WELCOME TO THE 1st FURTHER-FC WORKSHOP!

Clean Hydrogen Partnership

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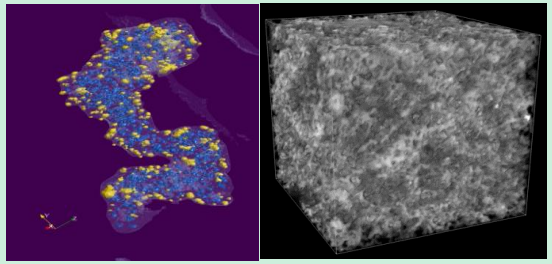
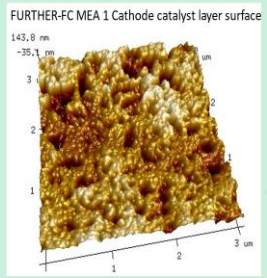
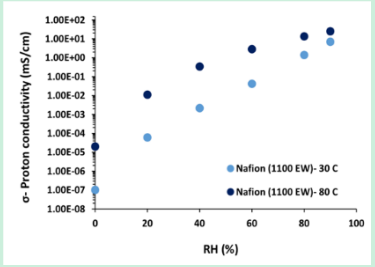
Multiscale characterization



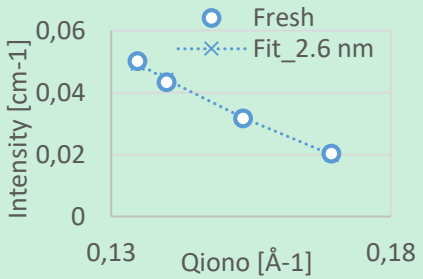
3D TEM and FIB/SEM



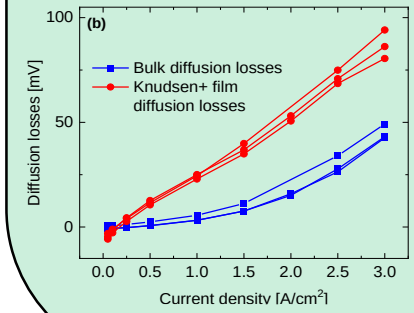
AFM



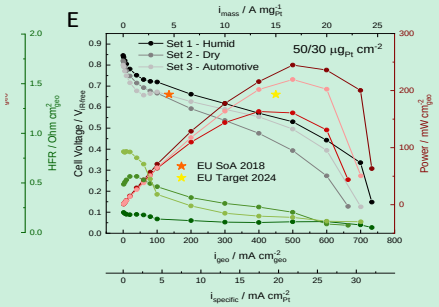
Ionomer transport properties



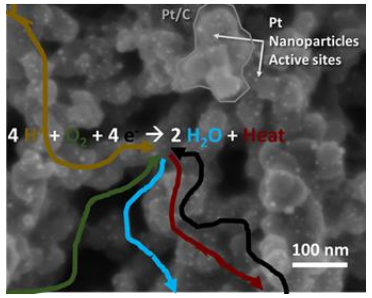
Ionomer swelling

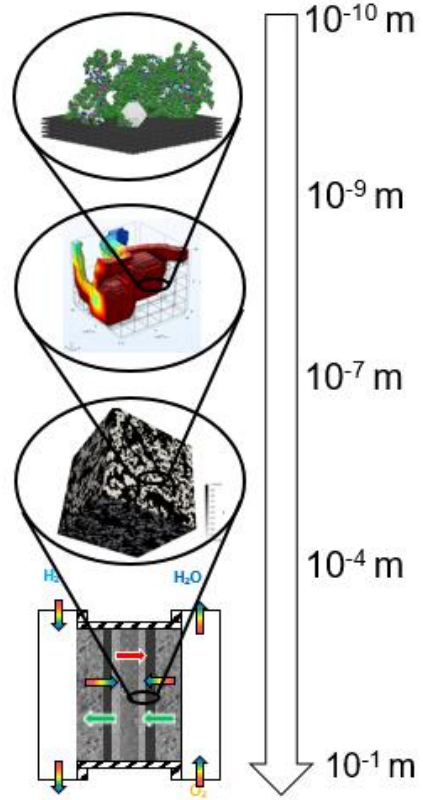


Mass transport losses



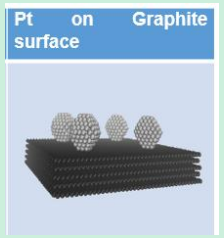
Ultra-thin electrode

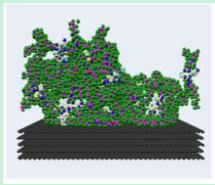


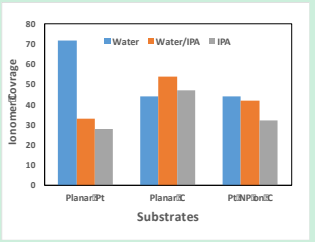


Multiscale modeling

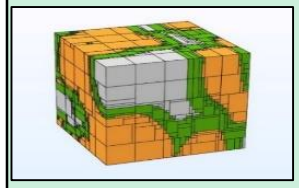
Ionomer film scale



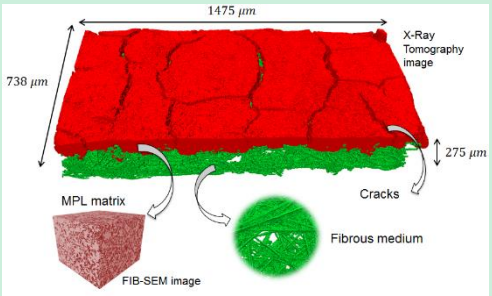




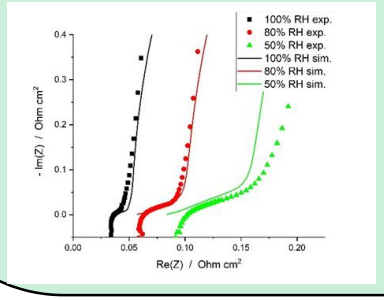
Sub μm scale

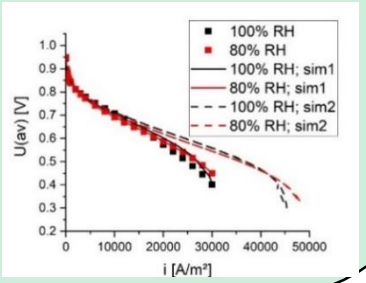


CCL scale



Cell scale





Coordinator: J. Pauchet (CEA); joel.pauchet@cea.fr

FURTHER-FC

Clean Hydrogen Partnership

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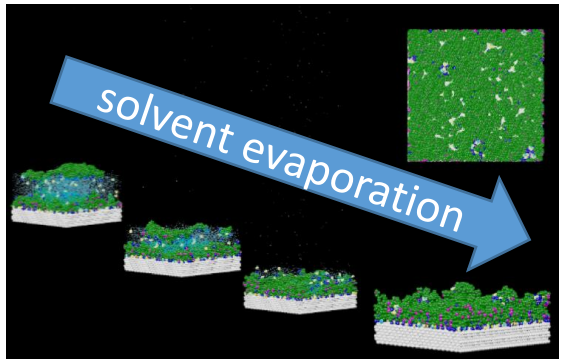
Further **U**nderstanding **R**elated to **T**ransport limitations at **H**igh current density towards future **E**lect**R**odes for **F**uel **C**ells

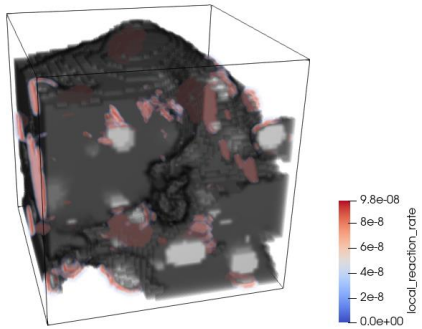
Multiscale Modelling

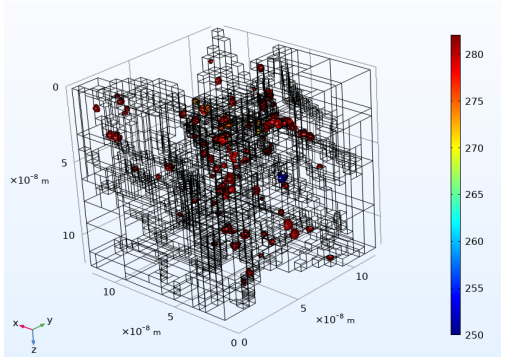
T. Jahnke (DLR), K. Gülicher (DLR), K. Karan (UCA), M. Maloum (INPT), M. Prat (INPT), M. Quintard (INPT), P. Schott (CEA) , J. Pauchet (CEA)

