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Modeling of Electrochemical Cells: Proton Exchange Membrane Fuel Cells HYD7007 – 01

Lecture 03. Electrode/Electrolyte Interface Structure

Dept. of Chemical & Biomolecular Engineering
Yonsei University
Spring, 2011

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Lecture Outline

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- Review of Macroscopic Structure
- Conceptual Models of Electrode/Electrolyte Interface
- Scanning Electron Microscopy
- Molecular Dynamics simulation
  - membrane/vapor interface
  - membrane/vapor/platinum interface
  - membrane/vapor/graphite interface
  - membrane/vapor/platinum/graphite interface

how fuel cells work: conceptual level

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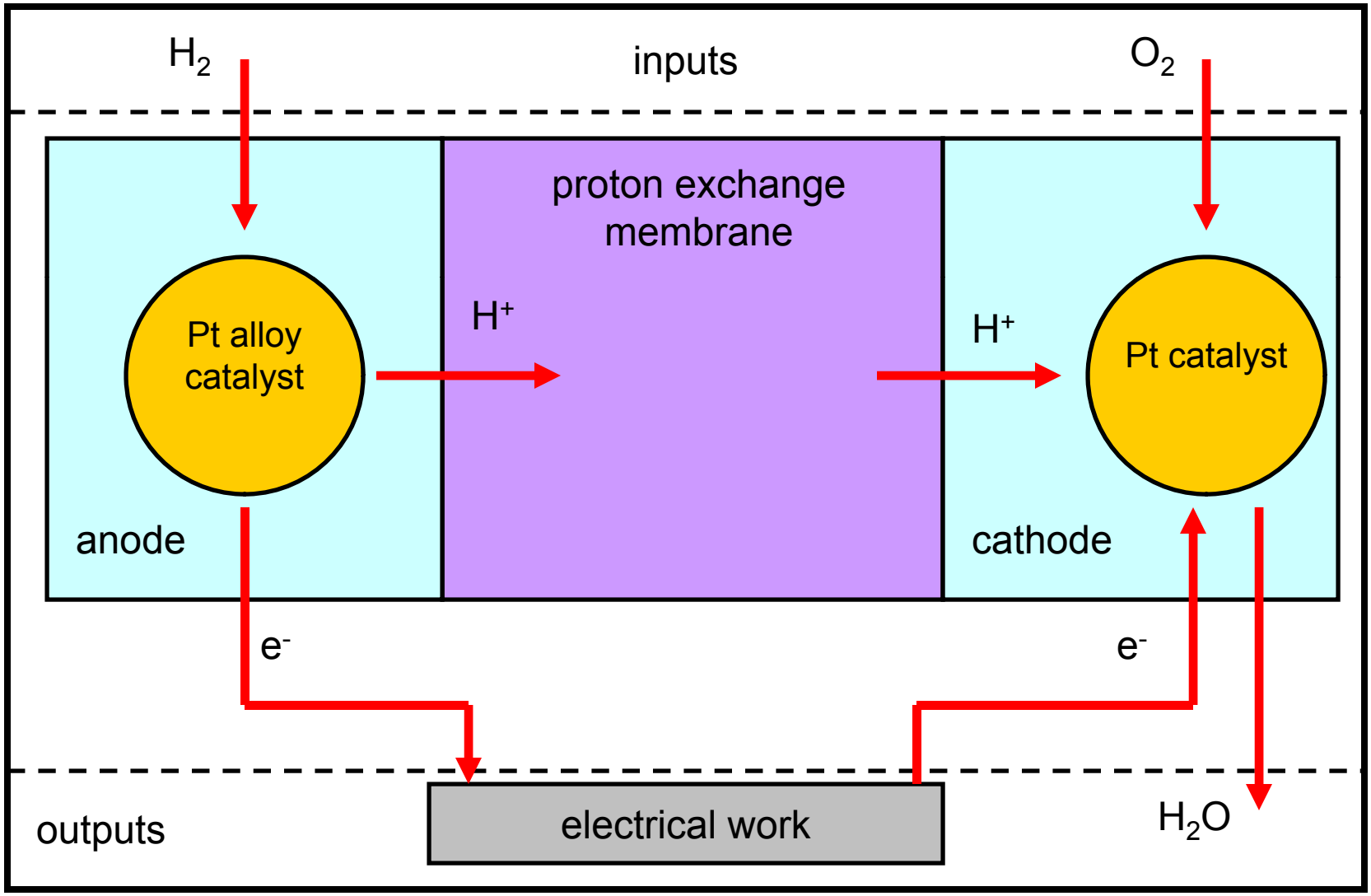

Overview of Structure

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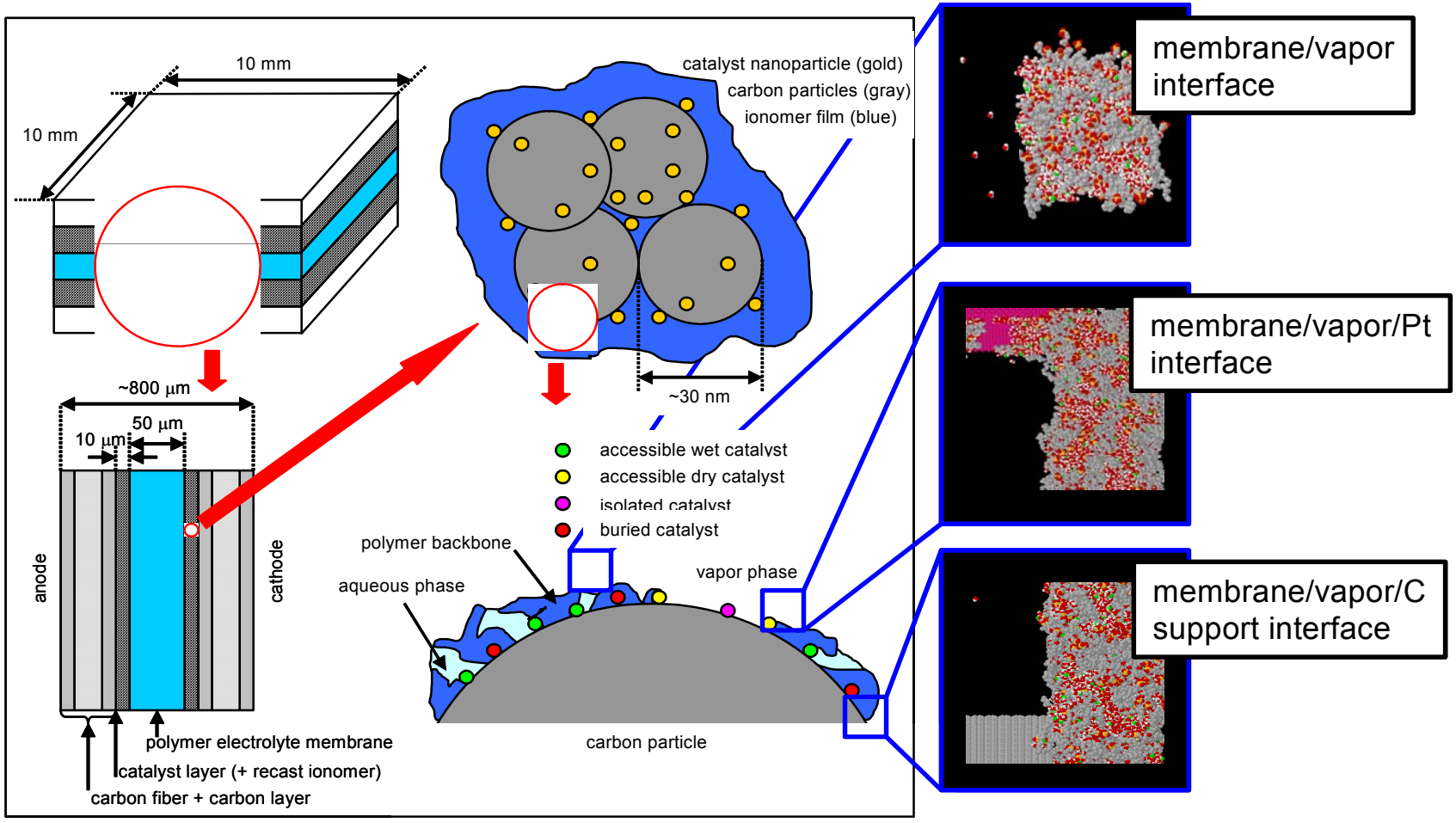
A membrane electrode assembly from the macroscale to the molecular scale



Ideal Catalyst Layer

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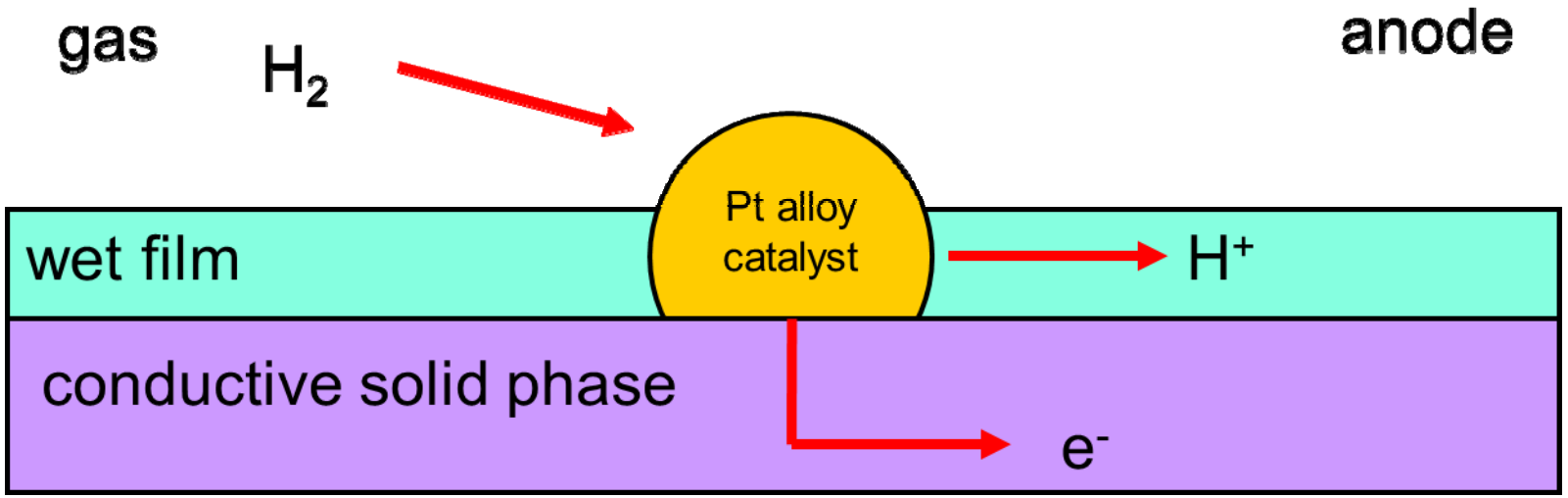
- ✓ **Large three phase interface area in the catalyst layer**
- ✓ **Efficient transport of protons**
- ✓ **Easy transport of reactant and product gases and removed of condensed water**
- ✓ **Continuous electronic current passage between the reaction site and the current collector**



Possible Problems in Catalyst Layer

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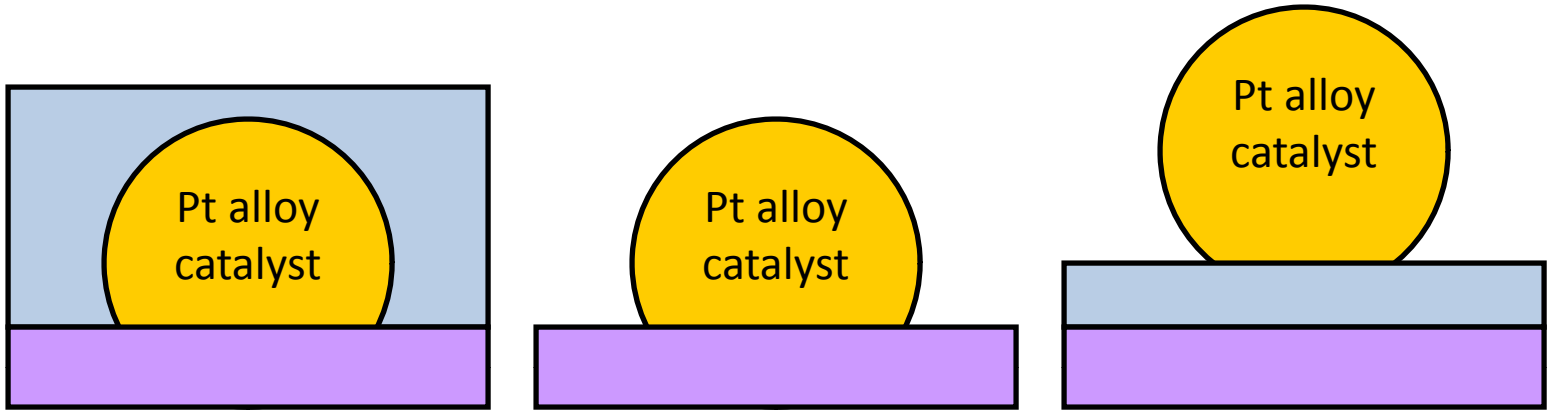

Too much film:
Barrier to H_2.

Too little film:
Barrier to H^+.

Detached catalyst,
Barrier to e^-.

Too much film: mass transfer resistance for H_2 to reach the catalyst.

Too little film: no path for protons or hydronium ions to move from catalyst to PEM.

Detached catalyst: no path for electrons to move from catalyst to carbon electrode.

