SEVENTH FRAMEWORK
PROGRAMME

Artemis

Multi-scale modeling to boost fuel cell performance: From pore-scale simulations to better efficiency and durability

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Multi-Scale Modelling LAB – **SMaLL** (www.polito.it/small)

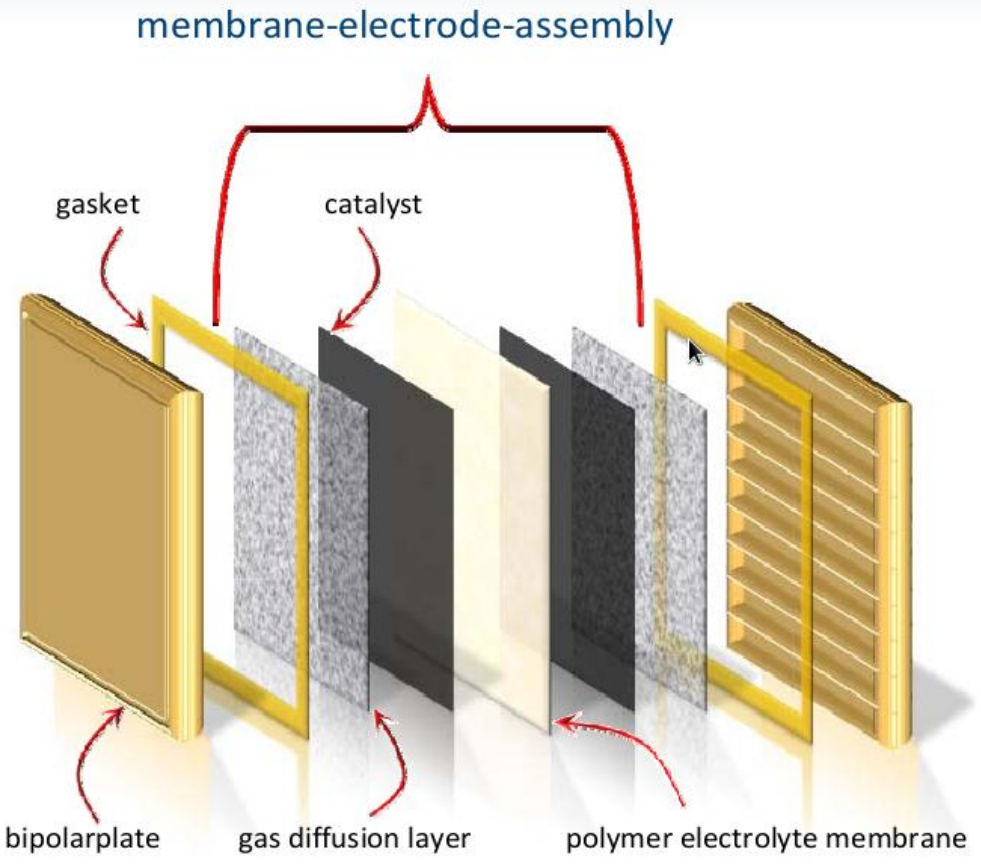
ARTEMIS (http://www.artemis-htpem.eu/)

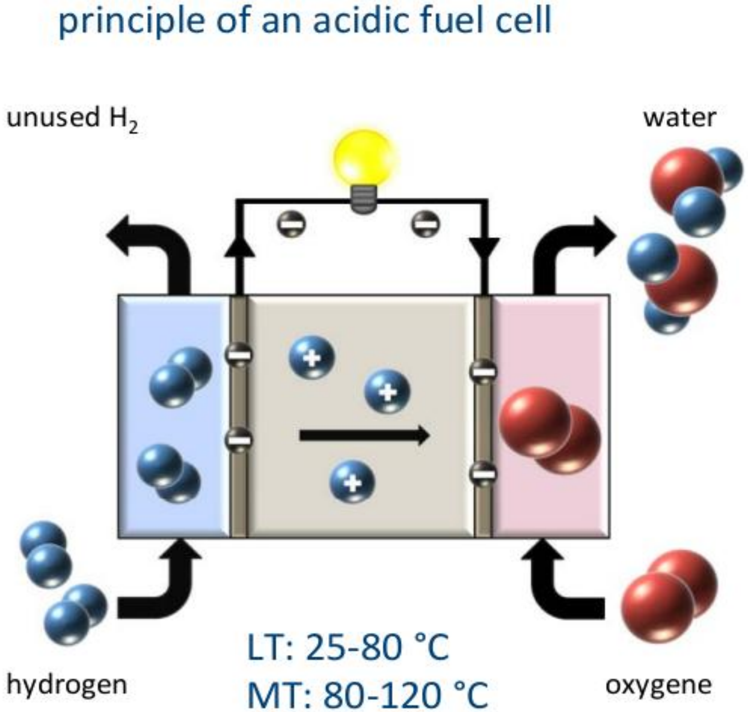
POLITECNICO DI TORINO

SMaLL
multiScale ModeLing Laboratory

ECo MaTech
EUROPEAN CONFERENCE ON
MATERIALS & TECHNOLOGIES
FOR SUSTAINABLE GROWTH

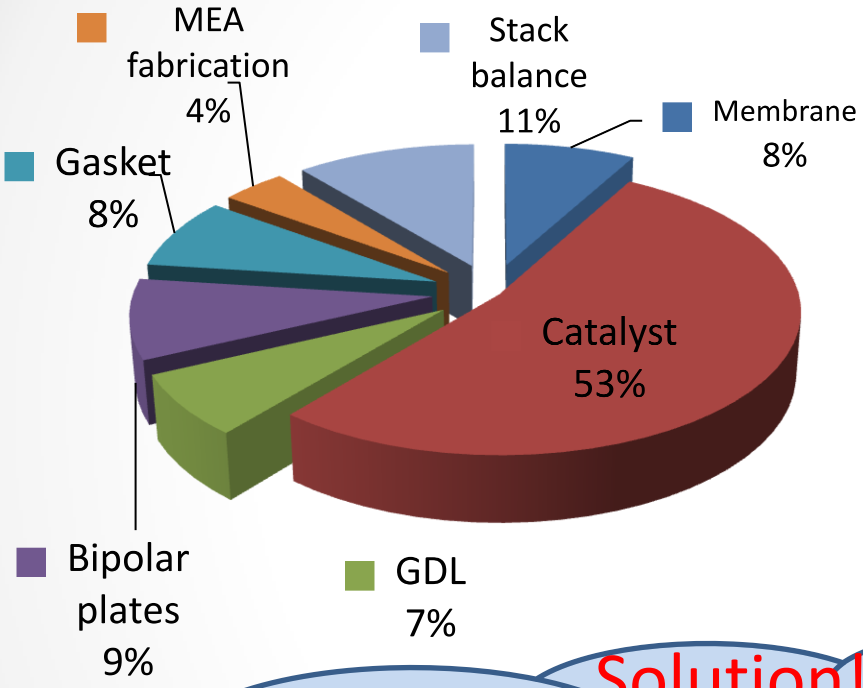
Motivation: High Temp. PEM Fuel Cells





LT: 25-80 °C
MT: 80-120 °C
HT: 120-200 °C

HT PEMFC: main issues



Two main issues preventing widespread commercialization of PEMFC:

- ➢ High cost
- ➢ Durability (degradation)

Study case:

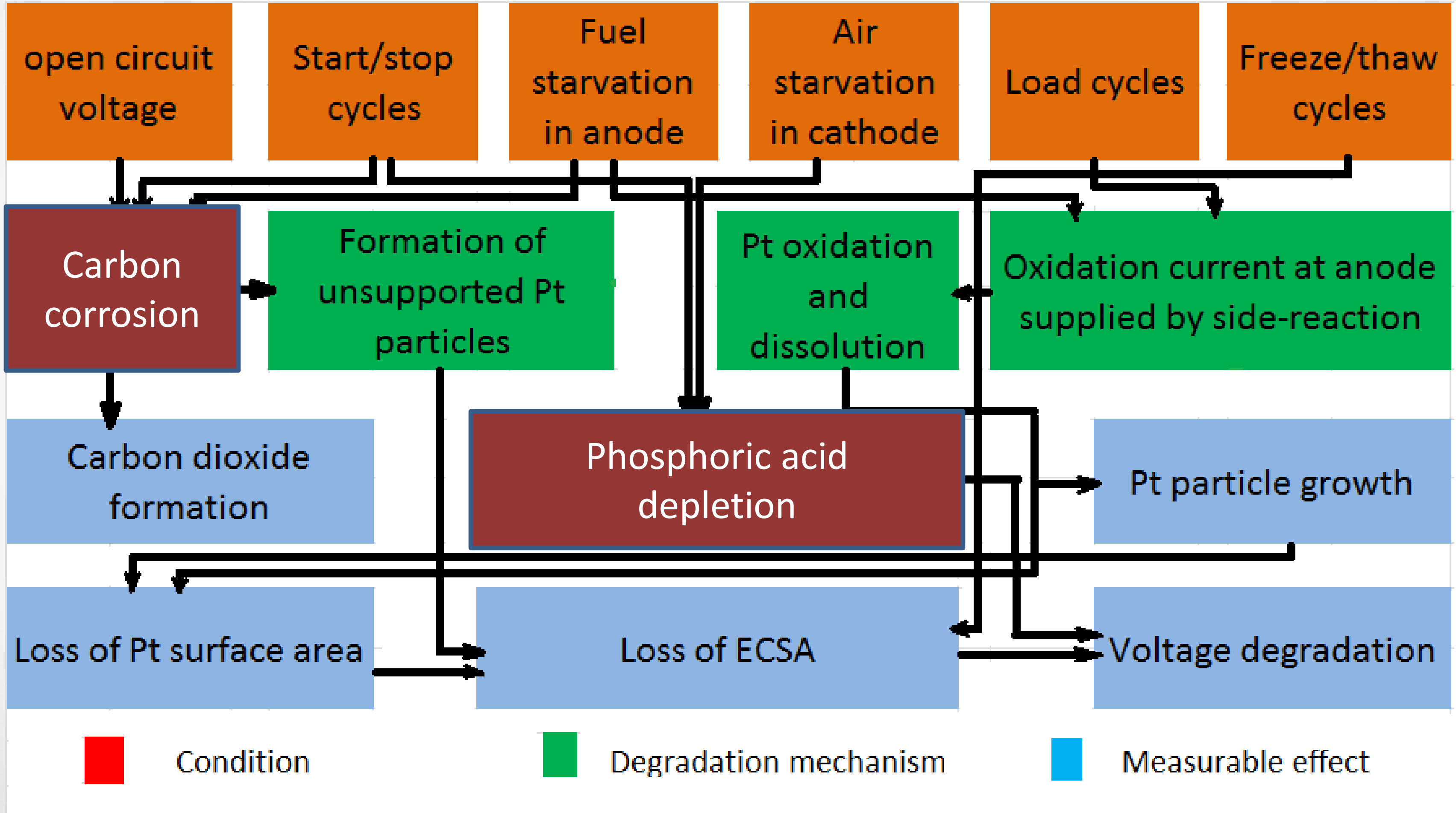
Electrode = Catalyst + GDL

- – the most expensive (~60% of full cost of cell)
- – the most vulnerable part prone to degradation processes

Solution!!!

Optimization of Pt loading of catalyst layers and analysis of carbon support via investigation of the undergoing physico-chemical mechanisms of degradation processes

HT PEMFC: degradation of electrodes


open circuit voltage

Start/stop cycles

Fuel starvation in anode

Air starvation in cathode

Load cycles

Freeze/thaw cycles

Carbon corrosion

Formation of unsupported Pt particles

Pt oxidation and dissolution

Oxidation current at anode supplied by side-reaction

Carbon dioxide formation

Phosphoric acid depletion

Pt particle growth

Loss of Pt surface area

Loss of ECSA

Voltage degradation

🟥 Condition

🟩 Degradation mechanism

🟦 Measurable effect

Degradation of electrodes: phosphoric acid loss

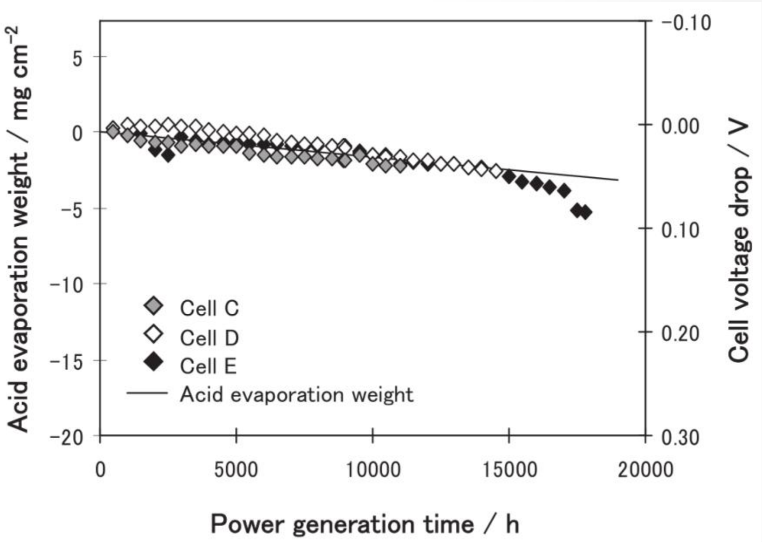
Phosphoric acid depletion :