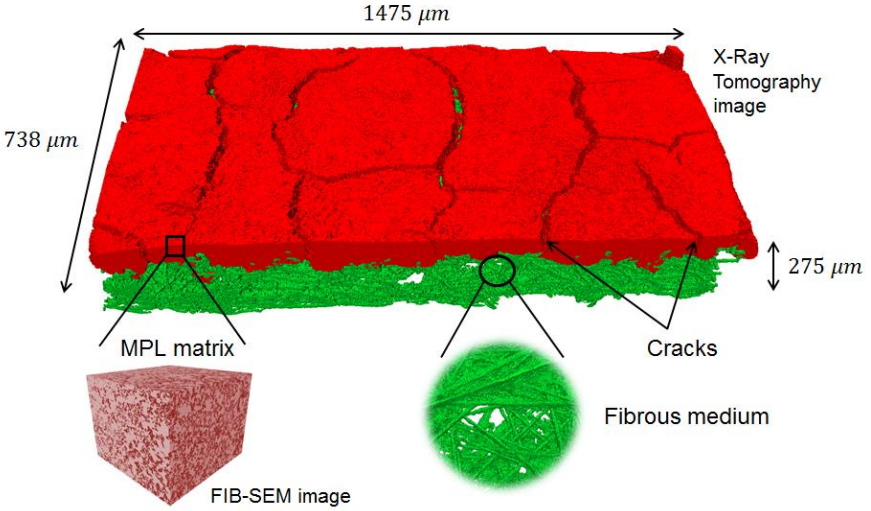
Content of the presentation

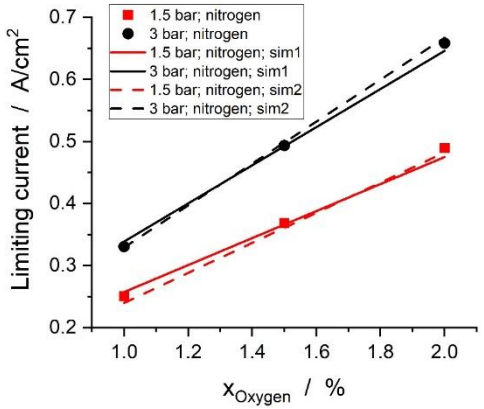
1. Objectives multiscale modeling
2. Coupling between the scales
3. Modeling of ionomer films with MD
4. Modeling of catalyst layer on sub-µm scale
5. Microstructure resolved modeling of MPL and CCL
6. Single cell modeling







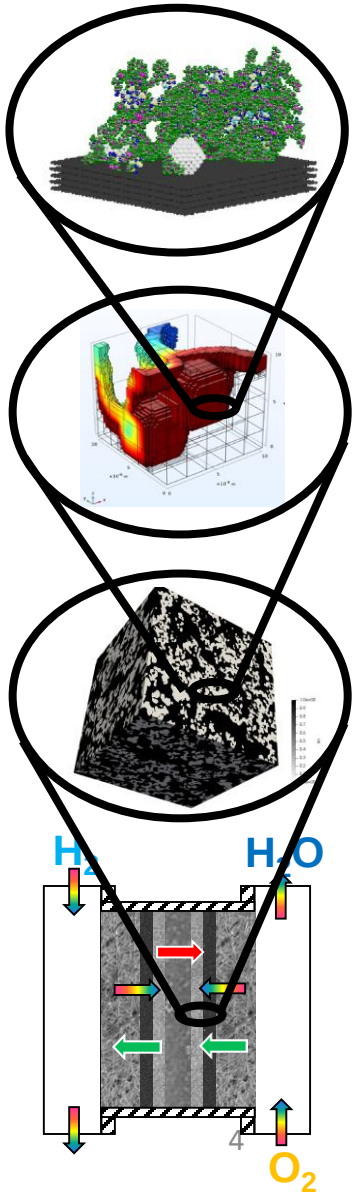




Objectives of the work described

Main objectives:

- Improved understanding of transport limitations by modeling of processes in the cathode catalyst layer at all relevant scales:
  - In the ionomer film with Molecular Dynamics
  - On the sub-micrometer scale with Lattice-Boltzmann modeling and Direct Numerical Simulation (DNS)
  - On the catalyst layer scale with DNS
  - On single cell scale with volume averaged models
- Upscaling from lower to higher scale models to connect lower scale mechanisms with cell performance
- **Main Goal: Identification of transport limitations and simulation based recommendations for improved CCL design and materials**

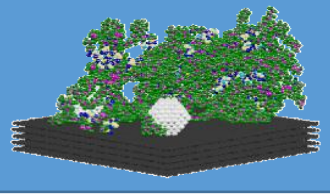


Coupling of models at different scales

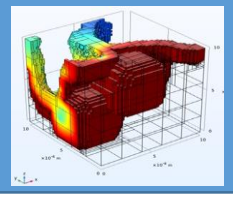
Effective equations

- Properties and transport coefficients of ionomer film
- Improved transport equations from upscaling
- Local reaction rate $i(\Delta\varphi, c_i)$
- Transport properties in CCL: Capillary pressure saturation relations, relative permeabilities, saturation dependent tortuosities,…
- Effective reaction rate

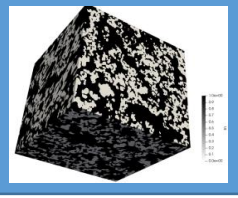
Task 4.1: Transfers in the ionomer film



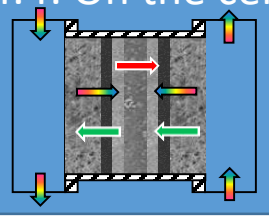
Task 4.2: Sub-µm structure scale



Task 4.3: On the catalyst layer scale



Task 4.4: On the cell level

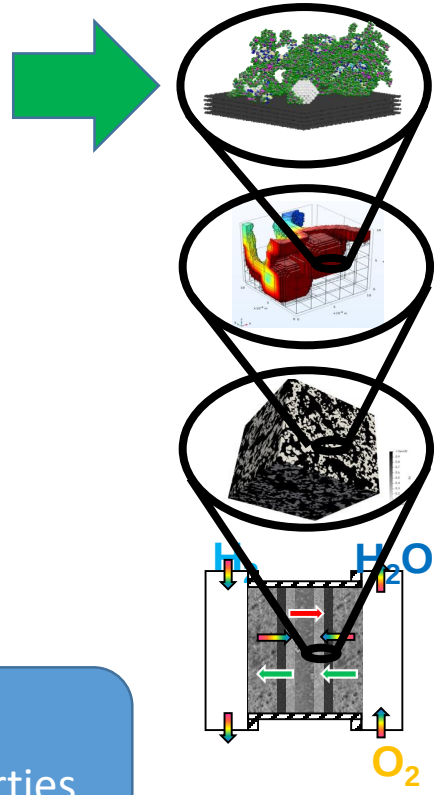


Boundary conditions & local conditions

- Boundary conditions on ionomer surface (c_i)
- Boundary conditions in secondary pores ($S, c_i, \Delta\varphi$)
- Local conditions (T)
- Boundary conditions for CCL ($S, T, c_i, \Delta\varphi$) depending on operating conditions (current density, RH, …)

Transfers in the ionomer film, MD

- **Objectives:**
  - Simulation of representative ionomer film structures in catalyst layer using Molecular Dynamics (MD)
  - Determination of the oxygen and water transport in/transfer to the ionomer films
  - Investigation of performance limiting processes on ionomer scale (poisoning by sulphonic group; Pt/ionomer interfacial water)
  - Simulation of water contact angle on ionomer surface



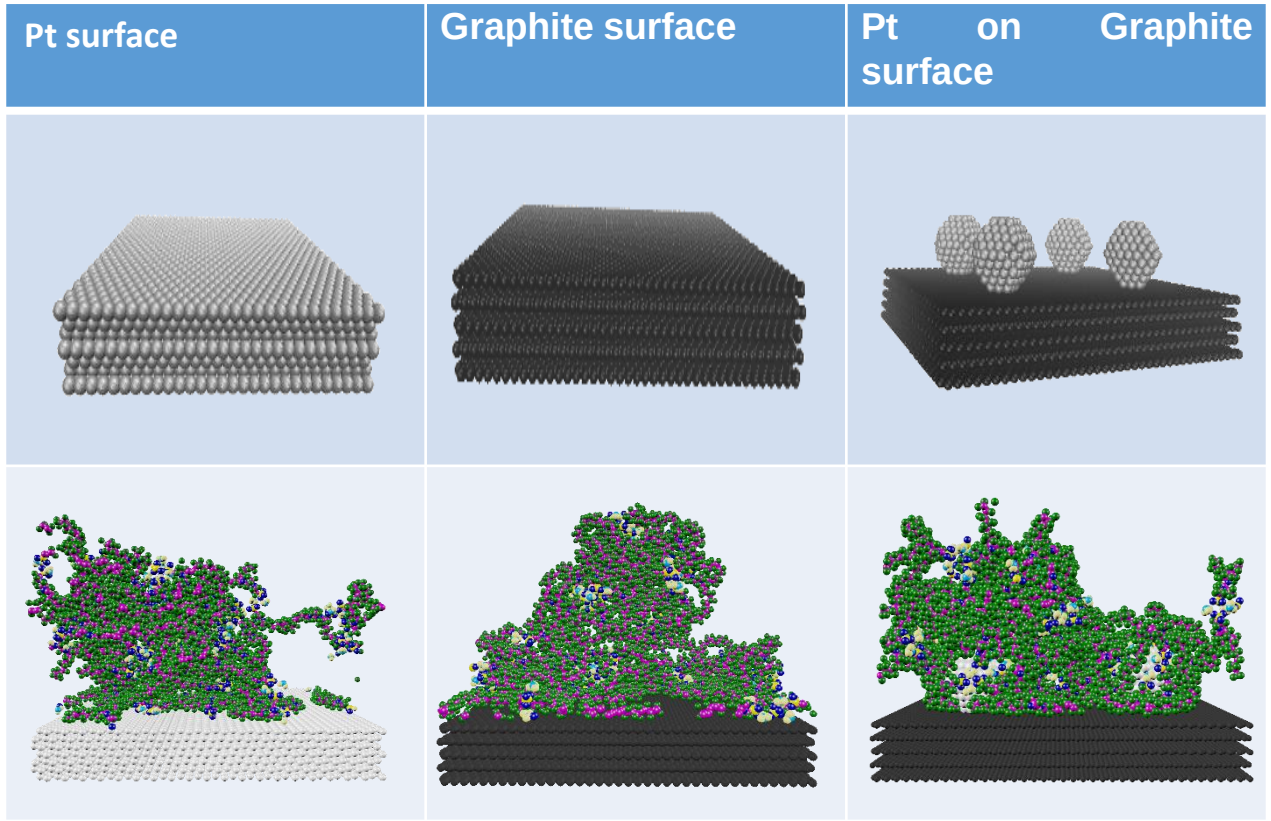
Input
AFM analysis of ionomer properties