Electrode/Electrolyte Interface

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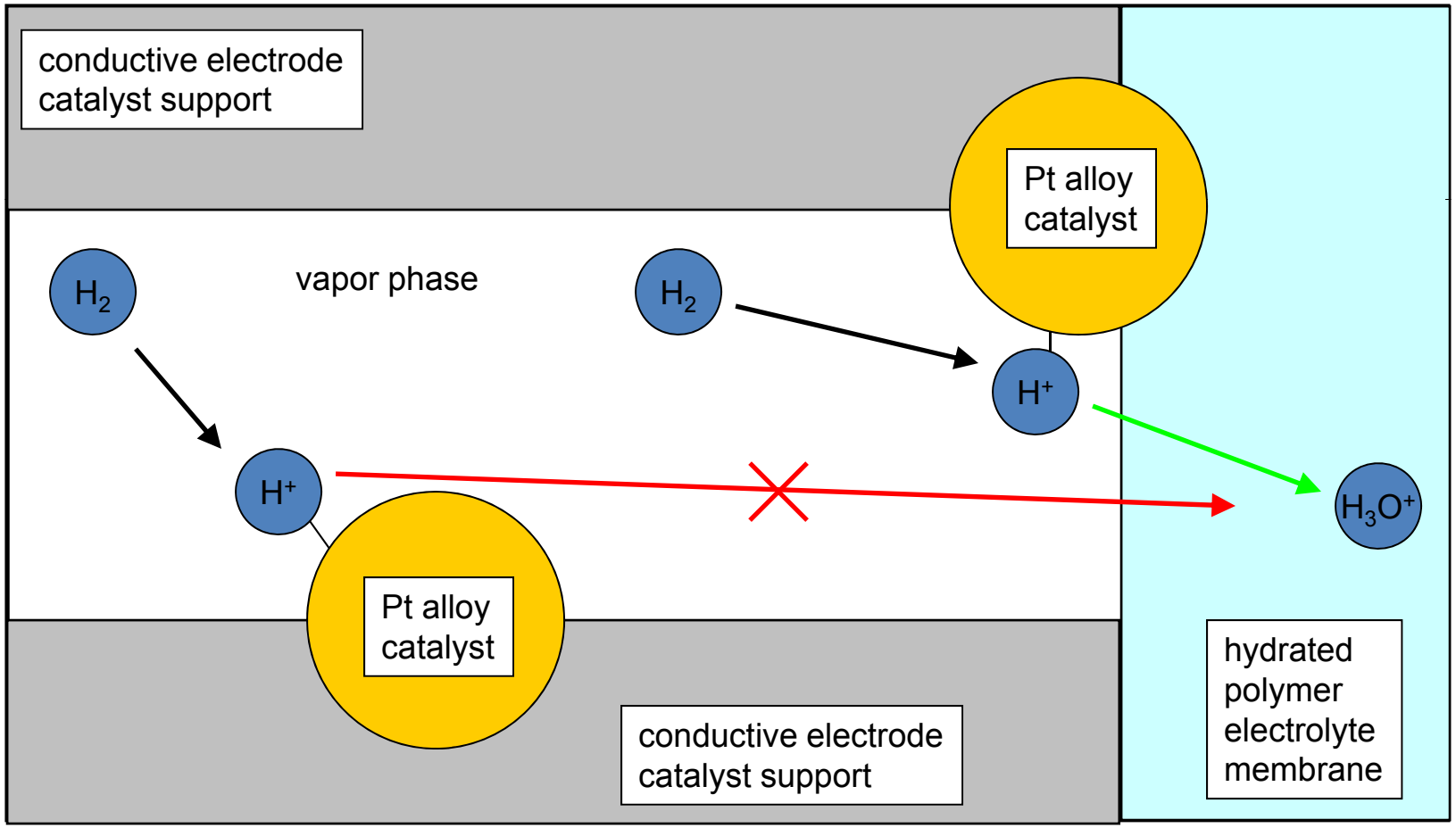
Non-Wetting Model: only Pt at electrolyte interface contribute



Electrode/Electrolyte Interface

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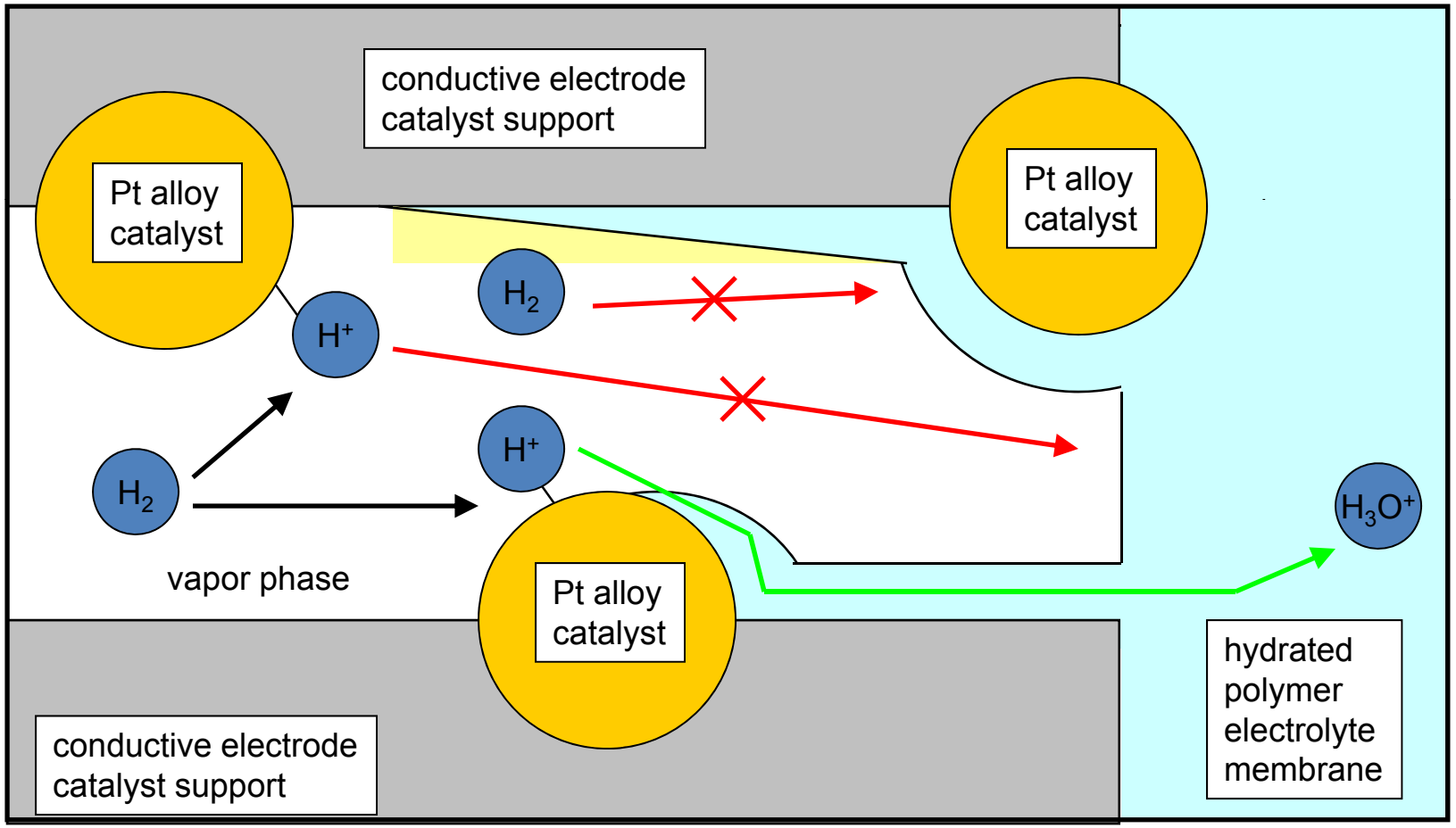
Wetting Model: only partially wet Pt contribute



Include recast ionomer in electrode

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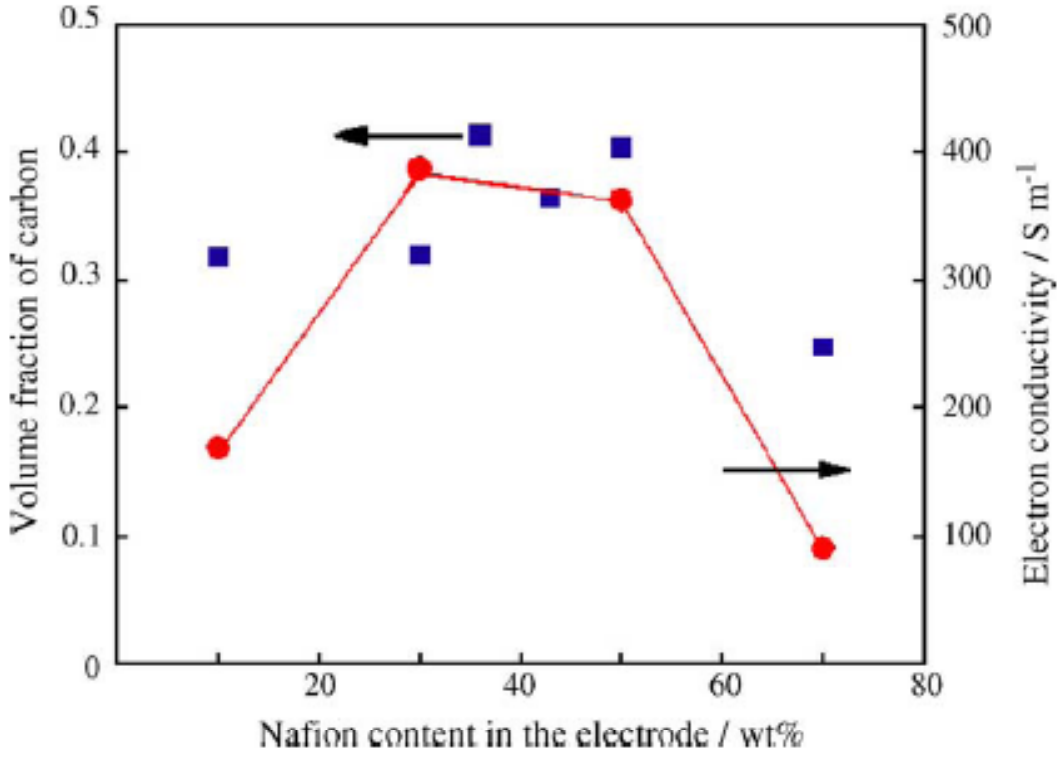

Fig. 6. (●) Electron conductivity and (■) volume fraction of carbon of the electrodes as a function of their Nafion content.

- optimum loading of recast Nafion in catalyst layer

P. Gode et al. / Electrochimica Acta 48, 2003.

Zeiss MERLIN SEM

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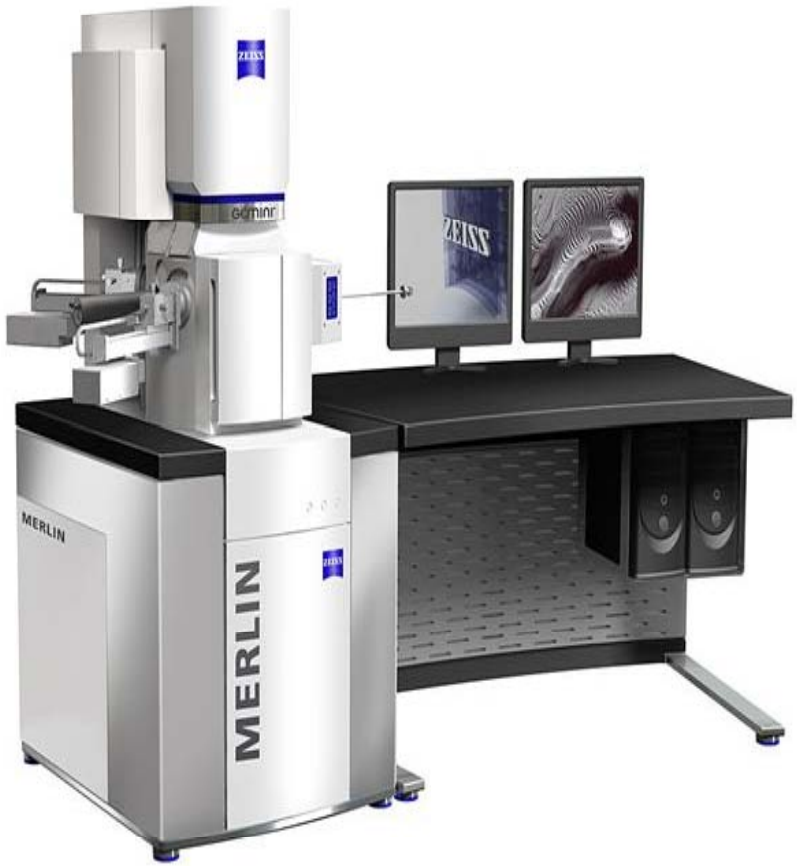

- ✓0.5 to 30keV energy range
- ✓High beam current
- ✓Unique “Gemini” optical design gives ultra high resolution across the energy range
- ✓Real time gas injection charge compensation – no coating required
- ✓Four quadrant BSE detector with “shape through shading” 3-D surface measurement and reconstruction
- ✓Peltier stage for temperature control of sample -40C to +100C
- ✓High performance SiDD system for X-ray microanalysis and mapping

Catalyst Layer Preparation

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5 weight% nafion (1100 EW) solution

