Clean Hydrogen Partnership
Co-funded by the European Union

FURTHER-FC Newsletter #3
Further Understanding Related to Transport limitations at High current density towards future ElectRodes for Fuel Cells

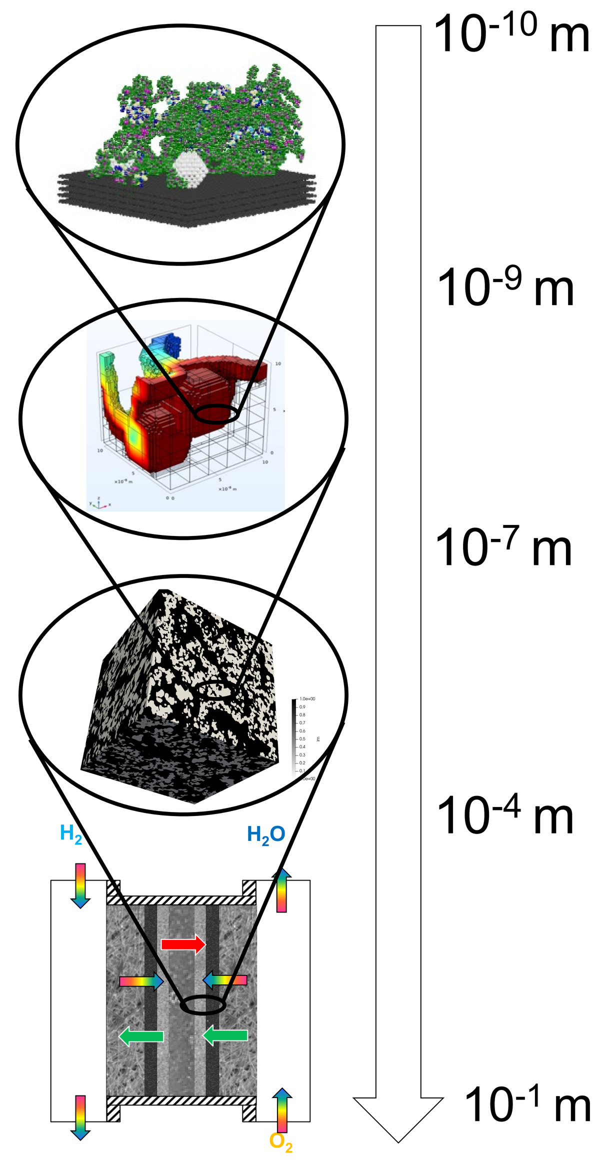
News: Multiscale modeling of PEMFC performance

