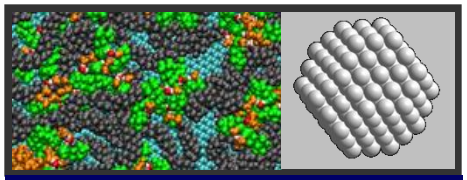
Modeling of Electrochemical Interfaces in PEFCs

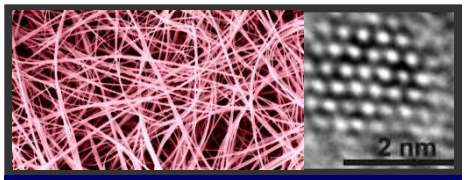
Kourosh Malek
M. Eikerling

MMM@HPC Workshop
Athens, Greece, Nov. 9th, 2012

Complexity!



Materials Modeling
Simulation

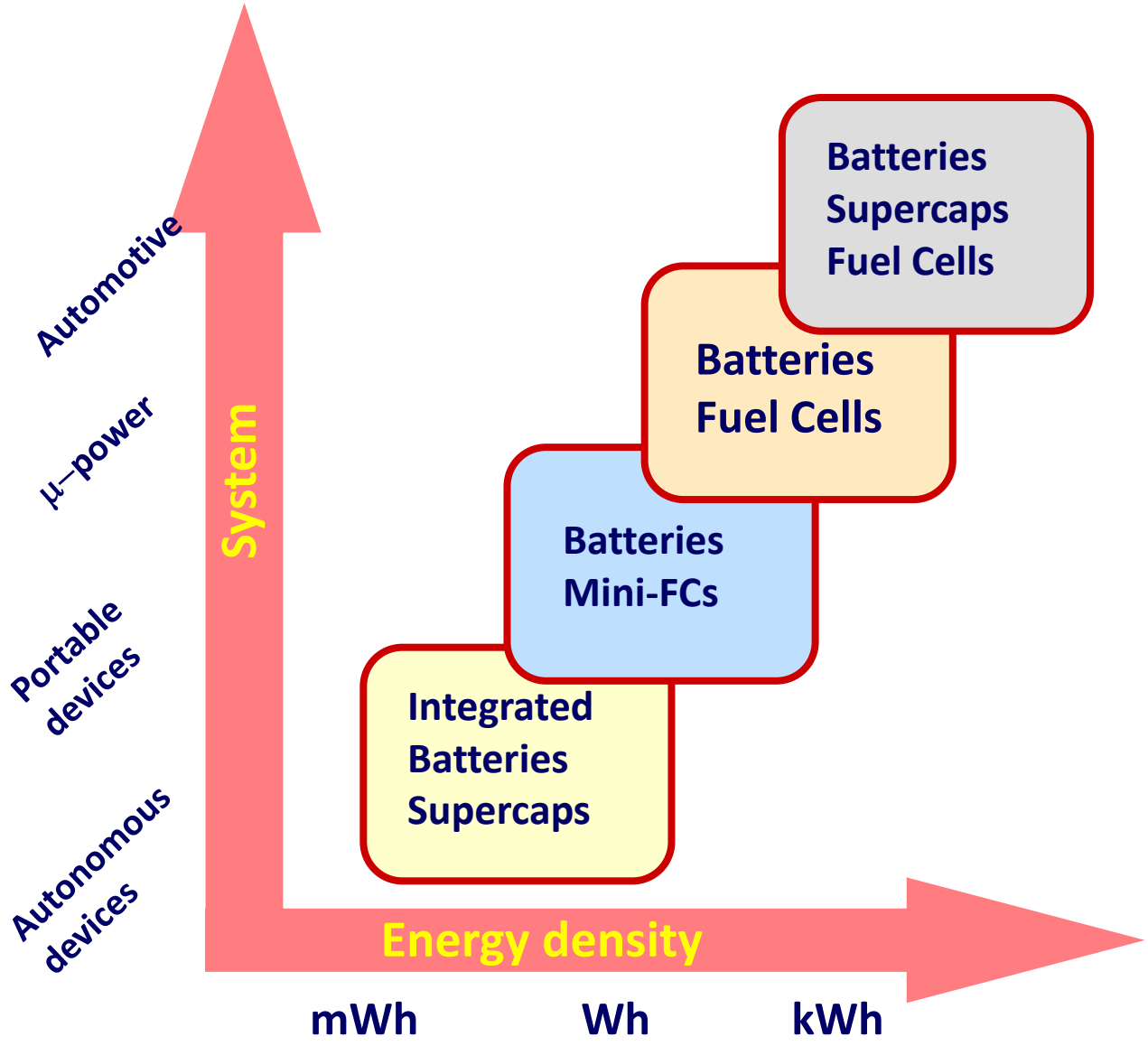


Fabrication
Characterization

Integration & Testing
Commercialization

Processes

Market

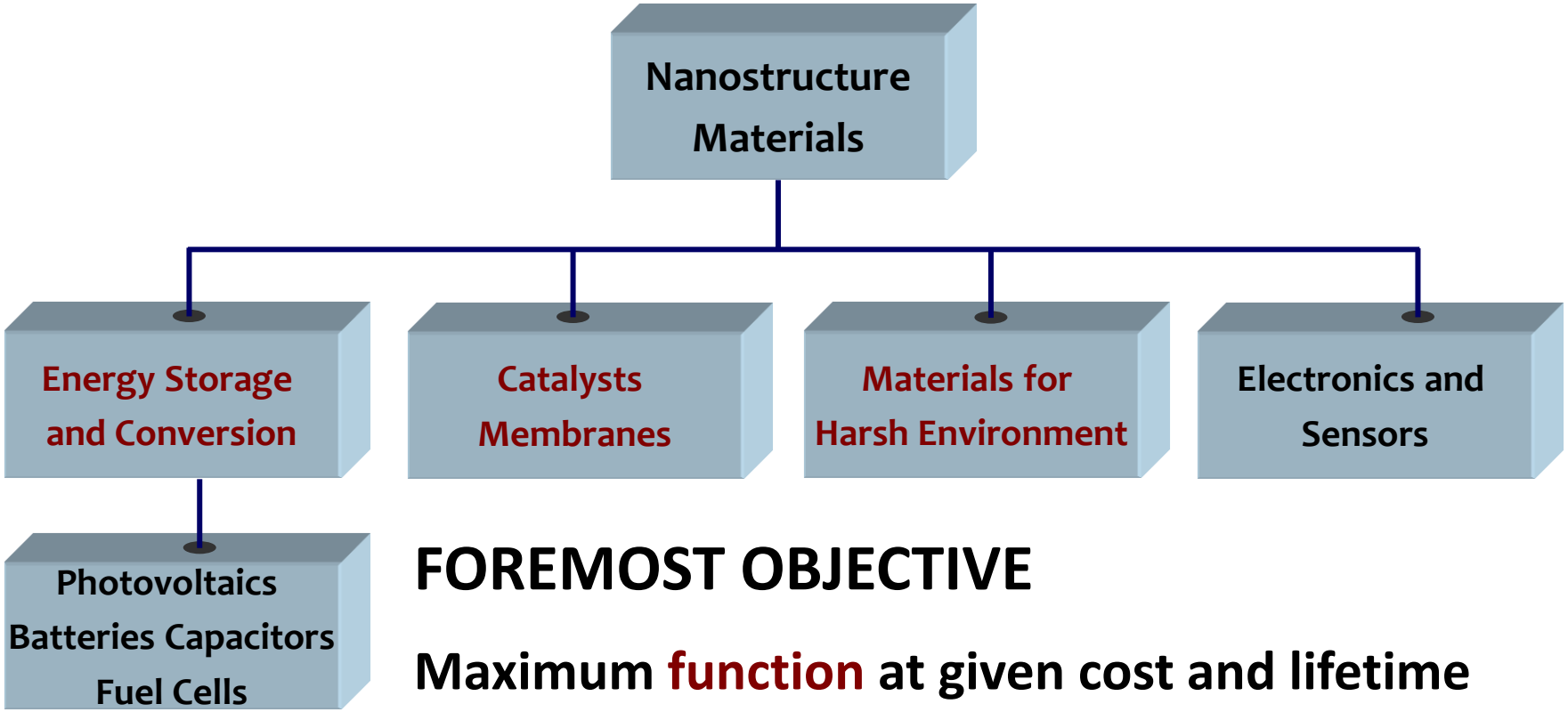


Adapted from P. Notten, 2010

Design Challenges

Materials Modeling

Accelerate material characterization	Improve critical reactions	Design with optimized properties	Understand key processes



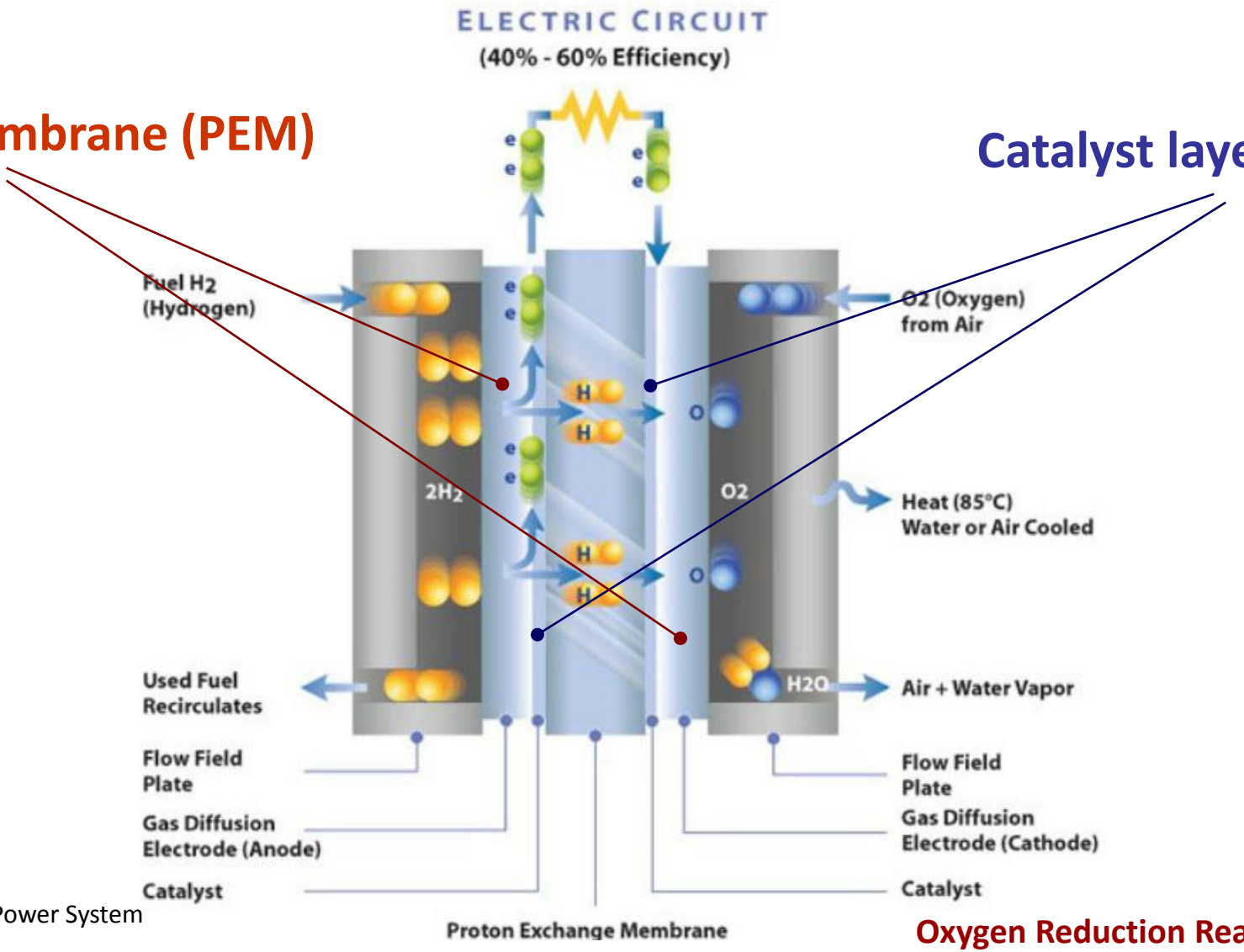
FOREMOST OBJECTIVE

Maximum function at given cost and lifetime

Fuel Cell Fundamentals

National Research Council Canada
Conseil national de recherches Canada
SFU
Canada

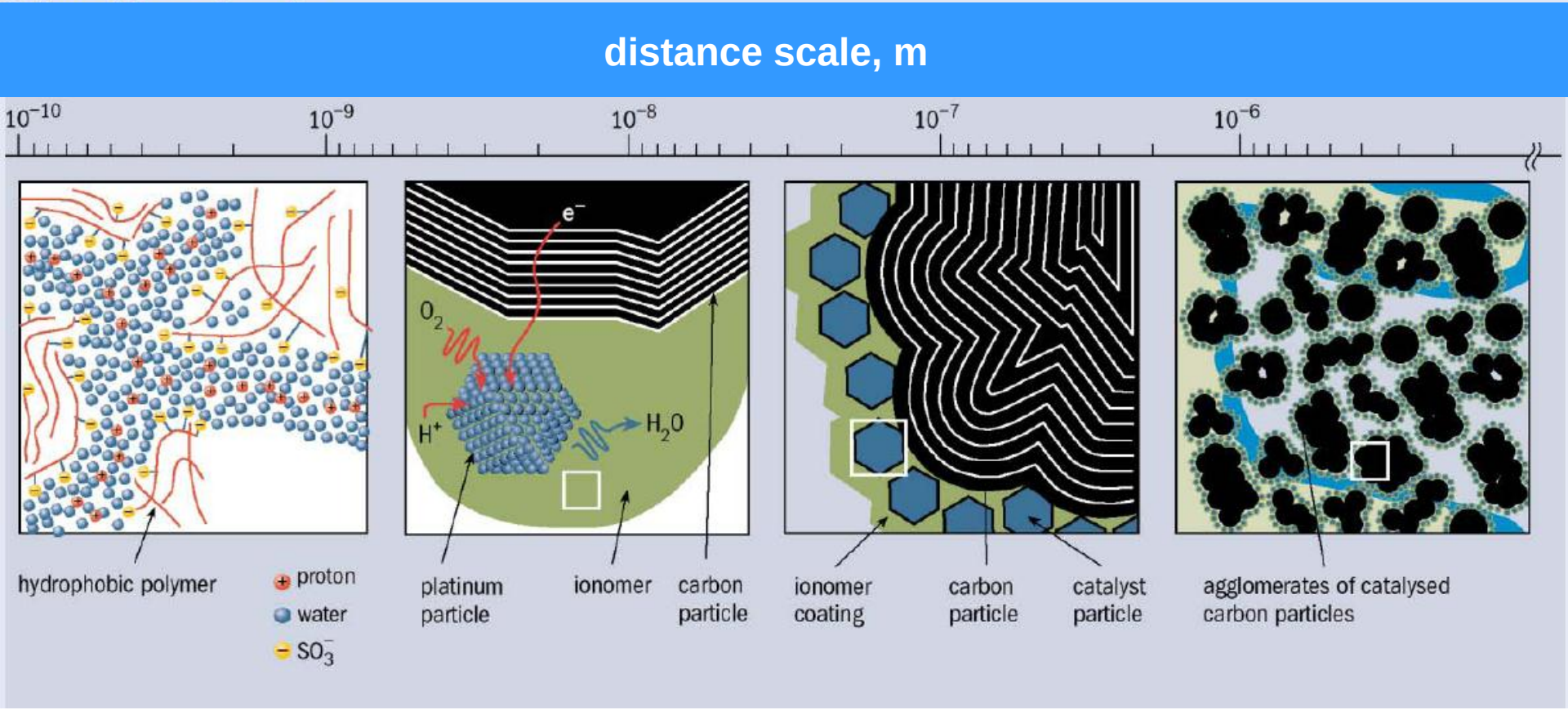
Polymer Electrolyte Fuel Cells



Ballard Power System

Oxygen Reduction Reaction (ORR)
Hydrogen Oxidation Reaction (HOR)