20 weight% Pt on Vulcan XC-72

solvent

deionized water

→ Catalyst ink → Sonication 15 min

→ Stir 12 h → Brush onto Nafion membrane

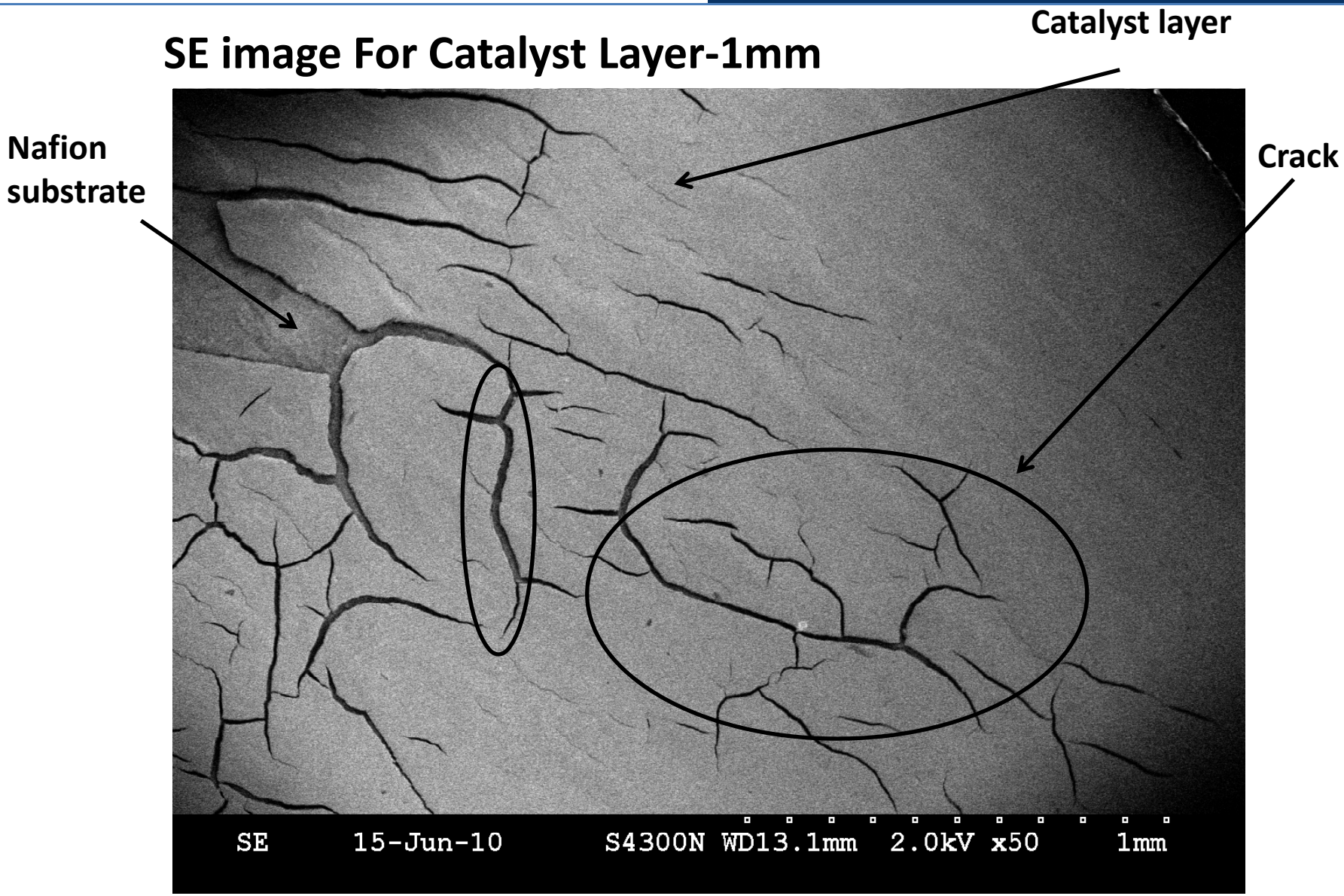
→ Oven dry for 12 h → Heat press 10 min 454 kgs/cm^2

→ 0.5 M/L H_2SO_4 wash 1 h → Deionized water wash overnight

→ Oven dry

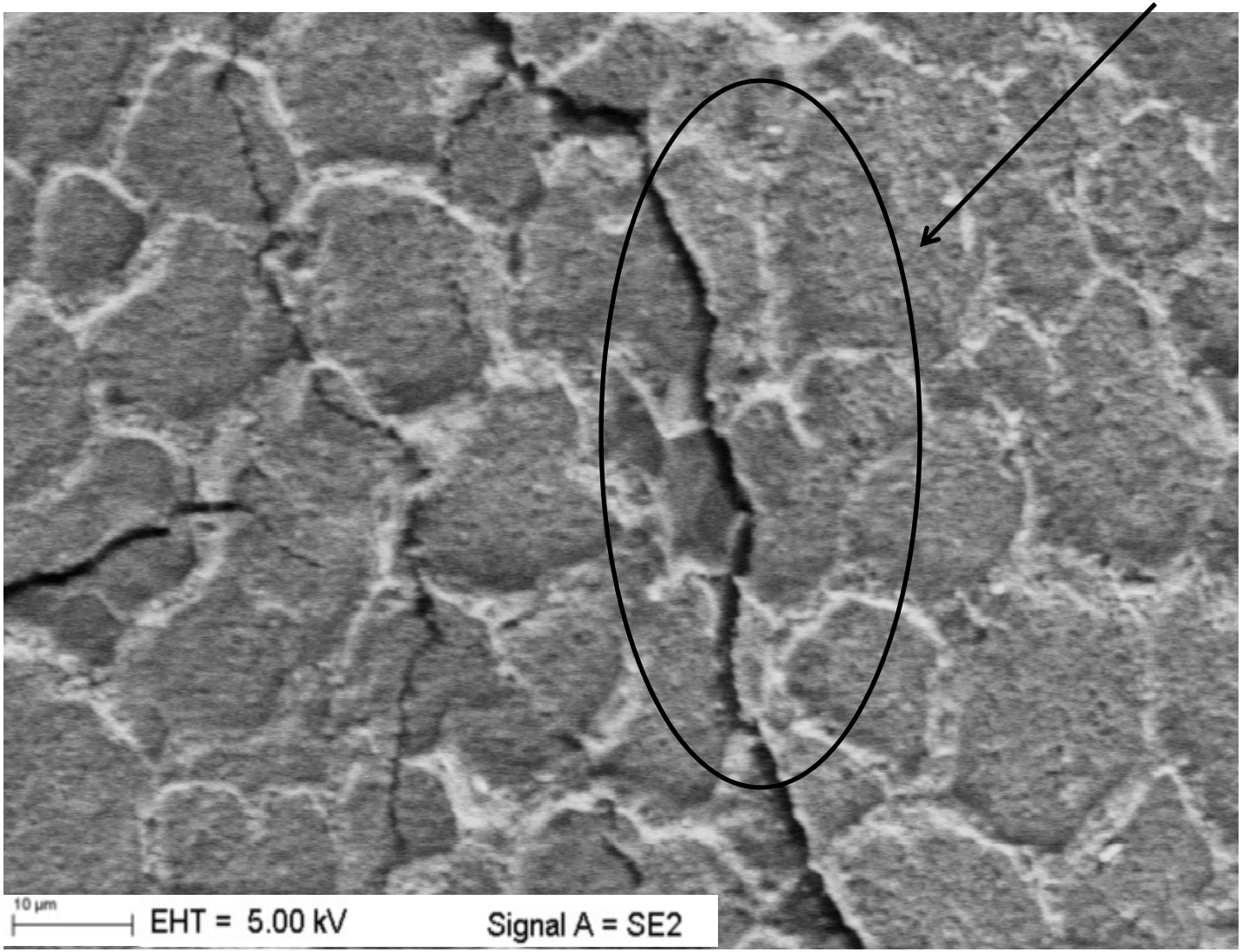
1 kgs/cm^2=0.098 mPa

SE image For Catalyst Layer-1mm

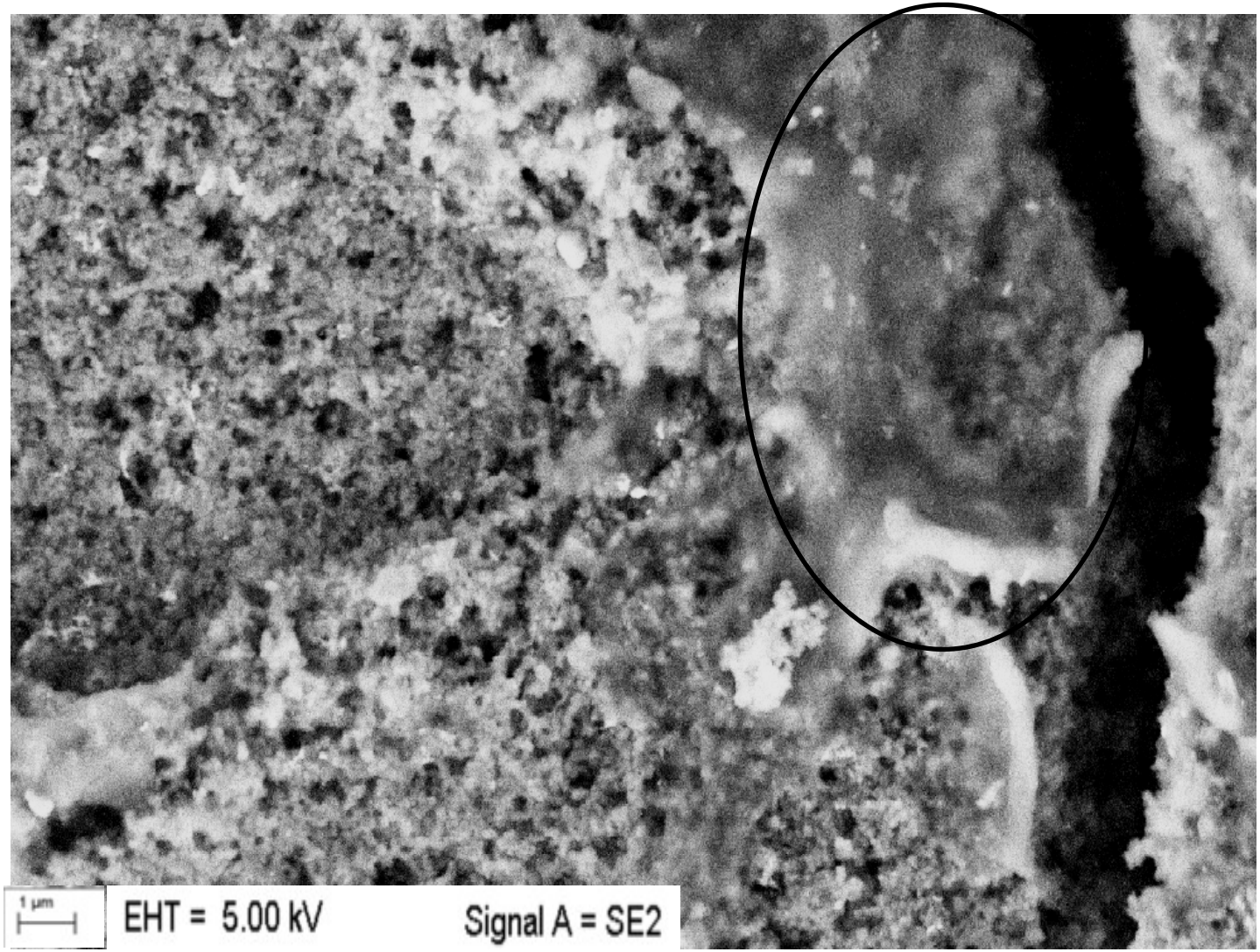


All the samples used here contains 76 weight% nafion.