Ambition

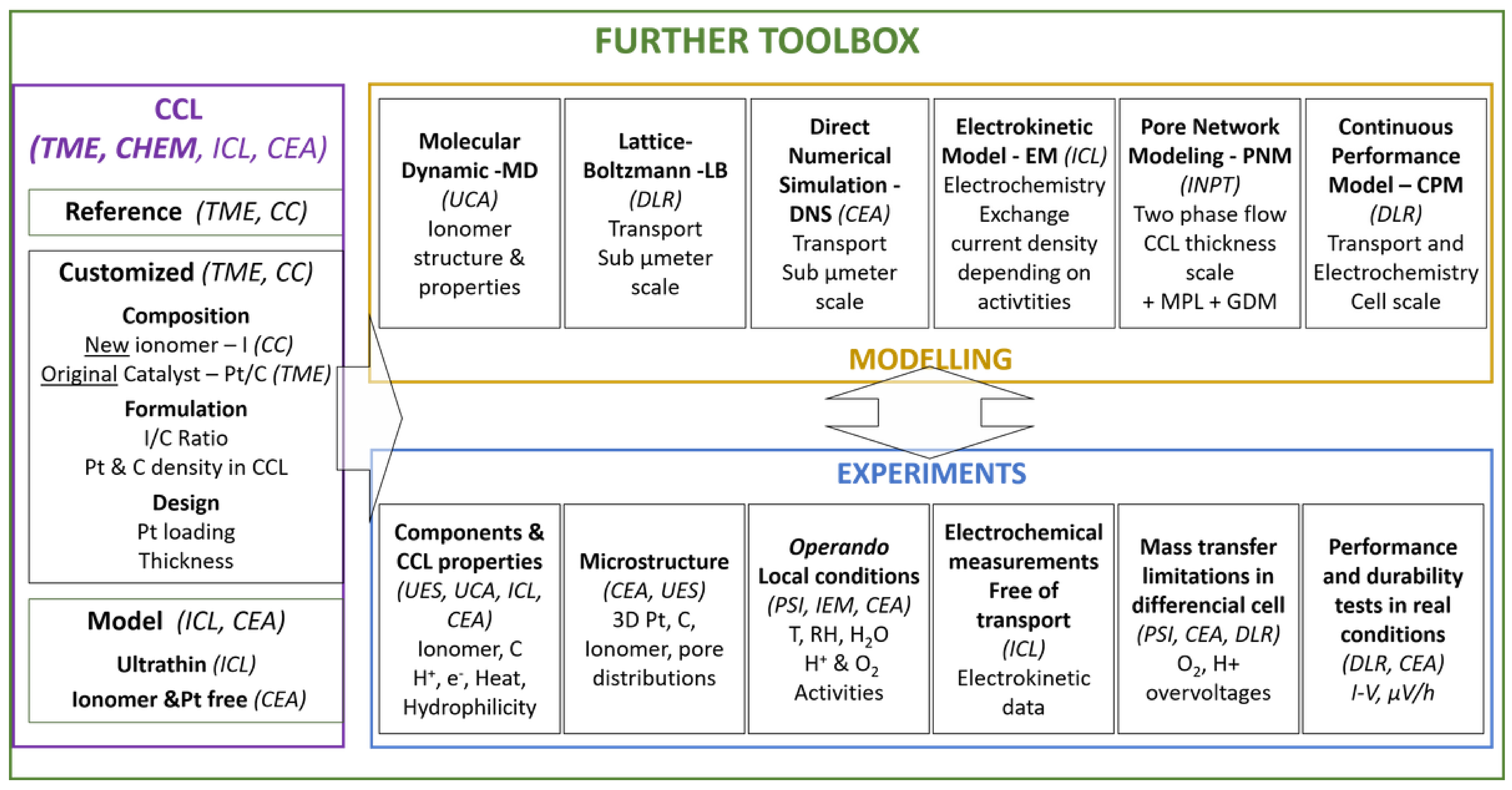
The identification of transport limitations and simulation based recommendations for improved Cathode Catalyst Layer (CCL) design and materials are among the main goals of the project Further-FC. To achieve these goals a **multiscale modeling** approach is developed, capturing the relevant processes on all length scales:

- Oxygen and water **transport in the ionomer film** with Molecular Dynamics
- **Mass transport and electrochemistry on the sub-micrometer scale** with Lattice-Boltzmann Modeling and Direct Numerical Simulation (DNS)
- **Mass and heat transport on the catalyst layer scale** with Pore Network Modeling and DNS
- Combination of all relevant processes at **single cell scale** with volume averaged models

To connect the approaches upscaling from lower to higher scale models is performed.



FURTHER-FC TOOLBOX



https://further-fc.eu/

Recent Results

Molecular dynamics on ionomer film scale (University of Calgary)

- **Realistic ionomer structure** on Pt/C (Platinum on Carbon) catalyst accounting for Pt nanoparticle (NP) morphology and ionomer organization in catalyst ink is critical first step for study of ionomer properties. Key findings are put together in a manuscript under review [1]
- **Self assembled ionomer** on three different substrates – planar carbon, planar Pt, and Pt NP on carbon – in different dispersion media were simulated (Figure 1).
- **Ionomer coverage** (Figure 2): Ionomer coverage on Pt is strongly influenced by dispersion media (28% coverage in isopropanol (IPA) to 72% coverage in water) but less so on carbon (44-54% coverage). Partial coverage is observed on Pt/C (32-44%)
- **Interfacial structure**: High abundance of sulfonic acid groups at Pt/ionomer interface is observed in water and lesser in IPA and IPA/Water mix (Figure 3). Expectedly, no ionic groups are seen at Carbon/Ionomer interface. Local structure analyses of SO_3^- (Figure 4) shows that two of the three oxygen atoms are bound to Pt and third atom is slightly away. Effectively SO_{3-} occupies three (3) Pt sites under no polarization or point of zero charge condition.