Design Challenge –
Problem of Scales

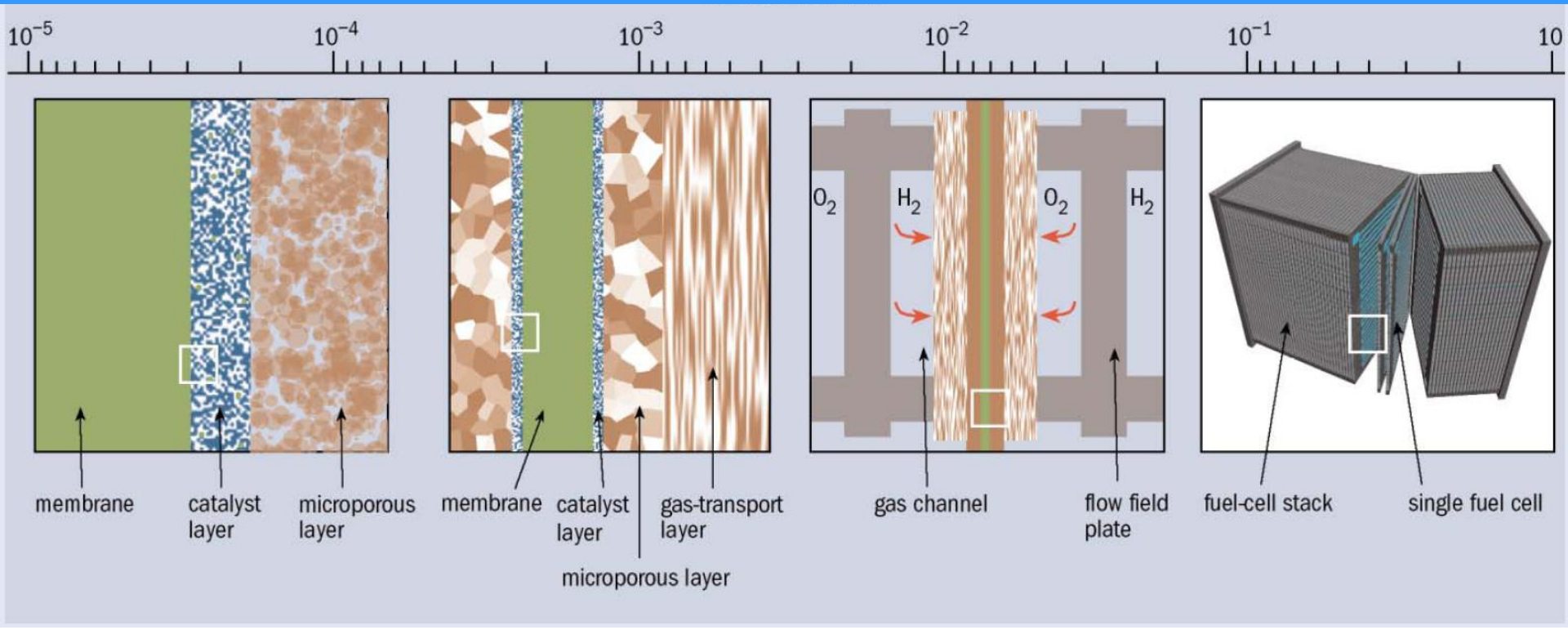


Electrochemical interfaces: Pt-C, Pt-W, Pt-O_2, C-W, Pt-ionomer, …

M.Eikerling & K. Malek, 2010

Design Challenge –
Problem of Scales

distance scale, m



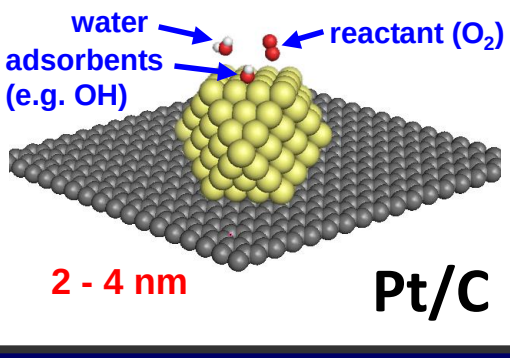
M.Eikerling & K. Malek, 2010

National Research Council Canada | Conseil national de recherches Canada

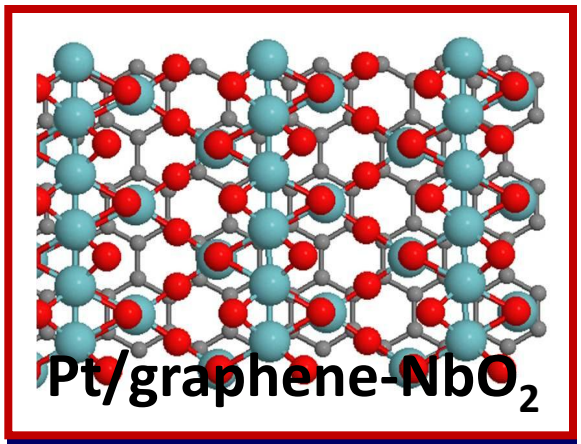
SFU

Canada

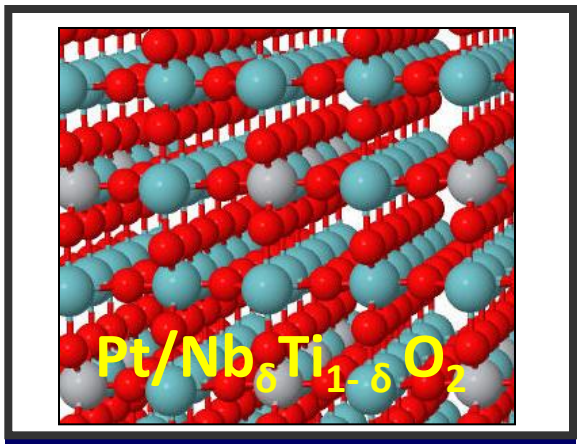
Modeling Fuel Cell Materials



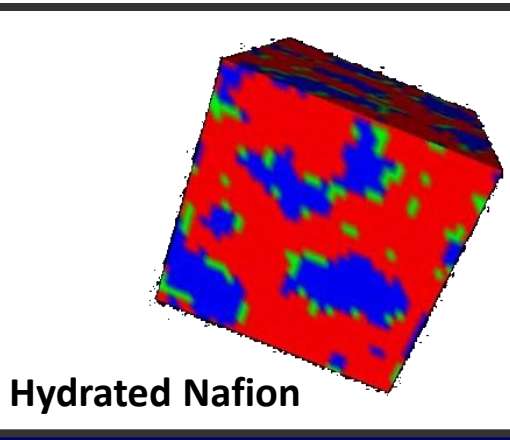
Fuel cell materials



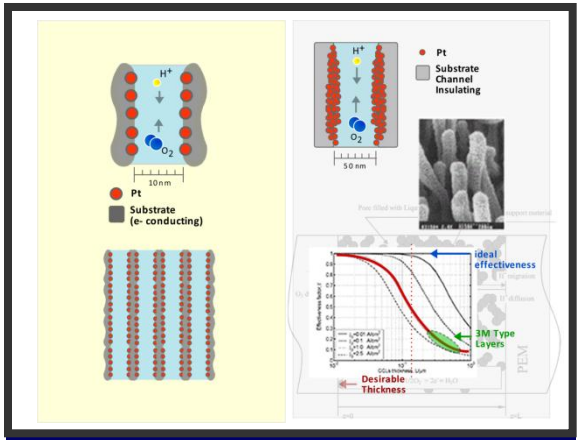
Nanostructured CL



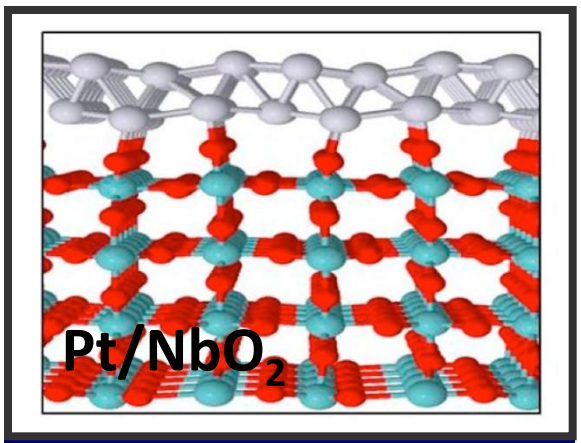
Support materials



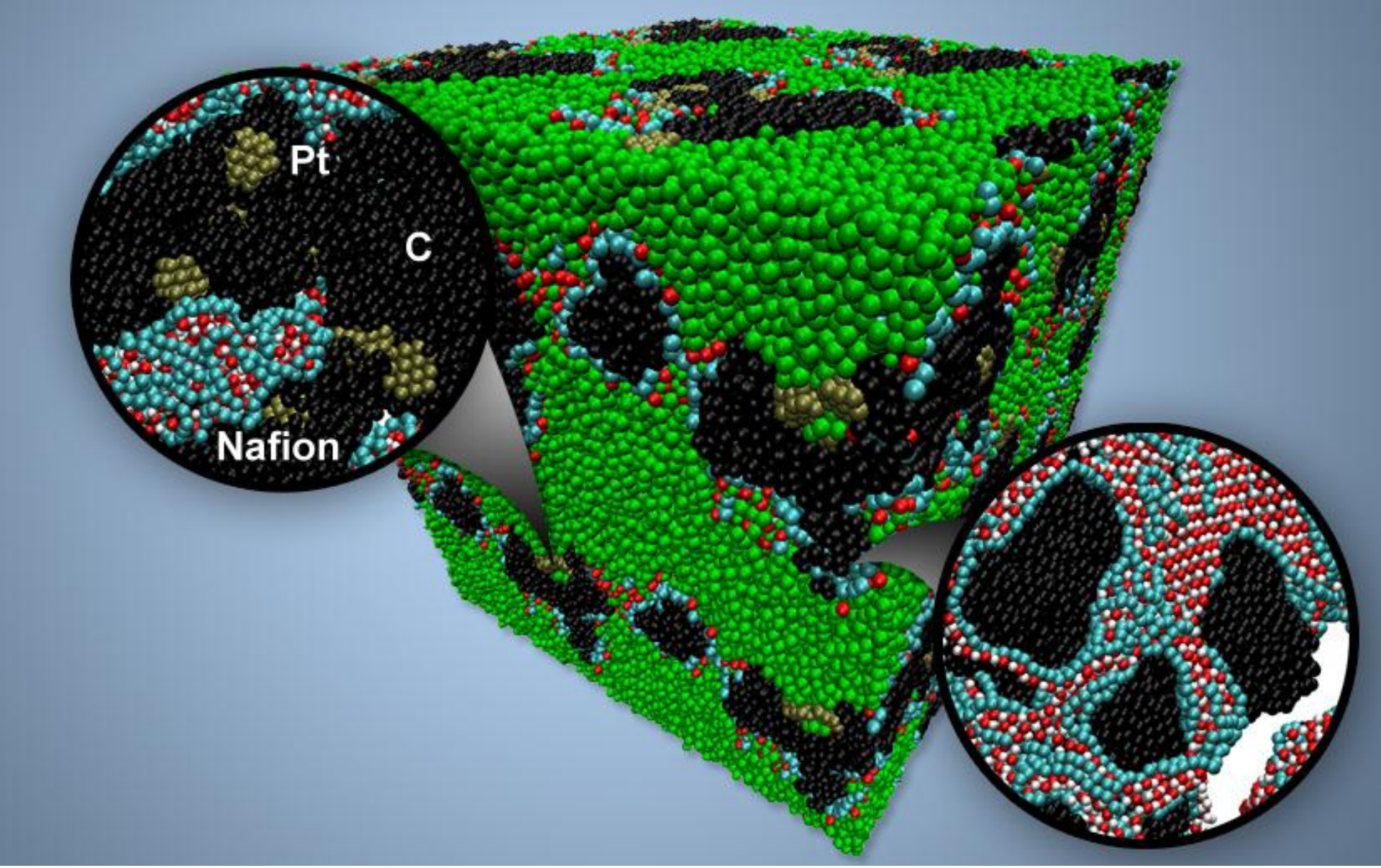
Polymer membranes



Nanostructured CL

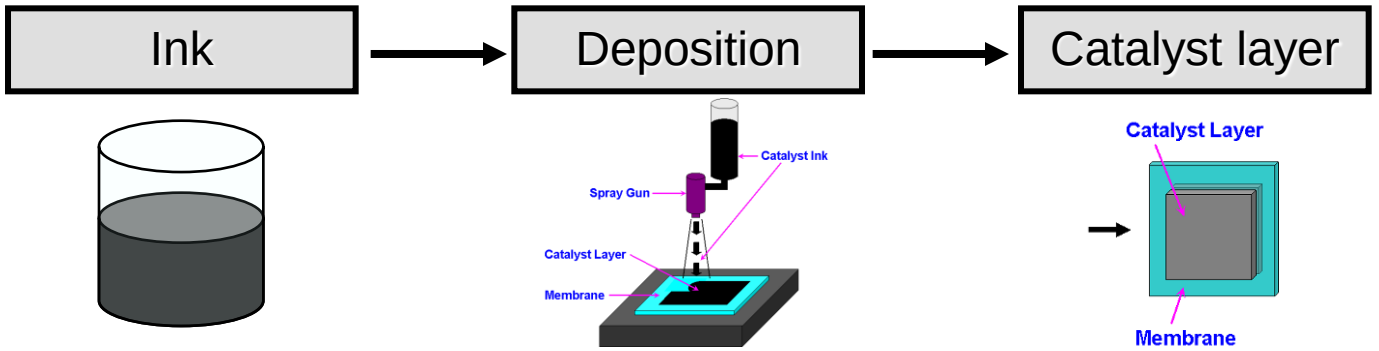


Support materials



CL microstructure formation

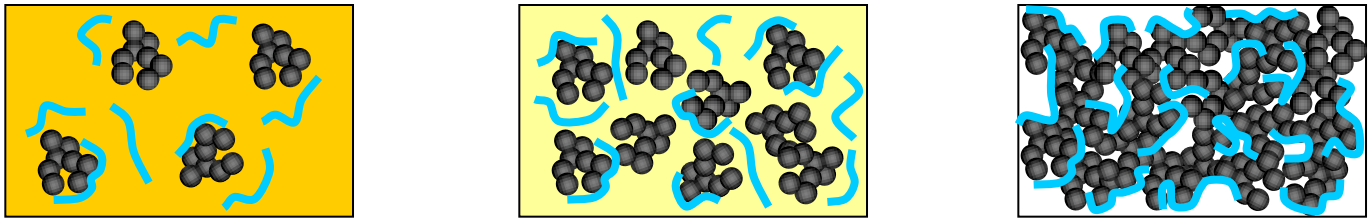
CL fabrication process



Solid ratio: low
Solvent: alcohol rich

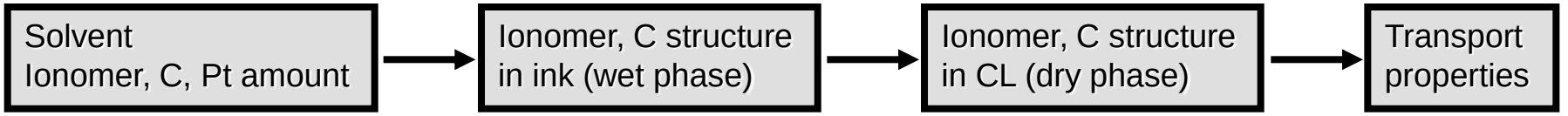
Solid ratio: medium
Solvent: water rich

Solid ratio: high
Solvent free



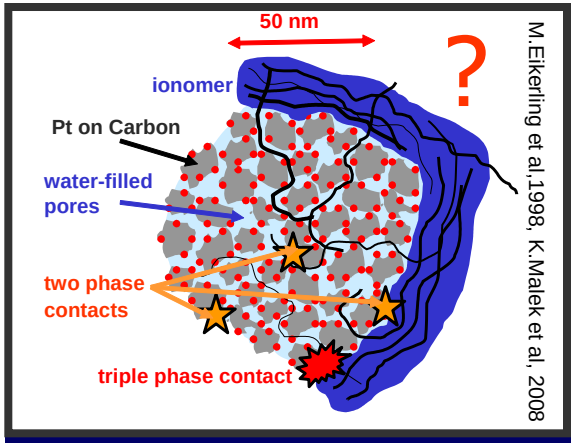
- Ionomer structure (rod like? adsorbed on C?)
- Carbon structure (aggregated? separated?)
- Structure change during drying process?
- Correlation with transport properties