→ Molecular Dynamics simulation →

Output
Transport properties of ionomer film

Transfers in the ionomer film, MD

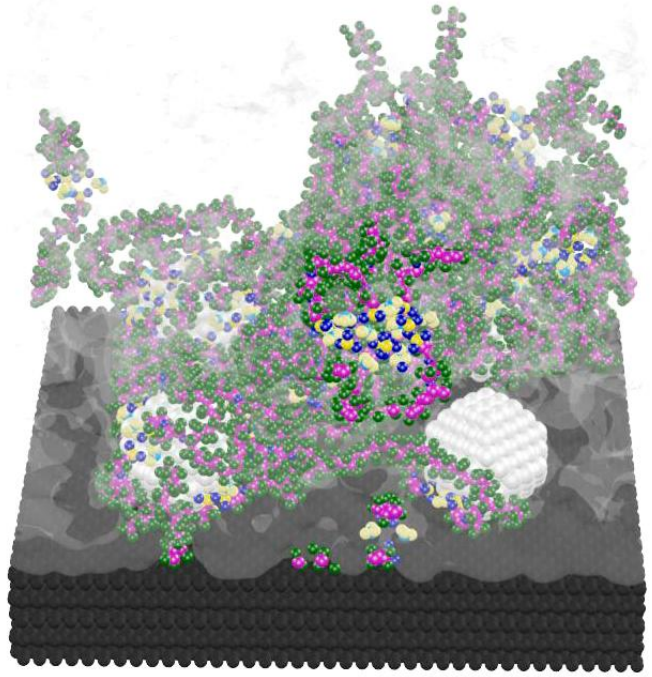
- **Results:**
  - Ionomer self-assembly process in the ink formulation stage is simulated
  - Effect of solvent on ionomer structure is investigated
  - Self-assembly is obtained for different substrates and different dispersions (water, isopropyl alcohol (IPA) and water-IPA mixture)
  - The ionomer coverage on carbon does not vary significantly (45%-54%) but that on Pt varies significantly (28%-72%) depending on the dispersion media; highest coverage (72% for water)



Self-assembly on different substrates in IPA

Transfers in the ionomer film, MD

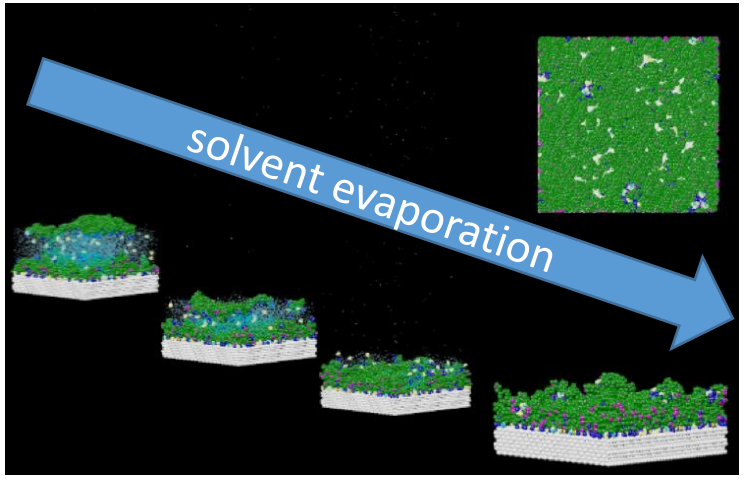
- **Results:**
  - Expectedly, no sulphonic groups are found at ionomer-carbon substrate indicating side chain orientation away from substrate
  - Abundance of sulphonic group on Pt-ionomer substrate depends on the dispersion used
  - Pt-ionomer interface reveals one sulphonic group blocks 3 Pt atoms via O-Pt interaction



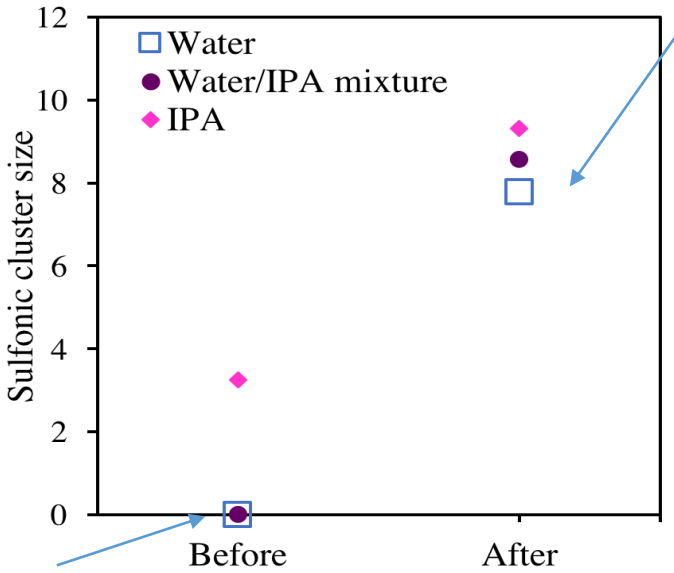
Influence of dispersion and substrate on ionomer-assembly simulated with MD

Transfers in the ionomer film, MD

- **Results:**
  - Simulation of solvent evaporation
  - Ionic cluster formation or cluster size increment is observed
  - Kinetically arrested structures can be envisioned



Drier film has 8-10 ion pairs (SO3-/H+) in a cluster or domain



No ionic cluster in self-assembled films (think ink stage) in water and water/IPA dispersions

Influence of solvent evaporation simulated with MD

Sub-micrometer structure scale

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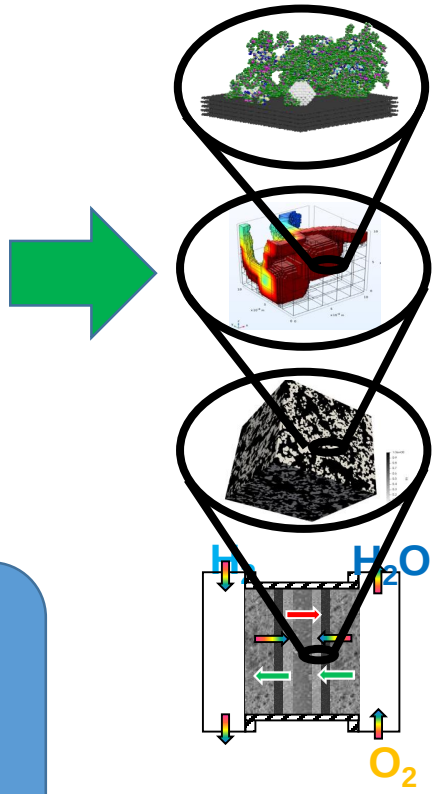
- **Objectives:**
  - Identification of transport losses on sub-µm scale
  - Development of DNS model and Lattice Boltzmann model for coupled transport and electrochemistry
  - Derivation of effective reaction rates
  - Investigations on the effect of CCL microstructure



Inputs
- Catalyst microstructure
- Catalyst and ionomer distribution
- Contact angles
- Properties of the ionomer depending on the water content
- Local conditions in CCL

→ DNS & Lattice Boltzmann →

Output
Microstructure-dependent effective reaction rate

Sub-micrometer structure scale

Clean Hydrogen Partnership
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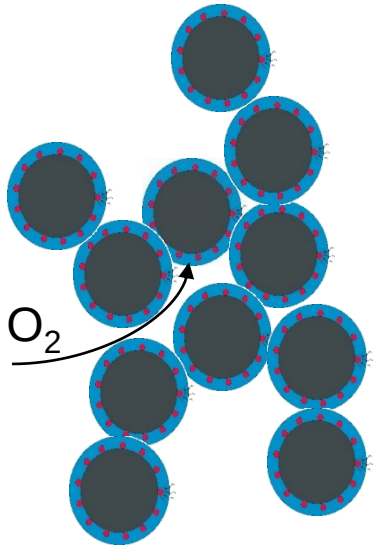
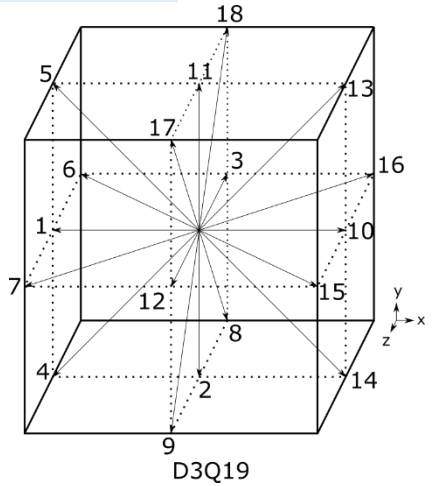
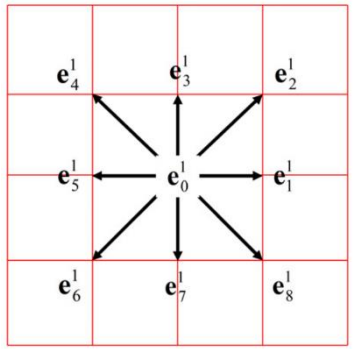
- **Lattice-Boltzmann model (LBM):**
  - Relevant processes to be described on sub-µm scale:
    - multi-component gas diffusion in pores
    - transport in ionomer film
    - electrochemistry on catalyst surface
    - liquid water transport
  - Lattice Boltzmann model (mesoscopic):