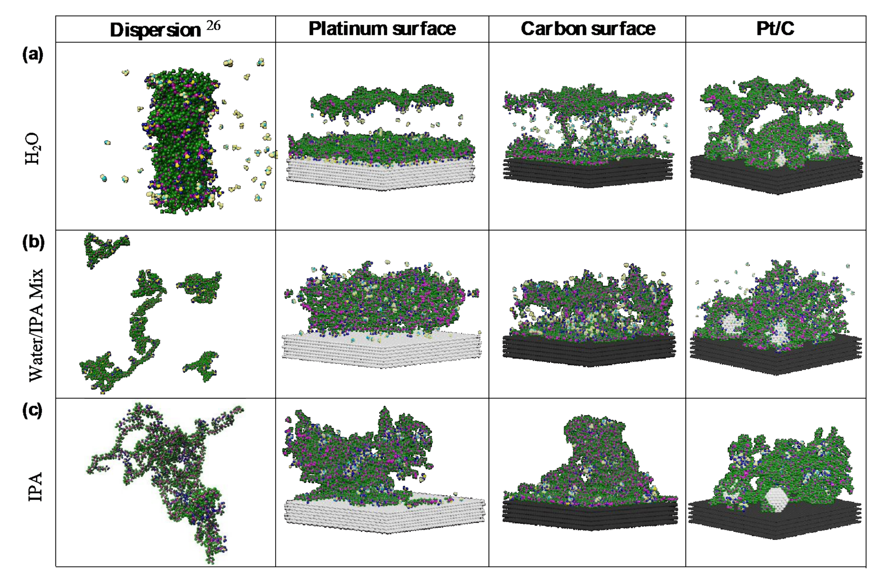


Figure 1. Self assembled ionomer on different substrates [1]

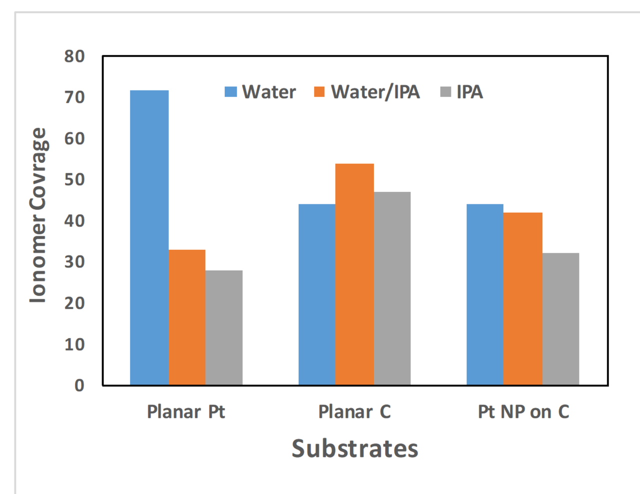


Figure 2. Effect of dispersion media on ionomer coverage on different substrates.

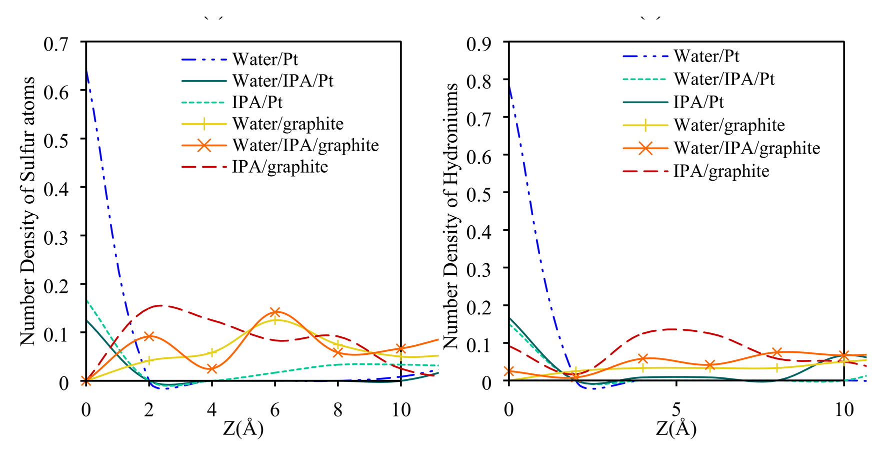


Figure 3. Abundance of sulfonic acid groups (a) and hydronoium ion (b) at the substrate ionomer interface [1]