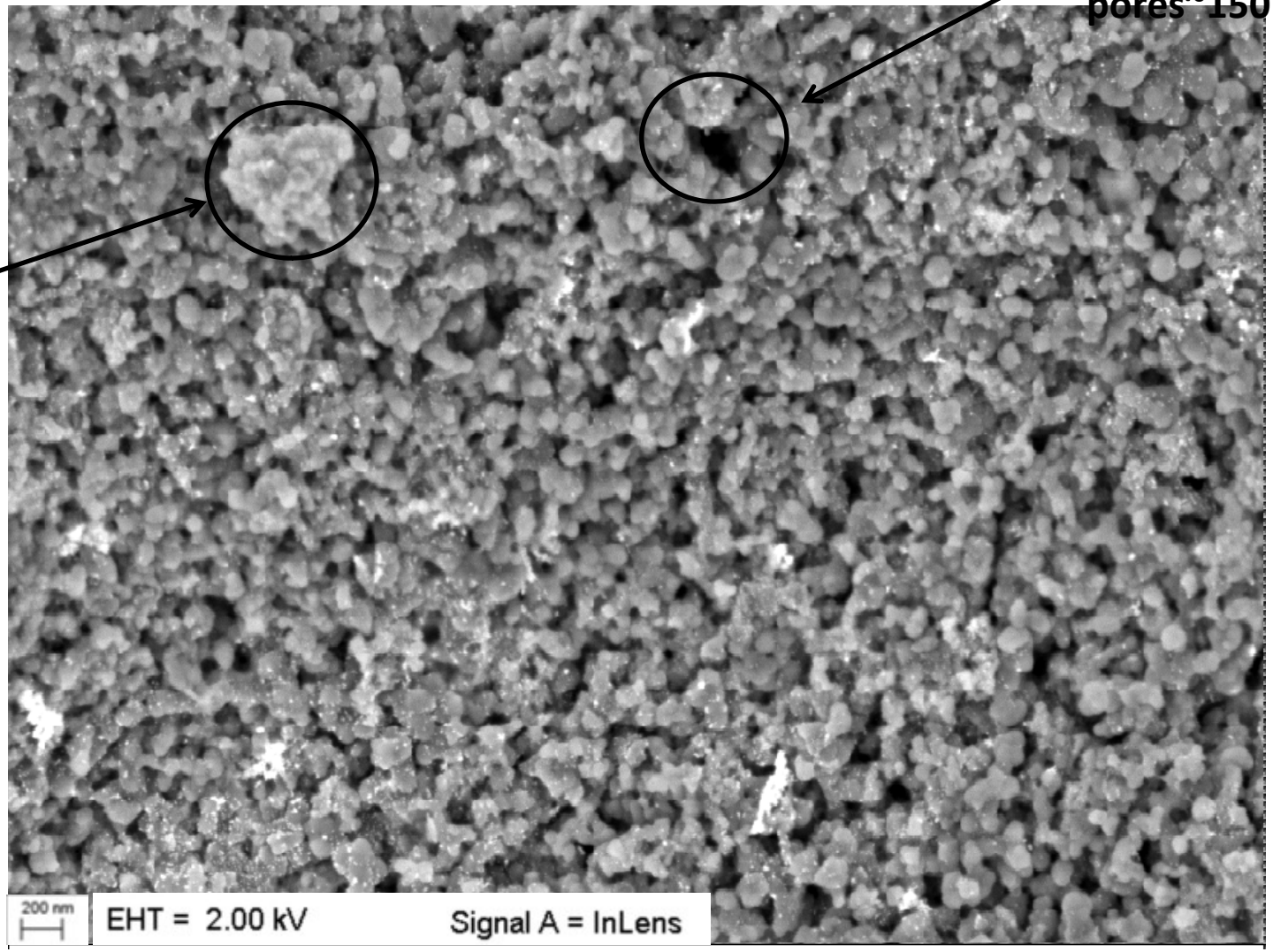
SE Image For Catalyst Layer-10μm



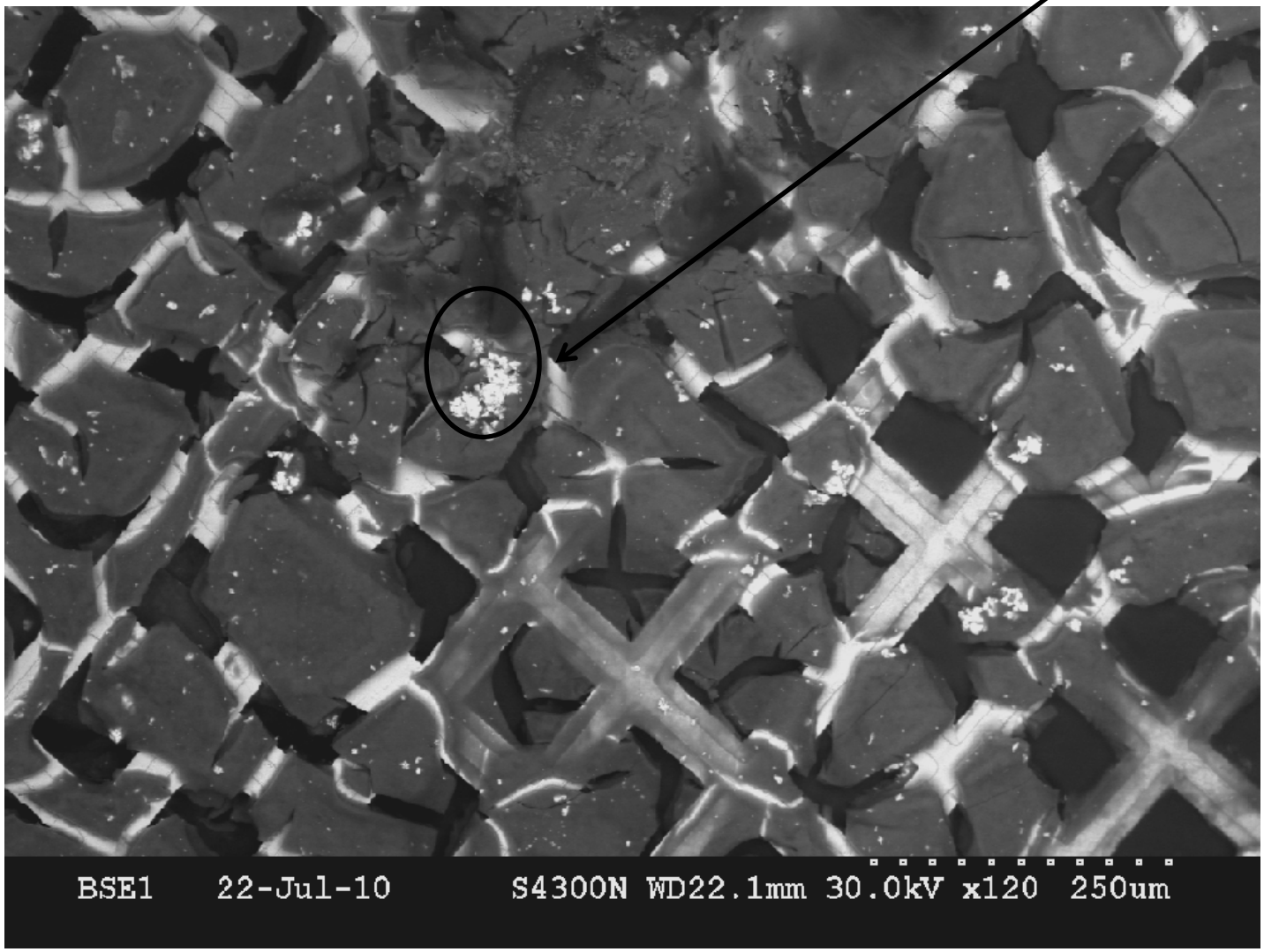
SE Image For Catalyst Layer-1μm



SE Image For Catalyst Layer-200nm



BSE Image for Catalyst Layer



Sample Current Image

$I_{sc}=I_b-I_{se}-I_{bse}$

Where

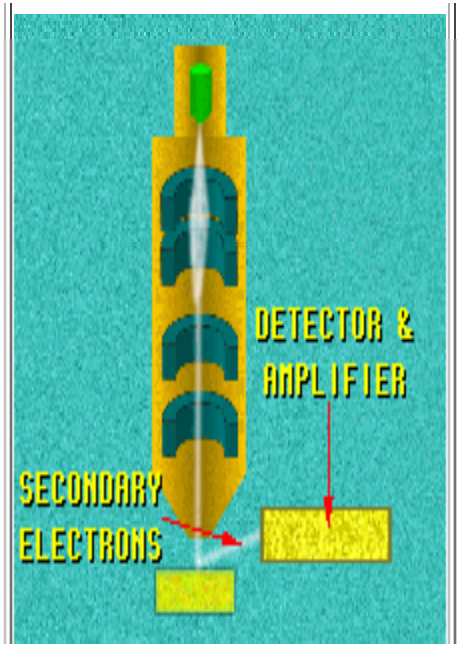
I_{sc} is the sample current.

I_b is the beam current.

I_{se} is the secondary electron current.

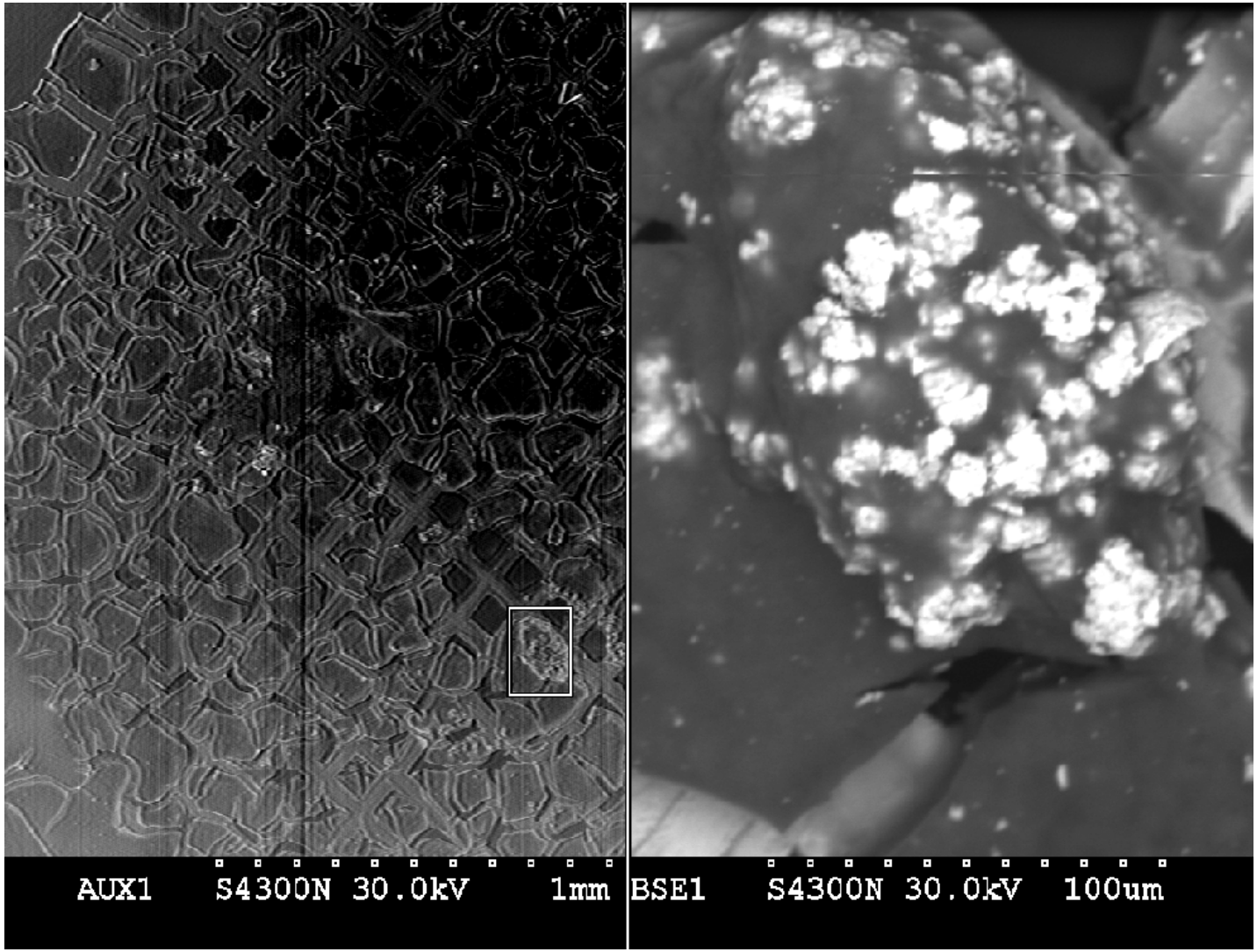
I_{bse} is the back scattered electron current.

Sample irradiation is determined by beam current. The brighter the sample, the higher conductivity the sample.



http://www.geneseo.edu/~nuclear/nuclear%20home%20page/Research/Present%20Research%20Projects/Spider%20Silk/current.htm

Sample Current Image and BSE Image



M4PP Microscopic Four-Point Probes

- ✓ M4PP gives us great enhanced spatial resolution of sheet resistance measurement.
- ✓ The M4PP we use has an electrode pitch of 10 µm.
- ✓ We are using probe 2 and probe 3.

