~~Mesoscopic~~ Modeling of PEMFC Catalyst Layers

Pore Scale

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Outline

- **Overview**
  – Fuel cell 101, PDE, CFD
- **Macroscopic CL models**
  – Volume averaging method
- **Mesoscopic modeling**
  – Pore scale model

Wuhan
Beijing
北京
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(Tsingtao)
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Hangzhou
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成都
Chongqing
重庆
Guangzhou
广州
Hong Kong
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Kaohsiung
City
Taiwan
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Pyongyang
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Seoul
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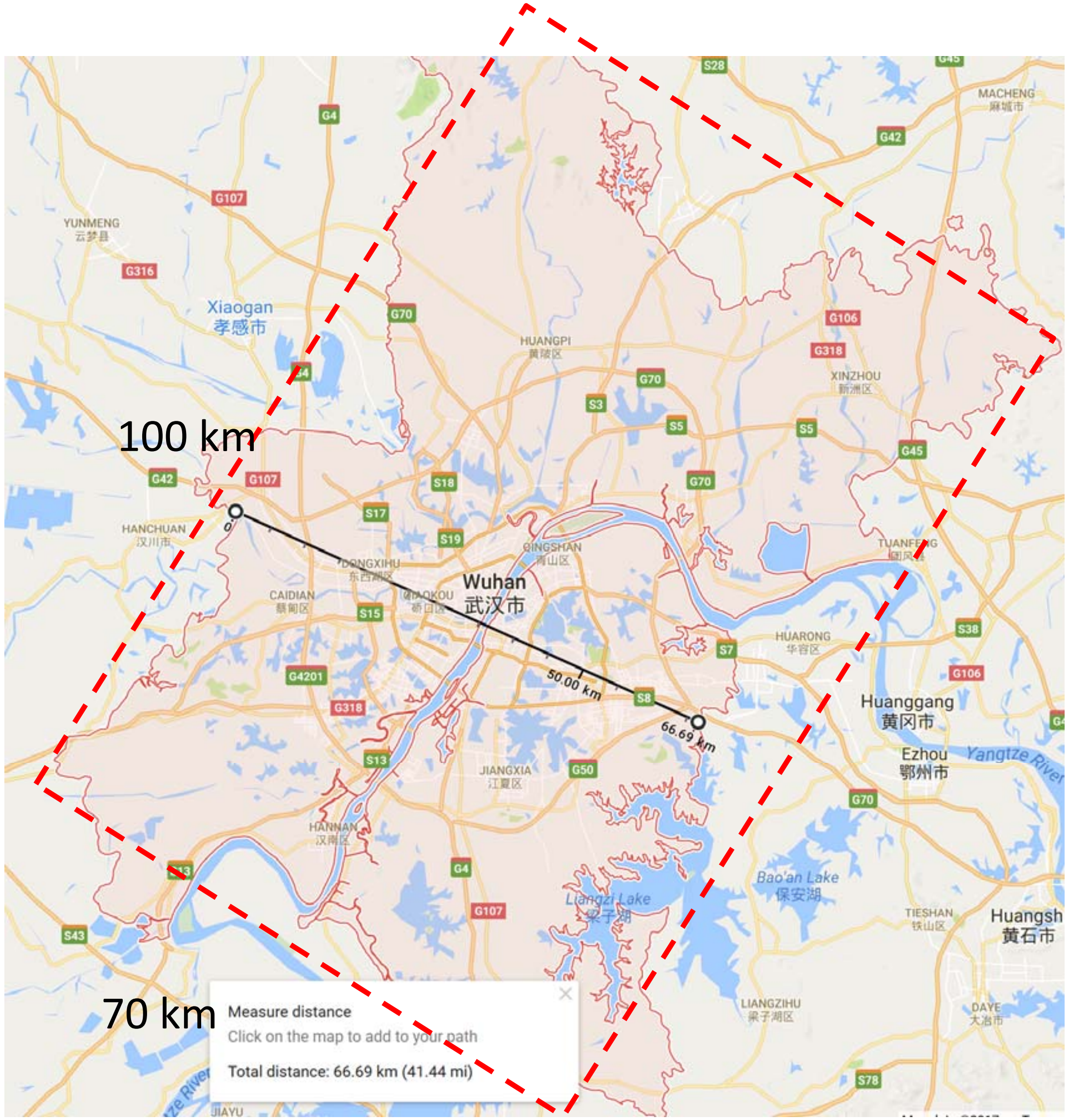
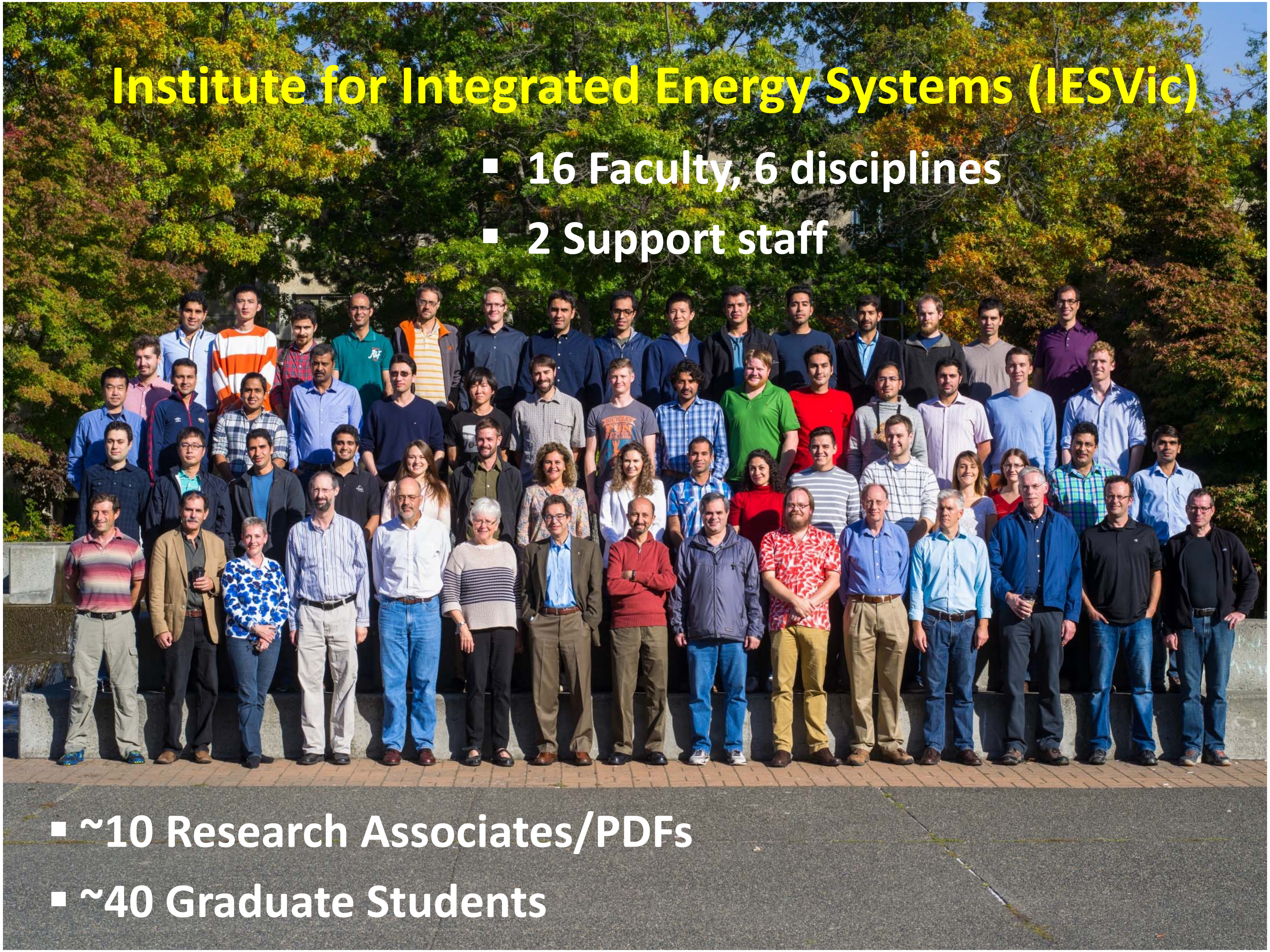
LIAONING
HEBEI
GANSU
SHANXI
SHAANXI
SHANDONG
HENAN
JIANGSU
HUBEI
ANHUI
SICHUAN
ZHEJIANG
GUIZHOU
HUNAN
JIANGXI
FUJIAN
YUNNAN
GUANGDONG
TSINGTAO