Input (Controllable parameters) → Output

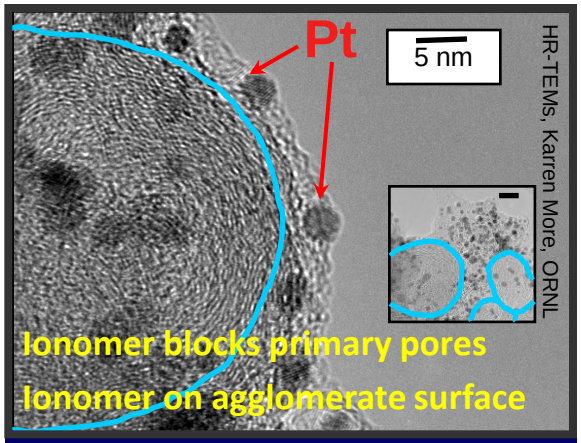


T. Mashio, Internal report

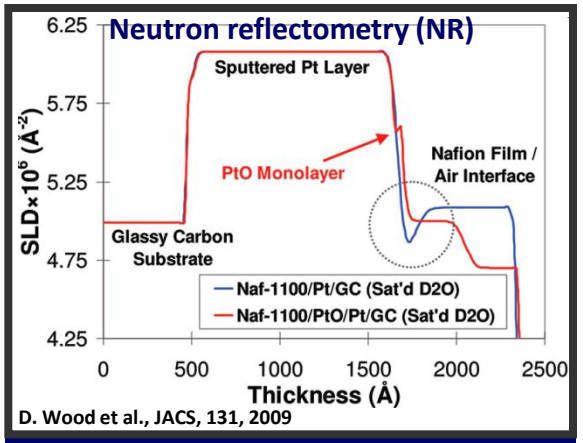
Apprehensions and controversial issues



Agglomeration?



Ionomer in agglomerates?

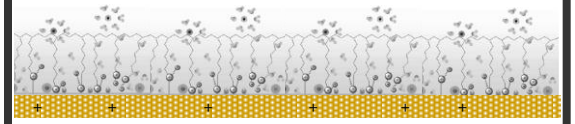


Interfacial structure

Sidechians on Pt: direct or indirect interaction?

Pt surface morphology

Pt surface charge /pot.



Subbaraman, Markovic et al, 2009-2010

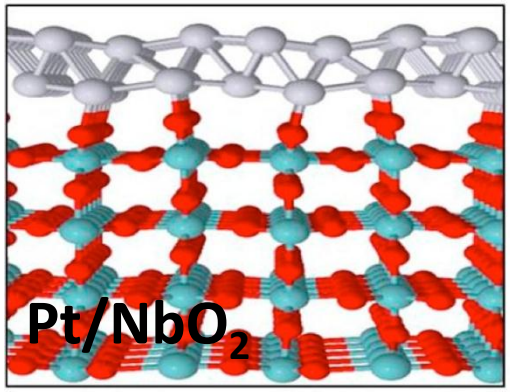
Ionomer: ORR foe / friend?

➔ Ratio of the electrocatalytically SA (accessible to e^- and proton) to the total surface area of Pt

➔ Material property measured by ex-situ experiments

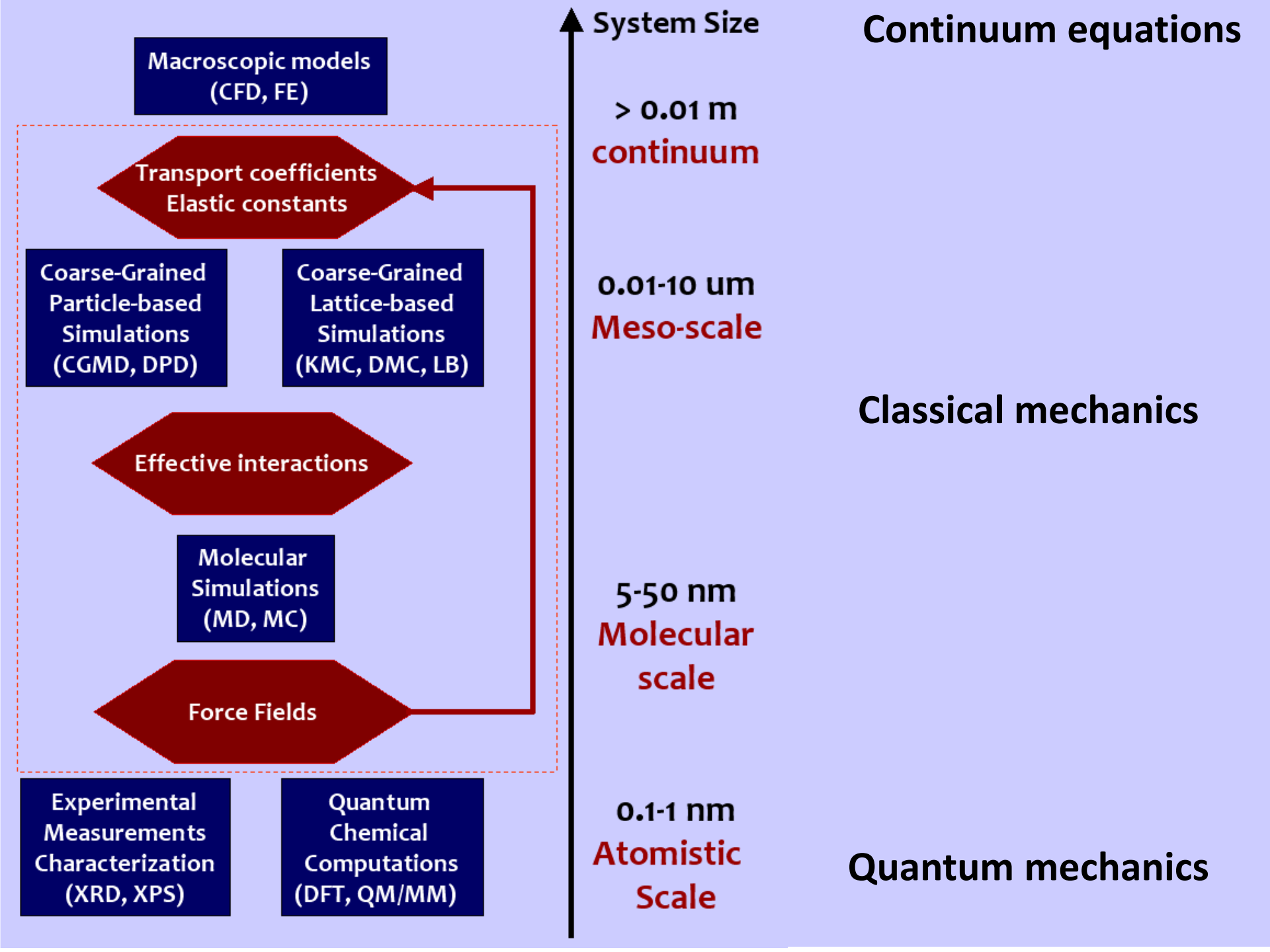
$$u_{Pt} = \frac{S_{ESA}}{S_{total}}$$

Catalyst utilization



Non-carbon supports

Methodology


Macroscopic models
(CFD, FE)
Transport coefficients
Elastic constants
Coarse-Grained
Particle-based
Simulations
(CGMD, DPD)
Coarse-Grained
Lattice-based
Simulations
(KMC, DMC, LB)
Effective interactions
Molecular
Simulations
(MD, MC)
Force Fields
Experimental
Measurements
Characterization
(XRD, XPS)
Quantum
Chemical
Computations
(DFT, QM/MM)
System Size
> 0.01 m
continuum
0.01-10 um
Meso-scale
5-50 nm
Molecular
scale
0.1-1 nm
Atomistic
Scale
Continuum equations
Classical mechanics
Quantum mechanics

Modelling approaches
pros and cons

Modeling of C-Pt-Nation interfacial structure

CGMD

- (+) Representing the ionomer network and more realistic structure of CL
- (-) Highly simplified representation of sidechains
- (-) Uncertainty of actual parameters and hydration energies

MD on extended surface

- (+) Hopefully more accurate representation of sidechains and more accurate hydration energies
- (-) Does not consider 3D network of ionomer
- (-) Effect of long-range interactions on nano-scale morphology of nafion

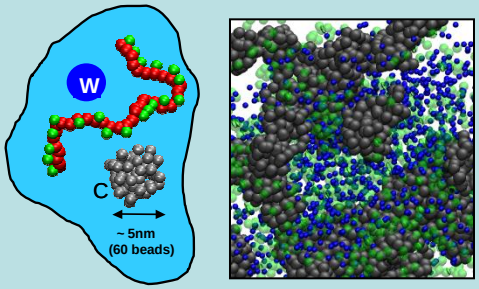
Alternatives

- Hybrid CGMD-AMD or implementing (mixed) atomistic models in CGMD

Advanced CL design

Step I → **Step II** → **Step III**

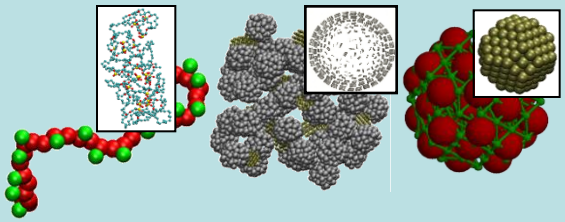
Model Development



Effect of solvent
(implicit solvent, Pt)

Versatile CGMD
Ionomer-free aggl.
Phase segregation

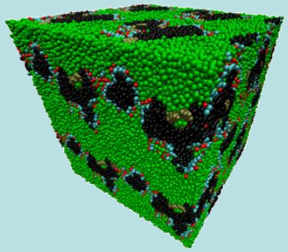
Model Refinement

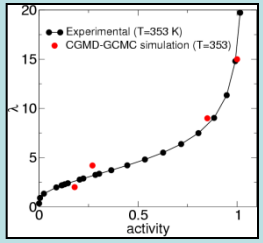


C ➔ Pt/C
(explicit Pt)

CGMD ➔ Physical model
➔ Experimental data

Model Validation





Composition-microstr.
(characterization)

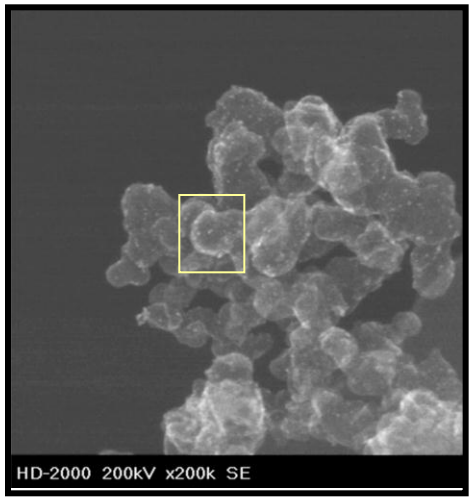
Water/gas ads.
Ionomer network
Water transport
Re-draw structural picture

Methodology

CG model

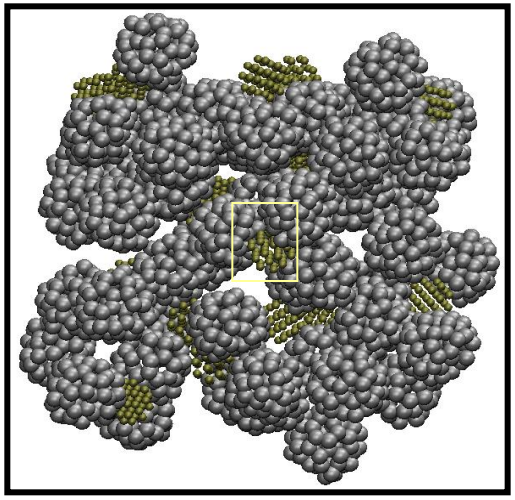
Multi-scale coupling scheme of Pt/C

Agglomerated Pt/C



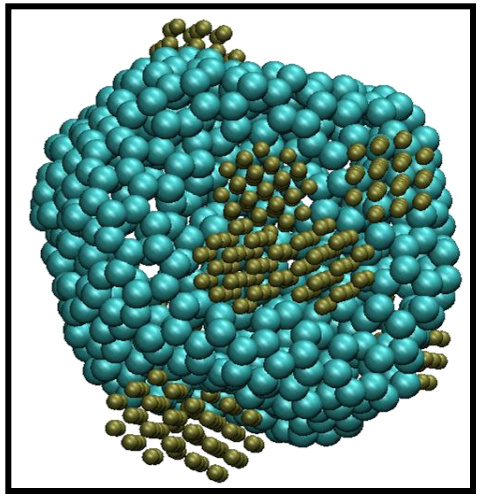
50 nm

Pt/C-primary particle



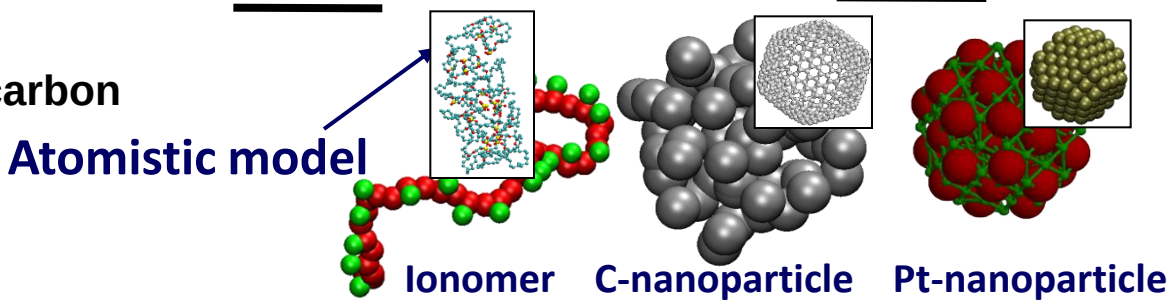
10 nm

Pt/C-nanoparticle



2 nm

CG models of ionomer, carbon and Pt nanoparticles



Methodology
CGMD simulations

Systematic meso-scale simulations

Coarse-Grained Molecular Dynamics

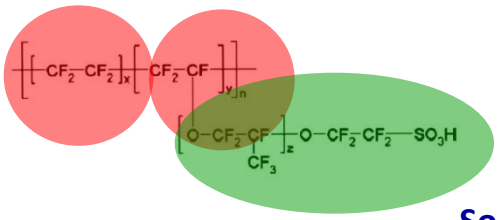
Parameterization

Modified MARTINI FF

σ = 0.47 nm

ε/K=674-217

supra-attractive to supra-repulsive



Coarse-grained model of Nafion, 20-unit oligomer, length ~ 30 nm

Validation

Boltzmann-inversion (MD vs. CGMD)