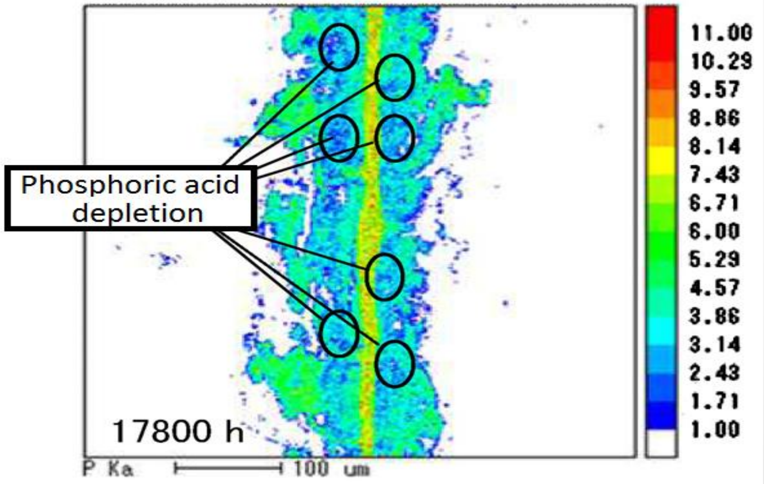
Loss of ionic conductivity → Voltage drop

- Acid loss may occur through several mechanisms such as :
  - diffusion
  - capillary transport
  - membrane compression
  - evaporation
  - leaching by condensed water during shutdown and cold start

  T. Sousa, M. Mamlouk, K. Scott*, Int. J. Hydr. En. 35 (2010) 12065
- PA loss as a function of flow rate, temperature, operating conditions

Y. Oono et al. , Journal of Power Sources, 210 (2012) 366



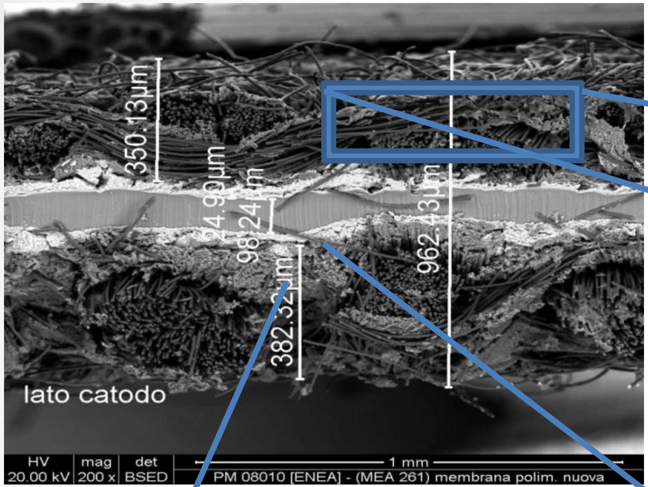


Pore-scale modeling of the fluid flow through the electrodes of HT PEMFC

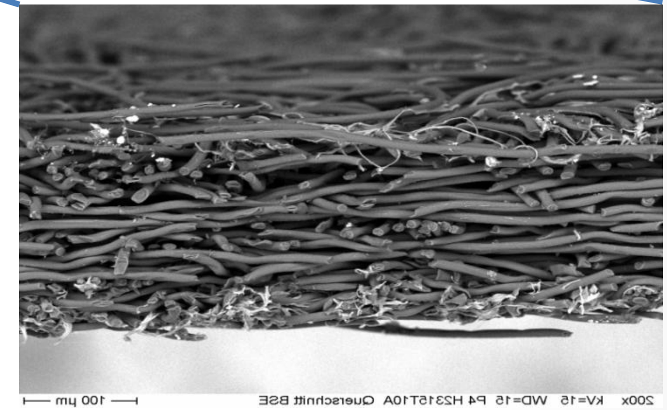
Morphological model: main steps

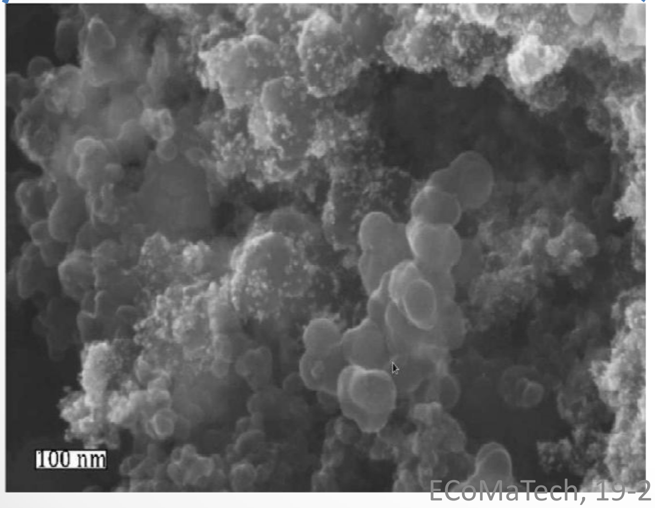
- Development of the reliable algorithm for reconstruction of micro-morphology of electrodes (GDL, CL)
- Challenge for numerical tools and mathematical models for specific degradation phenomenon
- Validate the proposed algorithm and numerical tools computing macroscopic transport coefficients
- Development of mitigation strategy using virtual realization of system

Reconstruction: MEA's real structure SEM images



GDL has mainly ordered structure
Example: **Celtec by BASF®**
Structure: woven (nonwoven) like
Approach: deterministic (stochastic)



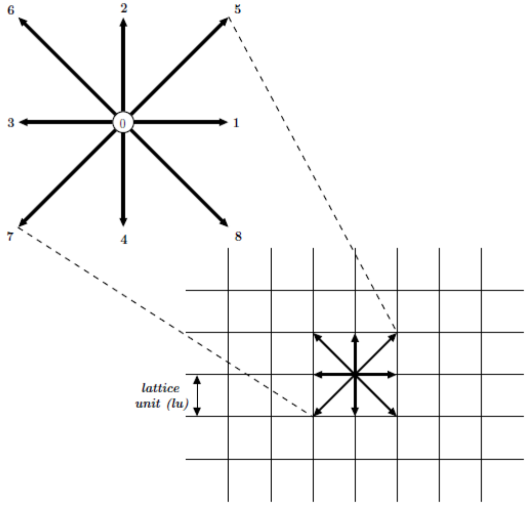


CL has irregular structure
Example: **Celtec by BASF® Vulcan XC – 72R**
Structure: aggregation of particles
Approach: stochastic based on
clusterization of particles

Numerical tool: Lattice Boltzmann Method

NUMERICAL TOOL?

- Very complex geometry
- Parallel computation
- Gas rarefaction effect



Computational domain size is ~100 Mcells

LBM is the discretization of not only physical space, but also velocity space, which means that particle velocities are restricted to a finite set of orientations.

