ²]	0.41	0.1
ECSA [cm ² /g _{Pt}]	48	23



Loss breakdown

- High local mass transport issue for low loaded CCMs

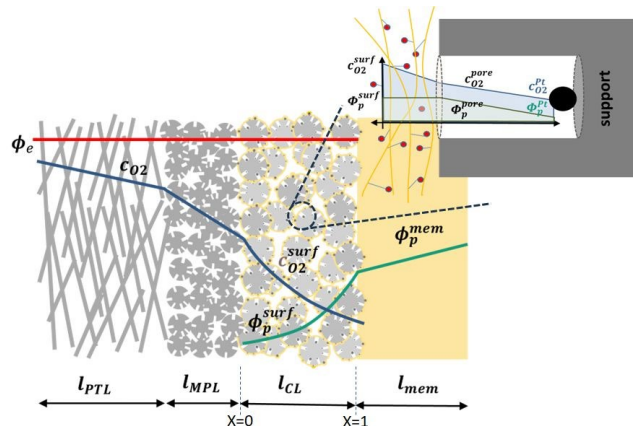


1D-Simulation of polarization curve

Example: CCM $Pt_{MSAC}^{0.41}$

MSAC catalyst with properties

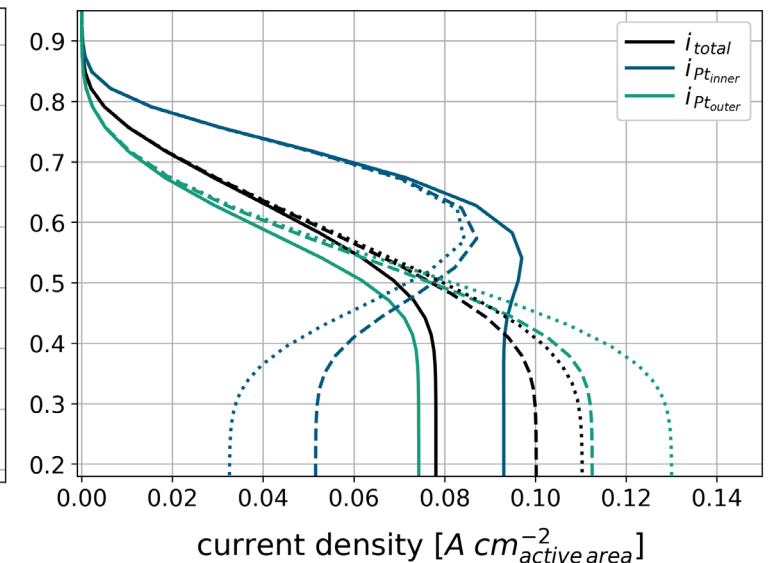
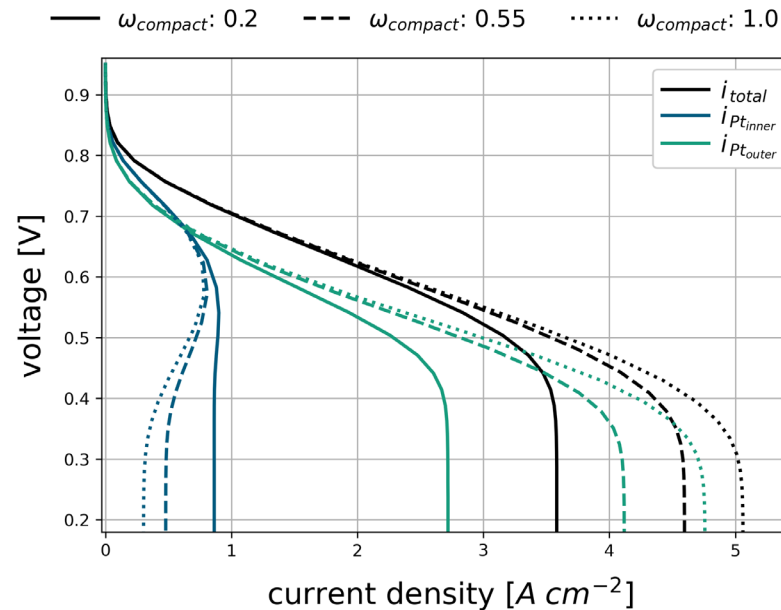
- $Pt_{inner} / Pt_{outer} = 38\% / 62\%$
- Loading = 0.1 mg/cm^2 ,
- ECSA = $48 \text{ cm}^2/\text{g}_{Pt}$



Impact of thinfilm compactness factor

- Higher diffusivity due to less compactness leads to higher limiting currents

- Normalized current density shows the high activity of Pt_{inner} due to less poisoning