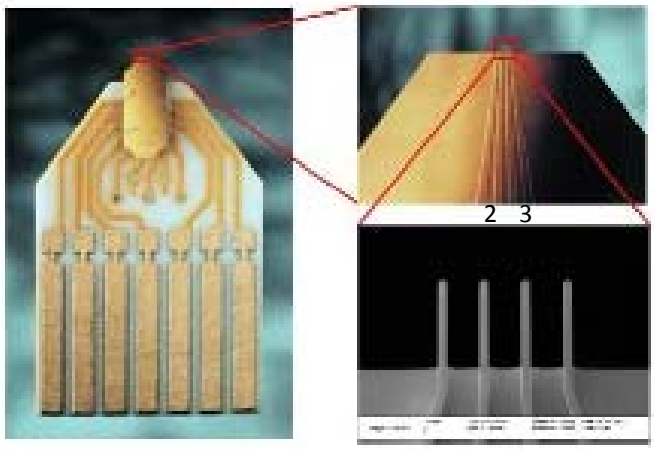
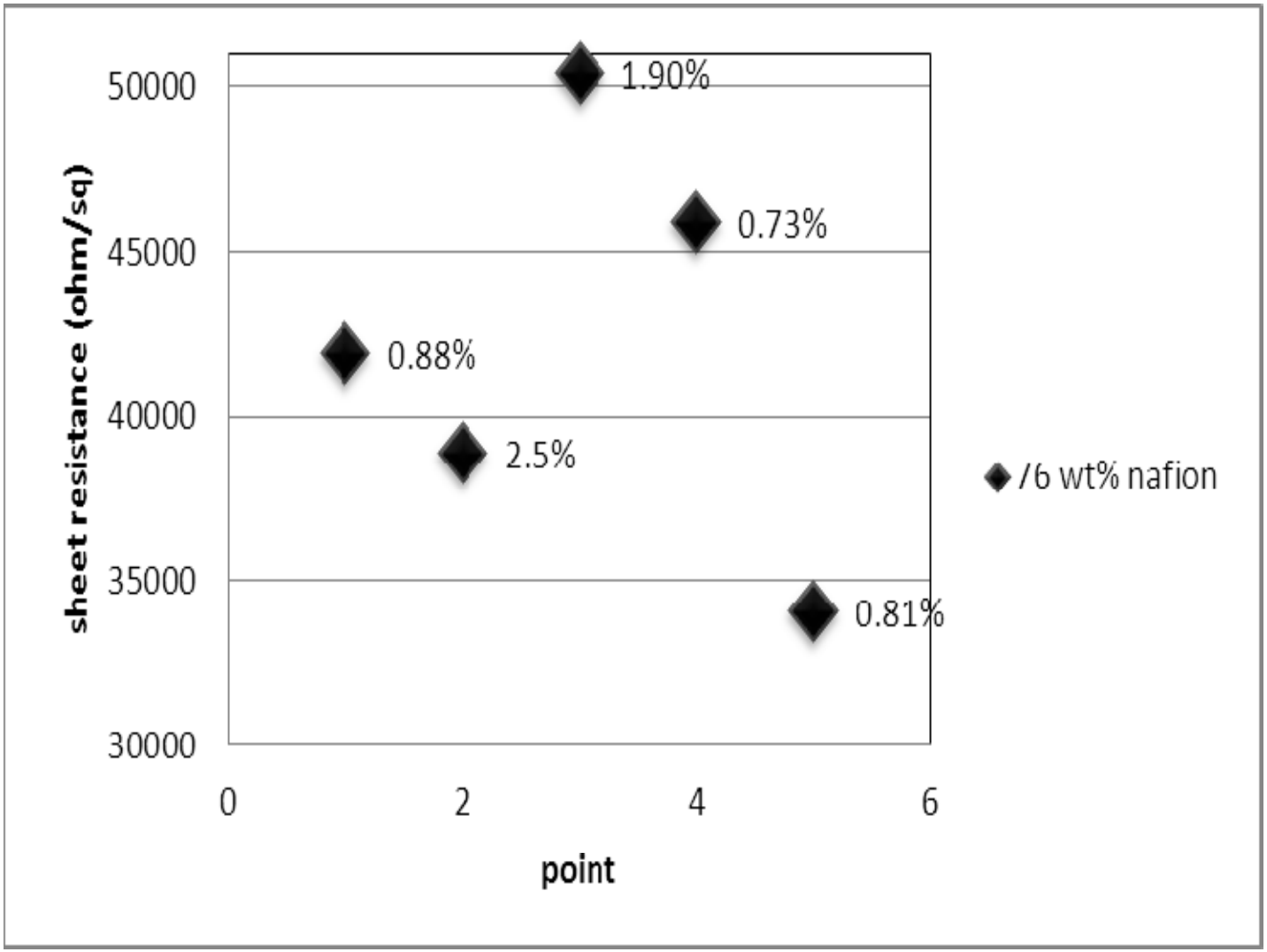


Figure 1-2: The Kleindiek Manipulator with a M4PP holder inserted

M4PP Data for 76 wt% Nafion Catalyst Layer



Microscopy observations

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- ✓ The interface of electrode and electrolyte is not homogenous.
- ✓ The surface is rough, porous and has cracks.
- ✓ Big size platinum agglomerate(~100 nm) is observed, which will greatly decrease the catalyst utilization rate.
- ✓ Carbon clusters (50-300 nm) is observed, and different pore size are formed accordingly.
- ✓ In plane sheet resistivity varies point to point.

Simulation of Interfaces

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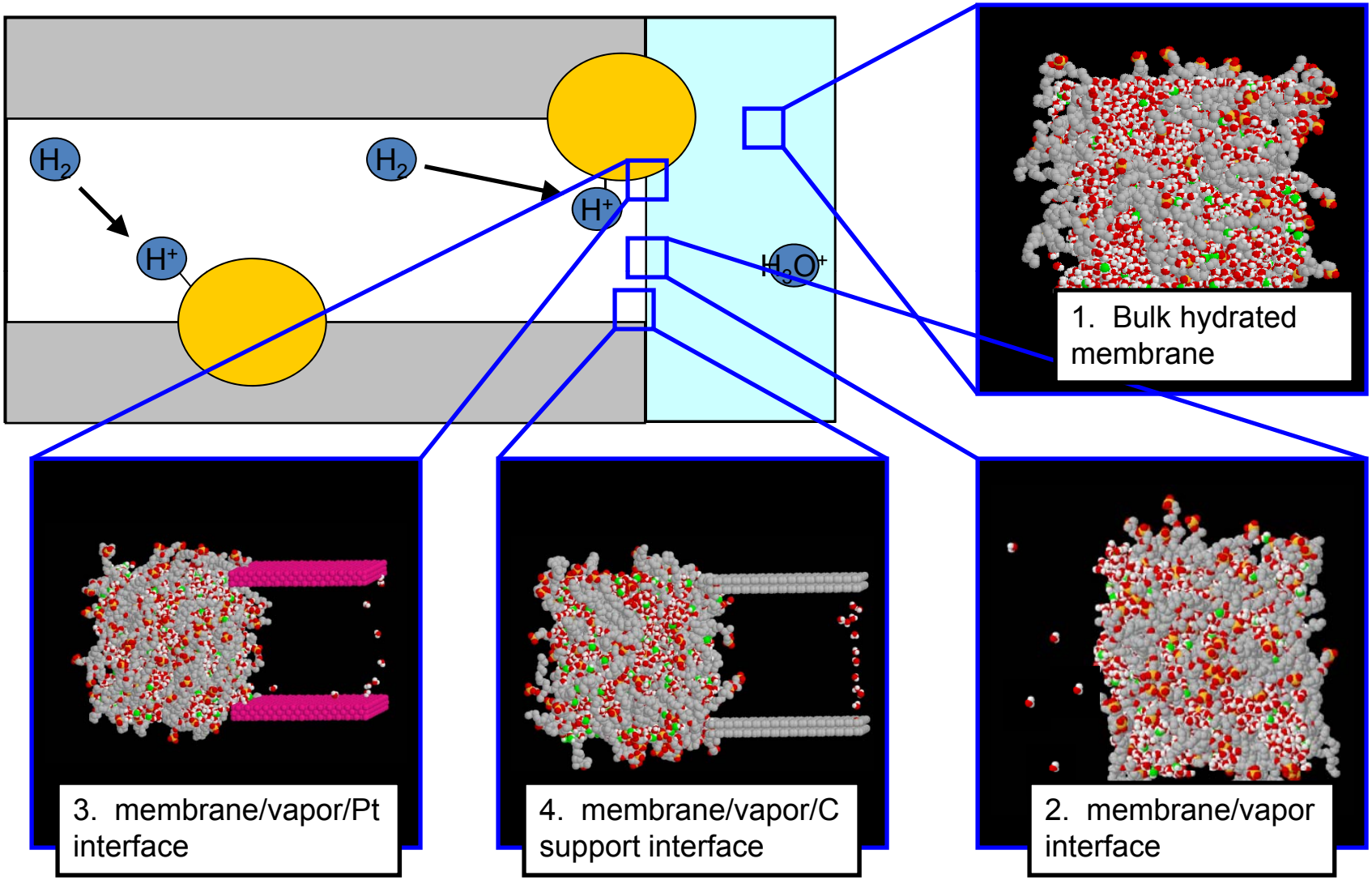

Simulation of Interfaces

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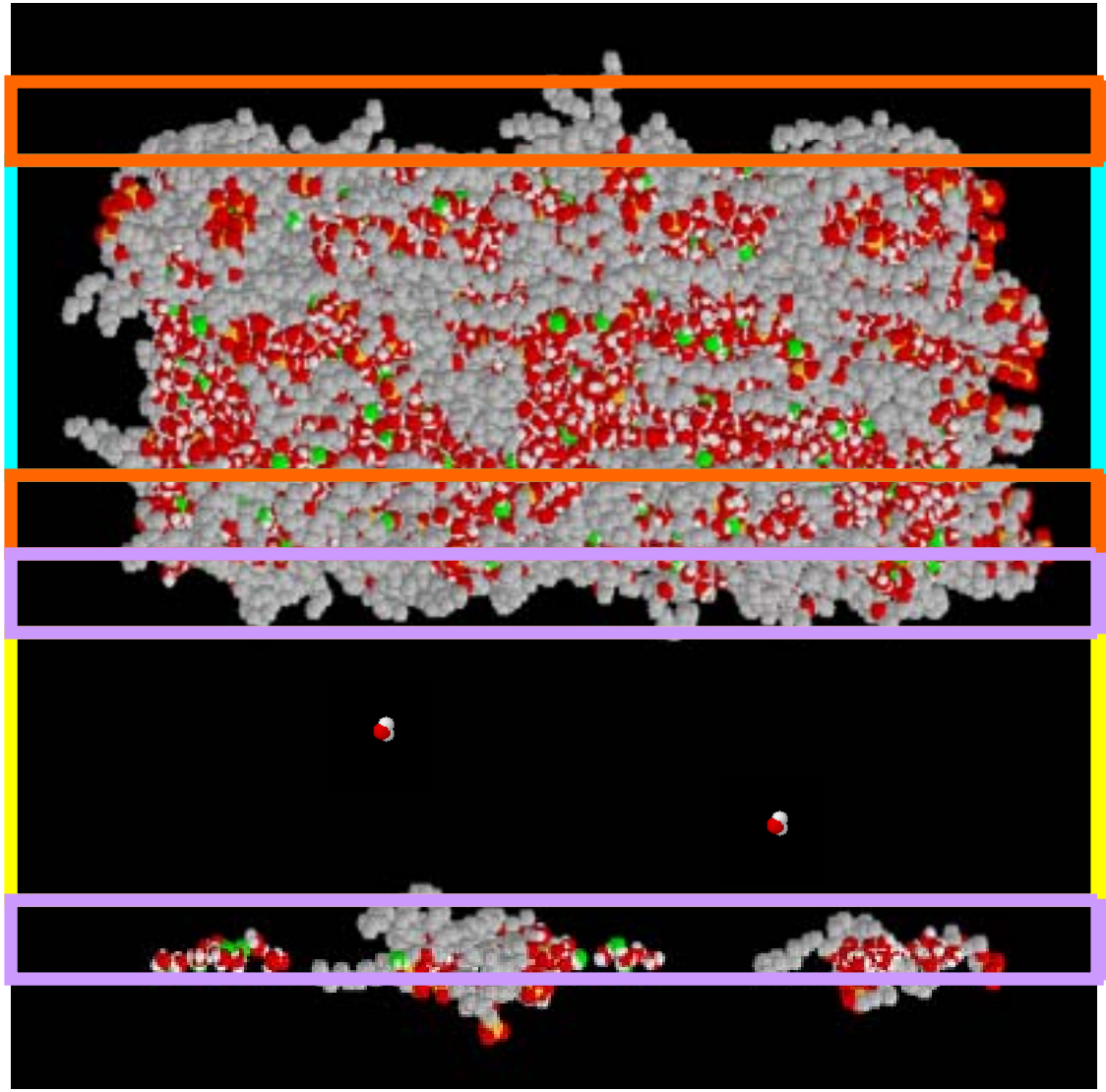
Nafion/vapor



Simulation of Interfaces

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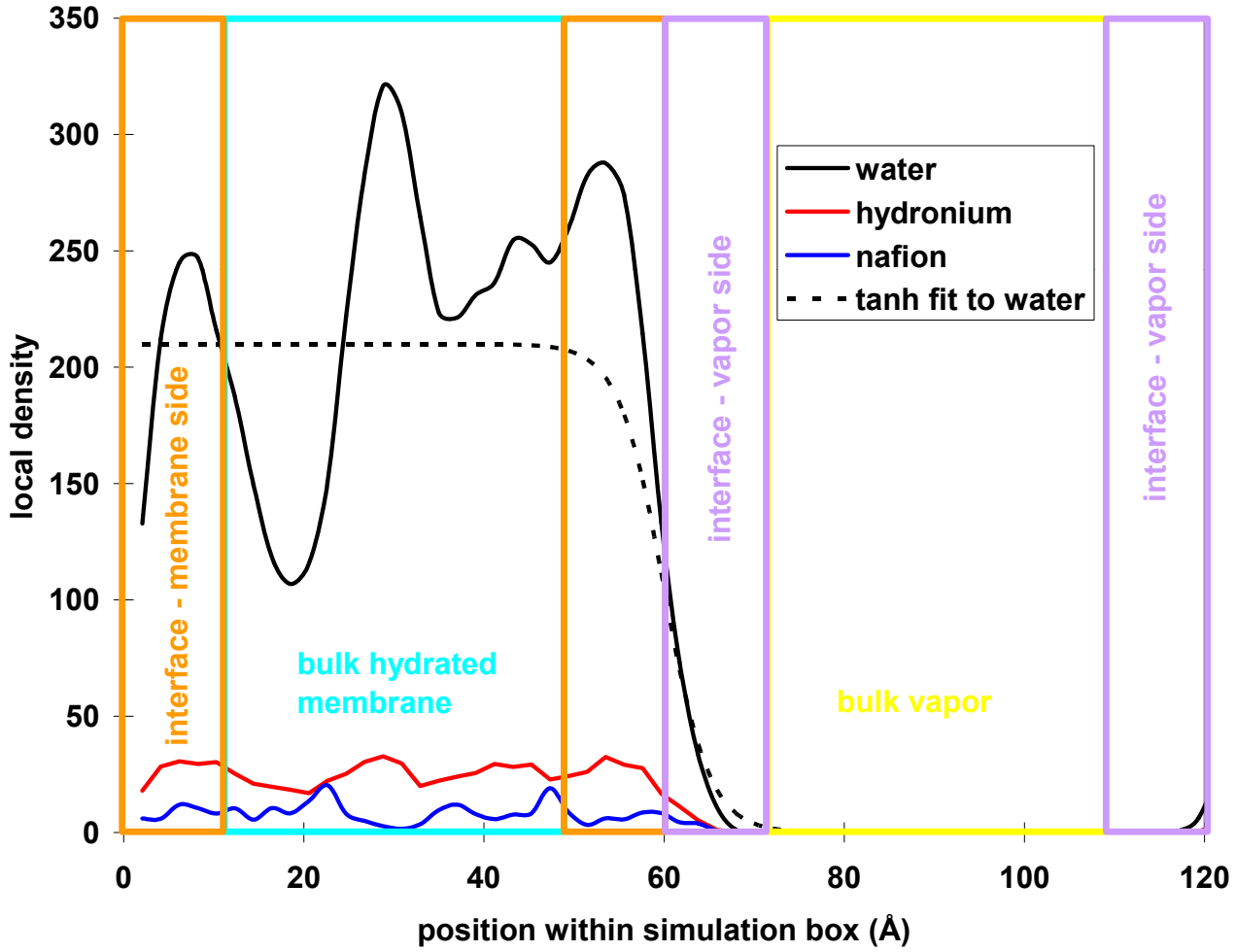
Density Profiles