Radial Distribution Functions (RDFs)

Experiment

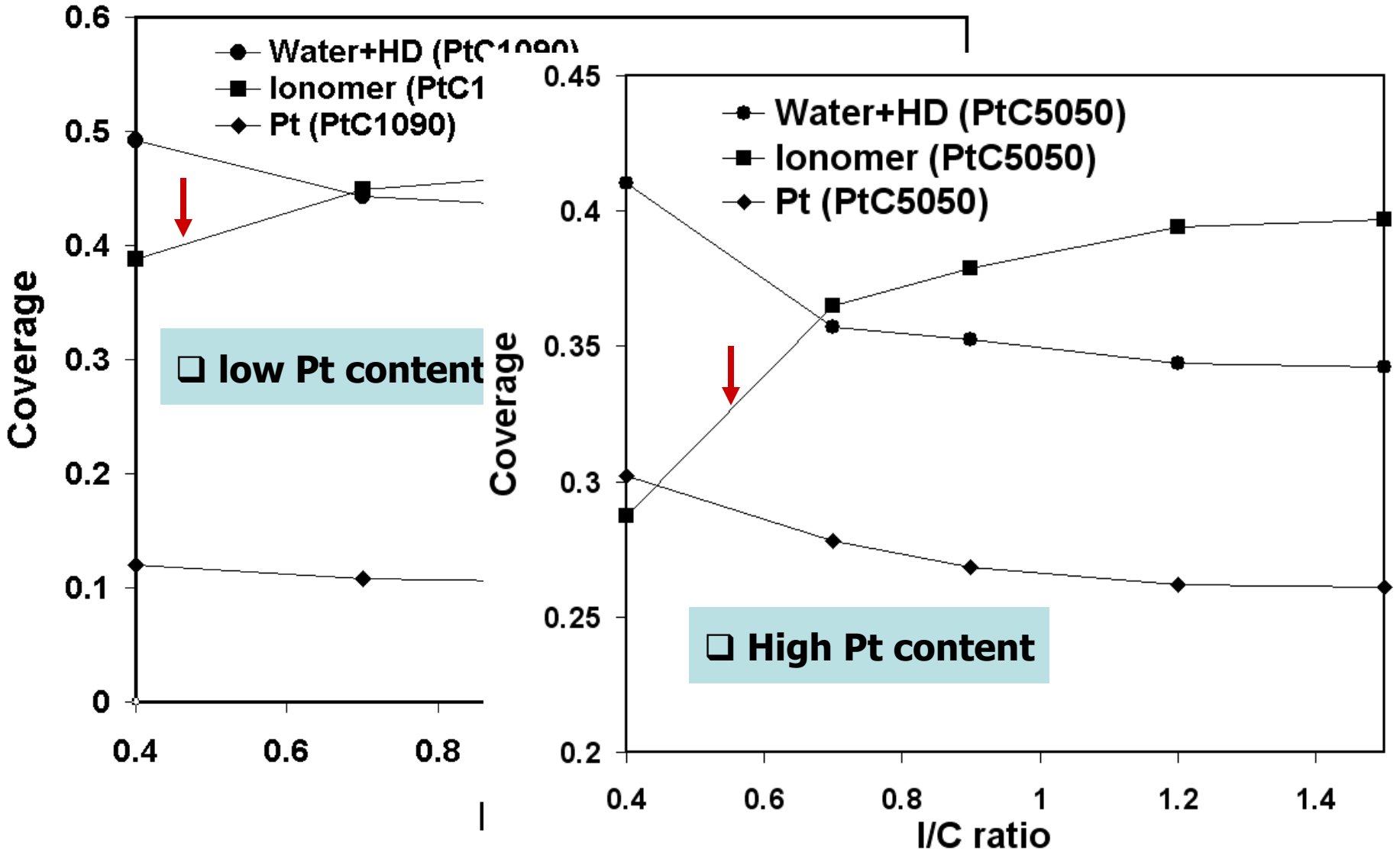
W-adsorption

Phases densities

$$g(r) = \exp(-V(r)/k_B T)$$

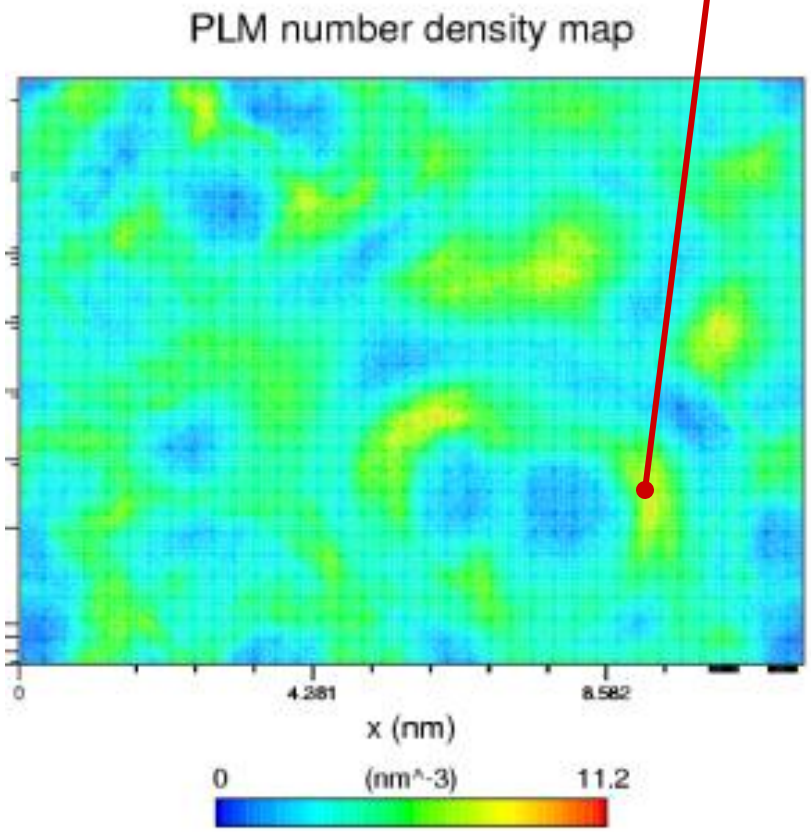
$$V^{i+1}(r) = V^{i}(r) - k_B T \ln(g_{atom}(r)/g^{i}(r))$$

Coverage on C

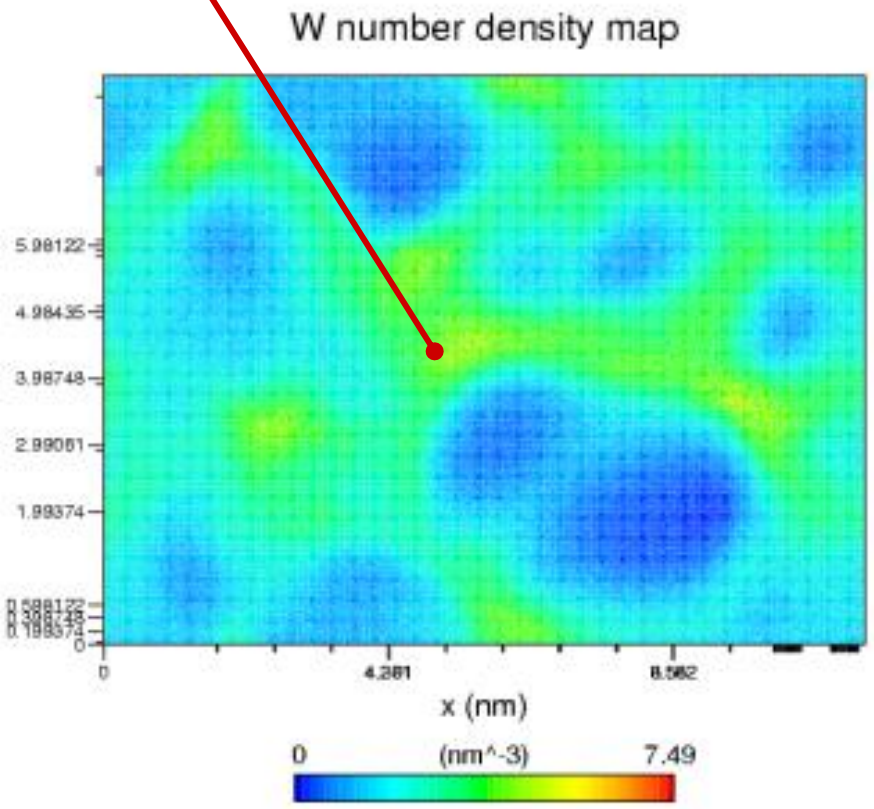


Nafion-water structure

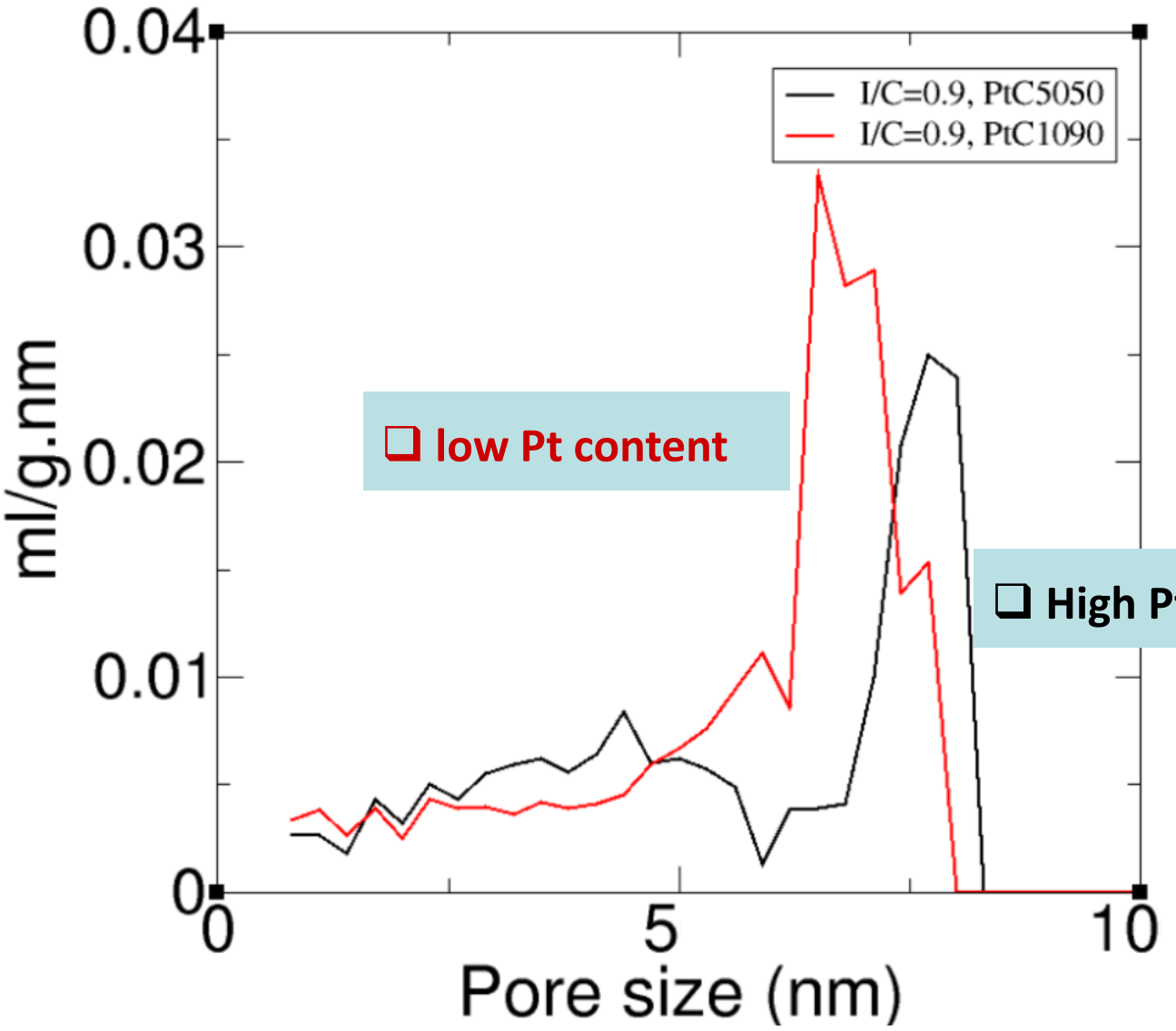
ionomer network



water network



PSD: role of Pt



❑ low Pt content

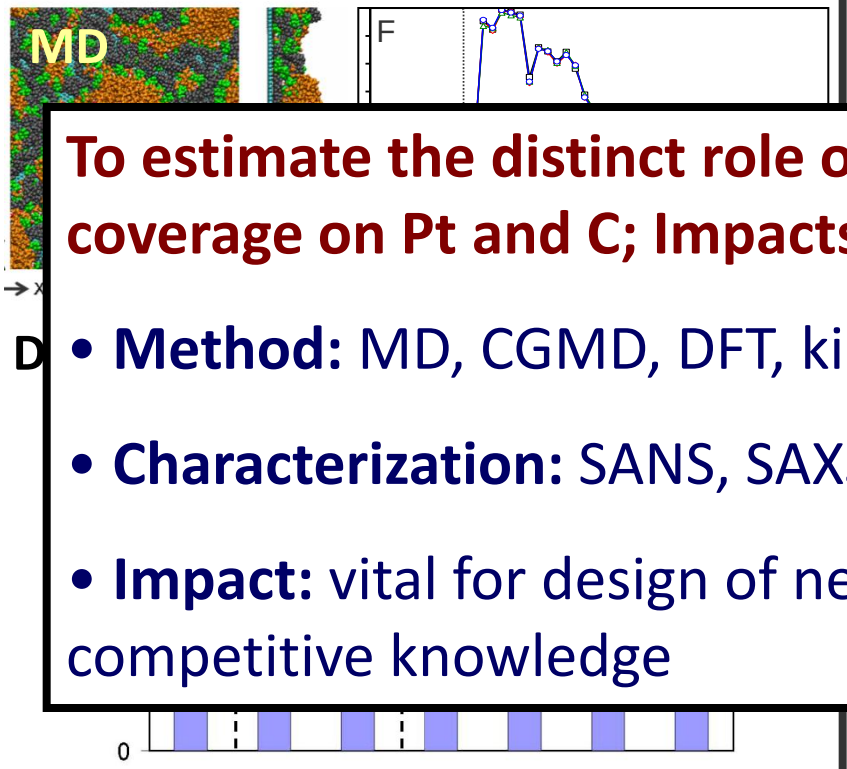
❑ High Pt content

Interfacial structure

Catalyst layer of PEFC

Interfacial structure and processes

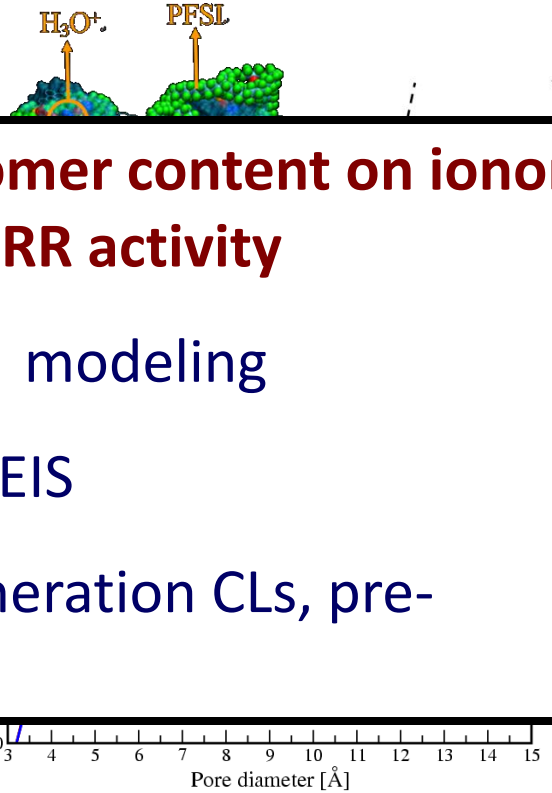
Ionomer → microstructure → ORR



T. Mashio et al. 2010

Effect of ionomer on ORR (MD, DFT)