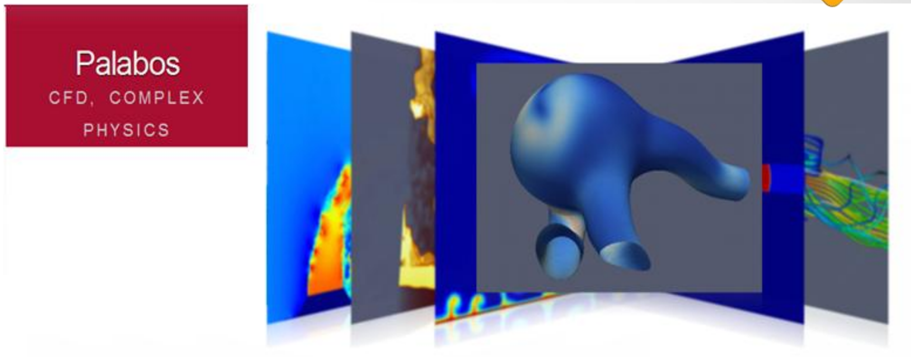
- LBM solves the following Lattice Boltzmann equation:

$$\underbrace{f_i(\vec{x}+\vec{e}_i\Delta t, t+\Delta t) = f_i(\vec{x},t)}_{\text{Streaming}} - \underbrace{\frac{[f_i(\vec{x},t) - f_i^{eq}(\vec{x},t)]}{\tau}}_{\text{Collision}},$$

- It should be noted that in this algebraic equation, “non-locality (streaming term, ***S***) is linear and non-linearity (collision term, ***C***) is local” [Sauro Succi, 2001]
- In LBM fluid models, like BGK or single relaxation time

Numerical tool: PALABOS

Palabos (www.palabos.org) is an open-source CFD solver based on the lattice Boltzmann method.

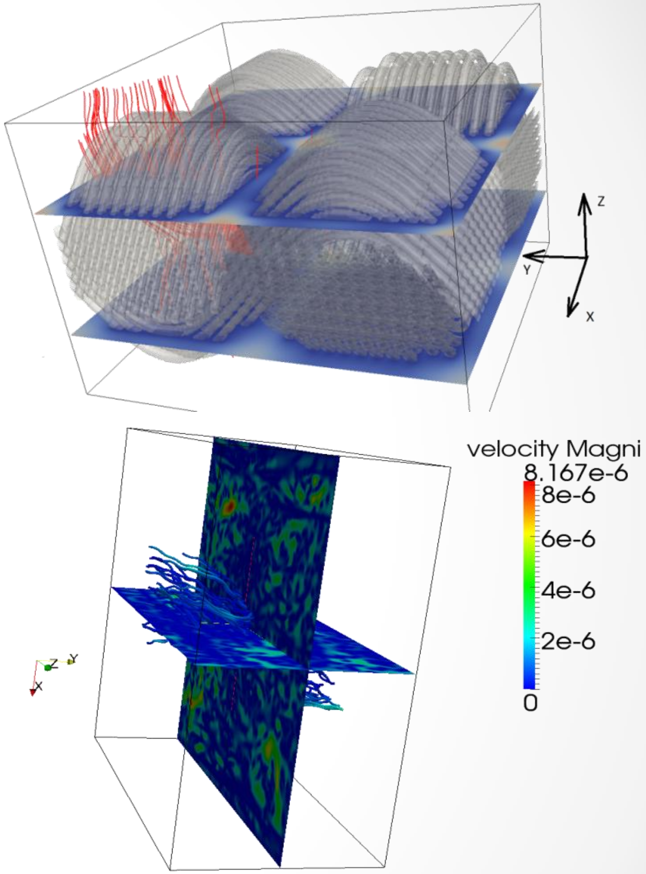


Palabos ingredients:

- Physics: In/weakly compressible, non-thermal Navier-Stokes equations; flows with body-force term, thermal flows with Boussinesq approximation, single-component multi-phase fluids (Shan/Chen model), free surface flows (volume-of-fluid approach), static Smagorinsky model for fluid turbulence.
- Basic fluid models: BGK, MRT, regularized BGK, LW-ACM, entropic model.
- Straight-wall boundary conditions: Zou/He, Inamuro, Skordos, regularized BC, simple equilibrium, bounce-back, periodic.
- Off-lattice boundary conditions: GUO model, generalized off-lattice BC.
- Grid: D2Q9, D3Q13, D3Q15, D3Q19, and D3Q27.
- Parallelism: parallelized with MPI for shared-memory and distributed-memory platforms, including I/O operations that are implemented in terms of MPI's Parallel I/O API.

Validation: Gas diffusion layer

Name	Woven [Celtec BASF®]	Non-woven [Freudenberg]
Thickness @0.025MPa	400 µm	256 µm
Computational domain	534 Mcells	67 Mcells
Fiber diameter	7 µm	7 µm
Porosity	0.78	0.75
Computed Permeability	$0.44\text{x}10^{-12}\ \text{m}^2$	$3.2\text{x}10^{-12}\ \text{m}^2$
Actual permeability	$0.50\text{x}10^{-12}\text{m}^2$	$2\text{-}3\text{x}10^{-12}\text{m}^2$

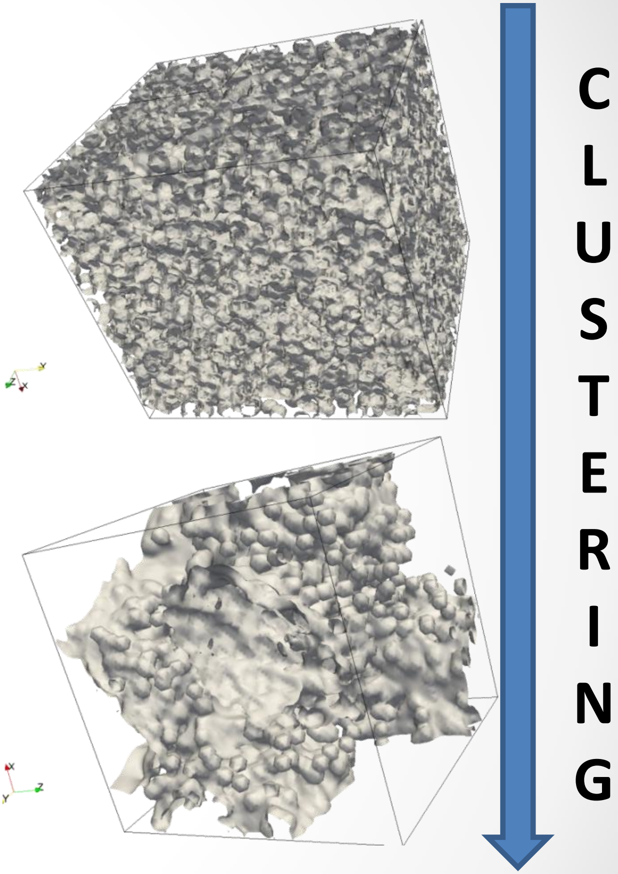


U. R. SALOMOV, E. CHIAVAZZO, P.ASINARI, **Pore-scale modeling of fluid flow through gas diffusion and catalyst layers for high temperature proton exchange membrane (HT-PEM) fuel cells**, CAMWA, pp. 19, ISSN: 0898-1221, DOI: 10.1016/j.camwa.2013.08.006