Nafion/vapor



Simulation of Interfaces

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Density as a function of moisture level

Nafion/vapor

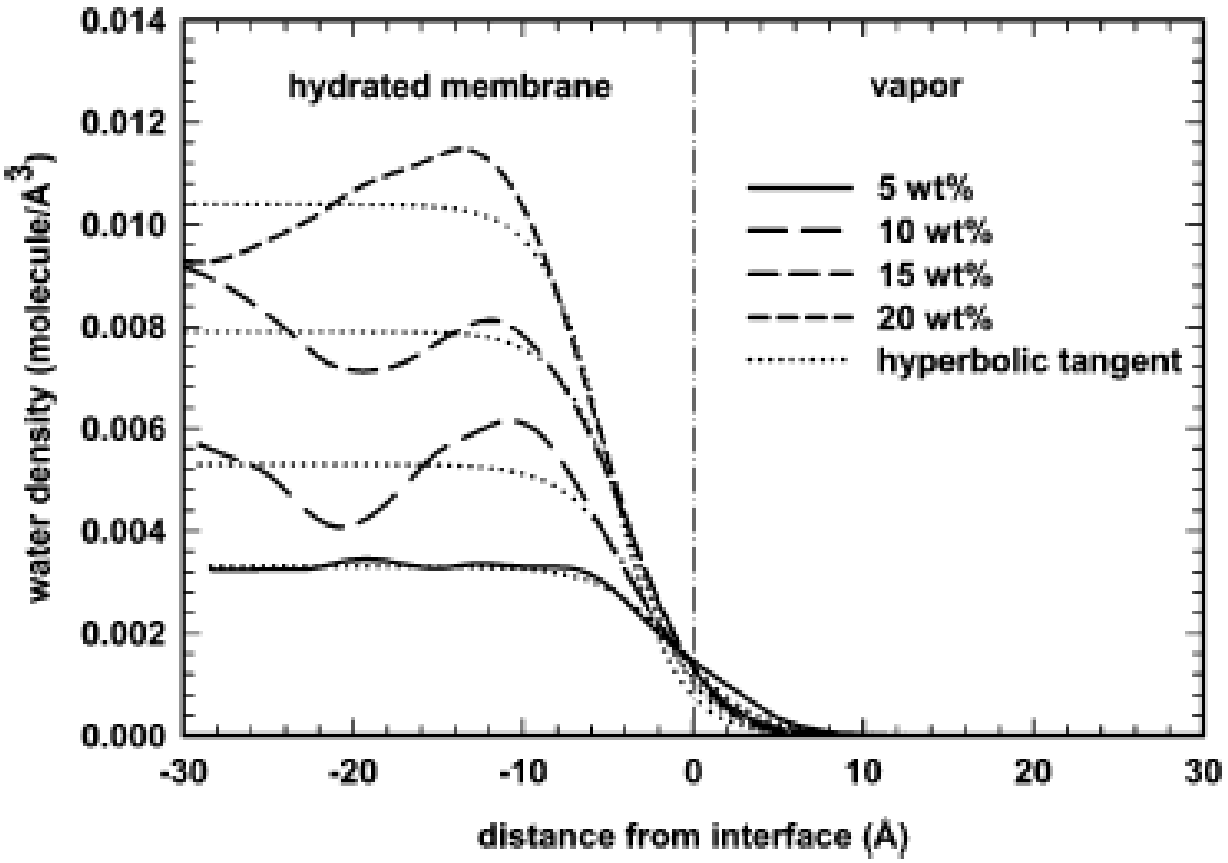

Figure 9. Density profile for water along the z direction with the hyperbolic tangent fitted for the water contents of 5 wt %, 10 wt %, 15 wt %, and 20 wt %.

Esai Selvan et al .J. Phys. Chem. C, 2008.

Simulation of Interfaces

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Hydronium ion hydration

Nafion/vapor

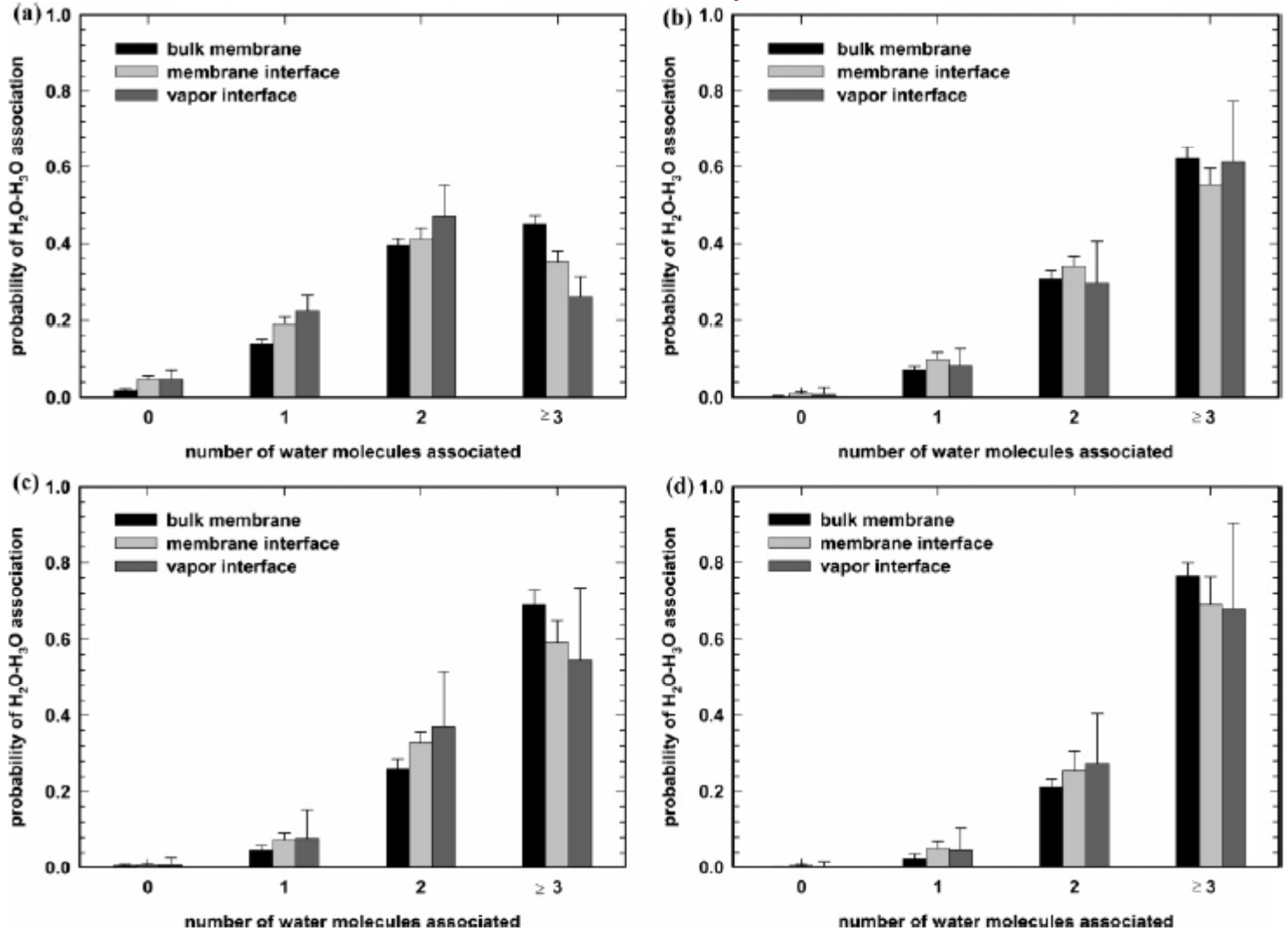

Figure 6. Distribution of hydrated hydronium complexes as a function of hydration number for water contents of (a) 5 wt %, (b) 10 wt %, (c) 15 wt %, and (d) 20 wt %.

Simulation of Interfaces

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Snapshots

Nafion/vapor

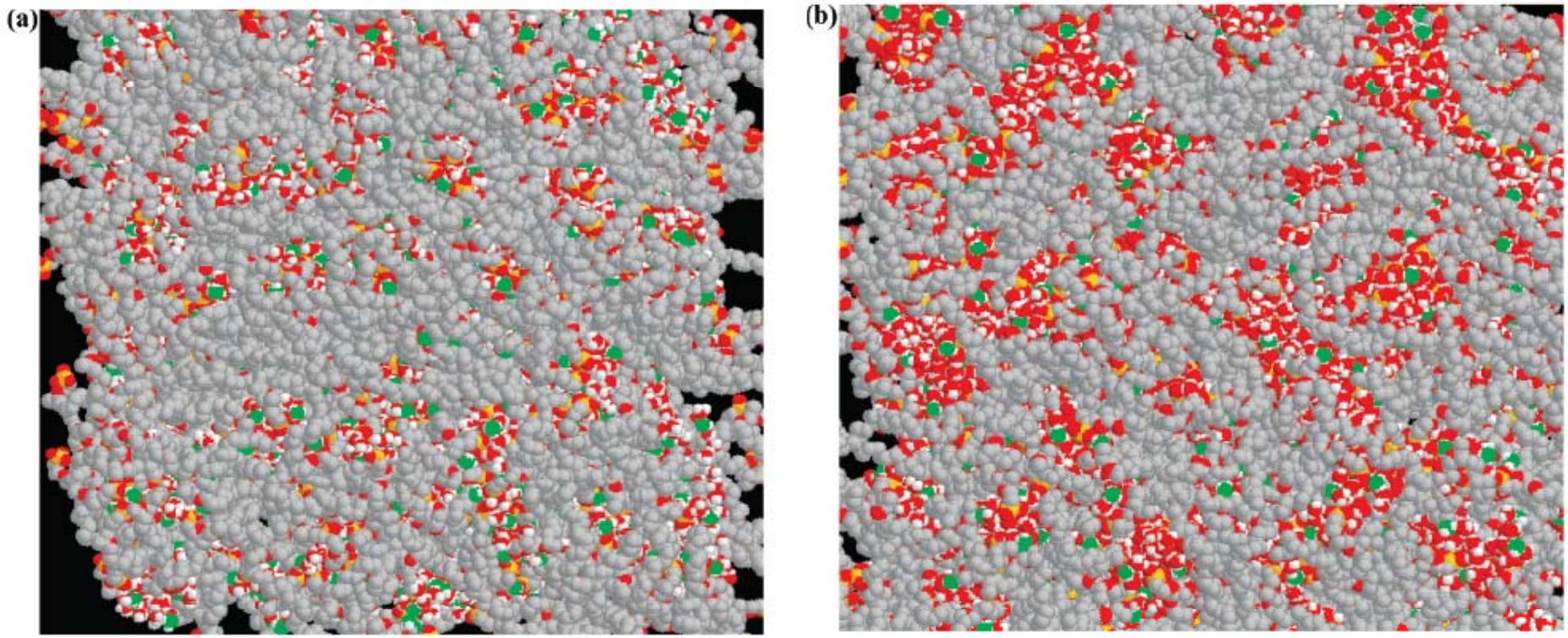

Figure 8. Snapshot taken normal to the interface from a MD simulation of hydrated Nafion at $T = 300$ K and nominal water contents of (a) 5 wt % and (b) 20 wt %. CF_2 and CF_3 pseudo-atoms are gray, H are white, S are orange, and O are red, except the O of H_3O^+, which are green for emphasis.

Esai Selvan et al .J. Phys. Chem. C, 2008.