Effect of carbon support



S. Ban et al. 2011, 2012

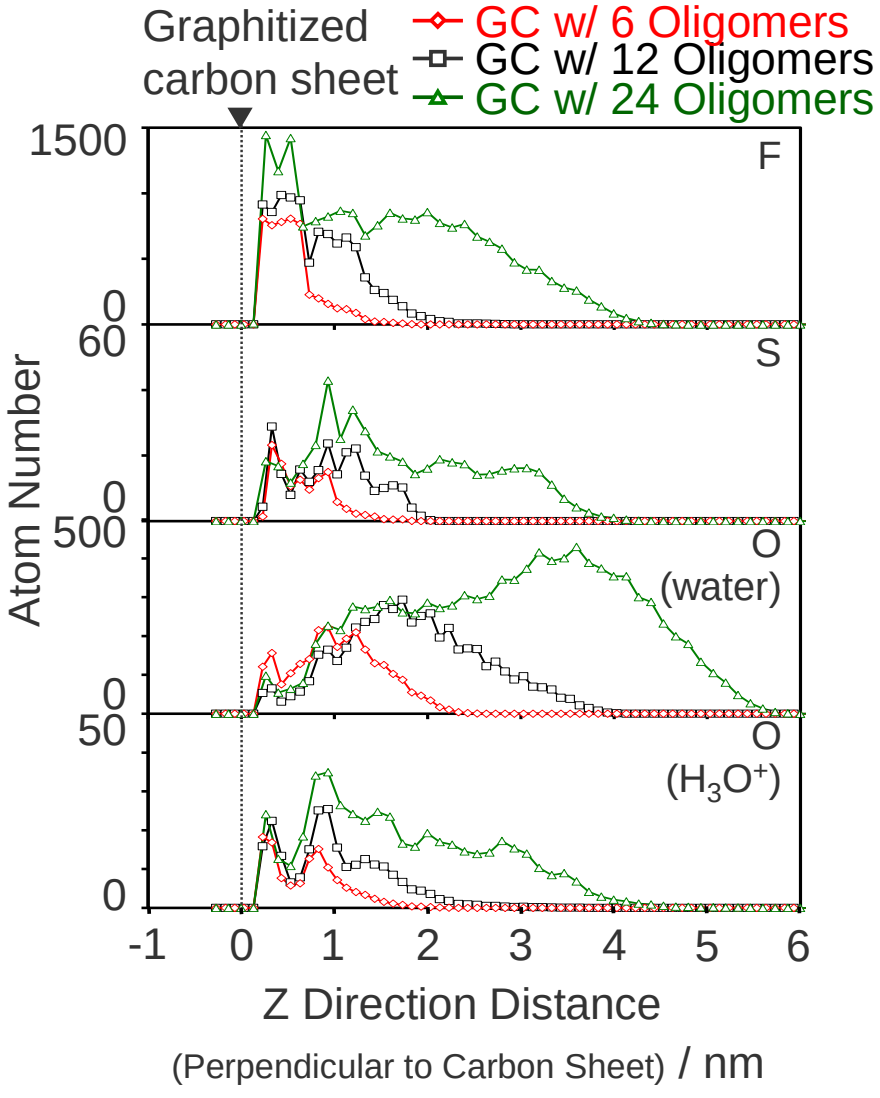
Effect of carbon model (MD)

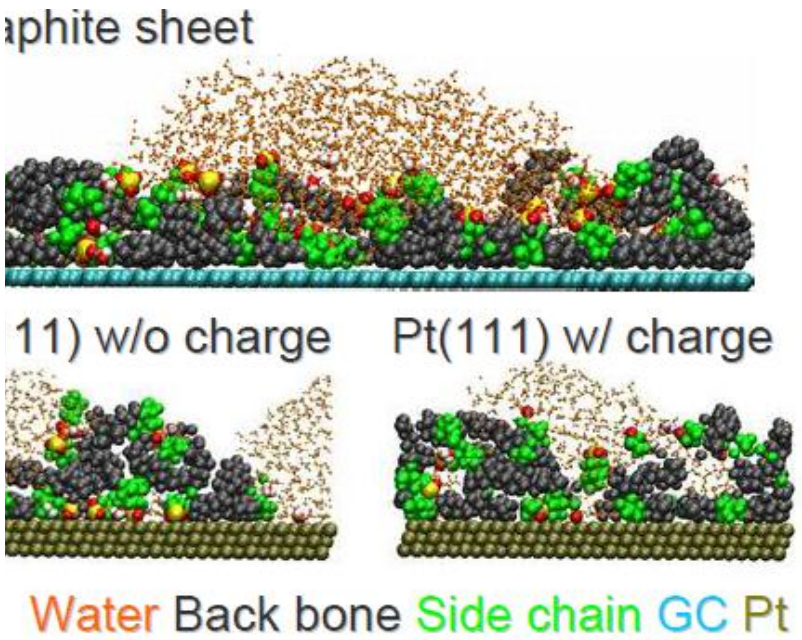
To estimate the distinct role of ionomer content on ionomer coverage on Pt and C; Impacts on ORR activity

- **Method:** MD, CGMD, DFT, kinetics modeling
- **Characterization:** SANS, SAXS, CV, EIS
- **Impact:** vital for design of new generation CLs, pre-competitive knowledge

Density profiles

extended surface





Slightly thicker Nafion film on Pt compared to that on graphite sheet.
Most of S atoms are adsorbed on Pt.
High H_3O^+ concentration on Pt in the case without surface charge.
High water concentration on Pt.

T. Mashio, K. Malek et al. J. Phys. Chem. C, 2010

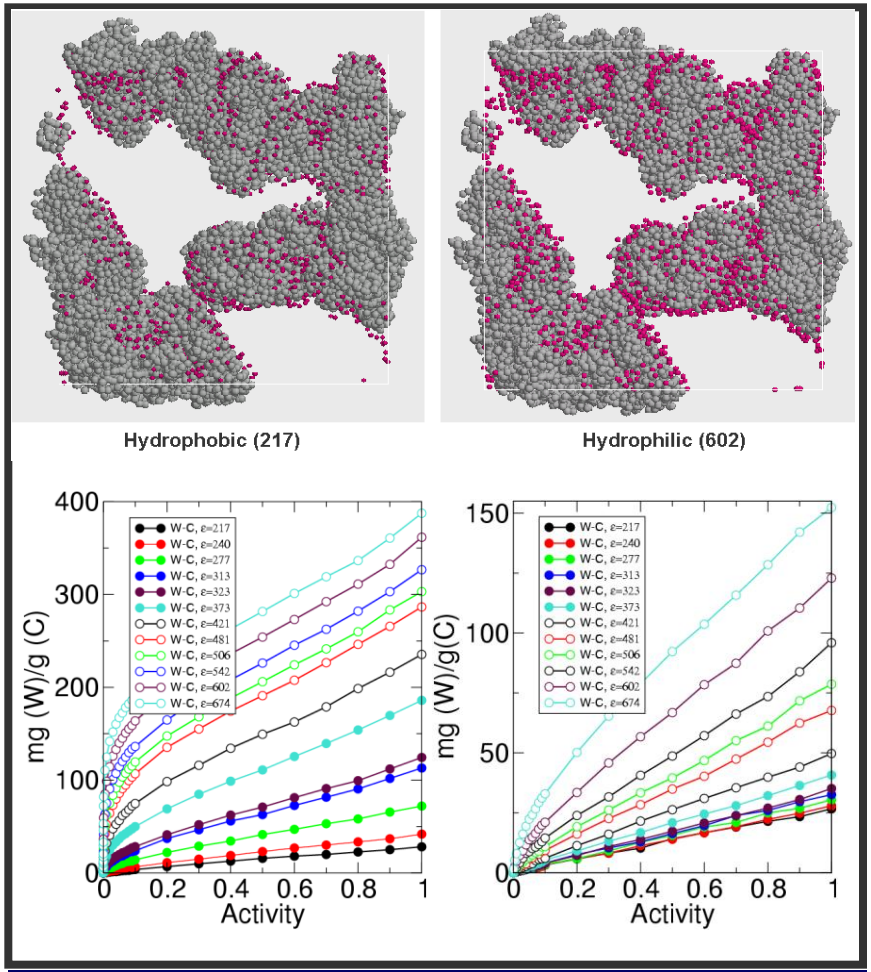
Parameterization

Constructing effective FF

Based on structural and thermodynamic properties

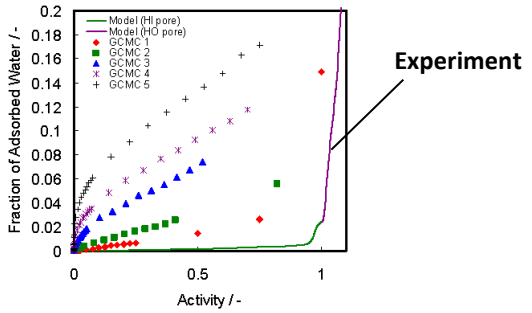
- Matching thermodynamic quantities
- **Boltzmann inversion (mixed or separate AA-CG)**
- **Force matching (adaptive, mixed AA-CG)**

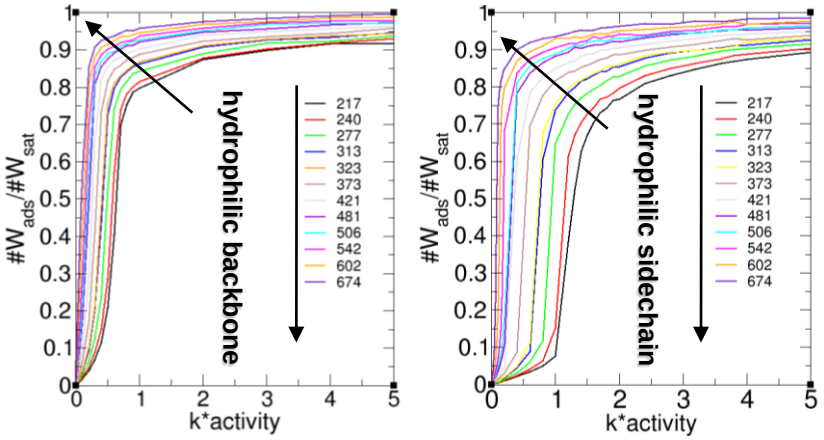
Effect of wettability



Water ads on C

Initial structure at 6% W (λ = 4.2)