- **10+** million population （#6 in China)
- ~**1.3 million** university students (#1 in the world)
- One of four FC R&D1 clusters in China




Institute for Integrated Energy Systems (IESVic)
▪ 16 Faculty, 6 disciplines
▪ 2 Support staff
▪ ~10 Research Associates/PDFs
▪ ~40 Graduate Students

Research at IESVic

http://www.uvic.ca/iesvic

Energy systems

Renewable energy

Clean transportation

Energy technology

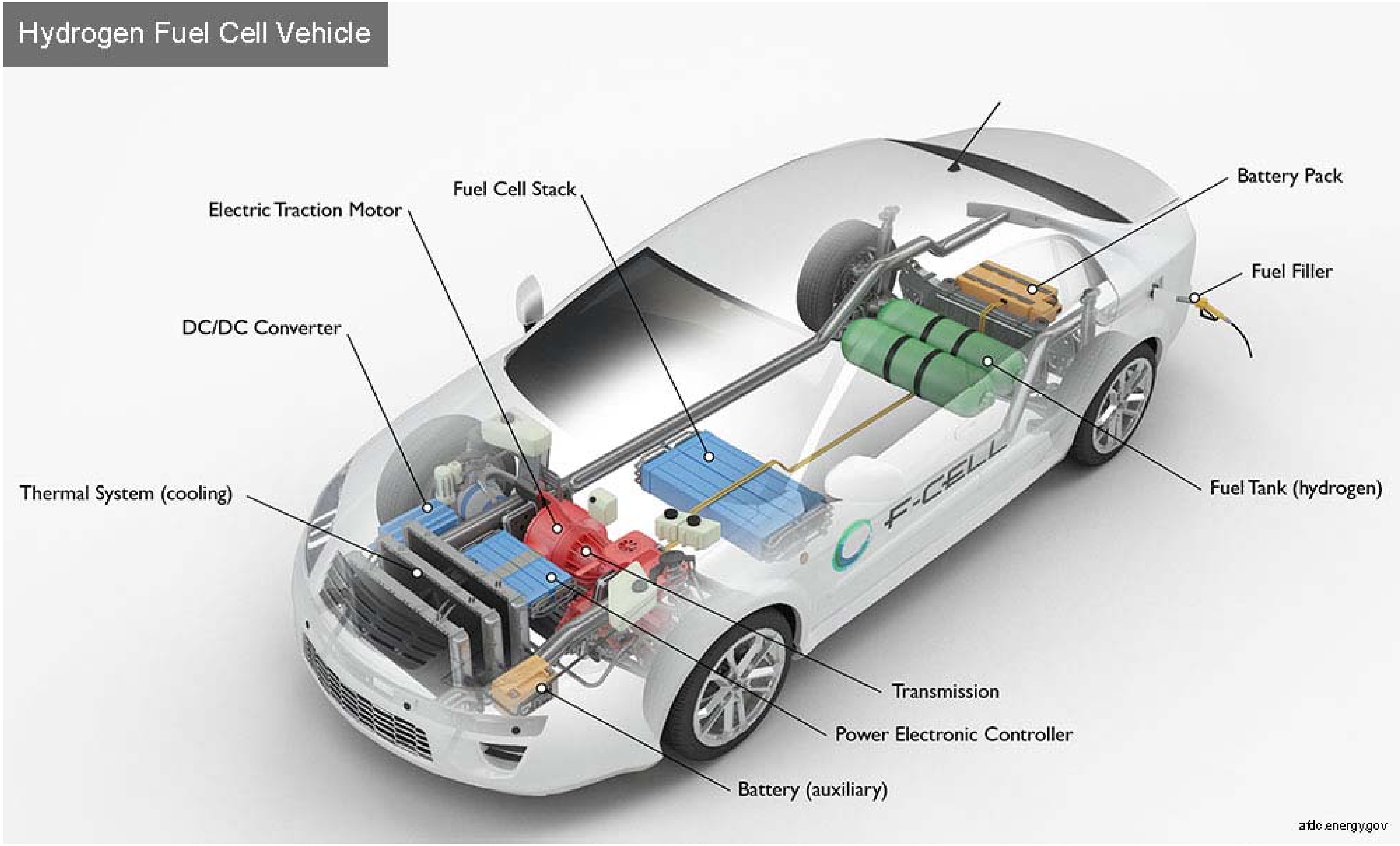
Sustainable communities

Human dimensions

EnVision 2019

May 2-3, 2019

Fuel Cell Vehicle (FCV)