Simulation of Interfaces

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Snapshots

Nafion/vapor

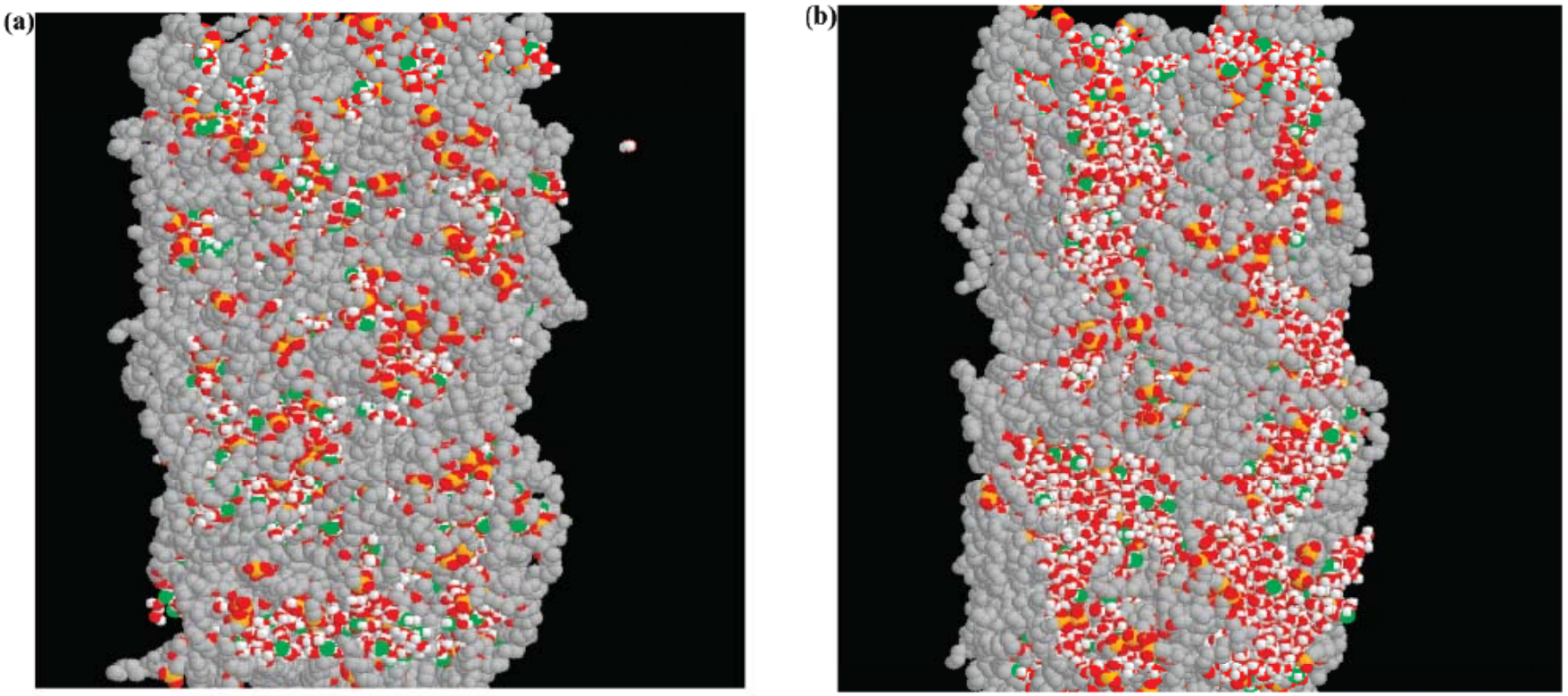

Figure 10. Snapshot taken parallel to the interface from a MD simulation of hydrated Nafion at $T = 300$ K and nominal water contents of (a) 5 wt % and (b) 20 wt %. CF_2 and CF_3 pseudo-atoms are gray, H are white, S are orange, O are red, except the O of H_3O^+, which are green for emphasis.

Esai Selvan et al .J. Phys. Chem. C, 2008.

Simulation of Interfaces

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Diffusion coefficients

Nafion/vapor

TABLE 4: Diffusion Coefficient of Hydronium Ions in the Interfacial Region, Perpendicular to the Interface[a]

water content (wt %)	$D_{\perp}^{BM}$ (10^{-11} m^2/s)	$D_{\perp}^{T}$ (10^{-11} m^2/s)	$\chi_{H_3O+}^{BM}$ (no unit)	$\chi_{H_3O+}^{I}$ (no unit)	ψ_z^{BM} (no unit)	ψ_z^{I} (no unit)	$D_{\perp}^{I}$ (10^{-11} m^2/s)
5	2.97	3.37	0.635	0.365	0.491	0.509	39.17
10	6.36	5.30	0.683	0.317	0.500	0.500	21.45
15	14.73	13.51	0.699	0.301	0.511	0.489	66.58
20	25.23	21.08	0.717	0.282	0.520	0.480	90.81

[a] $D_{\perp}^{BM}$, $D_{\perp}^{T}$, $D_{\perp}^{I}$: bulk membrane and total and interfacial diffusivity of the hydronium ions perpendicular to the interface. $\chi_{H_3O+}^{BM}$, $\chi_{H_3O+}^{I}$: fraction of hydronium ions in the bulk membrane and interfacial region. ψ_z^{BM}, ψ_z^{I}: length fraction of the bulk membrane and interfacial region.

TABLE 5: Diffusion Coefficient of Water in the Interfacial Region, Perpendicular to the Interface[a]

water (wt %)	$D_{\perp}^{BM}$ (10^{-10} m^2/s)	$D_{\perp}^{T}$ (10^{-10} m^2/s)	$D_{\perp}^{BV}$ (10^{-5} m^2/s)	$\chi_{H_2O}^{BM}$	$\chi_{H_2O}^{I}$	$\chi_{H_2O}^{BV}$	ψ_z^{BM}	ψ_z^{I}	ψ_z^{BV}	$D_{\perp}^{I}$ (10^{-10} m^2/s)
5	1.39	2.05	1.00	0.666	0.333	0.001	0.329	0.341	0.329	8.43
10	3.75	3.04	1.00	0.714	0.284	0.002	0.334	0.333	0.334	6.49
15	7.37	4.86	1.00	0.764	0.235	0.001	0.338	0.324	0.338	12.26
20	9.40	6.24	1.00	0.792	0.207	0.001	0.342	0.316	0.342	21.01

[a] $D_{\perp}^{BM}$, $D_{\perp}^{T}$, $D_{\perp}^{BV}$, $D_{\perp}^{I}$: bulk membrane, total, bulk vapor, and interfacial diffusivity of the water perpendicular to the interface. $\chi_{H_2O}^{BM}$, $\chi_{H_2O}^{I}$, $\chi_{H_2O}^{BV}$: fraction of water in the bulk membrane, interfacial, and bulk vapor region. ψ_z^{BM}, ψ_z^{I}, ψ_z^{BV}: length fraction of the bulk membrane, interfacial, and bulk vapor region.

There is no observed resistance to vehicular mass transfer at the membrane vapor interface.
There is likely a reduced structural diffusion of charge due to lower hydronium hydration.

Esai Selvan et al .J. Phys. Chem. C, 2008.

Simulation of Interfaces

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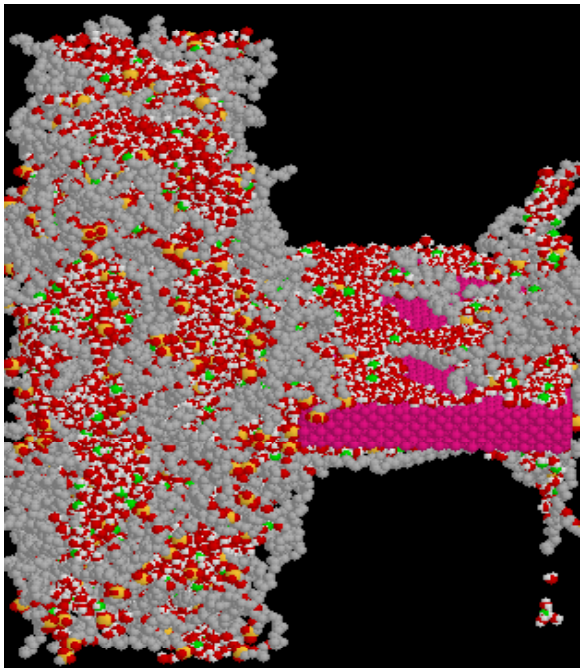
Snapshots

Nafion/vapor/catalyst(Pt)

λ = 3.44 (5 wt%)



λ = 11.83 (20 wt%)

CF = grey; O of H_2O and SO_3 = red; O of H_3O^+ = green;
S = orange; Pt = pink; H = white

There is no observed resistance to vehicular mass transfer at the membrane vapor interface.
There is likely reduced structural diffusion of charge due to lower hydronium hydration.

Liu et al .J. Phys. Chem. C, 2008.

Simulation of Interfaces

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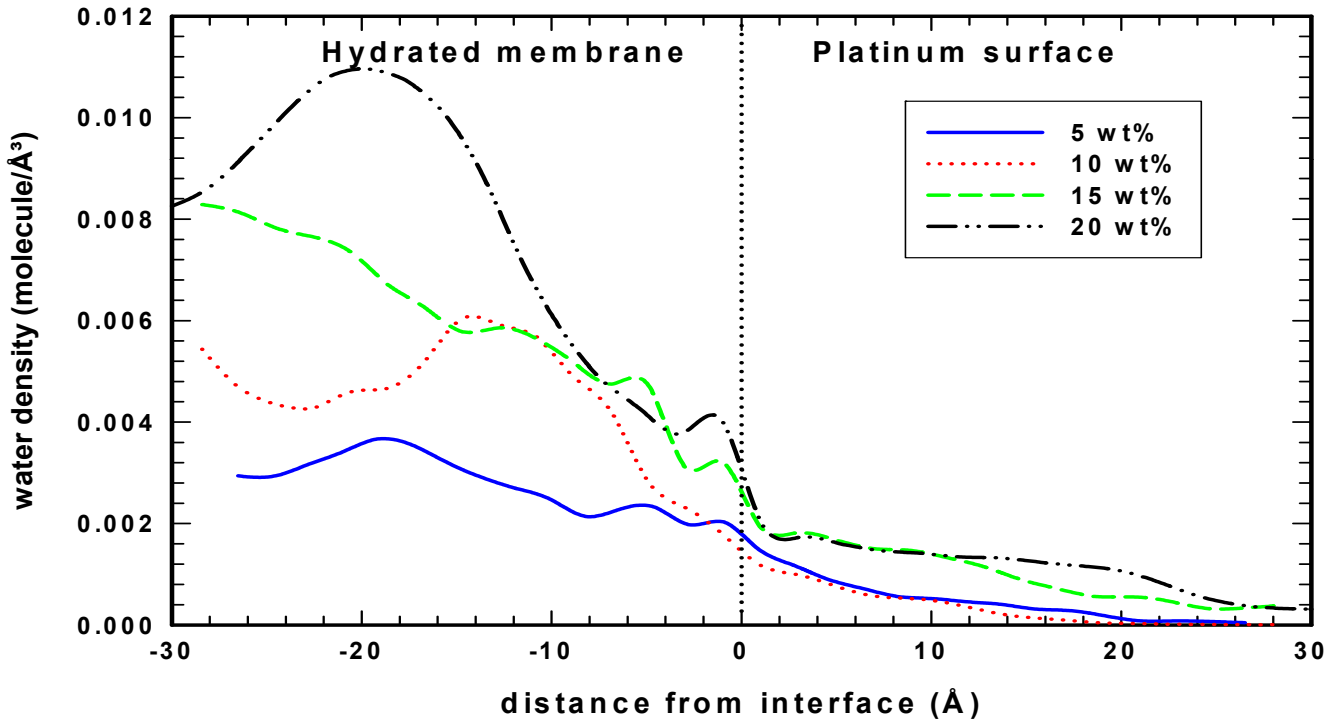
Nafion/vapor/platinum

density profile of H_2O



- a “dehydrated region” of the membrane near the interface
- a monolayer density of water on the catalyst surface

Liu et al .J. Phys. Chem. C, 2008.

Simulation of Interfaces

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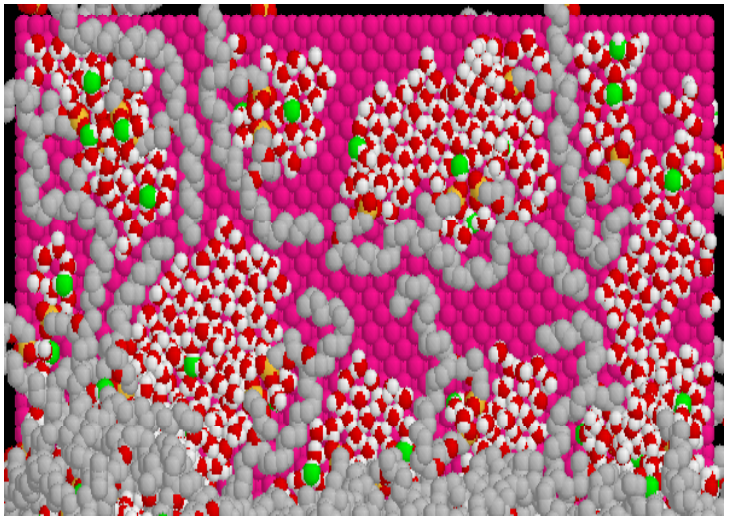
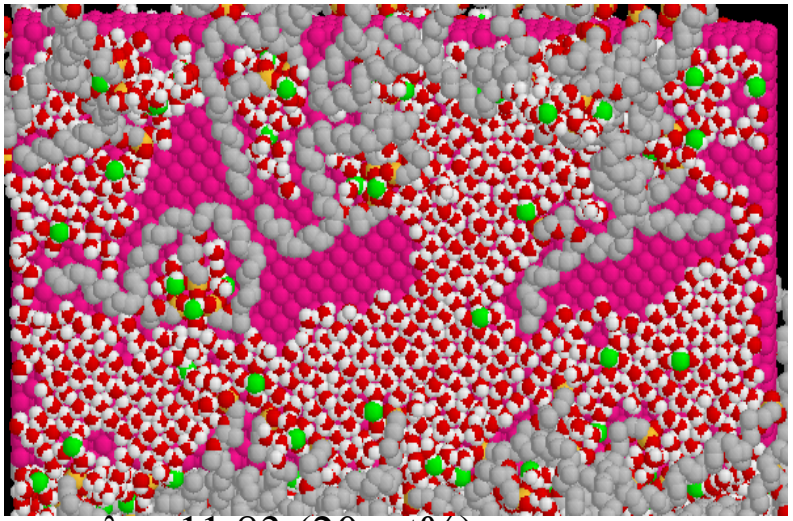
Nafion/vapor/platinum

snapshots of the catalyst surface



λ = 8.63 (15 wt%)



λ = 11.83 (20 wt%)

- each H_2O molecule has four nearest neighbors when the structure is stable
- the monolayer coverage of catalyst surface suggests H_2O molecules are from membrane phase, not from the vapor adsorption

Liu et al .J. Phys. Chem. C, 2008.