Validation: Catalyst layer

Clustering Name	40 nm	400 nm	1500 nm
Computational domain	8 Mcells	8 Mcells	16 Mcells
Carbon support particles diameter	40 nm	40 nm	40 nm
Computed Permeability	1.1×10^{-16} m^2	4.8×10^{-15} m^2	0.4×10^{-13} m^2
Actual permeability	1.0×10^{-13} m^2		

Increase of permeability



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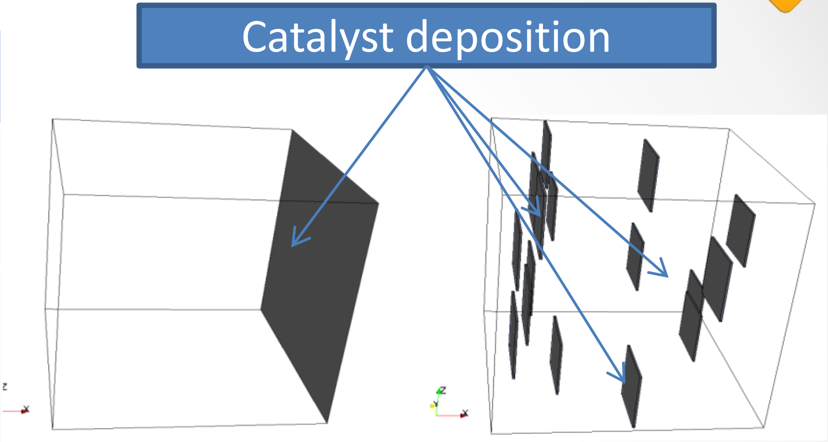
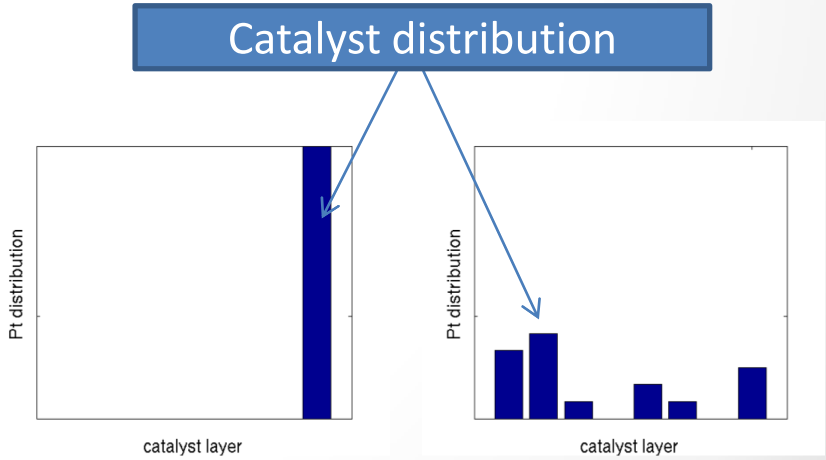
Validation: Effect of redistribution of Pt particles on flow field

Name	Non-distrib	Distributed
Computational domain	2.1 MNodes	2.1 MNodes
Average cluster size	1500 nm	1500 nm
Computed flow rate	$0.31x10^{-6}$	$2.3x10^{-6}$

Redistribution of catalyst particles inside the microstructure leads to considerable increase of mass flow rate.

This provides an additional tunable parameter of the morphological model.


Catalyst deposition

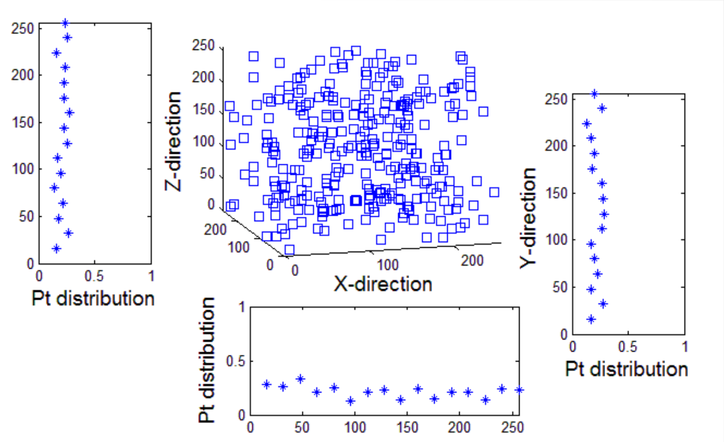

Catalyst distribution

Mitigation strategy: Redistribution of Pt particles in CL

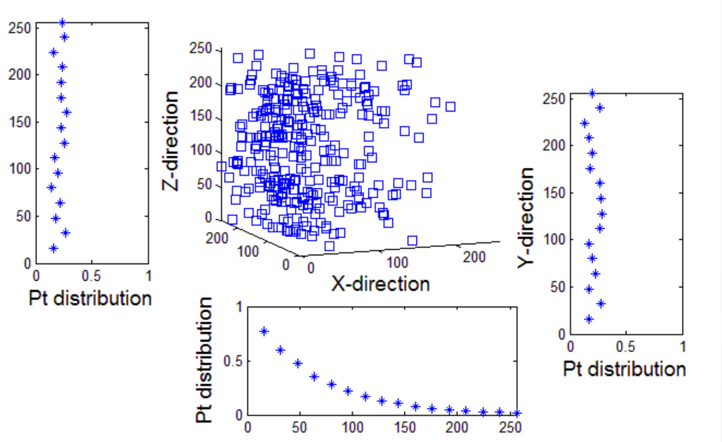
The goal of proposed morphological model is to design a strategy in order to enhance PEMFC performance and to mitigate degradation phenomena by improving mass transport processes.

Two virtual realizations of morphological model are considered in regards to Pt distribution:

1. Homogeneous
2. Exponential decay



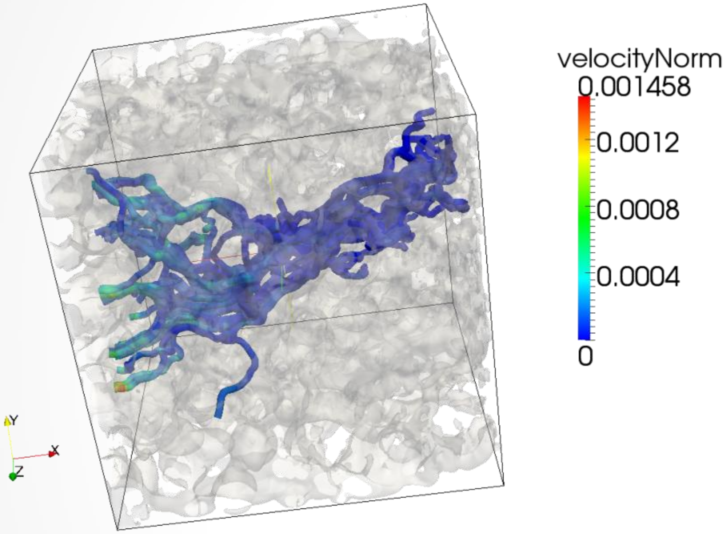
Homogeneous



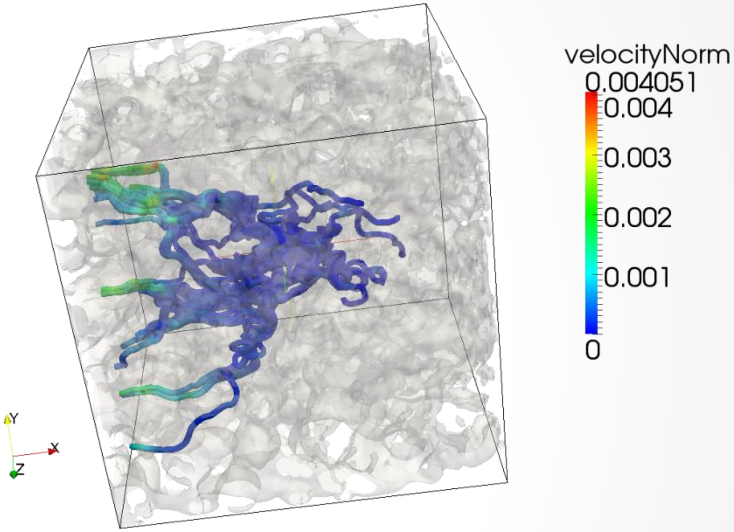
Exponential decay

Mitigation strategy: Results of pore-scale flow simulation

Homogeneous



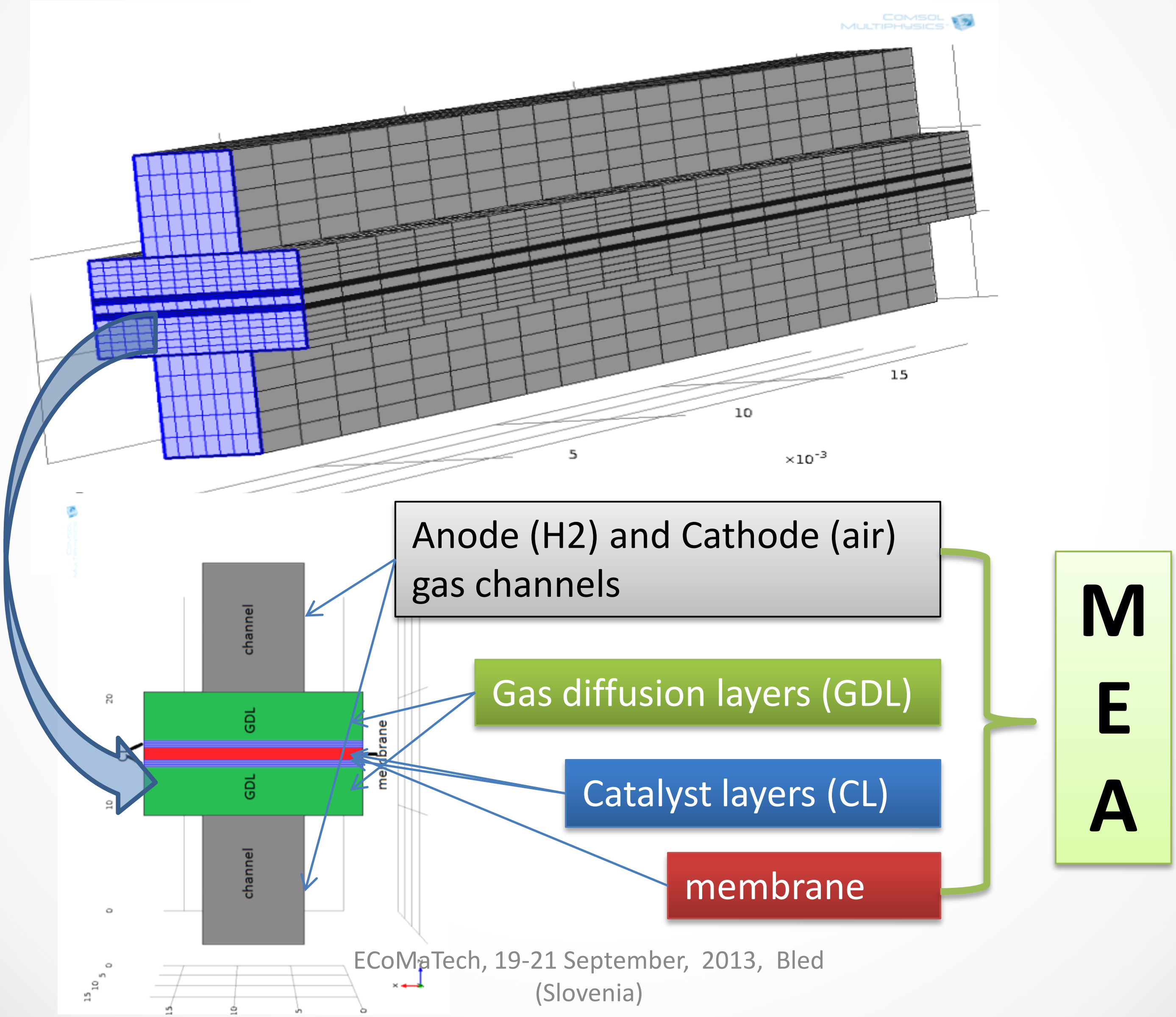
Exponential decay



There are quantitative changes (scale factor), but also qualitative changes in the flow field (streamlines). Thus, redistribution of catalyst particles inside the microstructure leads to considerable increase of overall mass flow rate and changing flow field near membrane (flow rate almost zero).