https://afdc.energy.gov/vehicles/how-do-fuel-cell-electric-cars-work

Working principle: PEMFC

PEM = Proton Exchange Membrane

Hydrogen oxidation

$$H_2 \rightarrow 2H^+ + 2e^-$$

Oxygen reduction

$$2H^+ + 2e^- + \frac{1}{2}O_2 \rightarrow H_2O$$

Net reaction

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$$

Chemical energy →Electrical energy + Heat

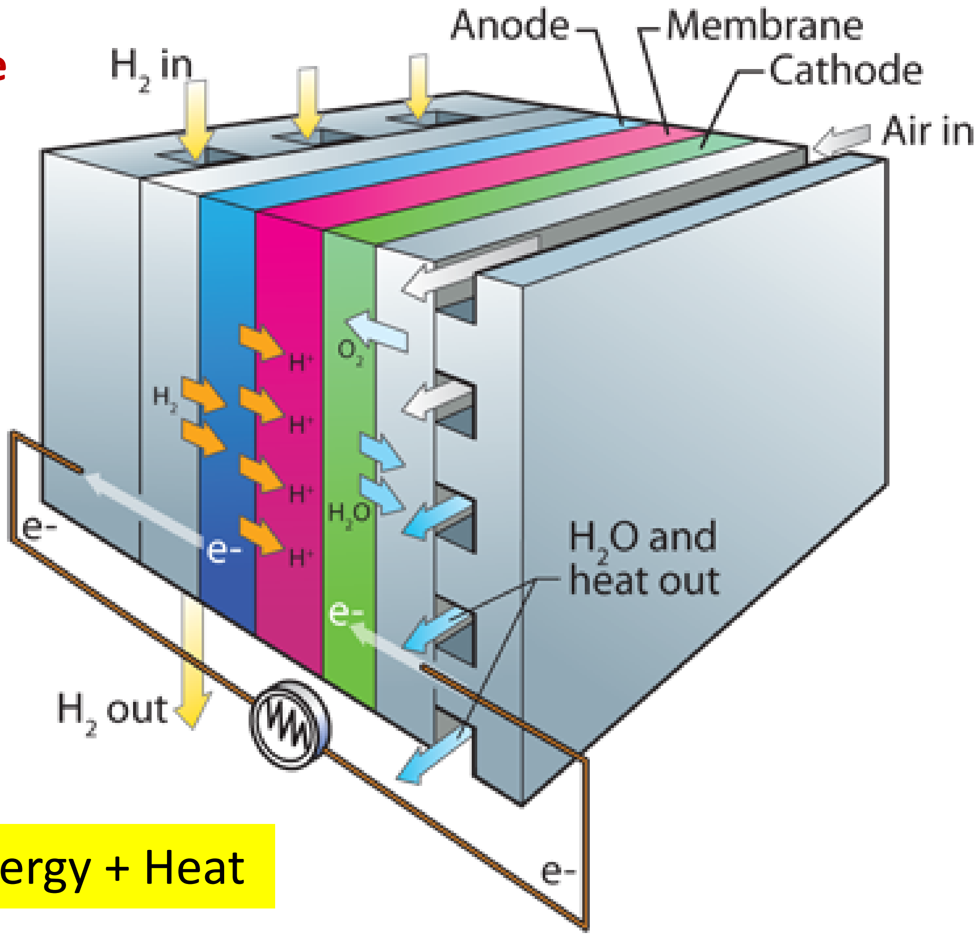
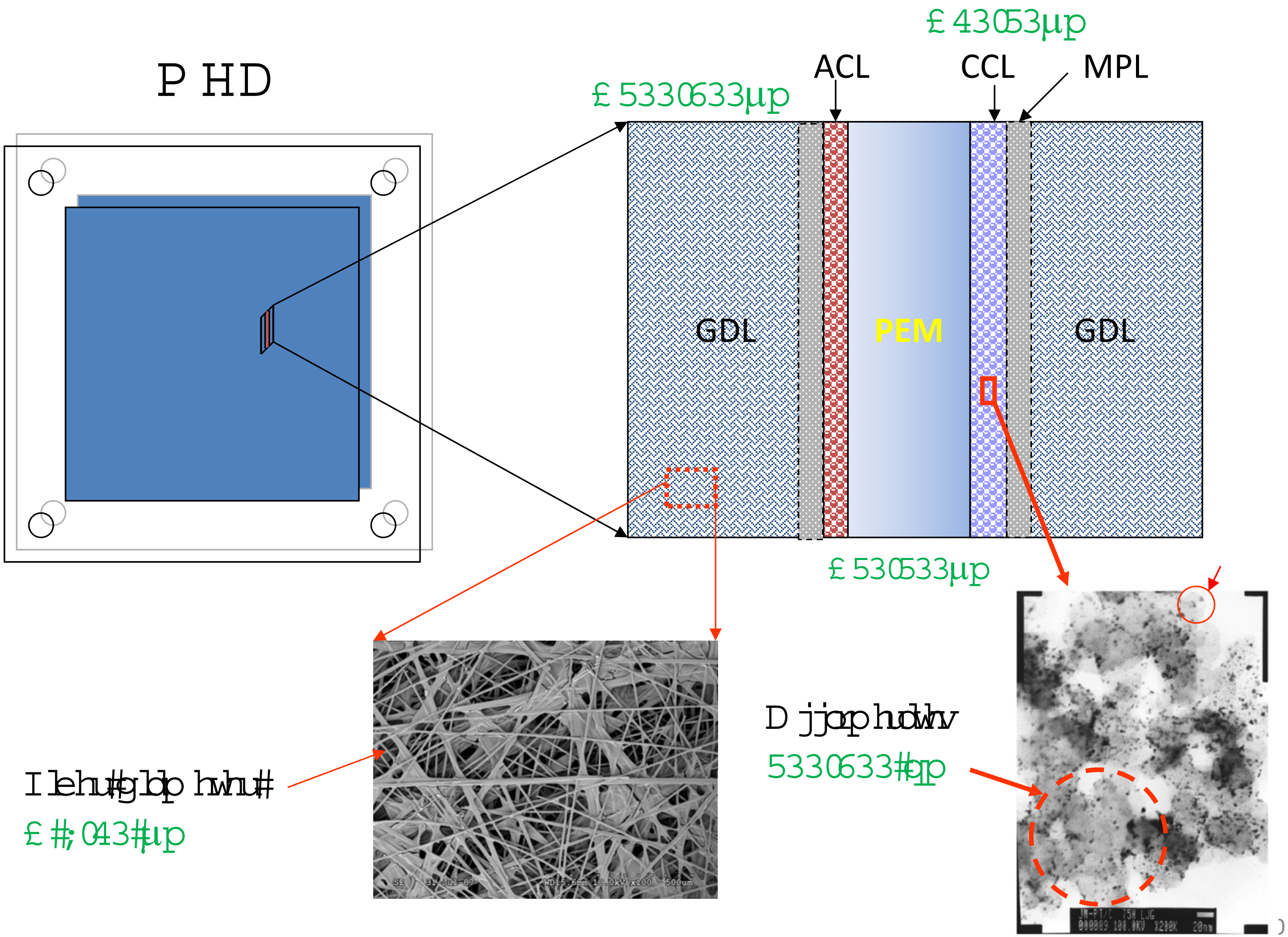
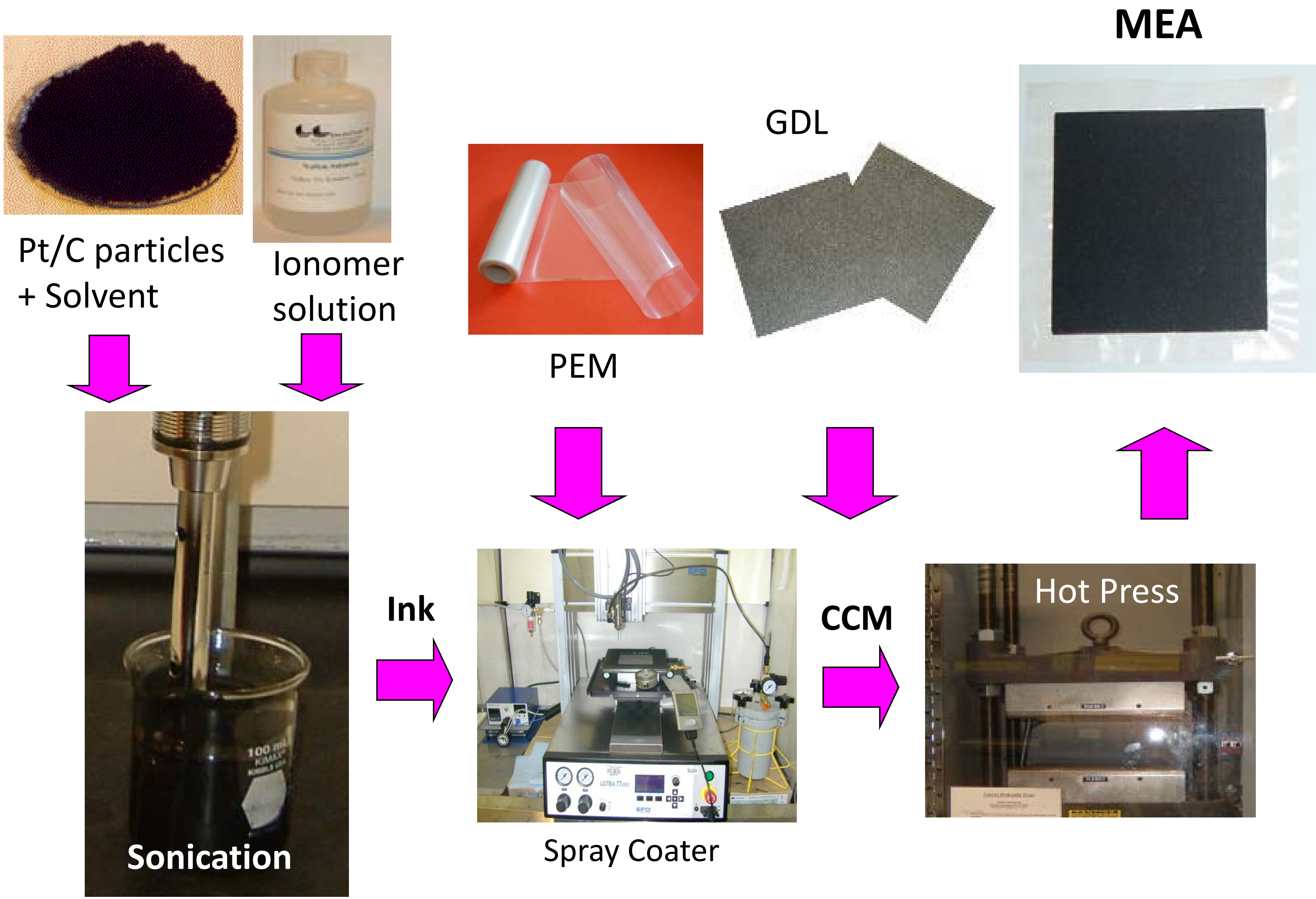