Simulation of Interfaces

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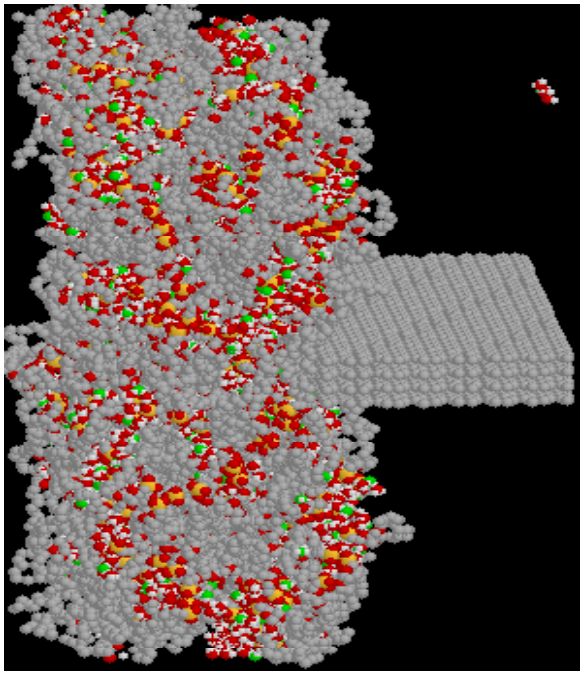
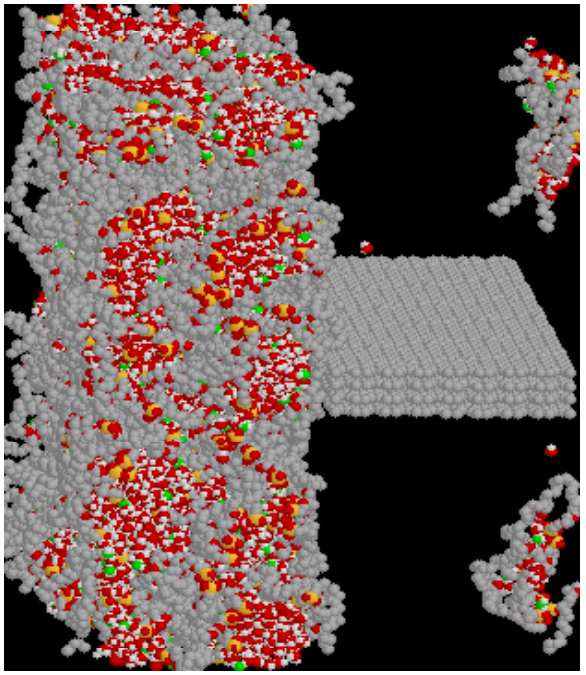
Nafion/vapor/graphite

simulation snapshots



λ = 3.44 (5 wt%)



λ = 11.83 (20 wt%)

CF_x and graphite = grey; O of H_2O and SO_3^- = red;
O of H_3O^+ = green; S = orange; H = white

Liu et al .J. Phys. Chem. C, 2008.

Simulation of Interfaces

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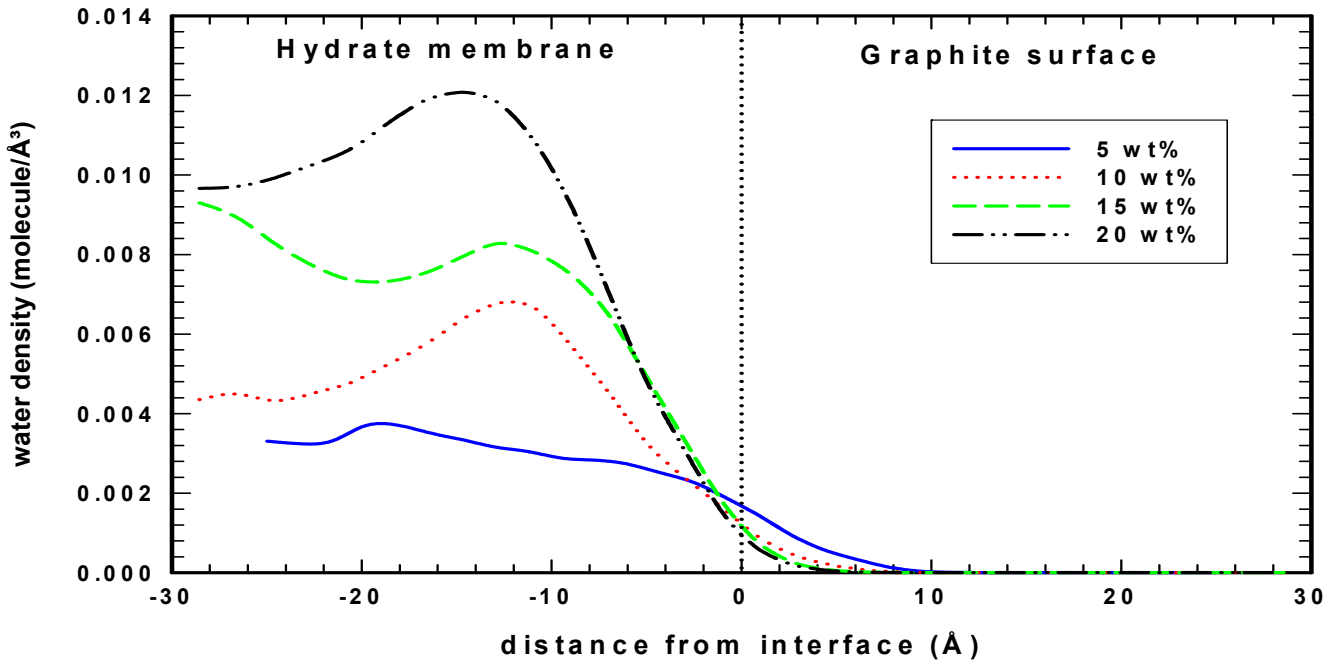
Nafion/vapor/graphite

density profile of H_2O



- a “dehydrated region” of the membrane near the interface
- no adsorption of H_2O on the graphite surface

Liu et al .J. Phys. Chem. C, 2008.

Simulation of Interfaces

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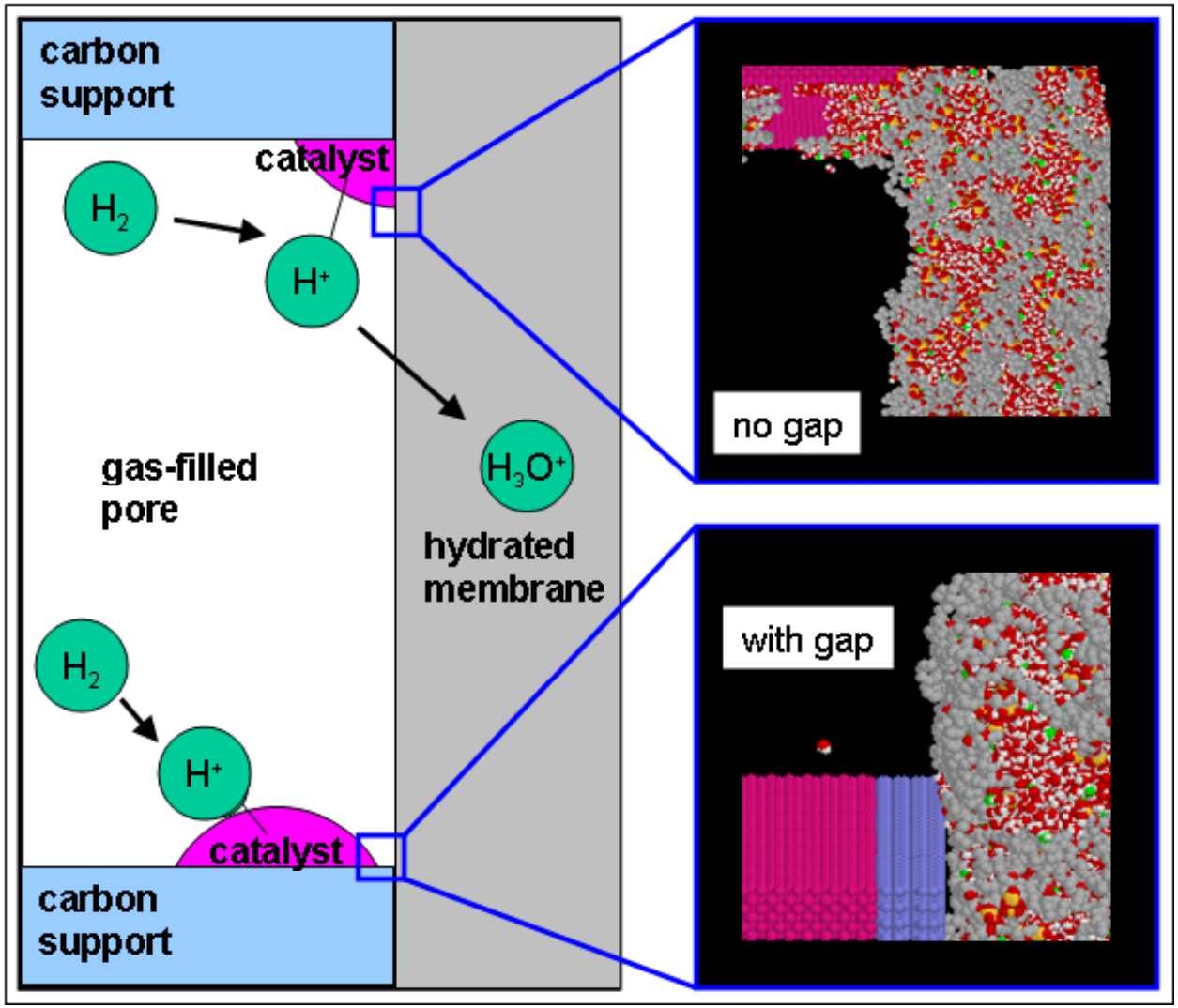
Can protons cross gaps?

Nafion/vapor/graphite/platinum



Liu et al .Fuel Cells, 2008.

Simulation of Interfaces

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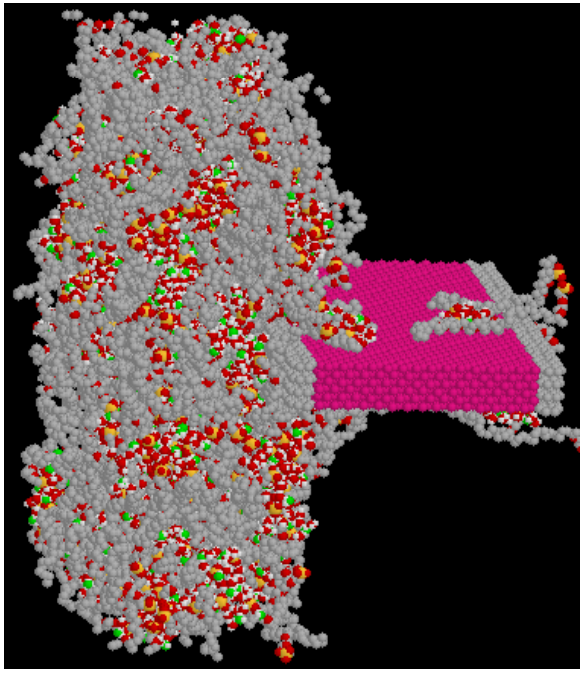
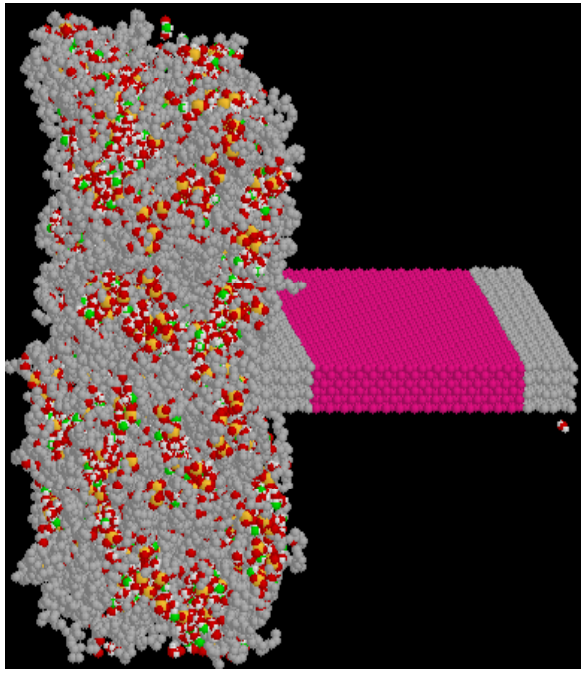
critical gap size



5 wt%, the gap size of graphite is 7.4 Å



5 wt%, the gap size of graphite is 14.8 Å

At all water contents studied, a gap of 15 Å is sufficient to completely disrupt proton transport.

Liu et al .Fuel Cells, 2008.

Conclusions

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Experiment and molecular simulation have given a pretty confident description of the molecular-level structure of electrode/electrolyte interface, including .

- a heterogeneous system, in which competition of three transport processes:
  (i) diffusion of molecular hydrogen to the catalyst surface,
  (ii) conduction of electrons from the anode, and
  (iii) diffusion of protons to the membrane
  are governed by the nanoscale structure of the interface.

- Molecular Dynamics simulation
  - membrane/vapor interface poses little resistance to vehicular component of transport
  - membrane/vapor/platinum interface is significantly wet by a mixture of water and ionomer
  - membrane/vapor/graphite interface is not wet by either water or ionomer
  - a small gap (~1 nm) between the catalyst and membrane is sufficient to disrupt proton transport.