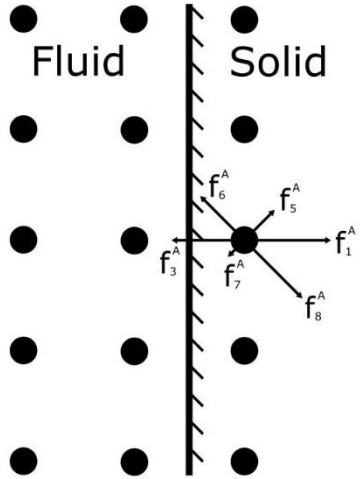
$$\frac{\partial f}{\partial t} + \boldsymbol{e} \cdot \nabla_{\chi} \boldsymbol{f} = \boldsymbol{\Omega}(\boldsymbol{f}) \rightarrow \boldsymbol{f_i}(\boldsymbol{\chi} + \boldsymbol{e_i}\boldsymbol{\Delta t}, \boldsymbol{t} + \boldsymbol{\Delta t}) = \boldsymbol{f_i}(\boldsymbol{\chi}, \boldsymbol{t}) + \boldsymbol{\Omega_{\sigma}^{i}}(x, t)$$

  - Collision operator for multi-component diffusion
  - Electrochemical reaction realized as modified bounce back boundary condition at platinum surfaces









Sub-micrometer structure scale

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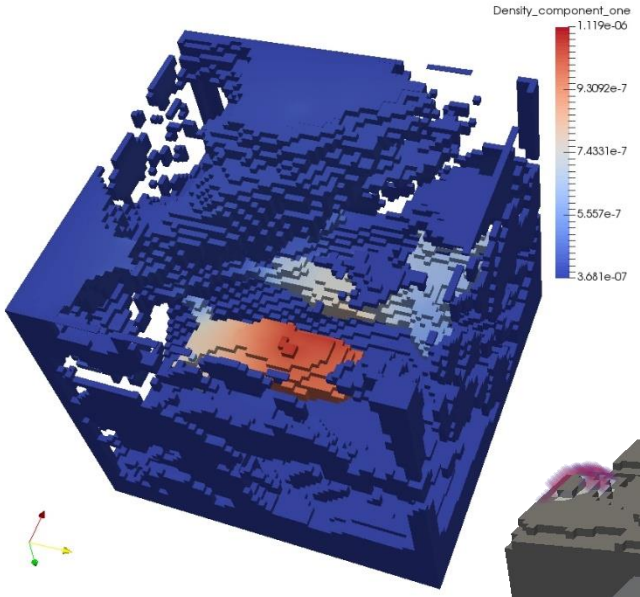
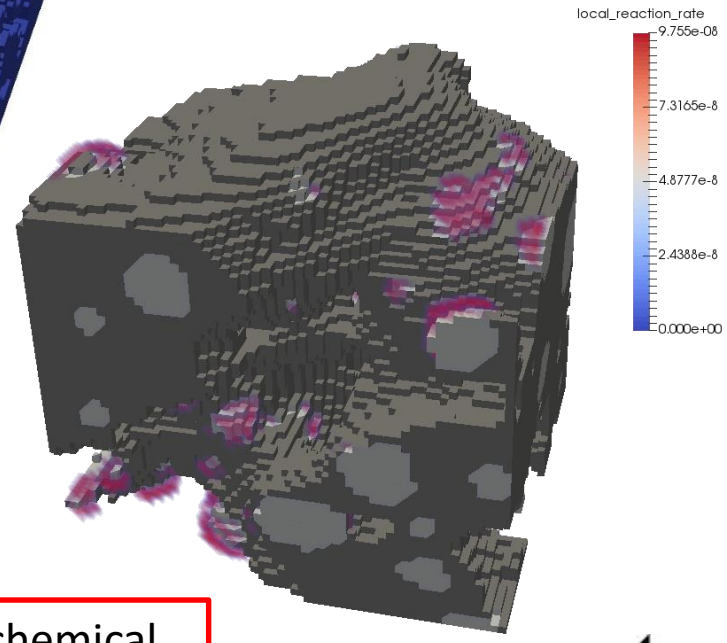
- **Results Lattice-Boltzmann model:**
  - CCL microstructures on sub-µm scale included from ADF-electron tomography
  - Domain size 60 voxel x 60 voxel x 60 voxel (8.65 nm x 8.65 nm x 8.65 nm)
  - Simulation of multi-component diffusion with electrochemical reactions
  - Formation of concentration gradients in nano-pores due to ORR





Successful first LB simulations of coupled diffusion with electrochemical reaction in three dimensions show variations in local reaction rate depending on microstructure

Sub-micrometer structure scale

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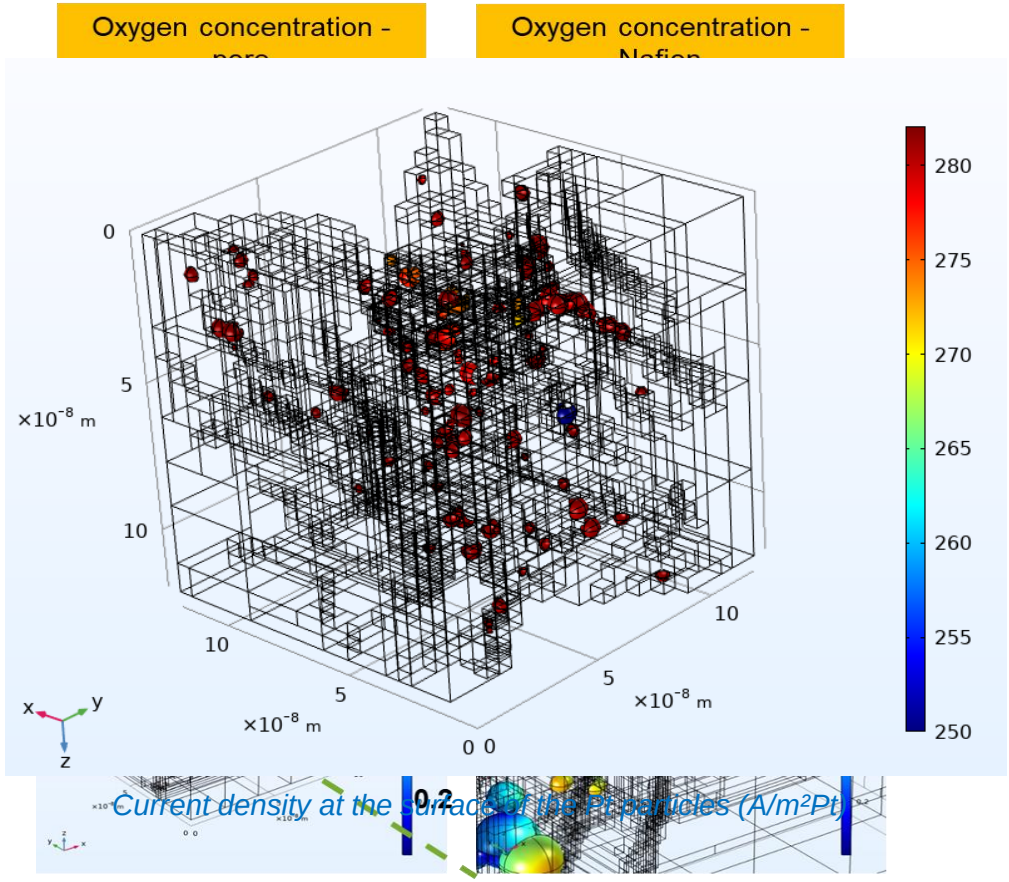
- **Results Direct Numerical Simulation (DNS):**
  - 3D structures of CCL on sub-µm scale constructed (carbon, ionomer, platinum particles)
  - Model includes gas diffusion, diffusion of O_2 in ionomer, proton transport, electrochemical reaction on Pt surface
  - First computation have been performed on CEA in-house MEA
  - The main transport limitation at local scale is the reactant diffusion through the ionomer
  - Similar analysis is ongoing for project CCL



Preliminary DNS results show expected heterogeneous distribution of local reaction rate. Competition effects between Pt particles observed depending on the particle distribution