Image source: Los Alamos NL

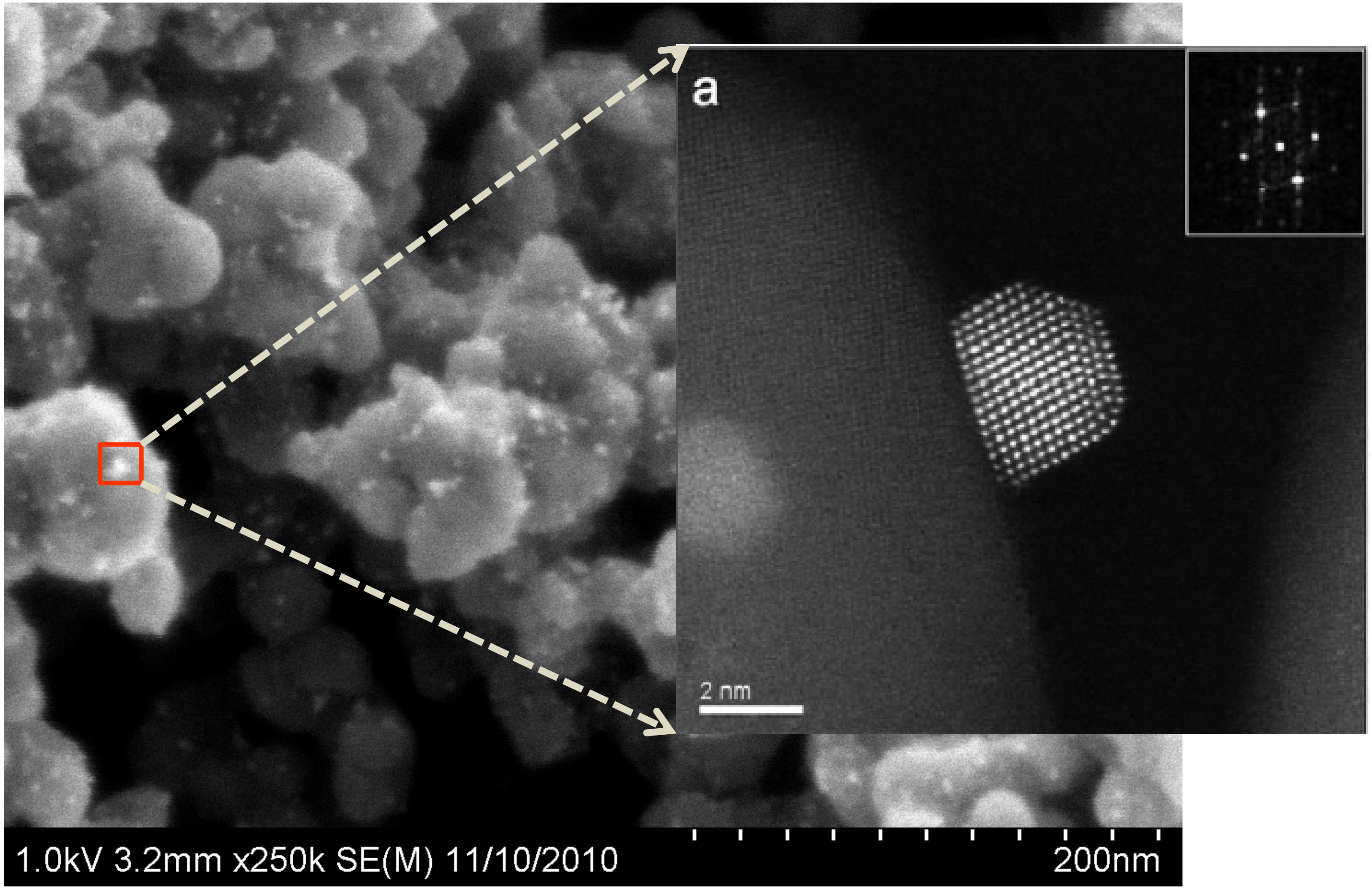
Membrane Electrode Assembly



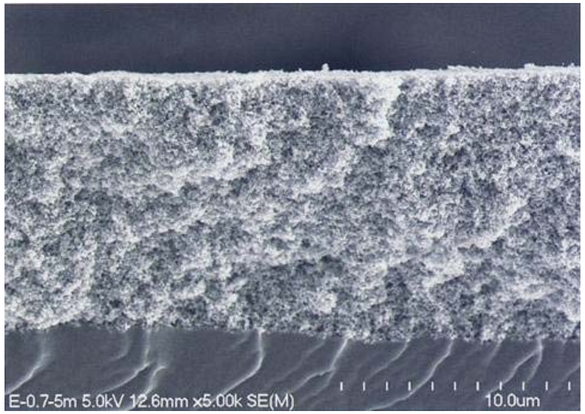
Steps to make MEAs



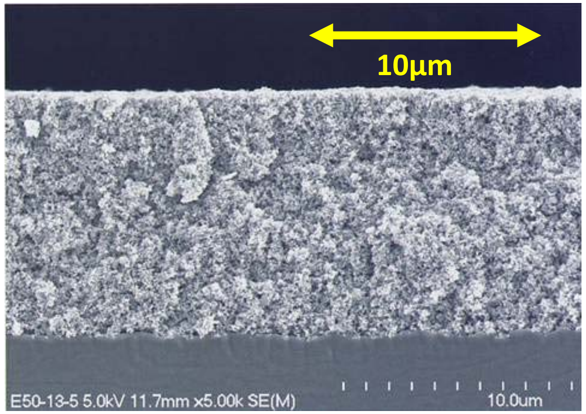
Catalyst layer



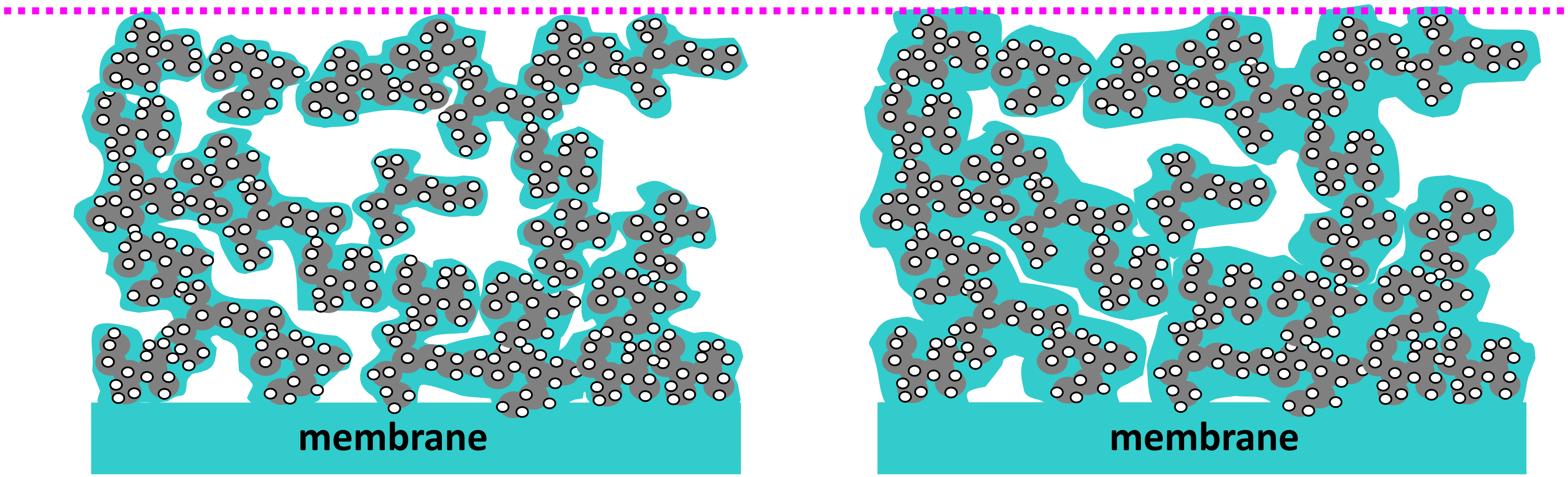
Microstructures



Low ionomer loading



High ionomer loading



LENGTH SCALES & TRANSPORT PROCESSES

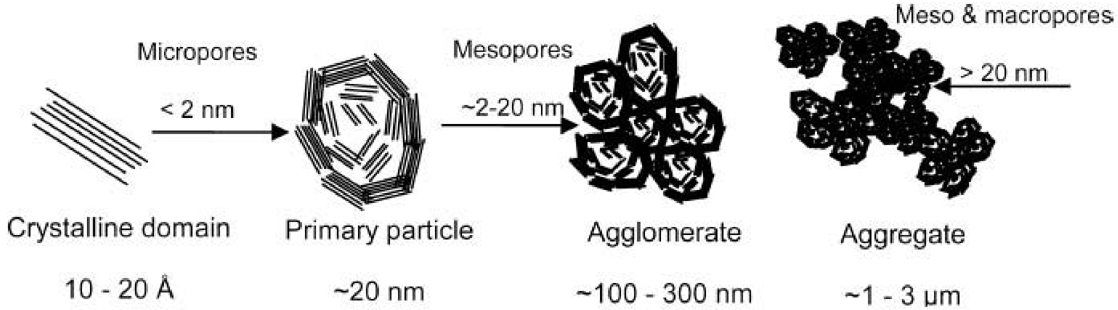


FIGURE 2. Schematic representation of the microstructures of carbon black supports: turbostratic crystalline domain, primary carbon particle, agglomerate, and aggregate of agglomerates. Representative micro-, meso-, and macropores are indicated by arrows.