W-backbone **W-sidechain**

Water ads on PEM

National Research Council Canada | Conseil national de recherches Canada

SFU

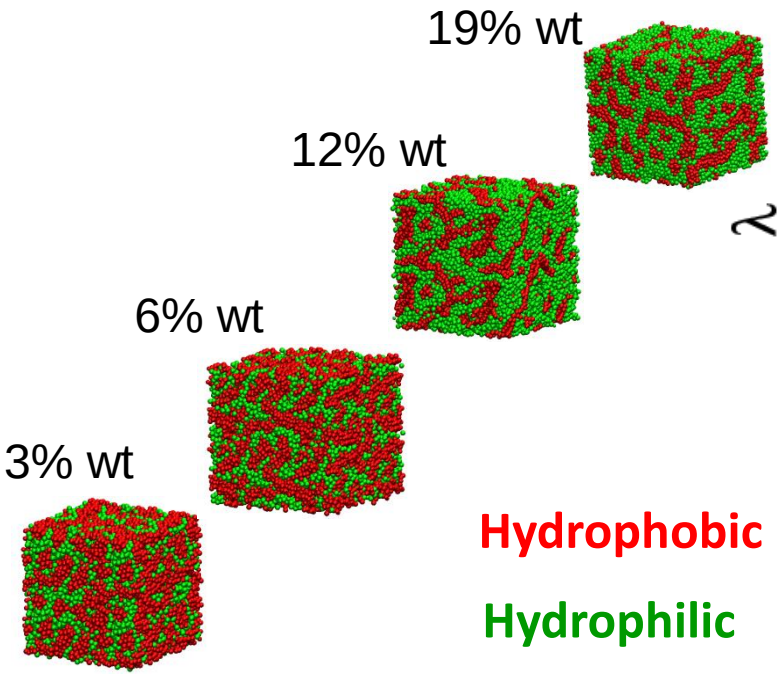
Canada

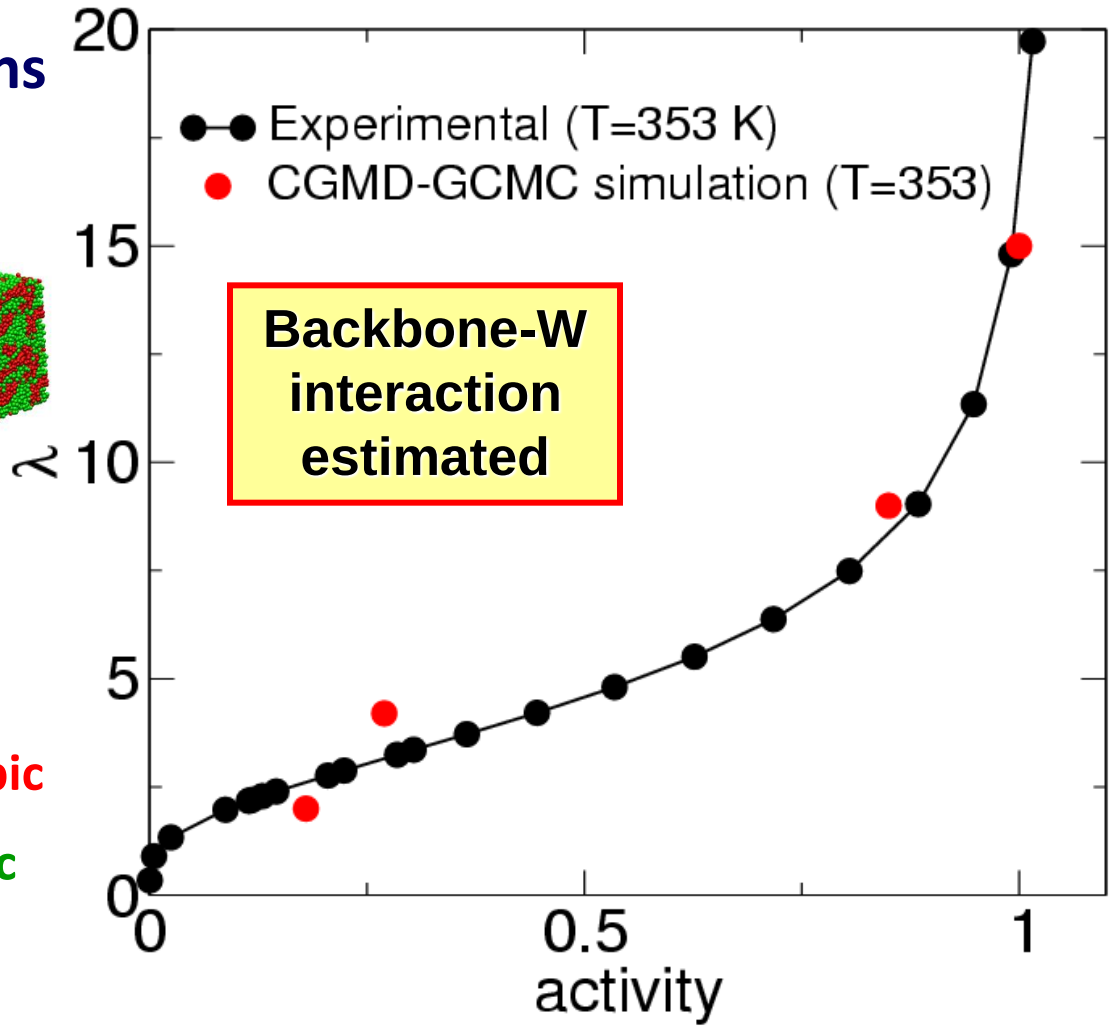
Water adsorption validation

- Validation

Water-Ionomer interactions

Ionomer/PEM structure





Parameterization
Boltzmann-inversion

$$g(r) = \exp(-\frac{V(r)}{k_B T})$$

$$V(r) = -k_B T \ln(g_A(r))$$

$$V^{i+1}(r) = V^{i}(r) - k_B T \ln(\frac{g_A(r)}{g^{i}(r)})$$

Parameterization mixed AA-CG

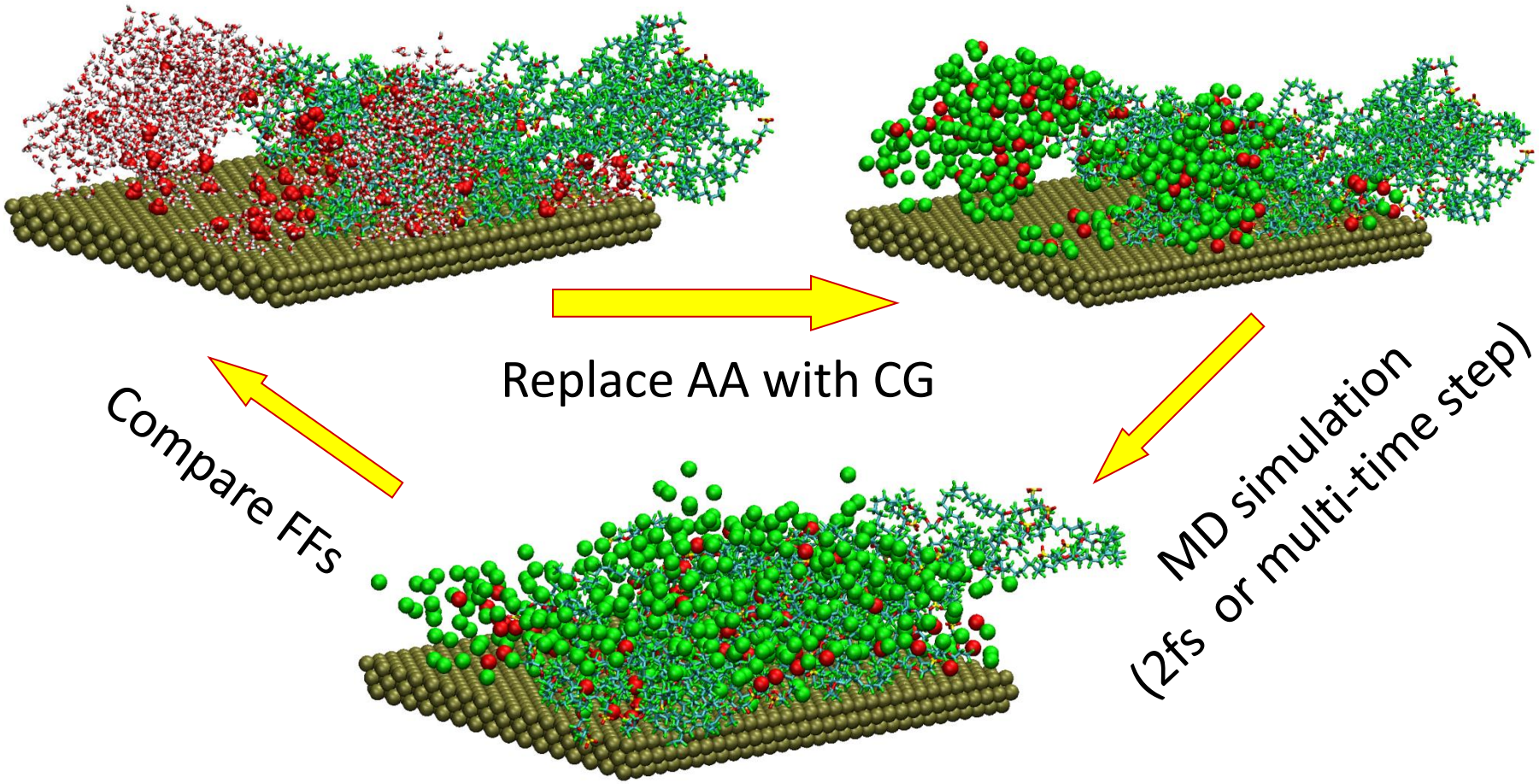
$$F_i^{atom} = \sum_{j \in atom, j \neq i} F_{ij}^{atom-atom} + \sum_{j \in CG} F_{ij}^{atom-CG}$$

$$F_i^{CG} = \sum_{j \in atom} F_{ij}^{atom-CG} + \sum_{j \in CG, j \neq i} F_{ij}^{CG-CG}$$

$$\vec{F}_{i,m}^{CG} = \sum_{j \neq i} f_{ij}^{CG}\left(\left|\vec{R}_{ij,m}^{CG}\right|\right) \frac{\vec{R}_{ij,m}^{CG}}{\left|\vec{R}_{ij,m}^{CG}\right|} \qquad \varepsilon = \frac{1}{3MN} \sum_{i=1}^{N} \sum_{m=1}^{M} \left|\vec{F}_{i,m}^{ref} - \vec{F}_{i,m}^{CG}\right|^2$$

S.Izvekov, G. A. Voth, 2005, 2006

Extended surface configurations



Parameterization
mixed AA-CG

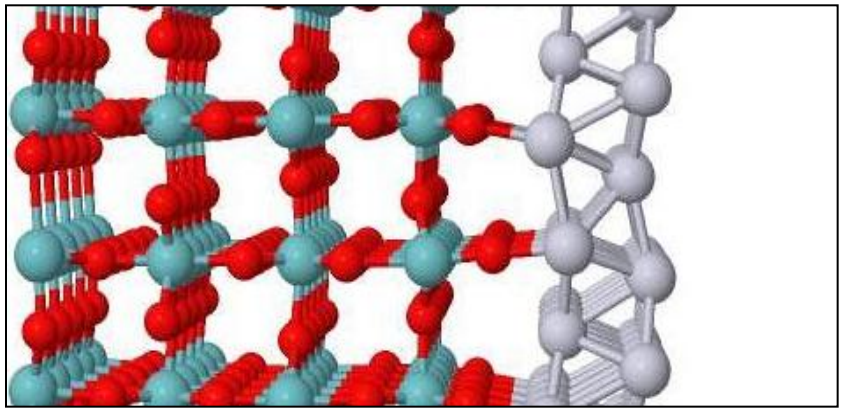
Challenge:

- **Creating a seamless connection between low- and high resolution zones**
- **Multiple-time step algorithm**

Solution: mixed-resolution Hamiltonian

- **Bead size from 0.37 nm (UA) to 0.47 nm (C, Pt)**

Pt/Nb_xO_y system



Li Zhang, L. Wang, Chris M.B. Holt, Kourosh Malek, Titichai Navessin, Michael H. Eikerling, David Mitlin, JPCC, 2010.

Methodology

- Density functional theory (DFT) calculations using the Vienna Ab-initio Simulation Package (VASP).

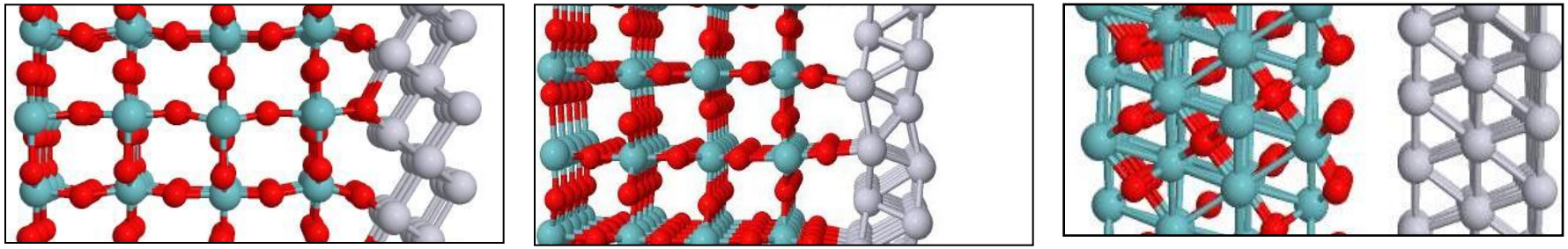
- The non-local exchange and correlation energies were calculated with the Perdew-Wang (PW91) functional within generalized gradient approximation (GGA).

- The total energy calculations during relaxation procedure were done with the linear tetrahedron method with Blöchl correction