Sub-micrometer structure scale

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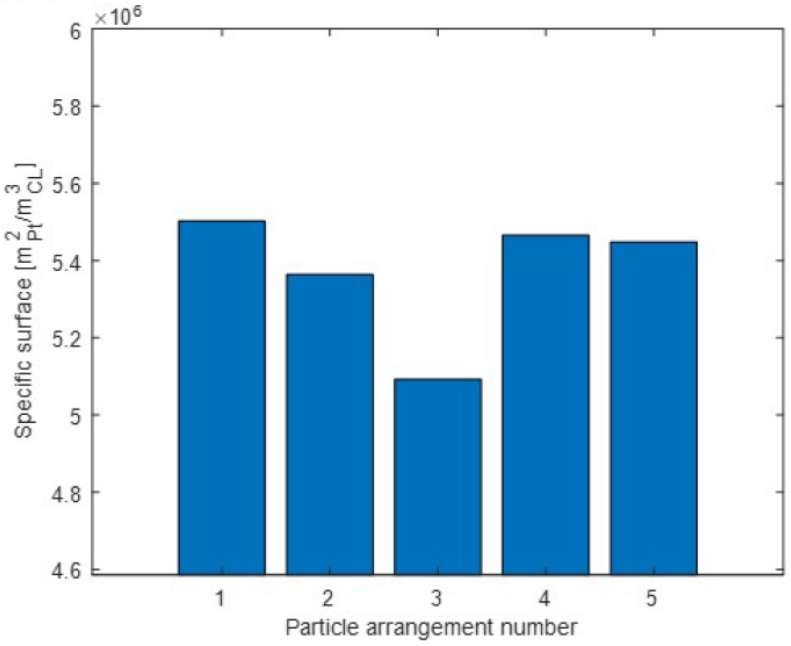
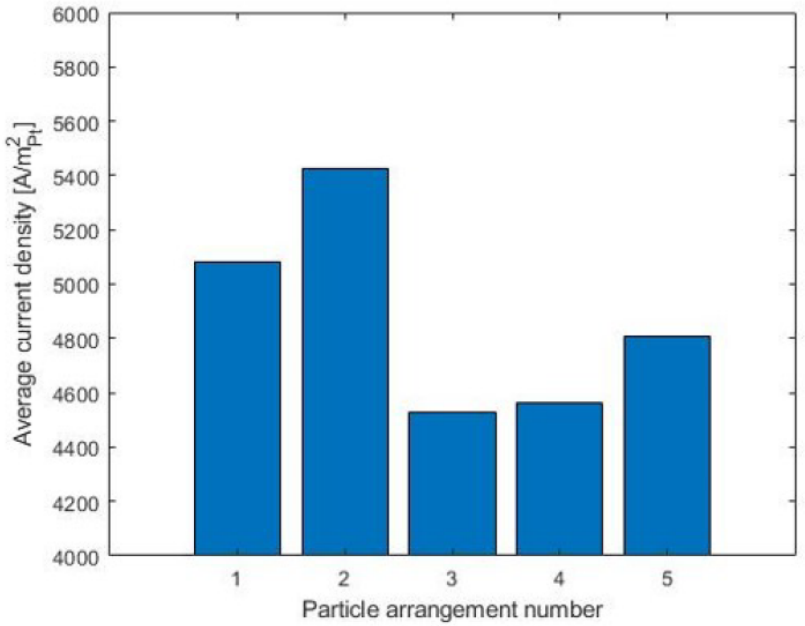
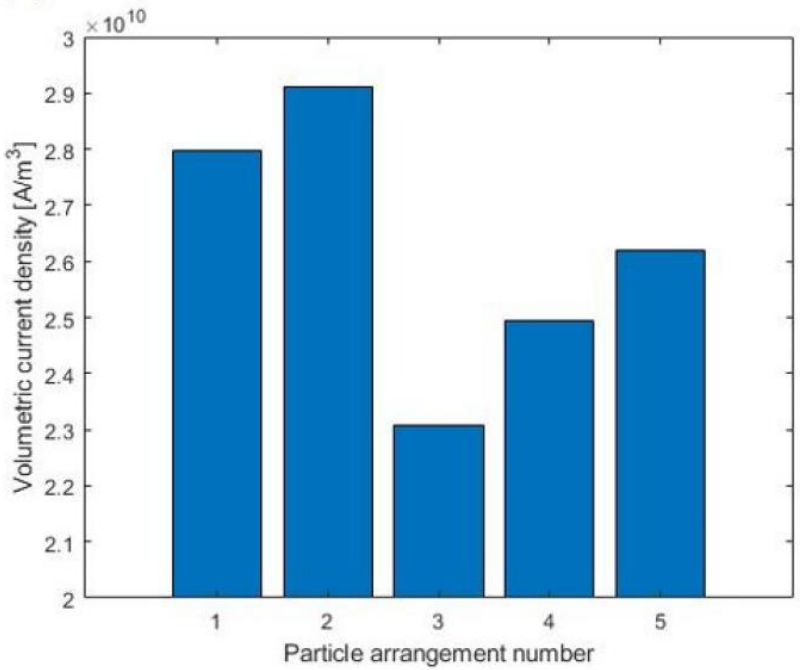
Results: Effect of the platinum particles positions for a given local carbon structure







- 5 random positionings have been tested
- The specific surface varies slightly due to particles location (flat surface, edge, corner) and discretization constraints (finite number of particles)
- Depending on the distribution, the platinum usage varies, because of local diffusion limitation and interparticle competition effect
- As a result, the volumetric current densities is significantly affected by the particles distribution

Cathode Catalyst Layer scale

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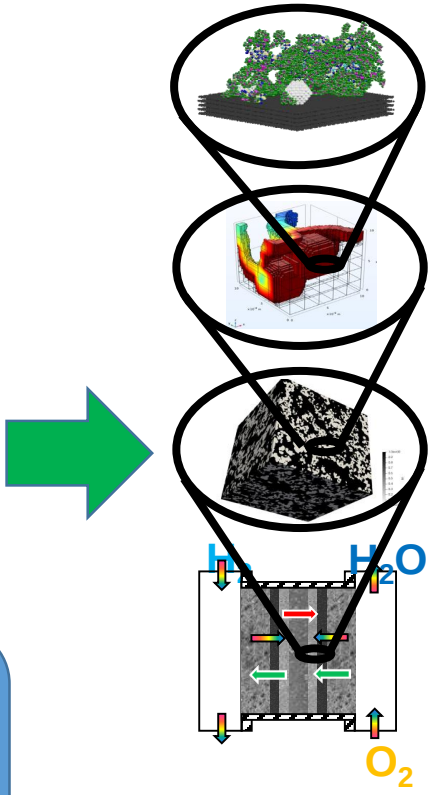
- **Objectives:**
  - Derivation of effective transport coefficients of MPL and CCL
  - Derivation of two-phase flow properties
- **Methodology:** Multi-scale approach:
  1. MPL computation (FIB-SEM)
  2. GDL computation (X-ray Tom.)
  3. GDL/MPL assembly (X-ray Tom.)



Inputs
- MPL/GDL/Catalyst microstructure
- Contact angles
- Catalyst and ionomer distribution
- Properties of the ionomer depending on the water content
- Improved description of electrochemical reaction
- Local conditions

→ DNS →

Outputs
- Volume averaged transport coefficients
- Effective contact angles

Cathode Catalyst Layer scale

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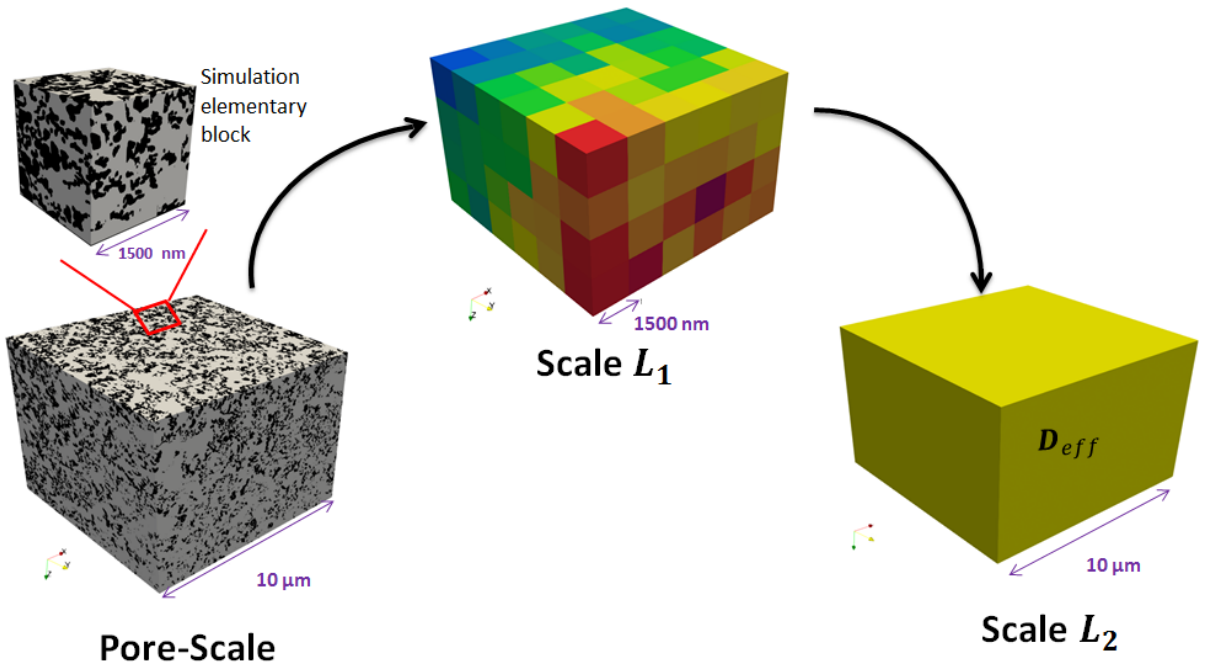
1. MPL computation (FIB-SEM)

- DNS using sequential approach
- Effective diffusion tensor has been computed
- $\frac{\partial c}{\partial t} = \nabla.(D(\boldsymbol{x})\nabla \mathrm{c})$ At pore scale
- $\frac{\partial C_{L_1}}{\partial t} = \nabla.(\epsilon(\boldsymbol{x})\boldsymbol{D_{L_1}}(\boldsymbol{x}).\nabla \mathrm{C_{L_1}})$ At first Darcy-scale
- $\frac{\partial C_{L_2}}{\partial t} = \nabla.(\epsilon\, \boldsymbol{D_{eff}}.\nabla \mathrm{C_{L_2}})$ At second Darcy-scale

- Same calculation method for thermal and electrical conductivity



Cathode Catalyst Layer scale

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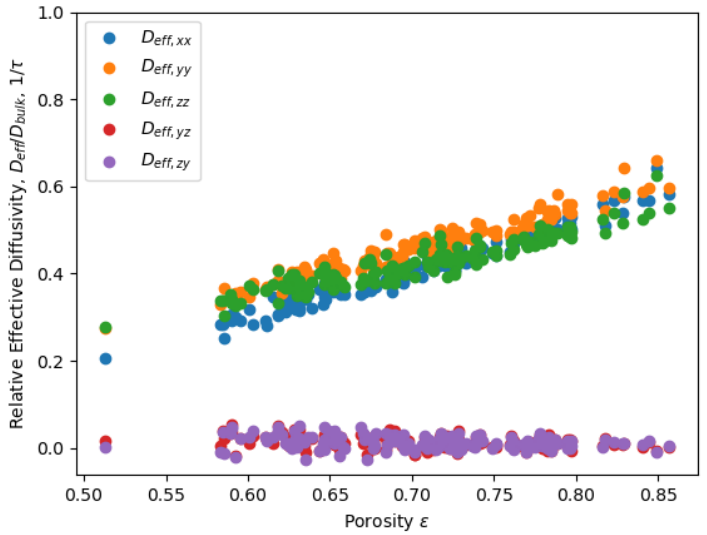
- **Results:**
  - Knudsen diffusion have a significative effect on diffusion in the MPL matrix