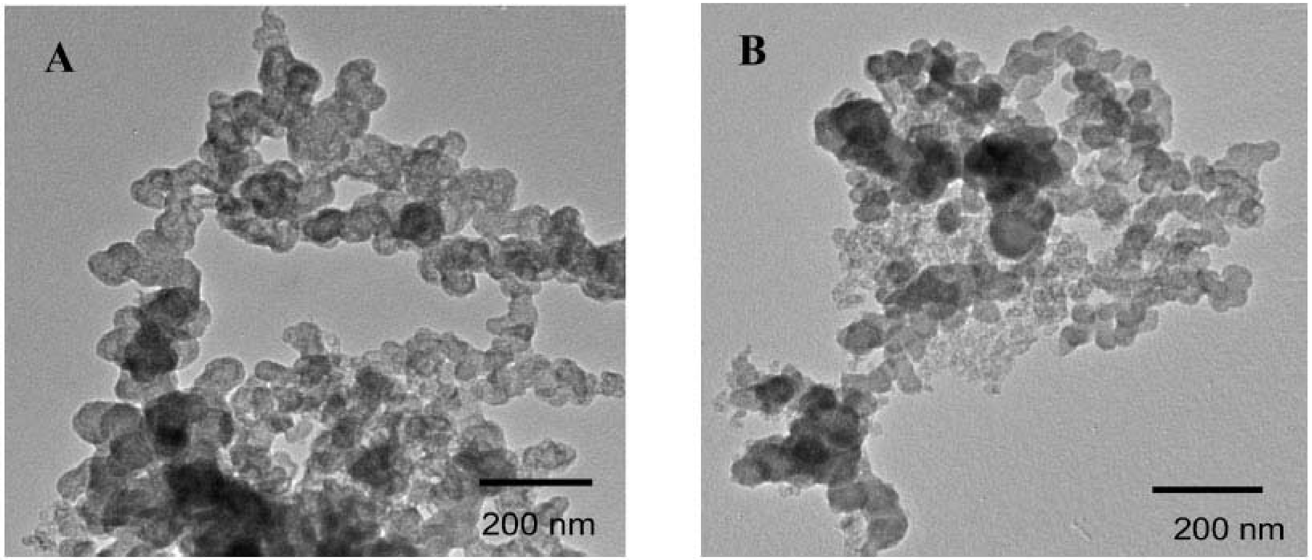
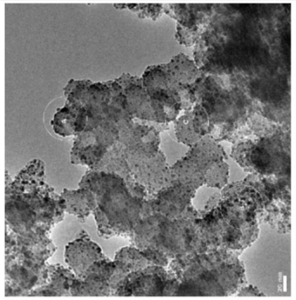


FIGURE 3. TEM micrographs of (a) Ketjen Black and (b) Vulcan XC-72 carbon aggregates.

Source:

On the Micro-, Meso-, and Macroporous Structures of Polymer Electrolyte Membrane Fuel Cell Catalyst Layers, Soboleva et al., (SFUF, NRC-IFCI), 2010, ACS Applied Materials & Interfaces



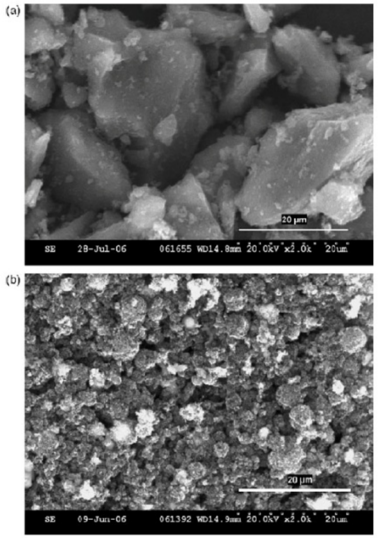
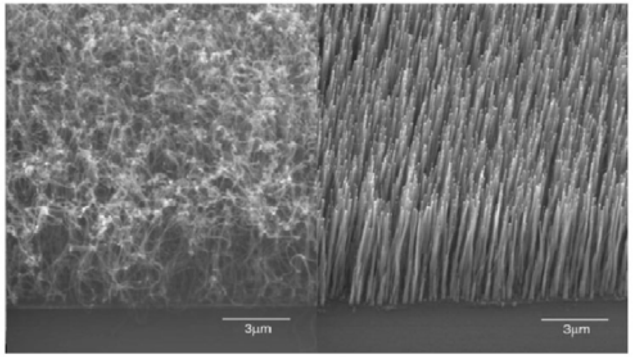
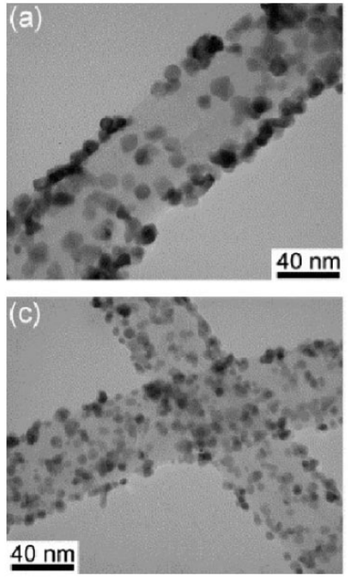


Figure 20.4. Scanning electron micrographs of a) aggregates obtained in a conventional electrocatalyst synthesis and b) aggregate size distribution of the electrocatalyst powders obtained by spray conversion. (Images courtesy of NRC-IFCI.)





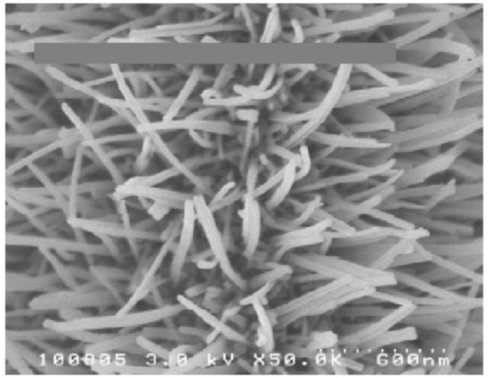


Figure 20.16. As-grown 3M, PR149 whiskers. (Image reproduced courtesy of 3M Corporation.)

Source:
Spray-based and CVD processes for synthesis of fuel cell catalysts and thin catalyst layers, R. Maric (NRC-IFCI)