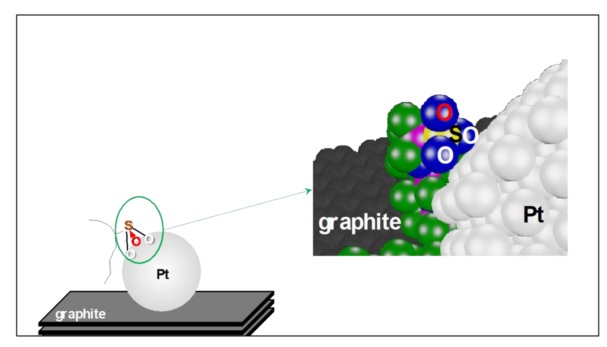


Figure 4. O-atom in SO_3^- orientation and coordination with Pt nanoparticle [1]

DNS on sub-µm scale (French Alternative Energies and Atomic Energy Commission)

DNS simulations : agglomerate modeling is now possible up to 32x32x32 voxels (=160x160x160nm), as shown in figure 5. The represented domain in the pores+ionomer phase.

Platinum particles are distributed randomly over the carbon surface, according to a pre-determined particle size statistical distribution. The particles are considered as half "flooded" spheres in the carbon (so half of the sphere is in contact with the ionomer).

For now, **3 different portions of the catalyst layer** have been simulated to evaluate the current density discrepancies (table 1). Differences are observed in performance, but more portions have to be simulated to be conclusive.

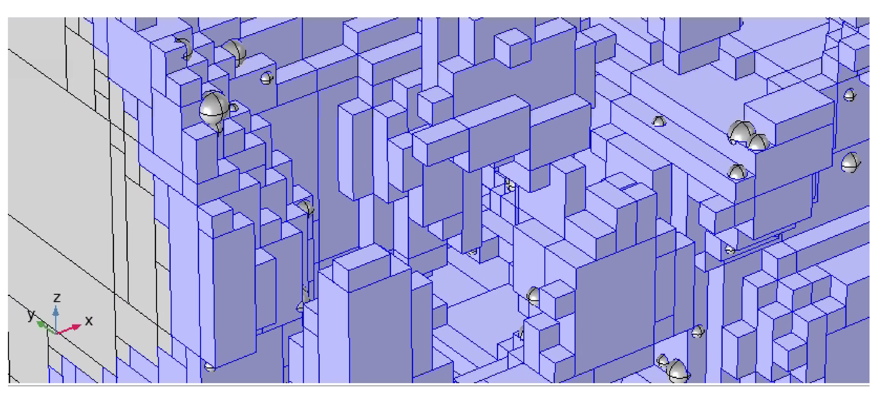


Figure 6. Platinum particle distribution

Location (i, j, k)	Volumic current density (A/m³)	Extrapolated frontal current density (A/m²)
25, 25, 1	$1.56*10^9$	$1.88*10^4$
25, 1, 25	$1.38*10^9$	$1.65*10^4$
1, 25, 25	$1.53*10^9$	$1.84*10^4$