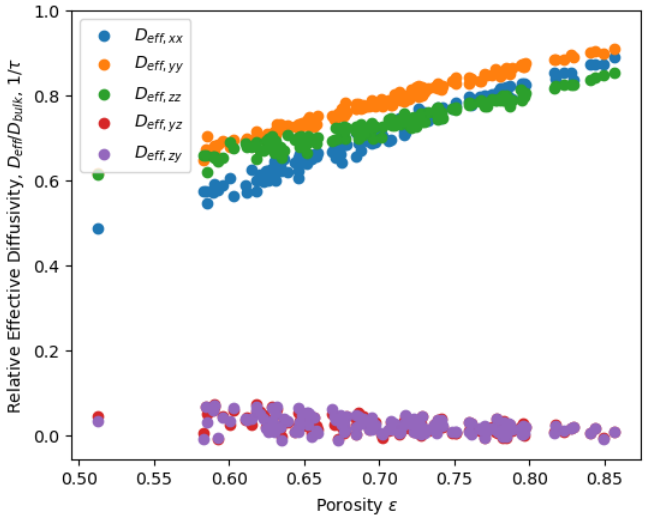
$$\frac{1}{D(\boldsymbol{x})} = \frac{1}{D_{bulk}(\boldsymbol{x})} + \frac{1}{D_{Kn}(\boldsymbol{x})}$$

$$D_{Kn}(\boldsymbol{x}) = \frac{d_p(\boldsymbol{x})}{3}\sqrt{\frac{8RT}{\pi M}}$$

With Knudsen diffusion



Without Knudsen diffusion



  - MPL effective diffusivity is isotropic at large scale

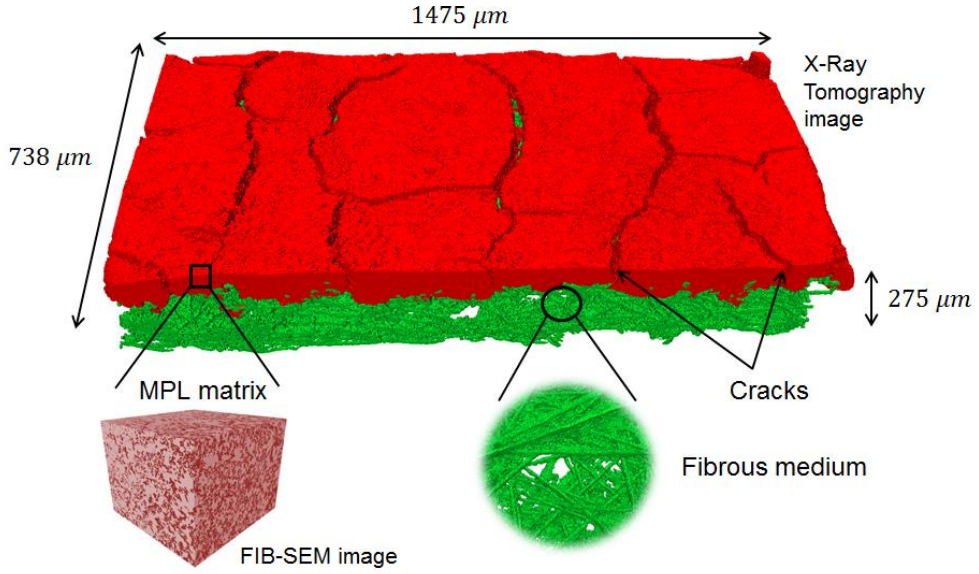
Successful calculation of full effective diffusion tensor based on MPL microstructure

Cathode Catalyst Layer scale

Clean Hydrogen Partnership
Co-funded by the European Union

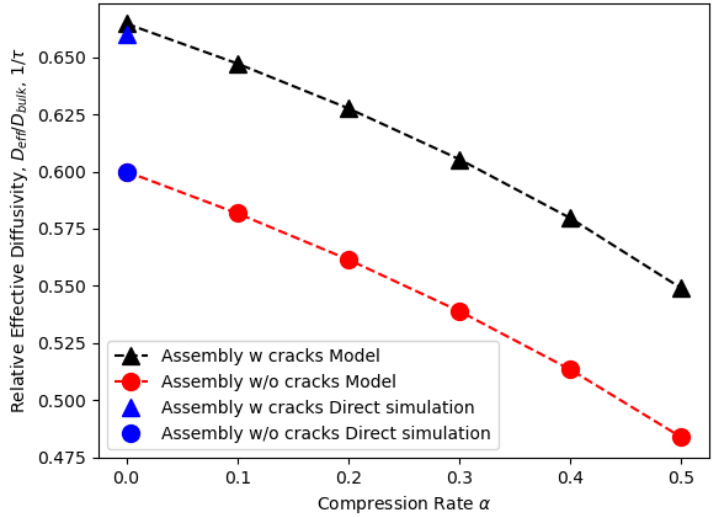
2. **GDL/MPL computation (X-ray Tomo.)**

- Cracked MPL reduces GDL diffusivity by 19% and uncracked MPL reduces GDL diffusivity by 25%



	GDL without MPL	GDL with cracked MPL	GDL with uncracked MPL
Thinkness (µm)	220	275	275
Porosity	0.88	0.81	0.80
Through plane relative diffusivity ($1/\tau$)	0.80	0.66	0.60
$\frac{D_{eff}}{D_{bulk}}(=\frac{1}{\tau})=(\frac{\epsilon-\epsilon_p}{1-\epsilon_p})^{\alpha}$	0.89	-	-
$\frac{D_{eff}}{D_{bulk}}(=\frac{1}{\tau})=\frac{1}{6}(\frac{4.7-1.7\epsilon}{2.7-1.7\epsilon}+\frac{9}{6.4-3.4\epsilon})$	0.88	-	-

- GDL compression effect via resistance model



Cathode Catalyst Layer scale

Clean Hydrogen Partnership
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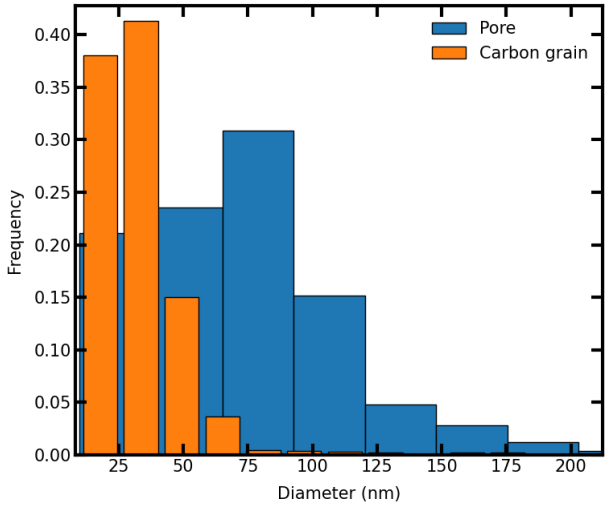
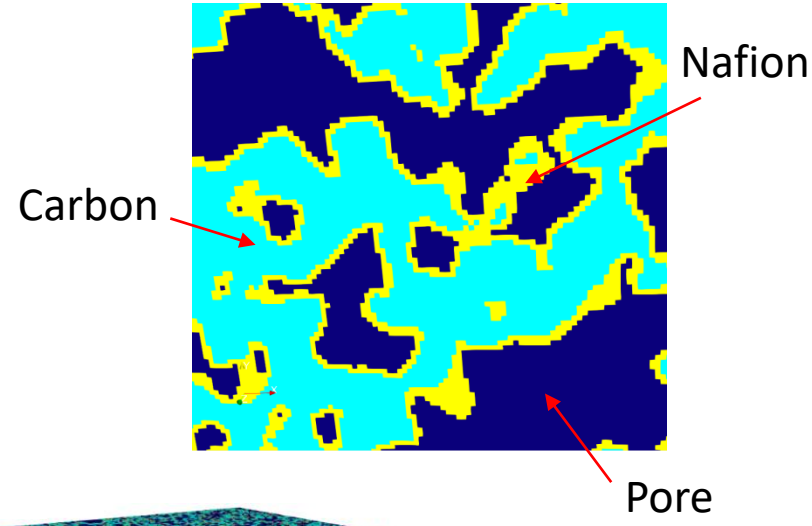
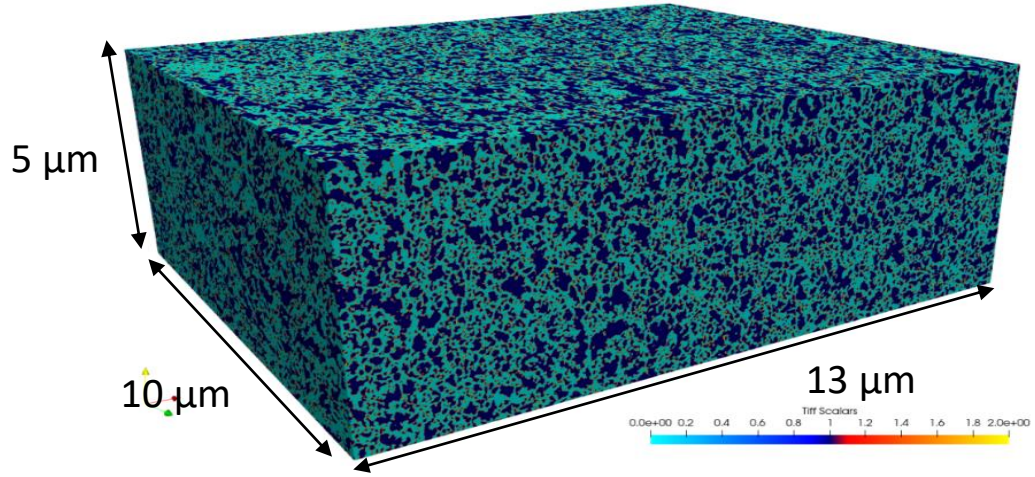
- **Results:**
  - Analysis of CCL microstructure:
  - Pore/Grain size distribution (from initial binary segmentation of FIB-SEM images)
    - carbon grain ~ 40 nm
    - pore ~ 80 nm
    - porosity equal to 0.55
  - Nafion voxel identification in solid phase using 3D distance map
  - volume fraction (I/C=0.77)