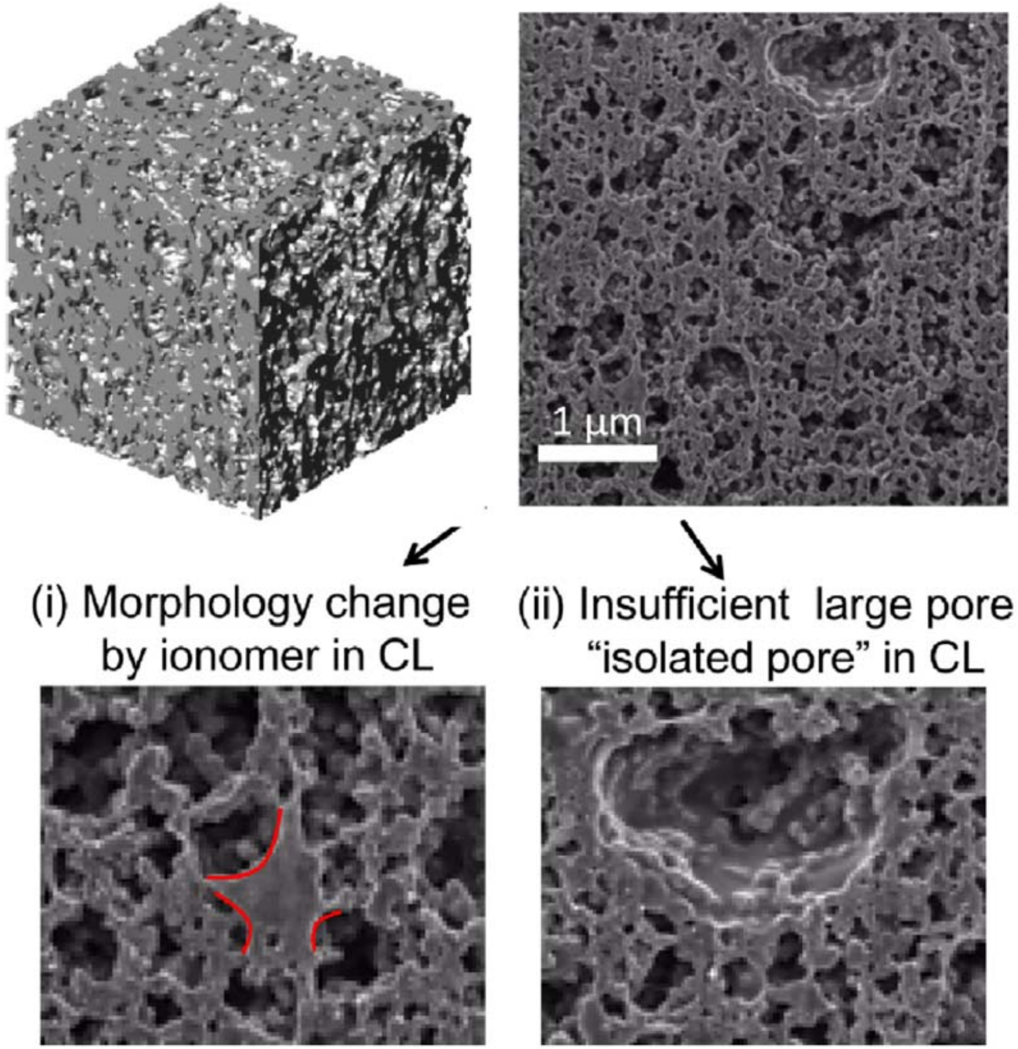
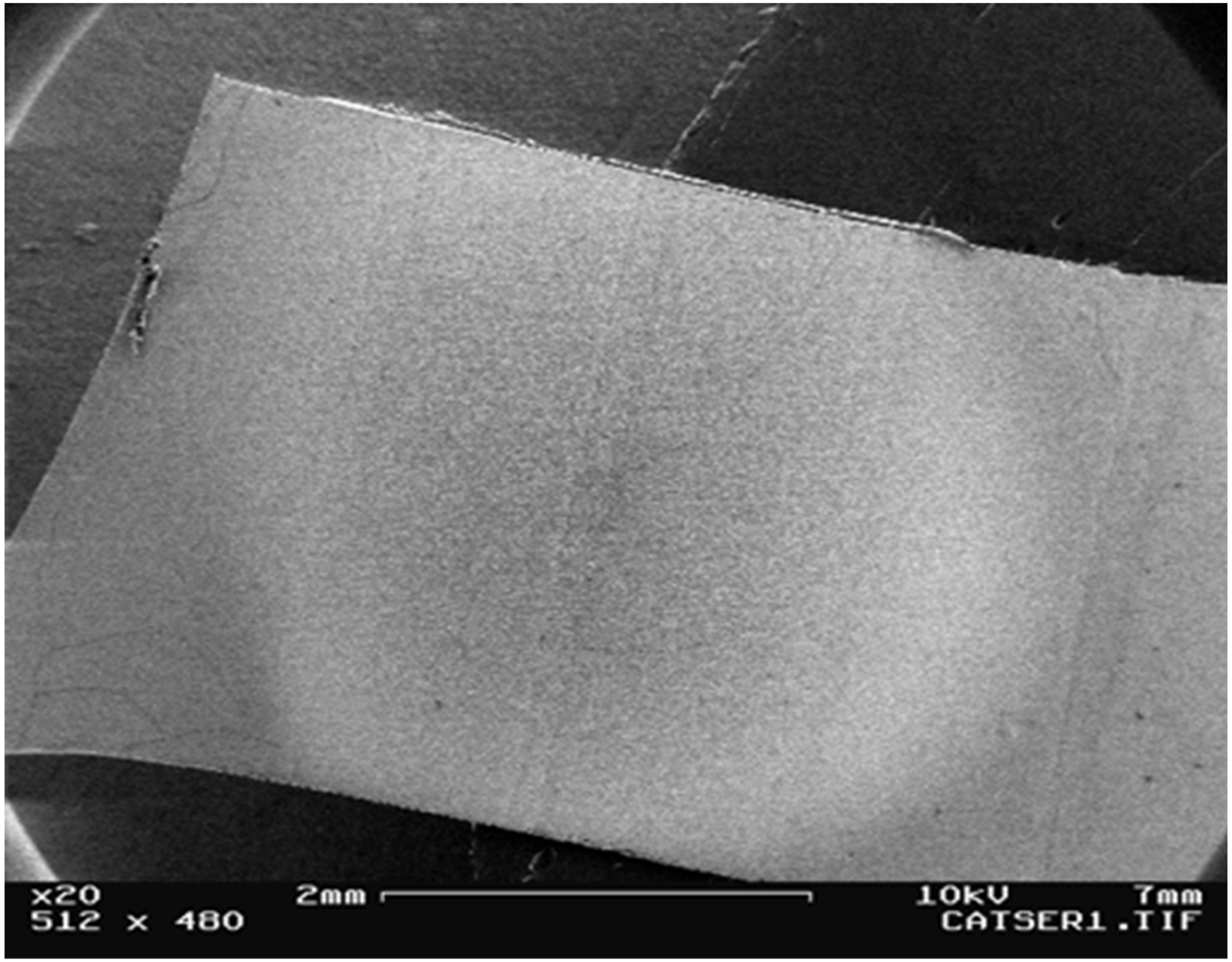


Fig. 2 – Cross-sectional view of CL obtained by FIB-SEM from Inoue et al. [32].

"Understanding formation mechanism of heterogeneous porous structure of catalyst layer in polymer electrolyte fuel cell", Gen Inoue, Motoaki Kawase, International Journal of Hydrogen Energy 41(2016)21352-21365