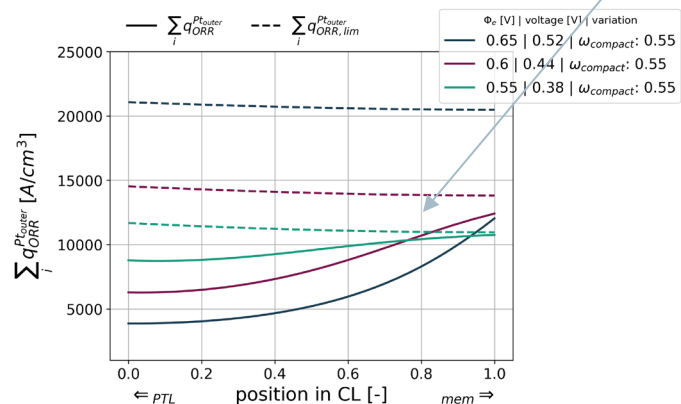
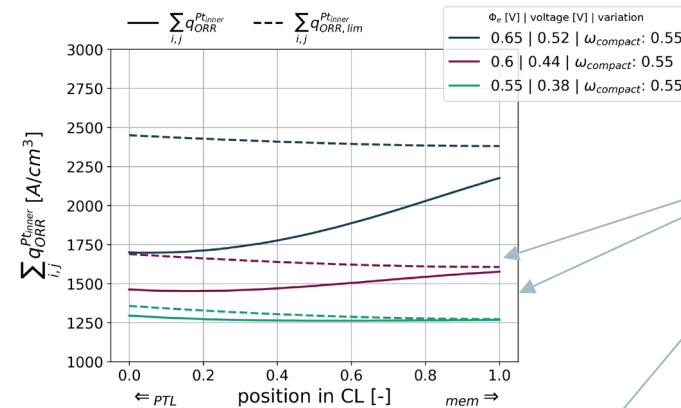
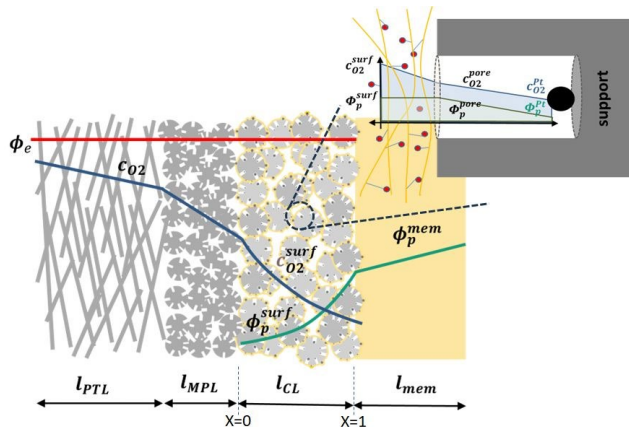


1D-Simulation of polarization curve

Example: CCM $Pt_{MSAC}^{0.41}$

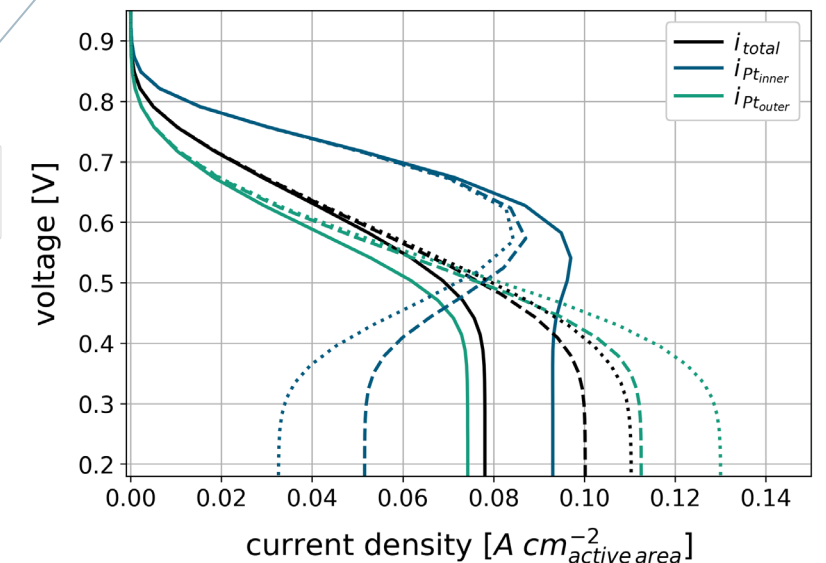
MSAC catalyst with properties

- $Pt_{inner} / Pt_{outer} = 38\% / 62\%$
- Loading = 0.1 mg/cm^2 ,
- ECSA = $48 \text{ cm}^2/\text{g}_{Pt}$