Microstructure analysis of CCL

Single cell scale

Clean Hydrogen Partnership
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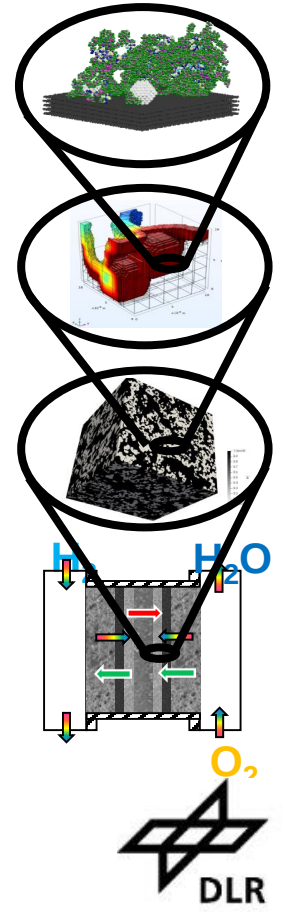
- **Objectives:**
  - Development and validation of single cell model including all relevant processes
  - Include improved sub-models and relations derived from lower scale models
  - Determination of the contributions of the different transport losses to the overall cell performance

Inputs
- Properties of cell components
- improved description of sub-micrometer scale and effective coefficients from LBM and DNS
- improved description of two-phase flow in porous electrodes
- dedicated electrochemical measurements for model validation

→ Cell model →

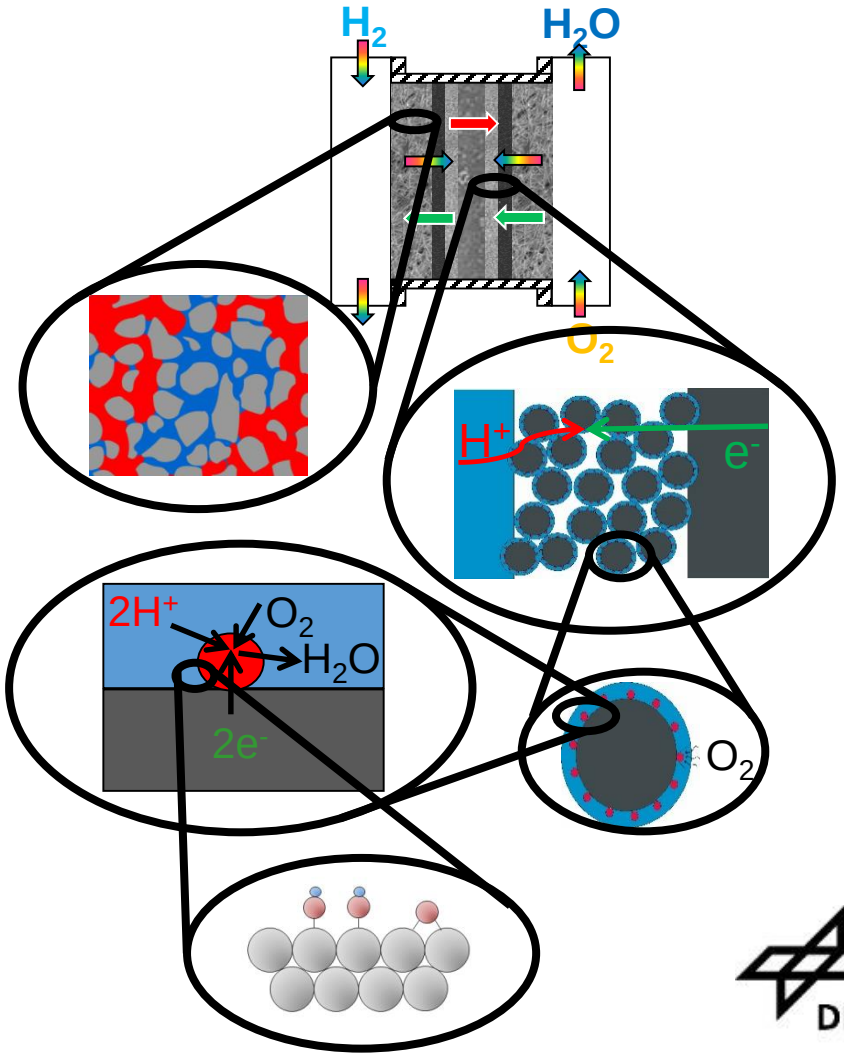
Output
- Transient simulations of cell performance
- Identification of contributions to performance losses



Single cell scale

Clean Hydrogen Partnership
Co-funded by the European Union

- **Approach:**
  - Development of macro-homogeneous 2D multiscale cell model including
    - Two-phase multi-component transport
    - Charge and energy transport
    - Transport resistance of ionomer film
    - Reaction kinetics including surface coverage effects
  - Parametrization and validation with dedicated ex-situ and in-situ experiments
  - Replacement of empirical relations by improved descriptions based on lower scale models



Single cell scale

Clean Hydrogen Partnership
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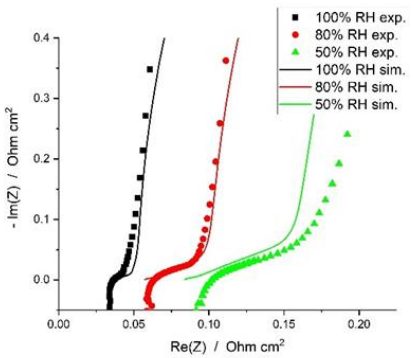
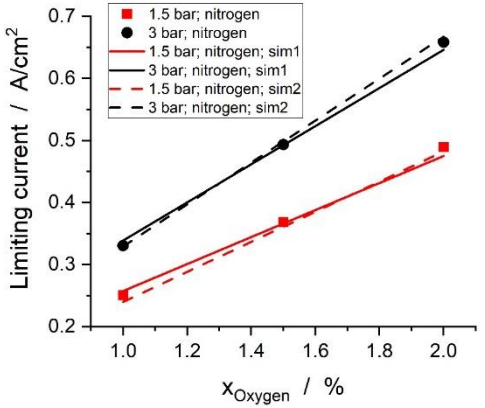
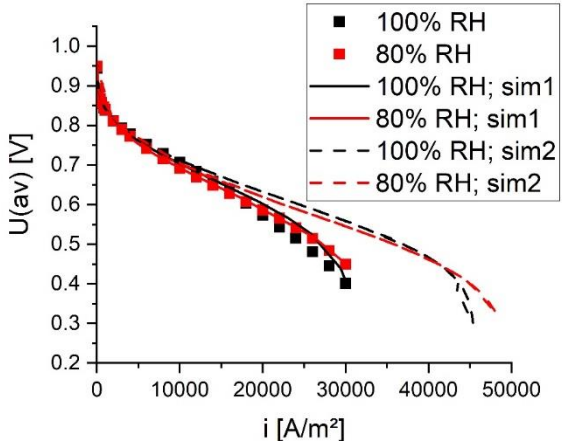
- **Results:**
  - Differential cell model has been implemented and parametrized for reference MEA in NEOPARD-X
  - Model validation has been started with dedicated electrochemical characterizations:
    - Polarization curves with various O_2 concentration in N_2 and He
    - EIS under H_2/air and various oxygen concentrations
    - EIS under H_2/N_2 (dedicated to determine protonic conductivity)
    - Limiting current measurements in nitrogen and helium
  - First results suggest the importance of the ionomer film resistance







First cell model is implemented and the in-depth validation ongoing

Multiscale-modeling: conclusions

Clean Hydrogen Partnership
Co-funded by the European Union

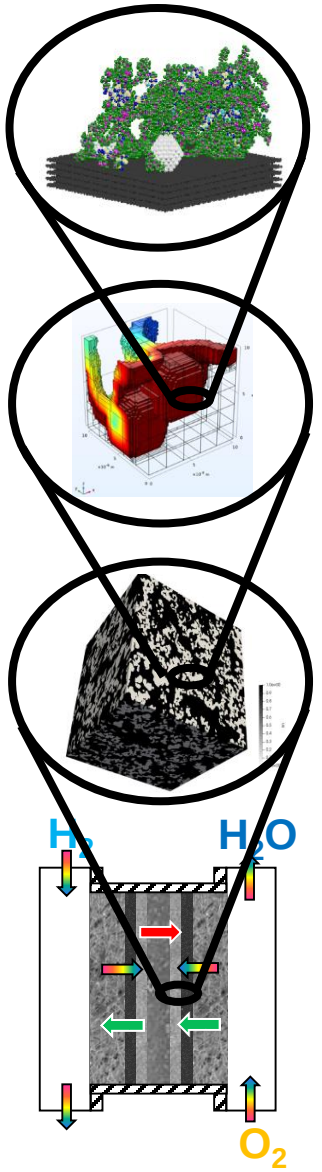
- Molecular Dynamics simulation of ionomer film:
  - Simulation of ionomer self-assembly and solvent effects
  - Simulation of solvent evaporation