High Temperature PEM FC single MEA performance simulation

Single MEA structure



Anode (H2) and Cathode (air) gas channels

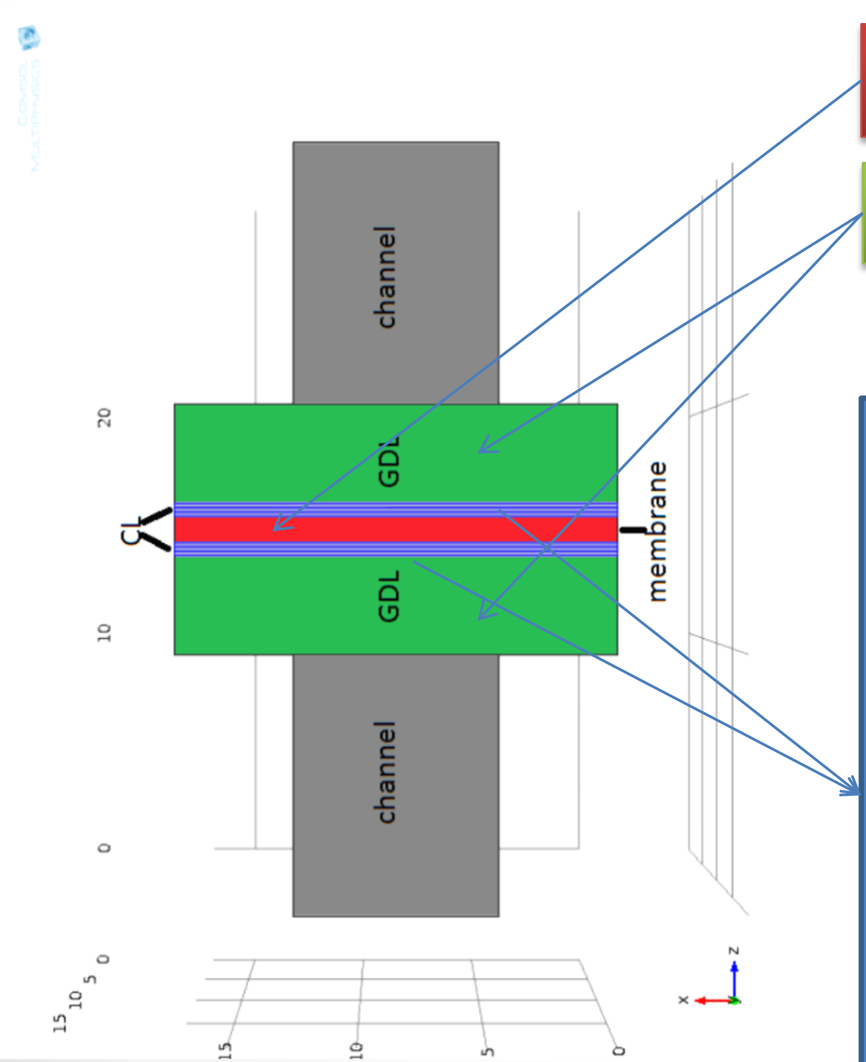
Gas diffusion layers (GDL)

Catalyst layers (CL)

membrane

M E A

MEA secondary current distribution



Electrolyte: Poisson equation

Electrodes: Poisson equation

$$\nabla \cdot i_l = Q_l,\ i_l = -\sigma_l \nabla \varphi_l$$

Porous electrodes: mixture of Poisson eqs of electrodes and electrolyte.

Electrode kinetics:

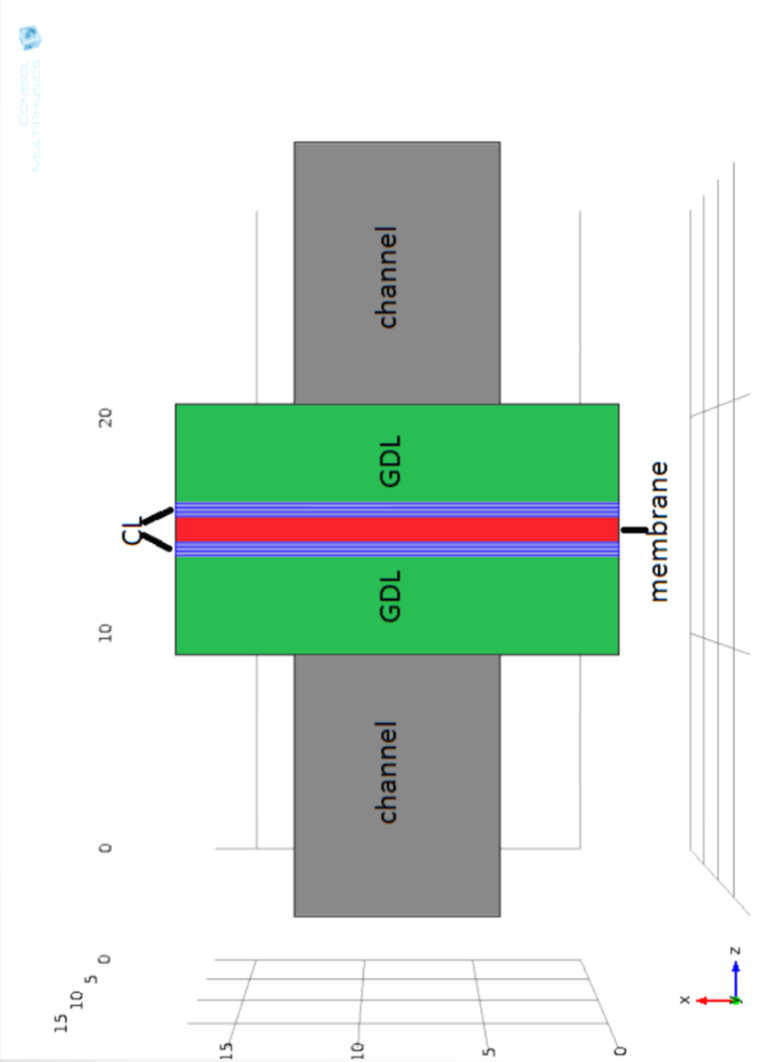
Linearized Butler-Volmer for anode CL

$$i_a = i_{a,0}\left(\frac{c_{H_2}}{c_{H_2,ref}}\right)^{0.5}\left(\frac{\alpha_a F \eta_a}{RT}\right)$$

Cathodic Tafel equation for cathode CL

$$i_c = -i_{c,0}\left(\frac{c_{O_2}}{c_{O_2,ref}}\right) exp\left(\frac{\alpha_c F \eta_c}{RT}\right)$$