Bending-back phenomena

- Local current generation in CL shows that Pt_{inner} operates closer to limiting current than Pt_{outer}



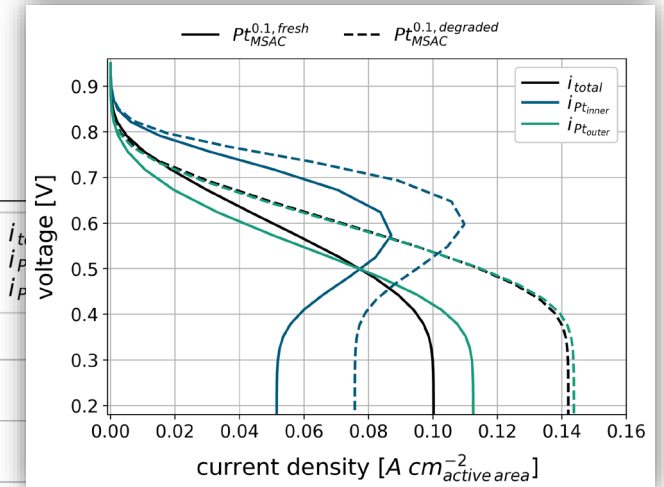
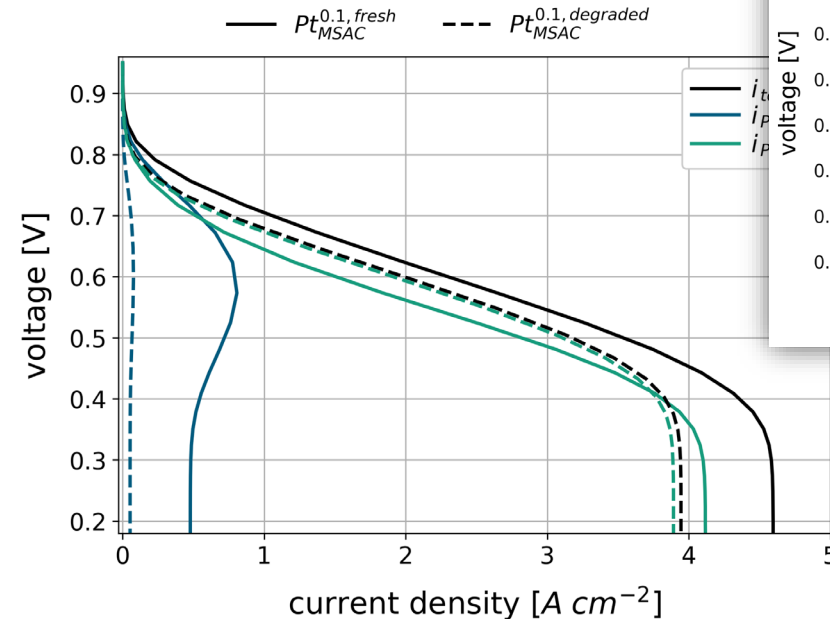
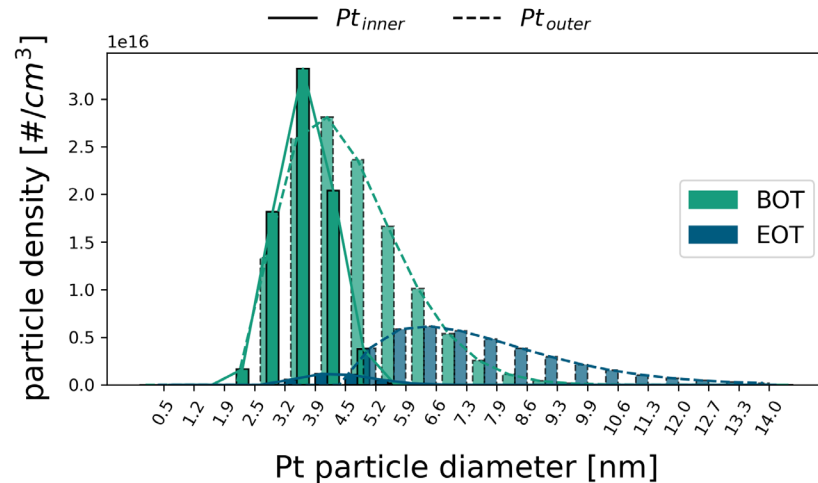
Impact of catalyst layer degradation on performance

Pt-redistribution via Ostwald ripening

Comparison of 'fresh' vs 'degraded' CCM

- Solely PSD is changed → no model parameter!