  →Derivation of ionomer transport properties
- DNS and Lattice Boltzmann modeling of the CCL on sub-µm scale:
  - Development of models describing transport and electrochemistry on sub-µm scale

  →Derivation of effective reaction kinetics depending on CCL microstructure
- DNS on MPL and CCL microstructures:
  - DNS in real MPL and CCL microstructures

  →Derivation of effective transport properties of MPL and CCL
- Volume averaged differential cell model
  - Coupling of transport processes in all layers and electrochemistry in a 2D cell model
  - In-depth validation with dedicated electrochemical characterization

  →Identification and quantification of performance losses



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Multiscale-modeling: Next steps

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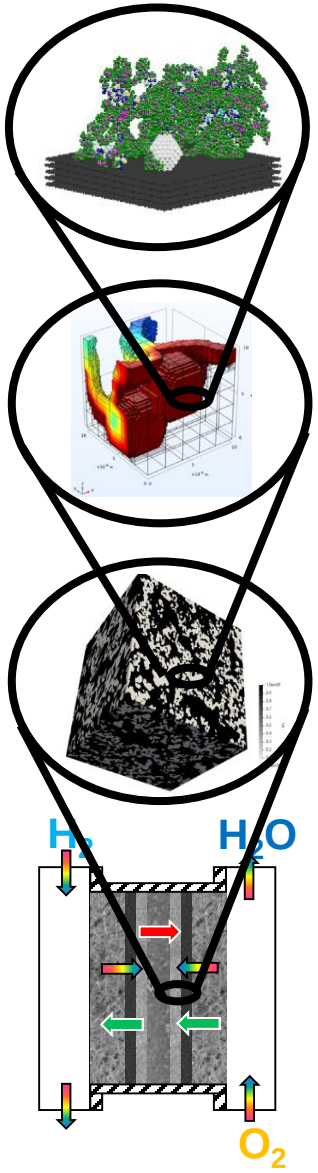
- **Molecular Dynamics simulation of ionomer film:**
  - Modeling material (H^+, O_2, water) transport through the dried ionomer films
  - Derivation of ionomer transport properties for higher scale models
  - Modeling of ORR and behavior of produced water with MD
- **DNS and Lattice Boltzmann modeling of the CCL on sub-µm scale:**
  - Extension of LBM taking into account the oxygen transport through the ionomer film and charge transport
  - Reference simulation with same microstructure with LBM and DNS to compare the approaches
  - Identification of microstructure dependent transport losses
- **DNS on MPL and CCL microstructures:**
  - Structure model of CCL microstructure including ionomer & platinum particles
  - Calculation of CCL transport properties
  - Computation of CCL water retention curve
- **Volume averaged differential cell model:**
  - Continue cell model validation with improved differential cell data (smaller cell area)
  - Include improved sub-models (effective reaction kinetics, two-phase transport) derived from lower scales when available
  - Analyze the contributions of the different processes to overall performance limitation



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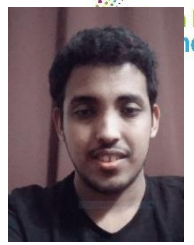
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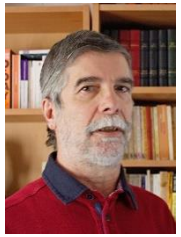
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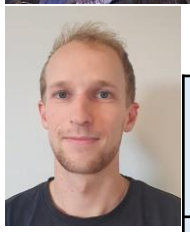
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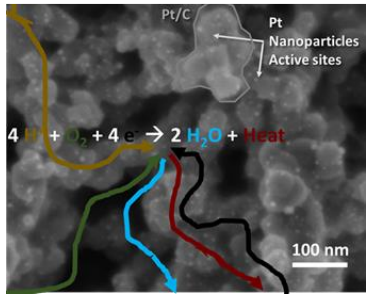
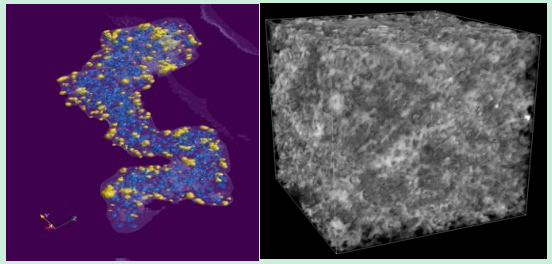
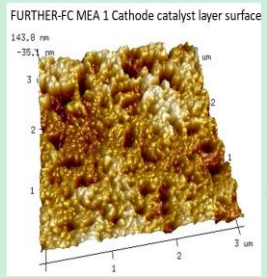
Thank you for your attention.
Your questions are welcome



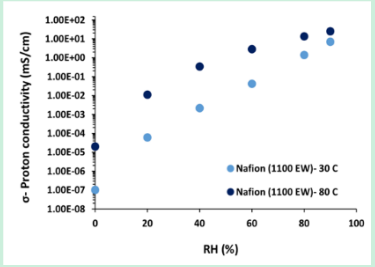
Multiscale characterization



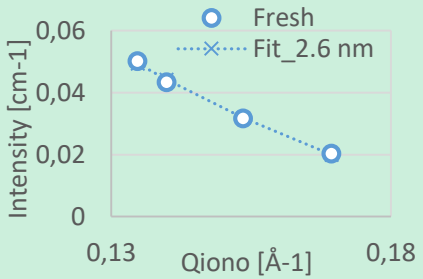
3D TEM and FIB/SEM



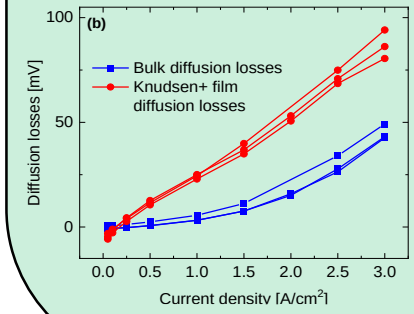
AFM



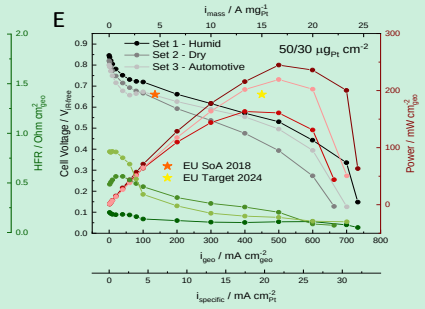
Ionomer transport properties



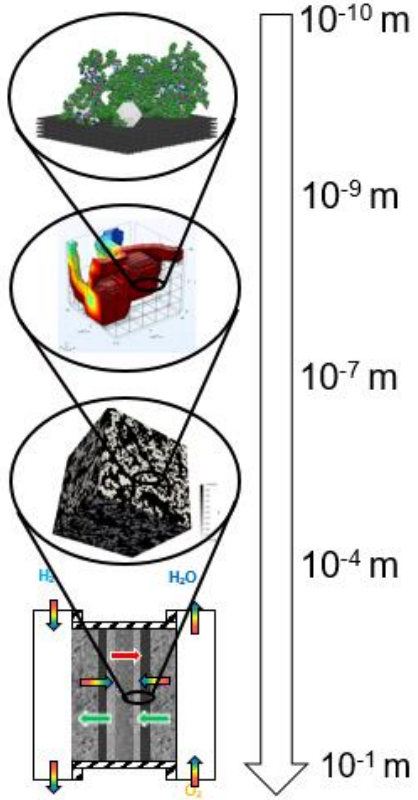
Ionomer swelling



Mass transport losses

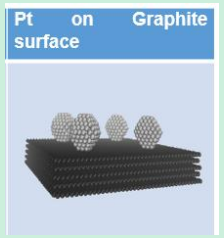


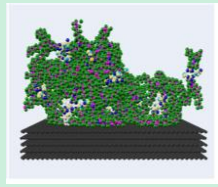
Ultra-thin electrode

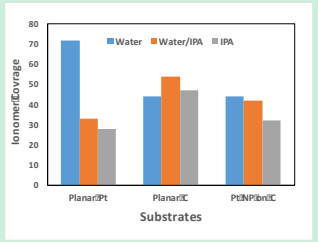


Multiscale modeling

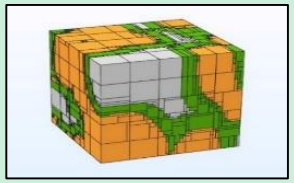
Ionomer film scale



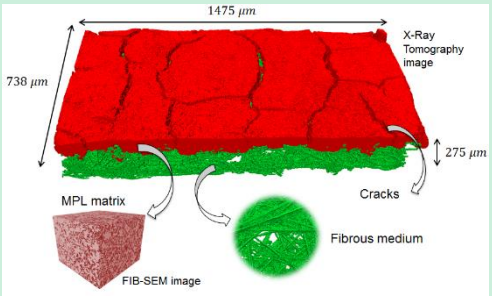




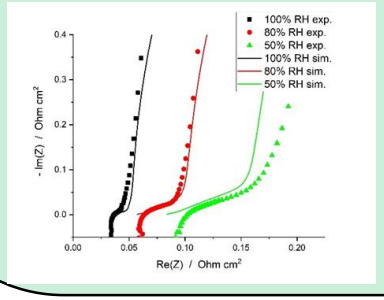
Sub µm scale

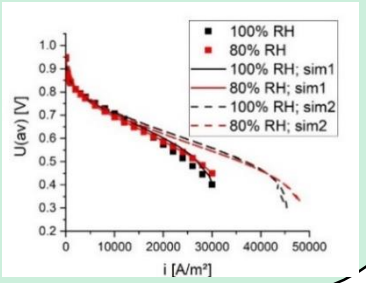


CCL scale



Cell scale





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Back-up slides