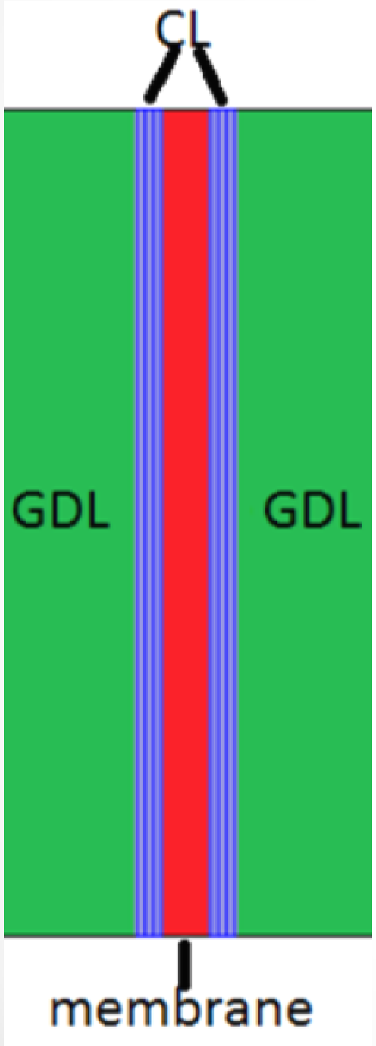
Transport mechanisms

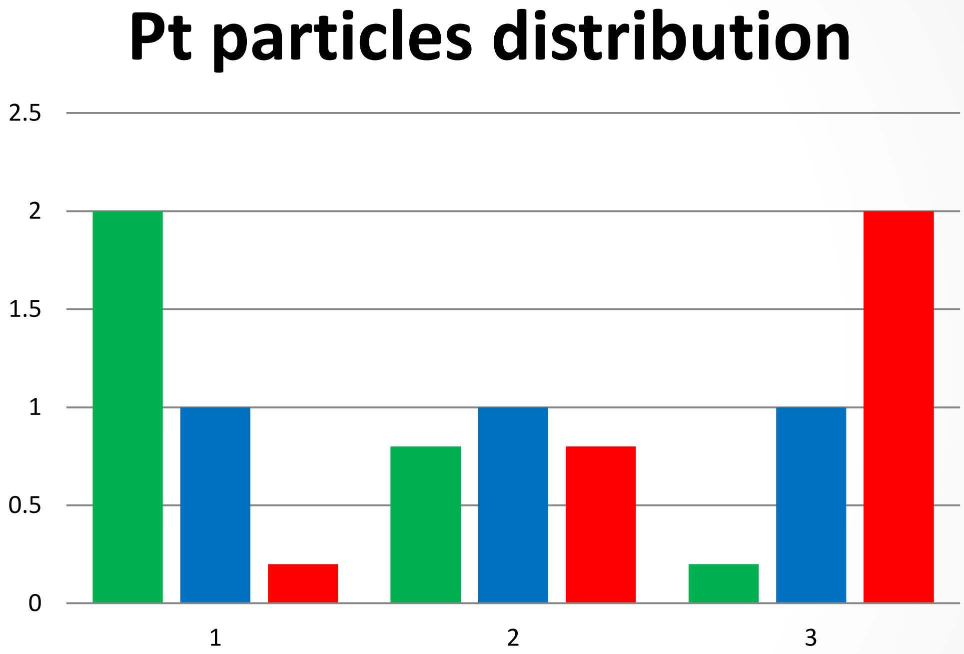


Transport of concentrated species:

- Compartments: Channel, GDL and CL
- Anode: Hydrogen and water
- Cathode: Oxygen, water and nitrogen
- Mass transfer : **Maxwell-Stefan** eqs (for LBM, see P. Asinari, PRE, vol. 80, 056701 (2009) and P. Asinari, PRE, vol. 77, 056706 (2008))
- Momentum transfer: Navier-Stokes and Brinkman equations
- Coupling with Poisson equations as sources and sinks at porous electrode (catalyst layer)

CL with different Pt distribution





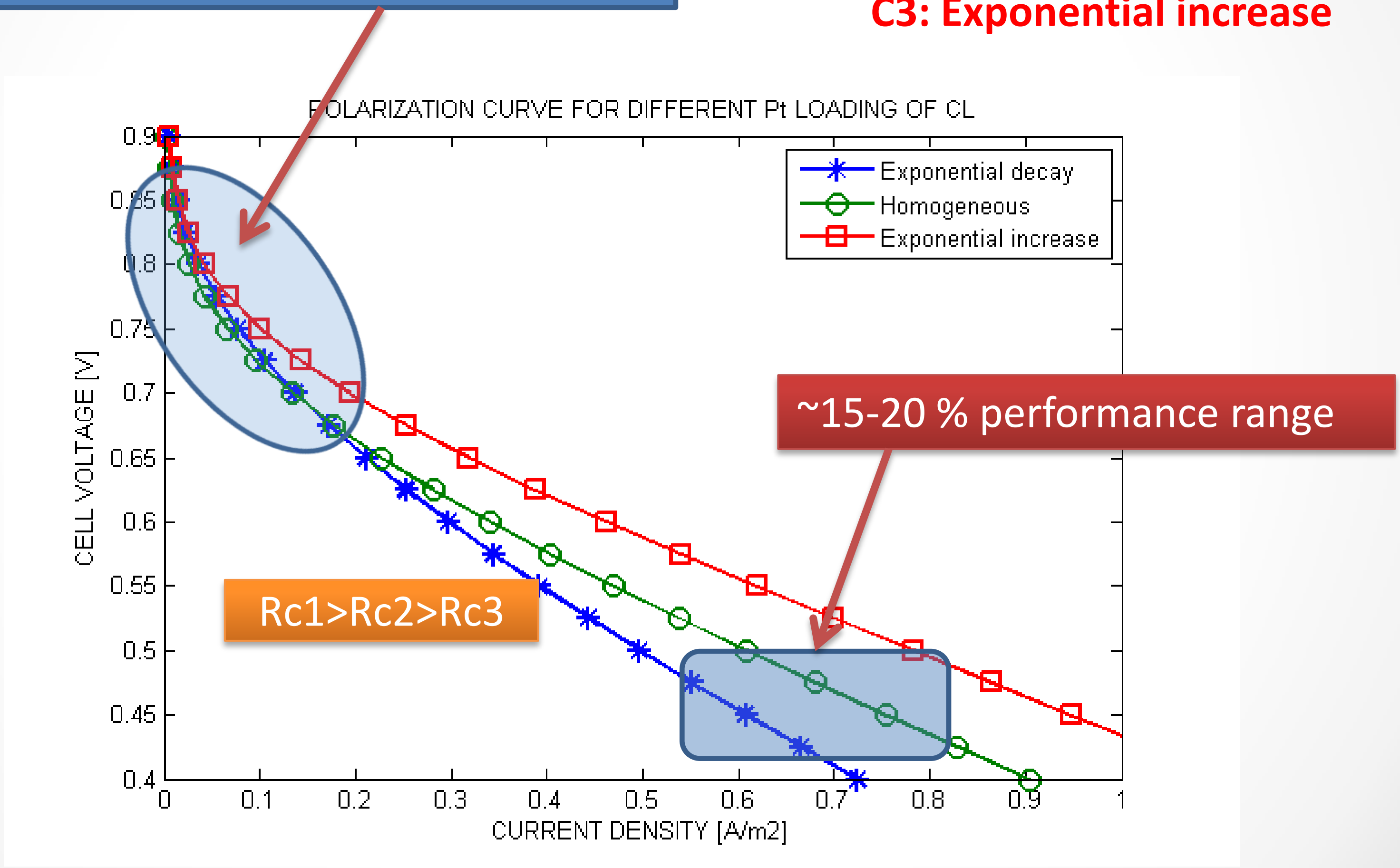
C1: Exponential decay

C2: Homogeneous (today)

C3: Exponential increase

Single MEA performance simulation

C1: Exponential decay
C2: Homogeneous (today)
C3: Exponential increase



Region with higher performance Pc1>Pc2

~15-20 % performance range

Rc1>Rc2>Rc3

Summary

Change flow field (no streamlines) in the region near membrane	Decrease phosphoric acid loss
Improve overall transport of gases through CL porous media	Enhance performance of PEMFC
Almost zero flow rate and its slope near membrane	Decrease possible crossover of gases through membrane
Provide longer path for transport of ions from reaction place	Increase Ohmic resistance

Thank you for your attention !

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