Table 1. Simulation results

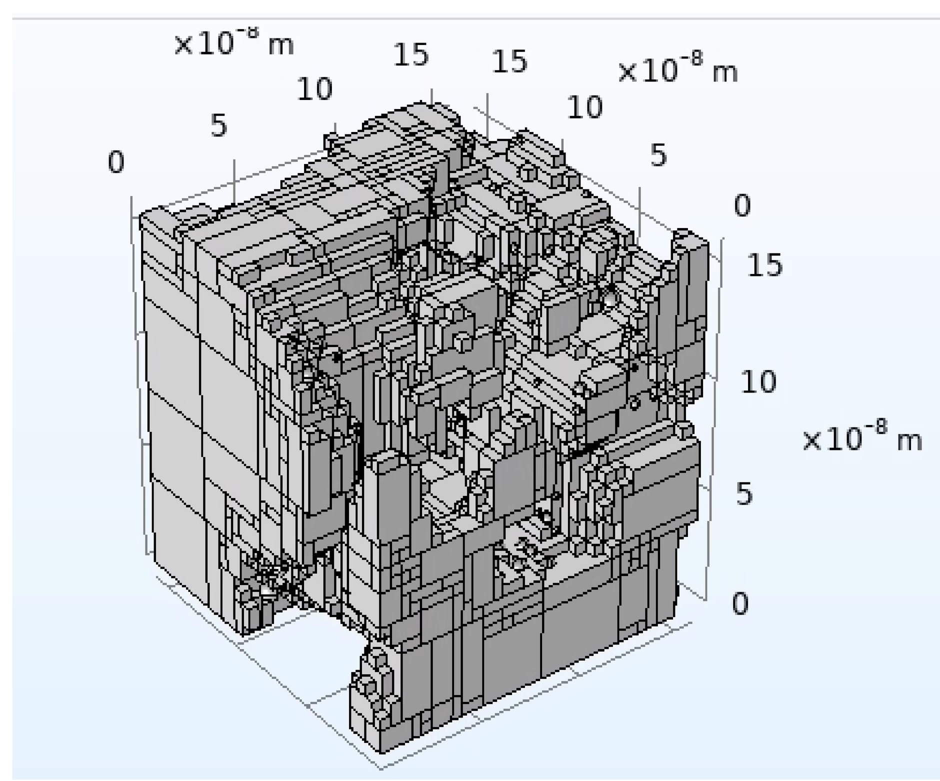


Figure 5. Example of DNS simulation domain

Reference:
[1] A. Tarokh, K. Karan, M. Khallgollah, M. Rioz, S. Ponnurangam (2022), J. Phys Chem C (under review)

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DNS and pore network modeling of MPL/GDL (National Polytechnic Institute of Toulouse)

DNS are performed on 3D digital images of component microstructures obtained by FIB-SEM (Focused Ion Beam Scanning Electron Microscopy, CCL) or a combination of FIB-SEM and X-ray tomography (gas diffusion layer, GDL).

This allows computing **macroscopic properties** such as,

- the effective diffusion tensor
- the thermal conductivity tensor
- the electrical conductivity tensor