ECSA = $48 \text{ m}^2/\text{g}_{\text{Pt}} \rightarrow 30 \text{ m}^2/\text{g}_{\text{Pt}}$
 $r_{\text{mean, inner}} = 1.63 \text{ nm} \rightarrow 2.14 \text{ nm}$
 $r_{\text{mean, outer}} = 2.49 \text{ nm} \rightarrow 3.86 \text{ nm}$
Fraction $\text{Pt}_{\text{inner}} = 38 \% \rightarrow 8 \%$

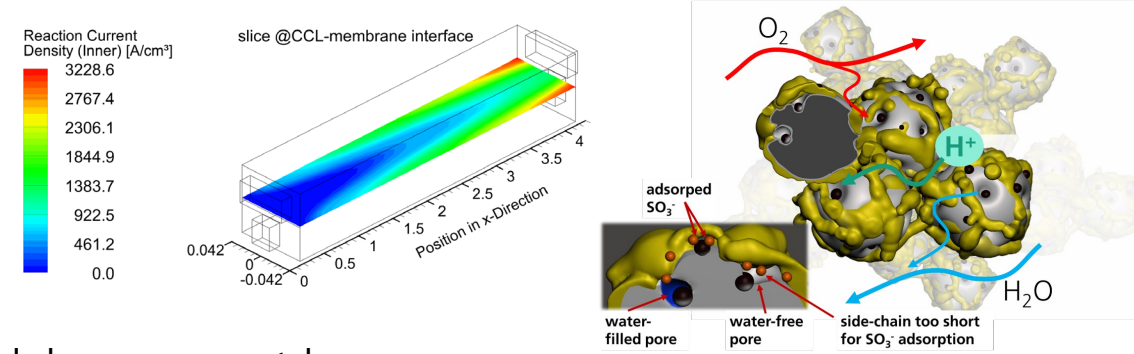


- The increase of normalized current density of the degraded CCM shows that the CL always suffers from mass transport (H^+ & O_2)
- Degraded CCM shows steeper drop in polarization curve in activation region
- Similar slope in ohmic region
- Lower limiting current

Conclusion

- Cathode catalyst layer model developed
 - Based on PSD
 - Classification of Pt_{inner}/Pt_{outer}
 - Ionomer poisoning of Pt_{outer} by simplified Langmuir competitive adsorption model
 - Local mass transport processes close to Pt particle
 - Fickian Diffusion of O_2 through (compact) ionomer thin-film
 - Fickian Diffusion of O_2 through primary pore (free or flooded)
 - Proton migration into pore

- Model agreement by
 - Limiting current density measurements
 - Mass activity measurements
 - Tafel analysis
 - CO stripping @ different RHs
 - CO displacement measurement (limited to potential range $<0.6V$)
- PSD with classification of Pt_{inner}/Pt_{outer} is difficult to measure, but essential!
- Model can analyze limiting processes with respect of support type or degradation level
- Model is implemented in AVL FireM (3D CFD)





PEMFC Performance Modeling Framework: Analyzing Pt Particle Size Distribution and Carbon Support Structure Impact

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A cathode catalyst layer model framework that accounts for the position of the platinum particles on the carbon support structure is proposed. Combining a discrete platinum particle size distribution (PSD) with the binary classification of whether the platinum particle is decorated on the support surface (Pt_{outer}) or buried inside the pore structure (Pt_{inner}) allows the differentiation of distinct loss mechanisms. Additional mass transport and proton accessibility issues are modelled for Pt_{inner} due to the extended diffusion path and worsened proton conduction inside the ionomer-free primary pores of the carbon support. Pt_{inner} particles suffer from the adsorption of sulphonic acid groups (ionomer poisoning) and the densification of ionomer thin film that builds a compact layer above the outer Pt particle. The influence of carbon support type such as high and low surface area carbon on the cell performance is simulated and discussed for different scenarios. A parameter study is conducted that gives insight into the complex interaction between the contribution of current generation obtained from Pt_{inner} and those from Pt_{outer} . The impact on mass activity and mass transport resistance is analyzed as well. The effect of PSD evolution on the cell performance is discussed.