Catalyst layer of PEFC

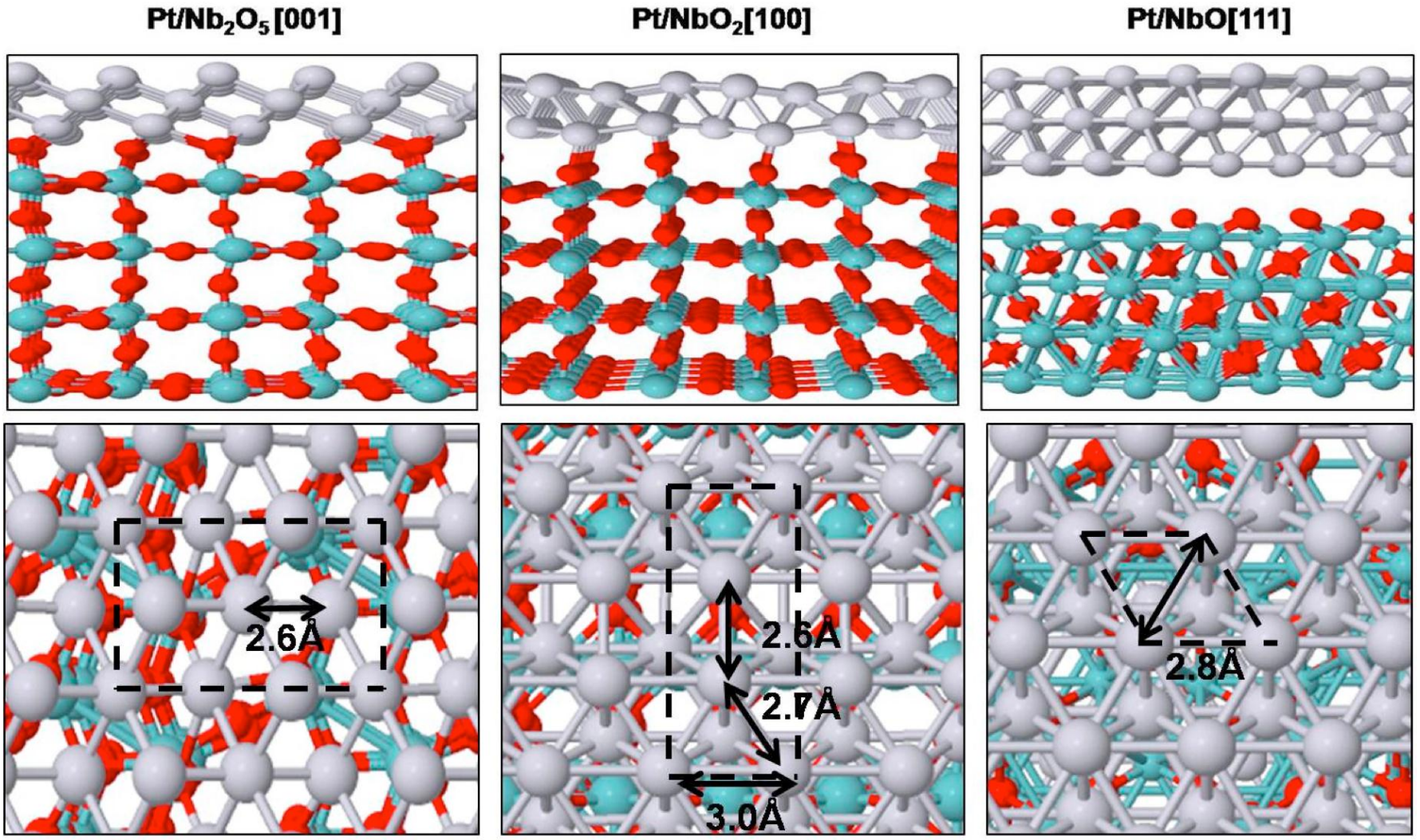
Non-carbon support materials

Pt/Nb_2O_5 **Pt/NbO_2** **Pt/NbO**



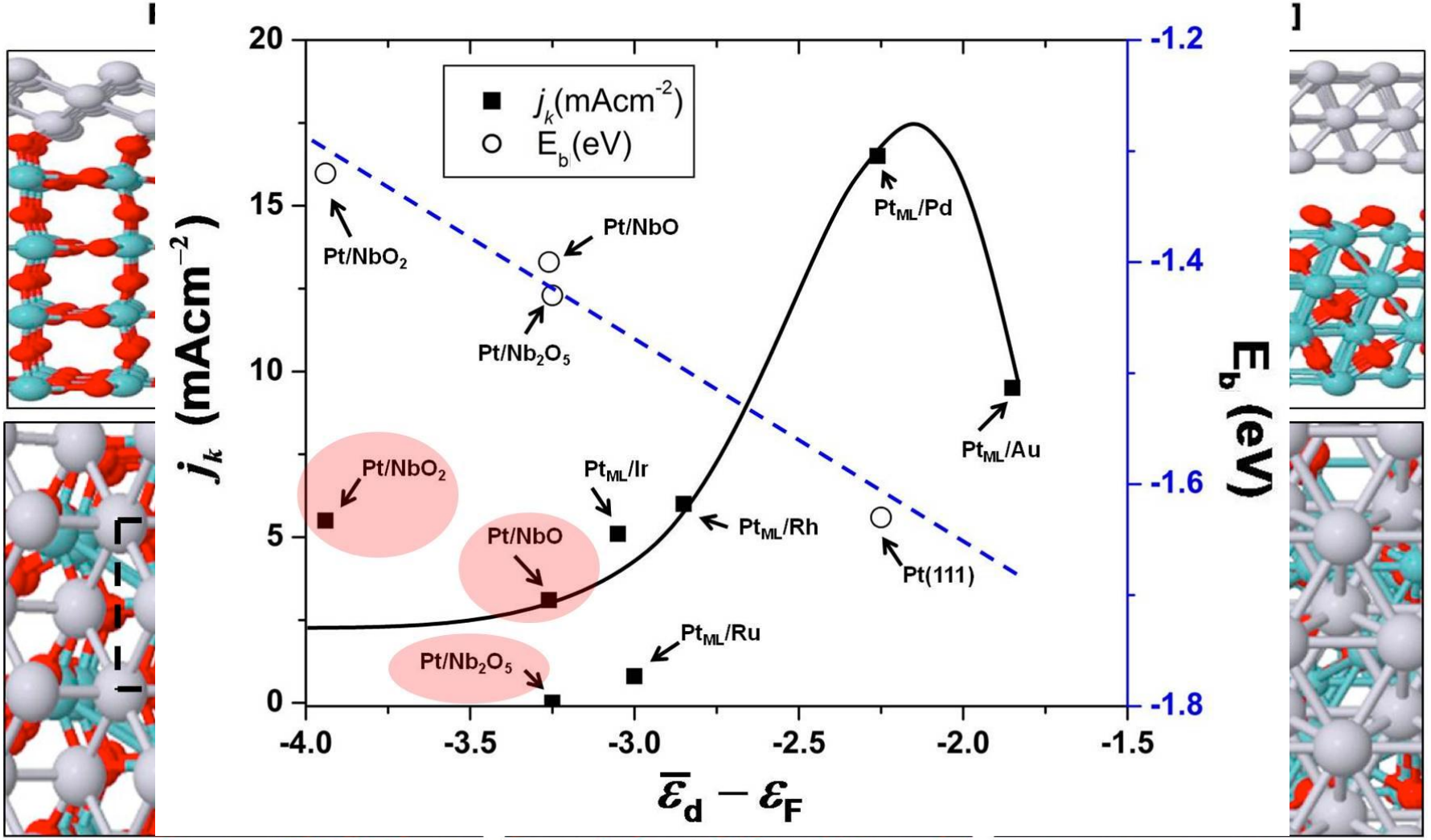
$$E_{ad} = (E_{tot} - E_{sub} - E_{Pt}) / N$$

Non-carbon support materials



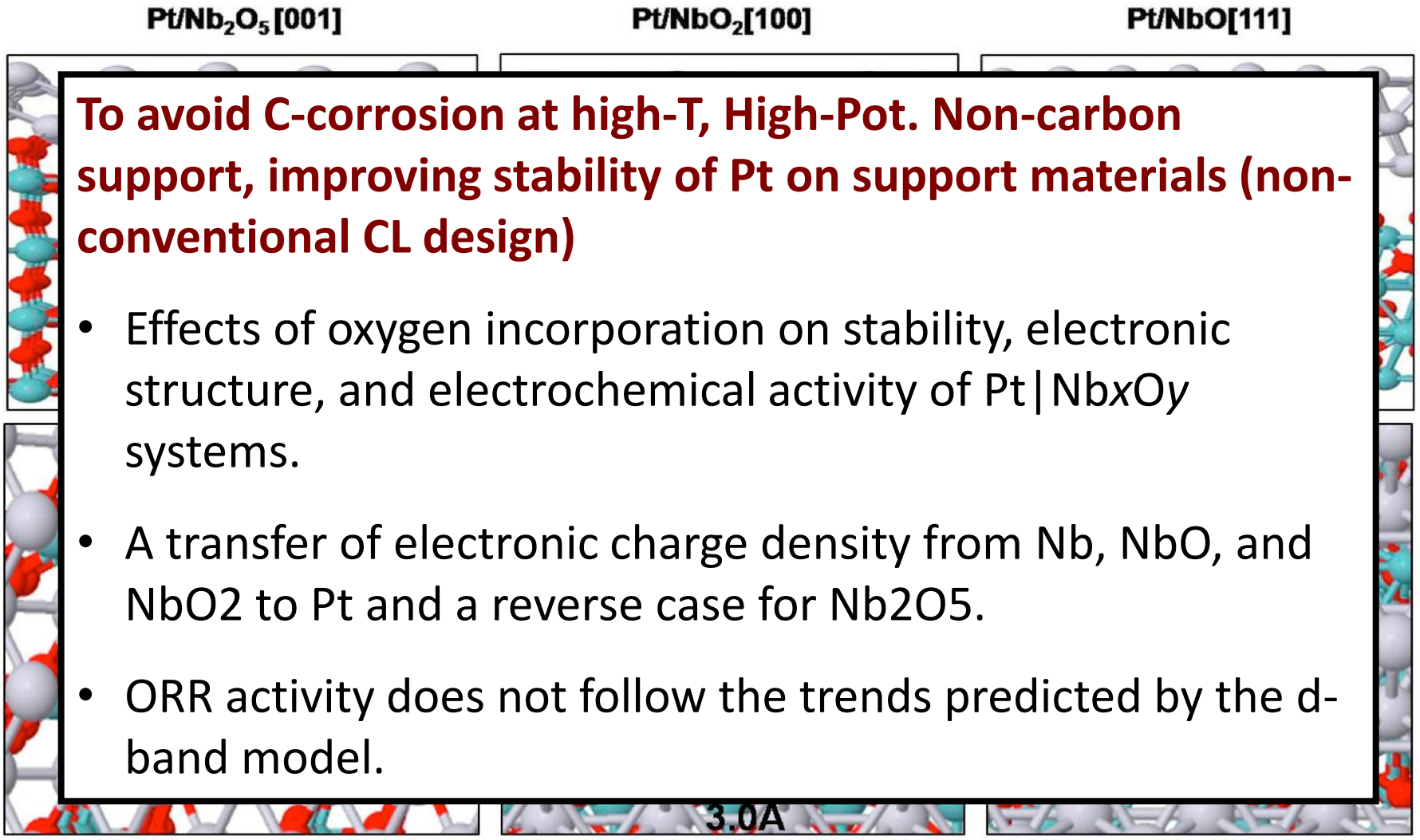
L. Zhang, Liya Wang et al. JPCC, 2010

Non-carbon support materials



L. Zhang, Liya Wang et al. JPCC, 2010

Non-carbon support materials

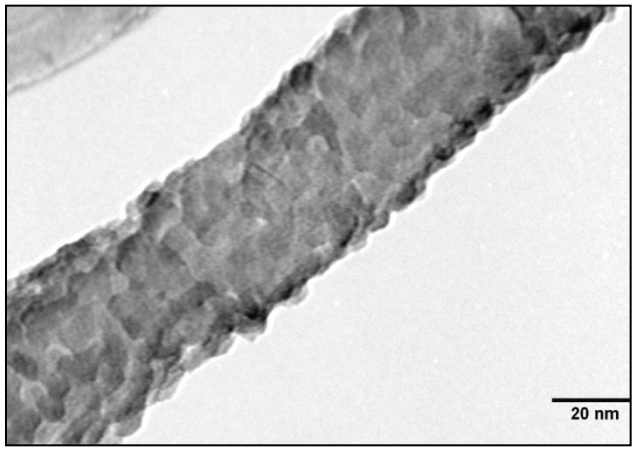


To avoid C-corrosion at high-T, High-Pot. Non-carbon support, improving stability of Pt on support materials (non-conventional CL design)

- Effects of oxygen incorporation on stability, electronic structure, and electrochemical activity of Pt|Nb*x*O*y* systems.
- A transfer of electronic charge density from Nb, NbO, and NbO2 to Pt and a reverse case for Nb2O5.
- ORR activity does not follow the trends predicted by the d-band model.

L. Zhang, Liya Wang et al. JPCC, 2010

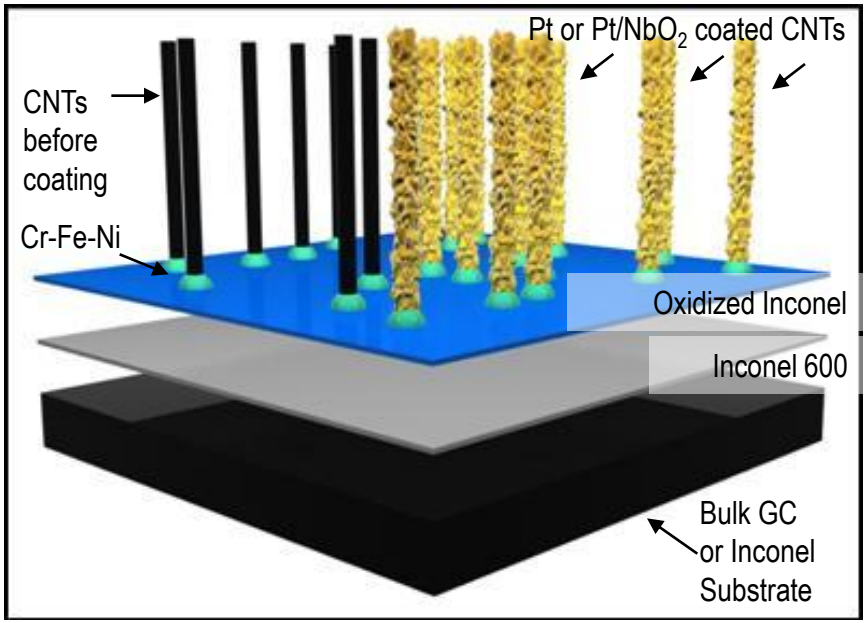
Pt/NbO_2/graphene system



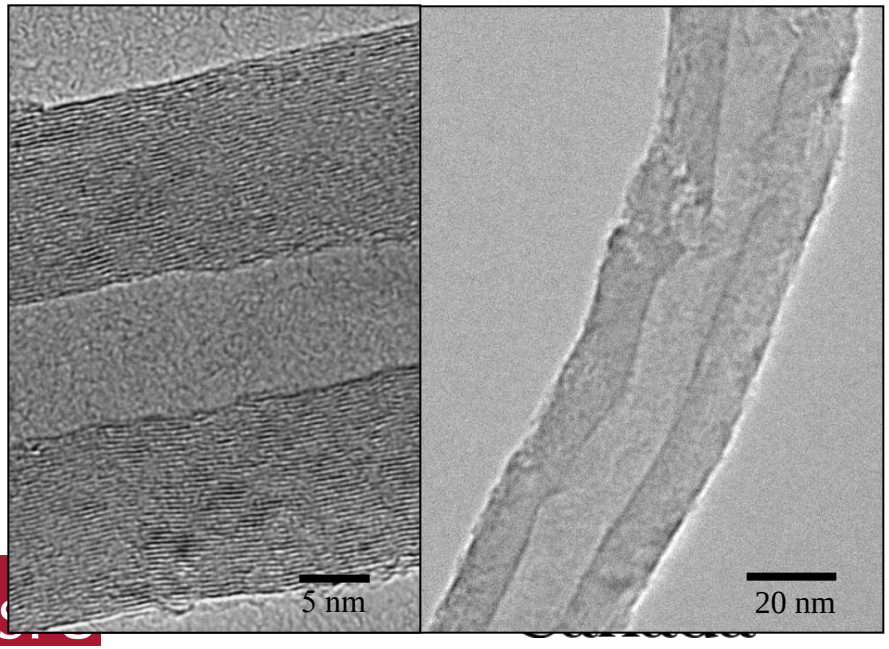
Li Zhang, L. Wang, Chris M.B. Holt, Beniamin Zahiri, Kourosh Malek, Titichai Navessin, Michael H. Eikerling, David Mitlin, Energy & Environmental Science, 2012.

3D Arrays of Pt and Pt/NbO_2 Functionalized CNTs

- Grow anchored 3D arrays of CNTs via CVD. I_G / I_D is 1.60, indicating good quality of as-prepared CNTs but with defects.
- Conformal coating of Pt or Pt/NbO_2 on the CNT arrays via PVD.
- *Geometrical thickness NbO_2 layers were 10 and 2 nm. The thickness of these layers when covering the CNTs was roughly 1 and 0.2 nm.*
- Platinum films mass loadings of 0.03, 0.09 and 0.15 mg/cm^2 (15, 45 and 75 nm by geometrical area).
- Electrochemical measurements were performed using a standard rotating disk electrode (RDE) system. Solutions were prepared from 70% $HClO_4$ (optima grade, Fisher Scientific) and Milli-Q water.
- A helical Pt wire counter electrode and a Cl^--free Hg/Hg_2SO_4 reference electrode
- ESA of Pt, i.e. A_{real} was determined by averaging the charge of the H_{ads} (Q') and H_{des} (Q'') peaks using $A_{real} = Q_H/qH_{upd}$, where qH_{upd} is 210 µC/cm^2

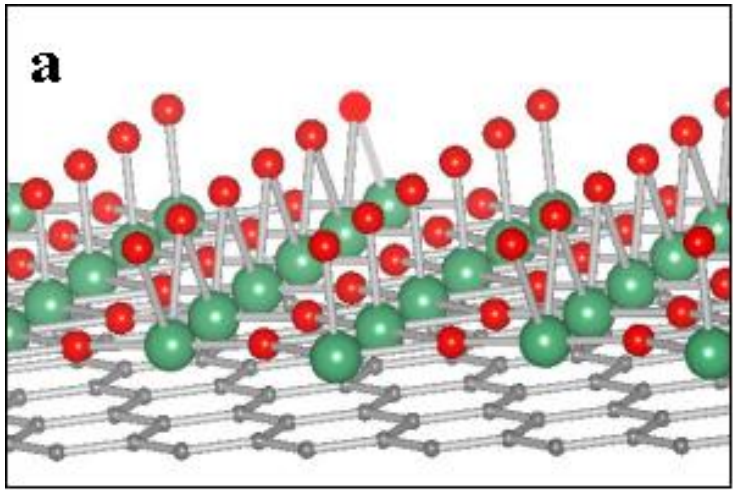


True substrate surface area vs. the geometric surface area ~ 12.