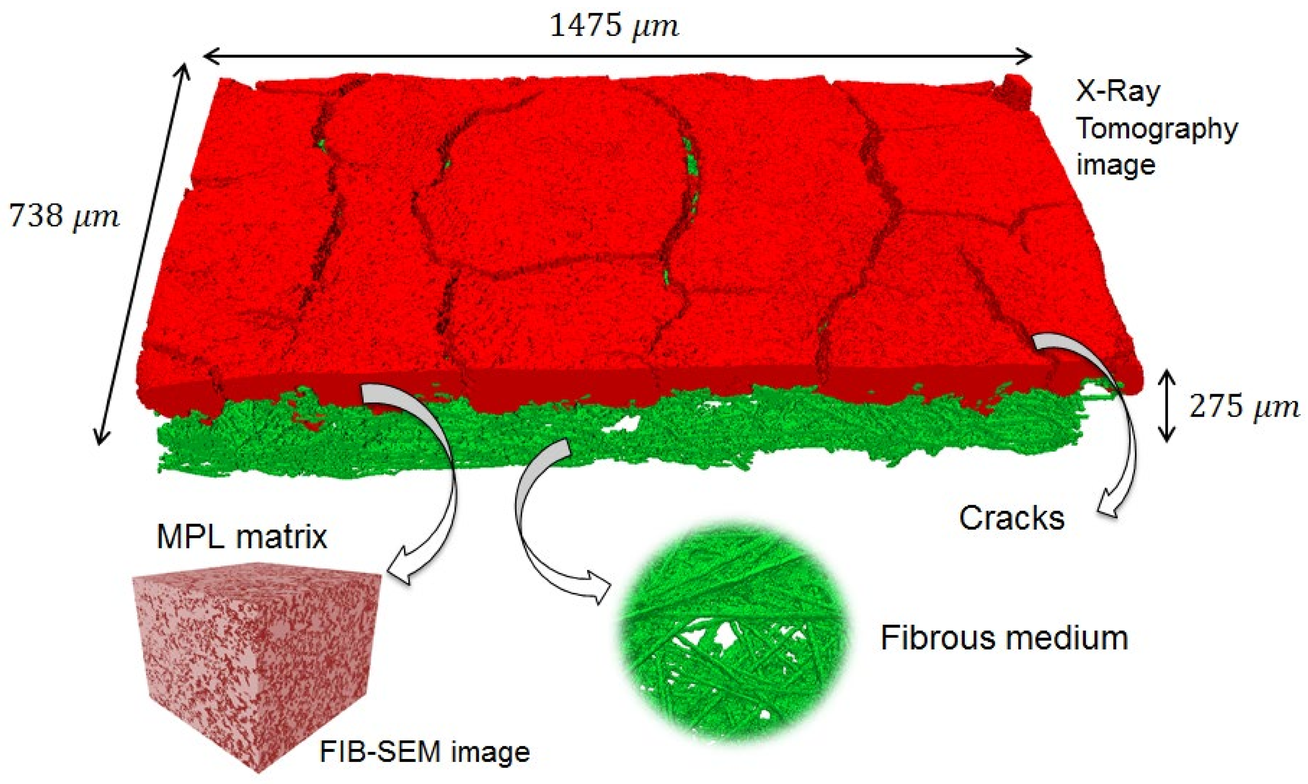

Figure 6. 3D digital image of GDL combining X-ray Tomography (fibrous medium, cracks) and FIB-SEM (MPL matrix)

- Simulations show the importance of Knudsen diffusion
- Impact of cracks in the MPL (MicroPorous Layer) on the oxygen diffusive transport through the GDL has been assessed.

Pore size distributions are determined by extracting the pore network from the 3D digital Images of microstructures using the open source softwares Porespy and OpenPNM

Results are in good agreement with experimental data obtained by Mercury intrusion porometry.