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Polymer electrolyte membrane fuel cells (PEMFC) are promising candidates for generating clean power in stationary and mobile applications. Despite over three decades of intensive research aimed at enhancing their performance and durability while reducing costs, the market introduction phase proceeds slowly. One significant challenge, aside from hydrogen availability, lies in the membrane electrode assembly (MEA), the core component of the fuel cell. Specifically, the cathode catalyst layer (CL) experiences high polarization losses under load, even with substantial platinum (Pt) loading, particularly after long-term operation due to CL degradation.

Efforts to optimize CL structure focus on its components: state-of-the-art electrodes typically consist of Pt or Pt-alloy catalysts, carbon support, and ionomer. A wide range of combinations regarding type, quantity, proportion, synthesis route, and fabrication process has been explored. Key factors include the Pt-to-carbon weight ratio (Pt/C wt%),¹ ionomer-to-carbon ratio (I/C),² Pt loading, Pt particle size distribution and location,³ support type^{3–5} and ionomer type categorized by equivalent weight (EW) and side-chain length.⁶ Most studies showed that it is not expedient to focus on improving the properties of the sole ingredients itself but on their mutual complex interaction and long-term stability. For instance, a highly active catalyst characterized by rotating disc electrode measurements does not necessarily translate to improved oxygen reduction reaction (ORR) kinetics in a high-performing MEA.^{7,8} Furthermore, the dispersion and deposition of catalyst particles on the carbon support within the CL are critical.^{4,9–11} A well-conducting ionomer network is essential for delivering protons to Pt sites for ORR, and the wetting properties of the ink formulation are crucial for establishing a large electrochemically active surface area (ECSA) while ensuring thin layers of ionomer above the catalyst particles. The optimal ionomer dispersion might occur when all Pt particles are covered and directly connected to the proton conduction network. This coverage should be achieved with a thin ionomer film to minimize the oxygen diffusion barrier and also to avoid excess ionomer loading which might contribute to premature degradation of the CL.^{12,13} However, recent studies indicate that direct contact between Pt and ionomer can lead to catalyst poisoning due to the adsorption of sulfonic acid groups,¹⁴ reducing area-specific activity to as low as 22% of a non-poisoned Pt in contact with water.¹⁵ The use of high surface area carbon (HSAC), such as Ketjenblack,

provides a rough surface with tiny nanopores for Pt deposition. This buried Pt appears to be protected from SO_3^- poisoning due to the ionomer's structure and stiffness, which hinders the penetration of these pores.^{4,16,17} Park et al.⁴ reported more than a threefold increase in mass activity for Pt on HSAC compared to low surface area carbon (LSAC). Ramaswamy et al.⁵ observed similar increases in activity (2.5–3.9 times, from 175 A g_{Pt}⁻¹ for Vulcan to 440–680 A g_{Pt}⁻¹ for Ketjenblack). These findings suggest that buried Pt particles remain electrochemically accessible as long as the fuel cell operates under sufficiently humidified conditions, due to finite proton conduction over a few nanometers into primary pores via complex transport processes on the pore wall or liquid water occupancy.^{18,19} In addition to poisoning effects, simulations reveal a strong oxygen diffusion barrier in the ionomer thin film near Pt, attributed to densification of the ionomer layer due to attractive forces between the Pt surface and ionomer molecules.^{20–22} Both poisoning and ionomer restructuring appear to be dependent on relative humidity (RH).^{22,23} Molecular dynamics simulations of highly oxygen-permeable ionomers (HOPs) indicate that both high permeation and mitigation of poisoning are due to the suppression of densely layered folding of polymer backbones near catalyst surfaces by the incorporated ring-structured matrix.²⁴ The interdependence of these properties and processes within the CL complicates the interpretation of performance data, as optimizing one property may lead to a decrease in another. To address these complexities, a performance model should incorporate through-plane transport of protons and oxygen in the CL via the ionomer and secondary pore network on a macroscopic scale.^{25–27} These processes must be coupled with micro- and mesoscale phenomena, including the adsorption of oxygen at the ionomer surface, oxygen diffusion, and proton migration within the ionomer thin film.²⁸ This includes considering the ionomer-free, open or water-occupied substructure of the carbon support and the unique properties of thin films, which differ significantly from bulk materials, as well as their interactions with Pt nearby.^{29,30}

The accessibility of oxygen at the reaction sites is critical and has been modeled at various levels of detail. Mashio et al.³¹ developed a mathematical model for local gas transport in a single carbon primary particle by merging the classical agglomerate model with local gas transport near a Pt particle, introducing two processes: gas transport through an ionomer thin film on the carbon particle's surface and through water inside the particle. To match experimentally measured gas transport resistances, they set gas permeability through the ionomer thin film to 10%–20% of that through the bulk



Thank You for Your Attention!

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