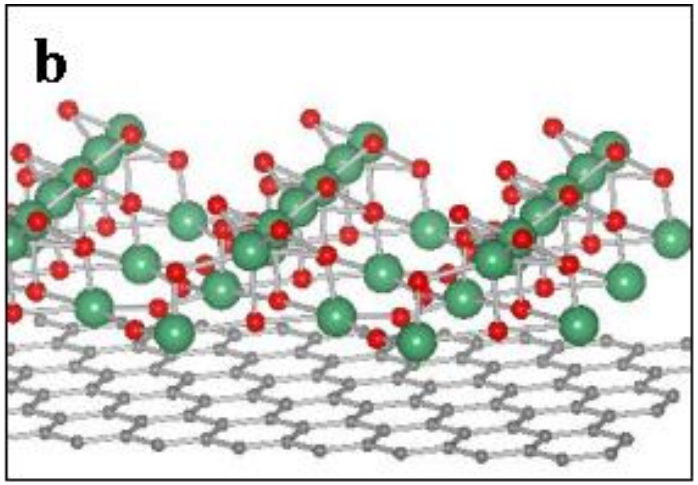


Model System

Initial structure



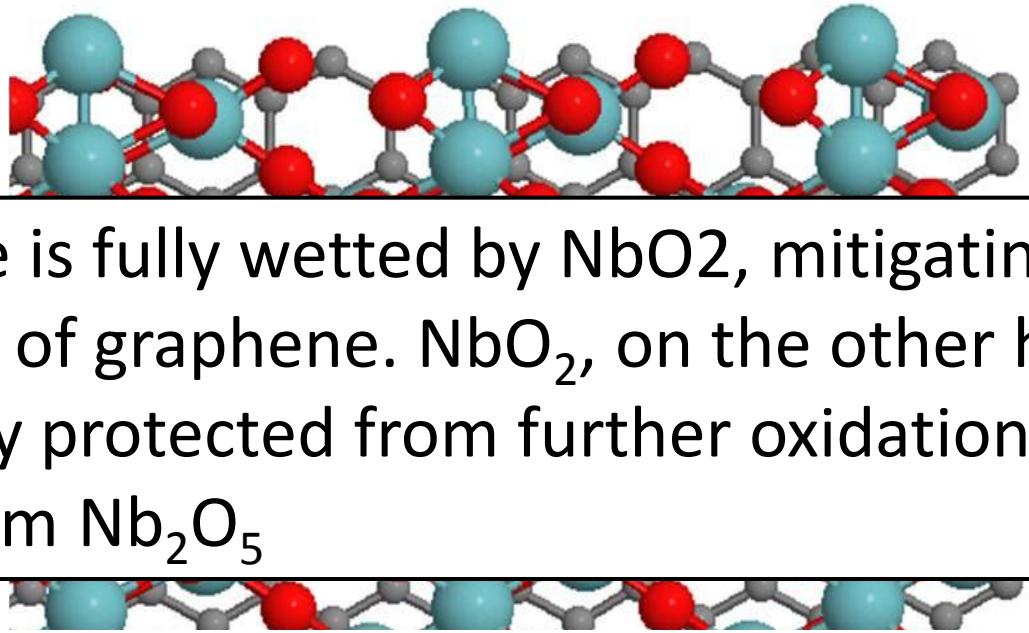
Relaxed structure



$$E_{ad} = \frac{1}{N}\left(E_{NbO_2/CG} - E_{CG} - E_{NbO_2}\right) \quad E_{ad} = -0.34(\text{eV per atom})$$

- **Pt is physisorbed on graphene with adsorption energy < -0.05eV**
- **-0.03eV for Pt(111)/graphene system**
- **NbO2 has a much stronger chemisorption-type interaction with graphene**

Stability



Graphene is fully wetted by NbO2, mitigating the corrosion of graphene. NbO_2, on the other hand, is effectively protected from further oxidation to the equilibrium Nb_2O_5

Top view of the atomic structure of the NbO_2/graphene bilayer system with the optimized geometry. Gray, cyan and red circles indicate C, Nb and O respectively.

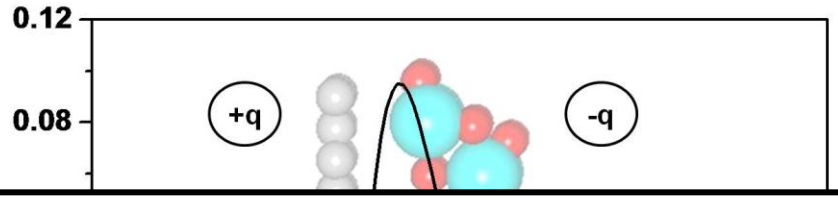
$$\Delta\gamma = \gamma_{NbO_2} + \gamma_i - \gamma_g \leq 0$$

Surface energy of add-layer + Interfacial energy - Surface energy of support

$$\gamma_{NbO_2} = \frac{1}{2A}\left(E^{slab}_{NbO_2} - E^{bulk}_{NbO_2}\right)$$

$$\Delta\gamma = -12\,\mathrm{eV/nm^2} < 0$$

Electronic structure



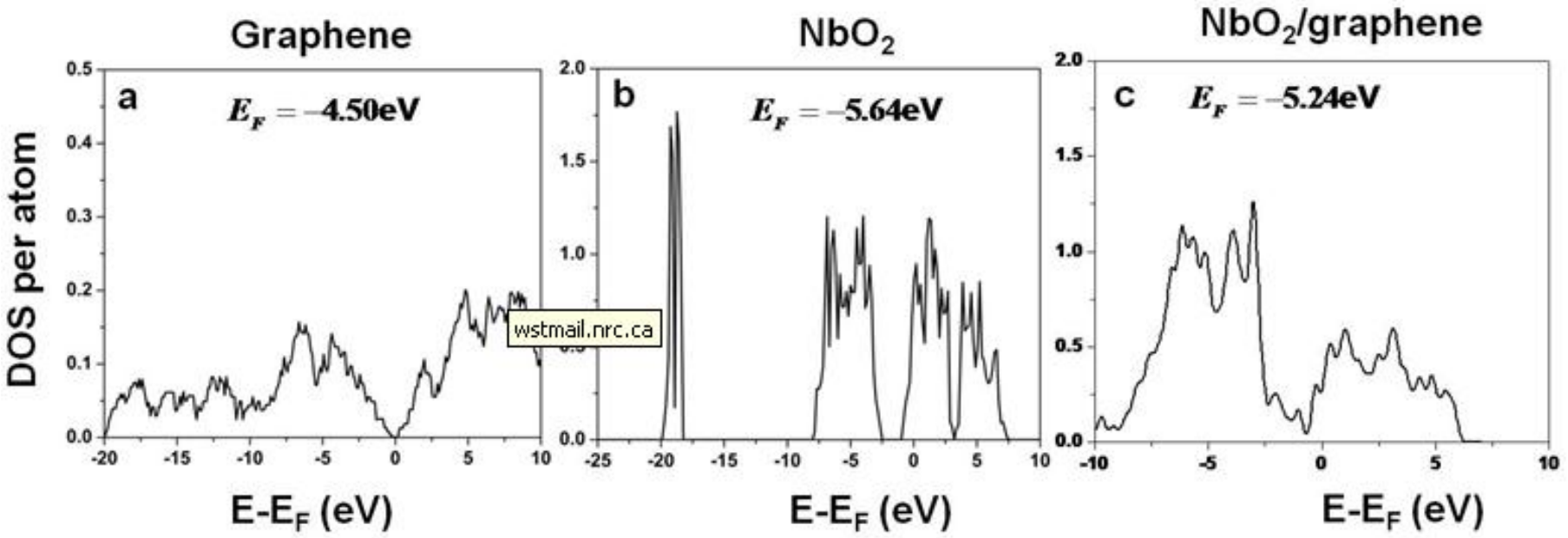
- The difference in Fermi energies between graphene (-4.5 eV) and the NbO_2 monolayer (-5.64)
- Net positive charge at graphene and a complex charge distribution in the NbO_2
- Due to the **electron transfer from graphene to NbO2** the number of electrons at the graphene sheet decreased by 0.01 per carbon atom.

Plane-average charge density of NbO_2/graphene system as a function of coordinate along surface normal

$$\Delta\nu_{p}(z) = \nu_{NbO_2/g}(z) - \nu_{NbO_2}(z) - \nu_{g}(z)$$

The plane-averaged electron density (e/Å) of **NbO2/graphene bilayer system** - **the isolated NbO2 layer** - **bare graphene**

DOS



- A good wetting between NbO_2 and graphene.

The two sublayers exhibit a strong chemisorption-type interaction.

- The graphene sheet injects a significant amount of mobile π electrons into the conduction band of NbO_2

- Further work: electrocatalytic properties of the graphene/NbO2/Pt system

Highlights

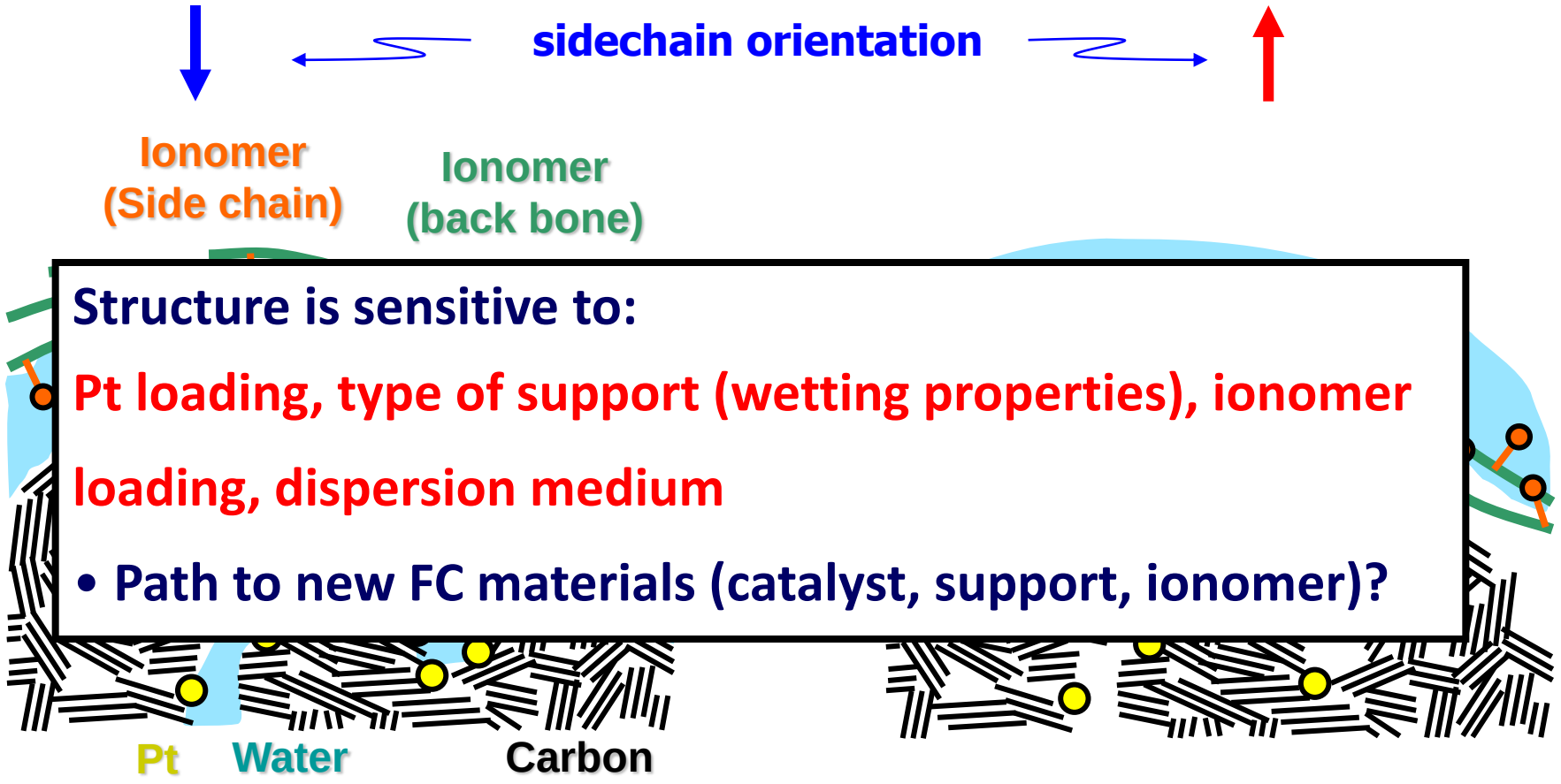
- **Evaluated effects of oxygen incorporation on stability, electronic Structure, and electrochemical activity of Pt|Nb*x*O*y* systems.**

Predicted a transfer of electronic charge density from Nb, NbO, and NbO2 to Pt and a reverse case for Nb2O5.

- **Highly corrosion-resistant electrocatalysts utilizing metal oxide coated carbon nanotubes as a support for Pt**

Gained further insights into changes in wetting properties, stability and electronic structure introduced by the insertion of the thin NbO2 film.

CL structural picture redefined!



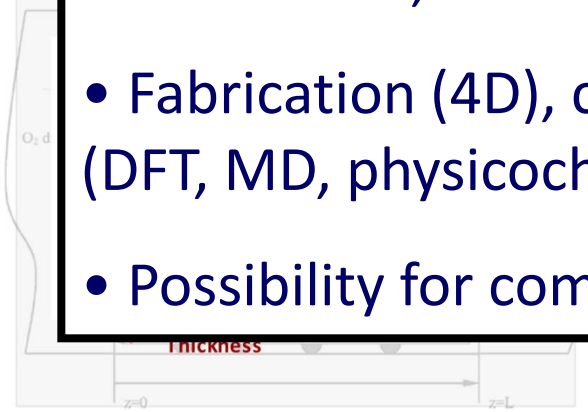
Modeling-based Design

Ultrathin Catalyst Layers

To design ultrathin, ionomer & carbon free CLs

NSERC-SPG (strategic)

- **Team:** NRC, Ballard, AFCC, SFU, UofA, Queen's
- Fabrication (4D), characterization, Pt deposition, modeling (DFT, MD, physicochemical modeling)
- Possibility for commercialization

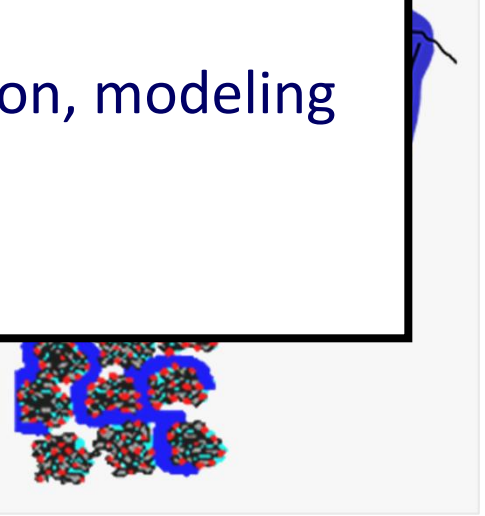


3M Design

~200 nm thick

NRC-SFU design proposal

- Ultrathin (< 100 nm)
- Conductive substrate
- Nanostructure



Conventional CL

~10 μ thick

Q. Wang, M. Eikerling, D. Song, and S. Liu, *Modeling of Ultra-thin Two-phase Catalyst Layers in PEFC*, J. Electrochem. Soc. 154, F95-F101 (2007).

Acknowledgeme

National Research Council Canada | Conseil national de recherches Canada

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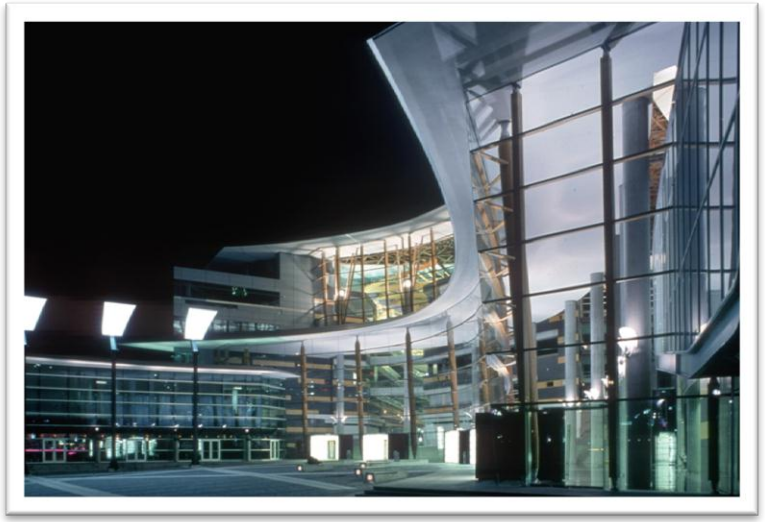

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