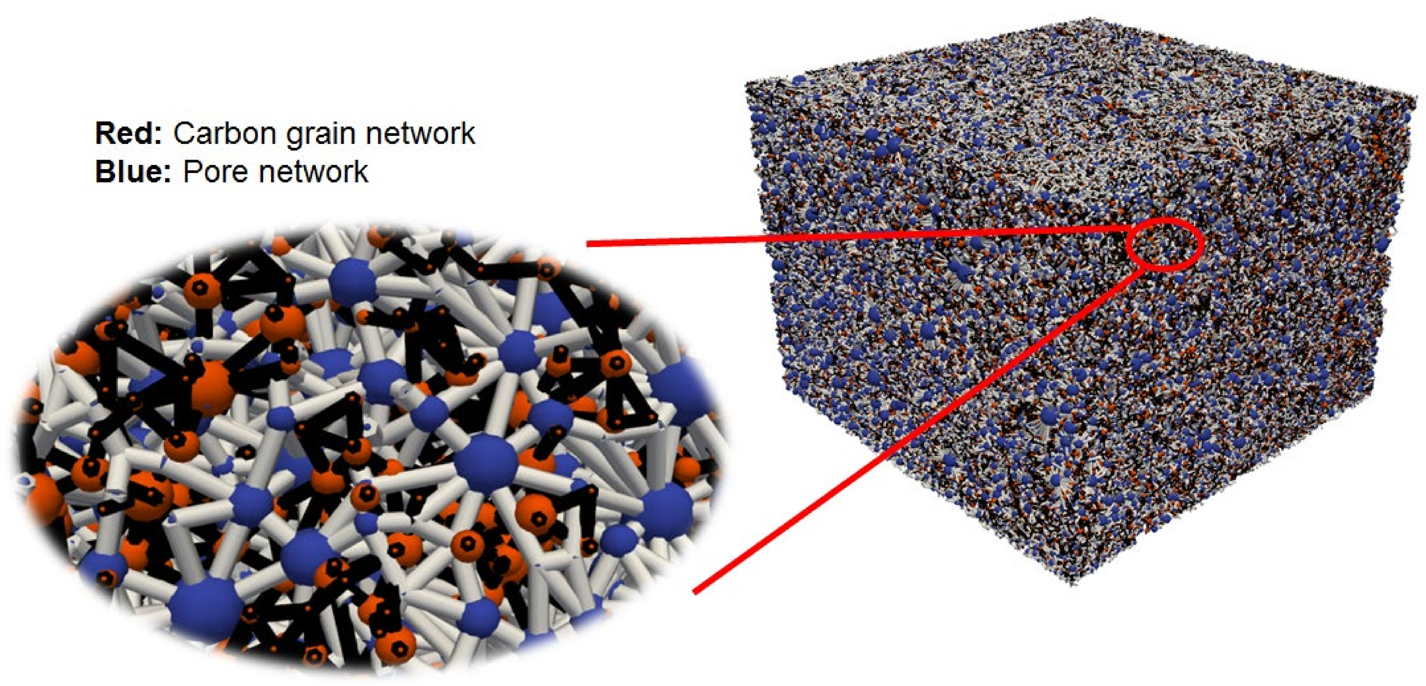

Figure 7. Pore and Carbon grain network extracted from a MPL matrix 3D FIB-SEM image using Porespy / OpenPNM

- Computations of effective properties on the extracted networks (solid phase network and pore network) are validated against DNS results.
- Network computations of effective properties are much faster than DNS

Volume averaged multi-scale modeling of single cells (German Aerospace Center)

A 2D differential cell model has been implemented in the DLR modeling framework NEOPARD-X. The model includes formulations for

- Two-phase multicomponent transport
- Energy transport
- Charge transport
- Water sorption kinetics
- Transport through the ionomer film
- Gas crossover through the membrane
- Hydrogen Oxidation Reaction (HOR) and Oxygen Reduction Reaction (ORR) kinetics
- Platinum oxide formation

In the course of the project the initial sub-models will be revised and improved based on the outcomes obtained from the lower scale models.

An **in-depth model validation** with dedicated experiments performed in differential cells is on-going in order to identify the accuracy and limitations of the current model. These experiments include

- Polarization curves with various O_2 concentration in N_2 and He
- Impedances under H_2/air and various oxygen concentrations
- Impedances under H_2/N_2
- Limiting current measurements in nitrogen and helium

First simulation results suggest the importance of the ionomer film resistance as well as of the cracks in the MPL for an accurate description of the cell performance.

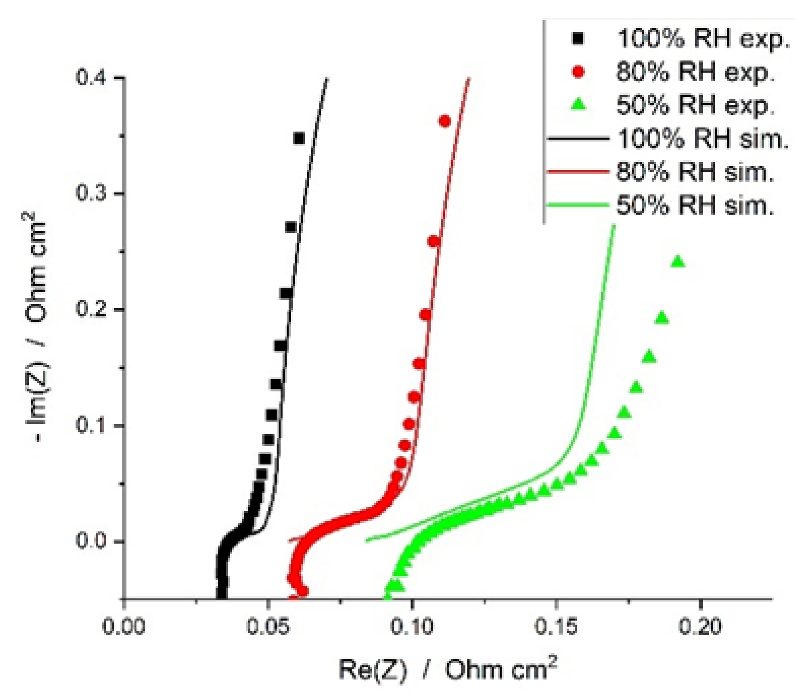

Figure 8. Validation with impedances under H_2/N_2

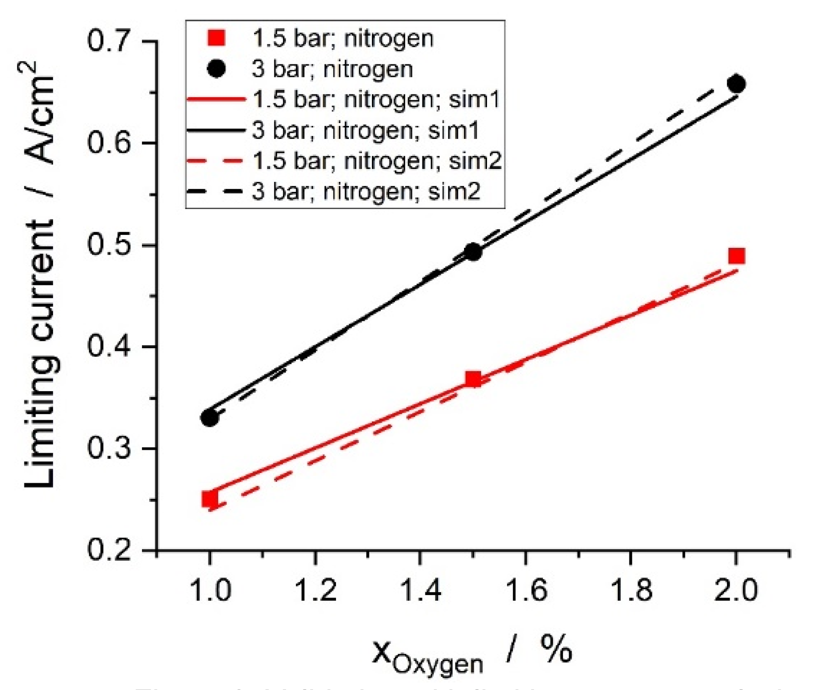

Figure 9. Validation with limiting current analysis

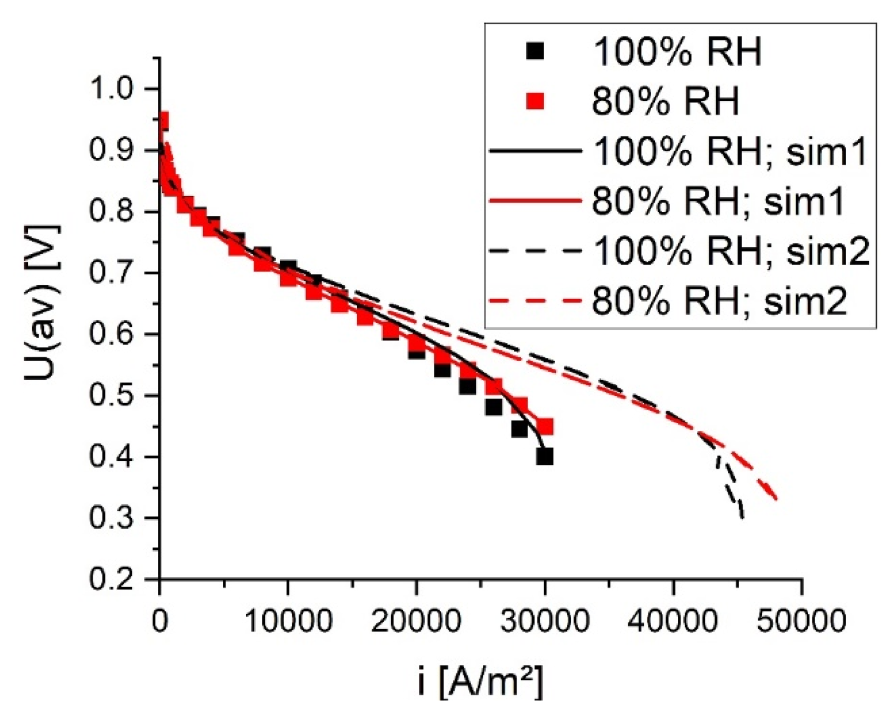

Figure 10. Validation with polarization curves

Acknowledgement

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Contacts:
tobias.morawietz@hs-esslingen.de
joel/.pauchet@cea.fr