SEM images at different magnifications

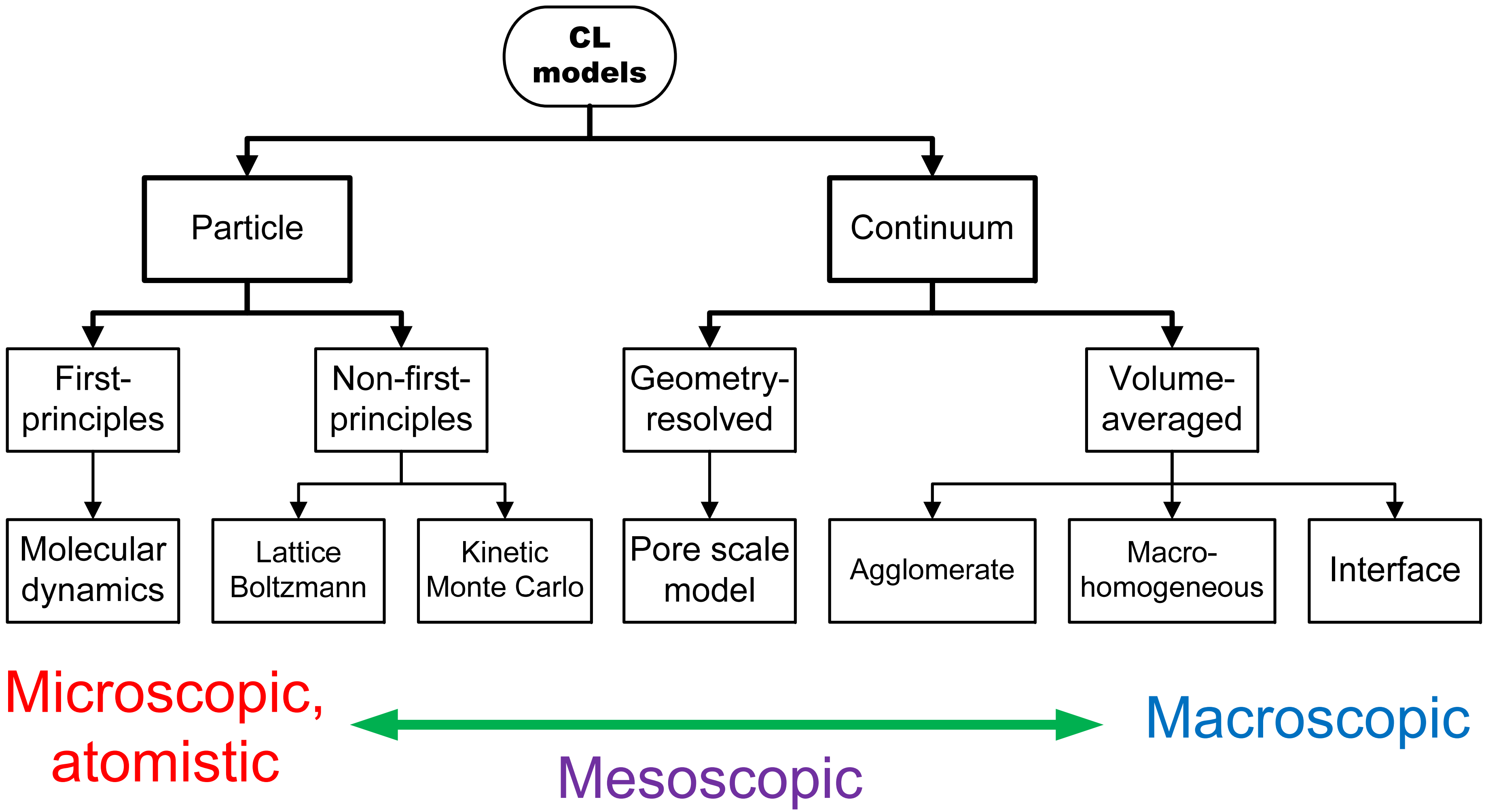


Quantitative description of porous media

- **Process-independent**
  - Porosity, tortuosity
  - Pore size distribution
  - Multi-point statistics*
- **Process-dependent**
  - Effective transport properties
  - Effectiveness

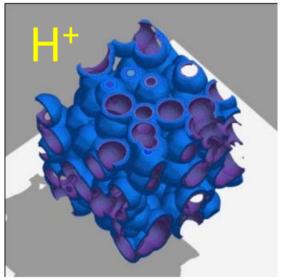
** "Stochastic Characterization and Reconstruction of Porous Media", Lalit Mohan Pant, Ph.D. dissertation, University of Alberta, 2016*

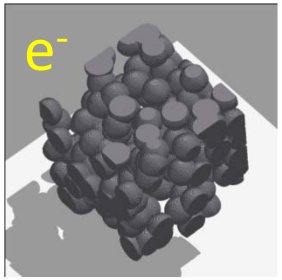
Classification of CL models

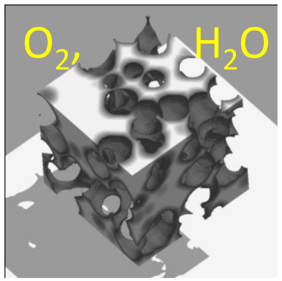


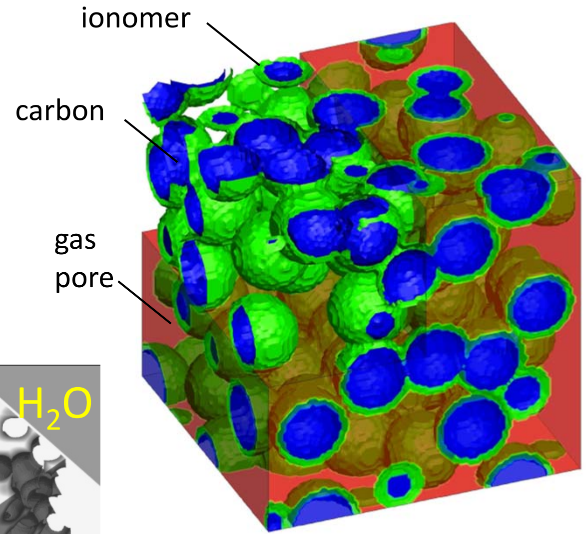
Salient features of transport phenomena in PEMFC catalyst layer

- Multiple species in separated phases
- Reactions taking place at phase boundaries
- Transport closely coupled
- Water exists in different forms

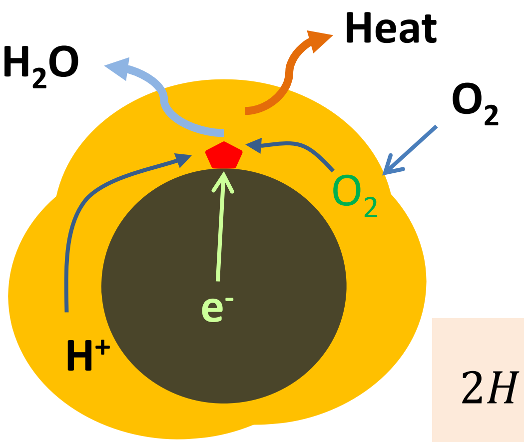






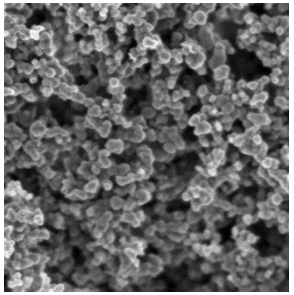


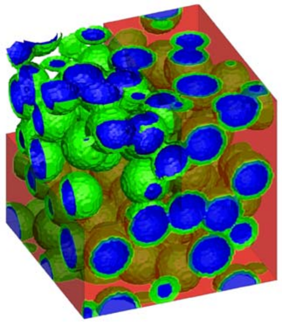
Cathode CL

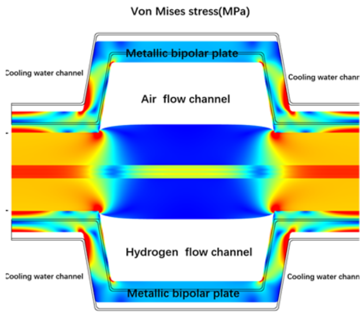


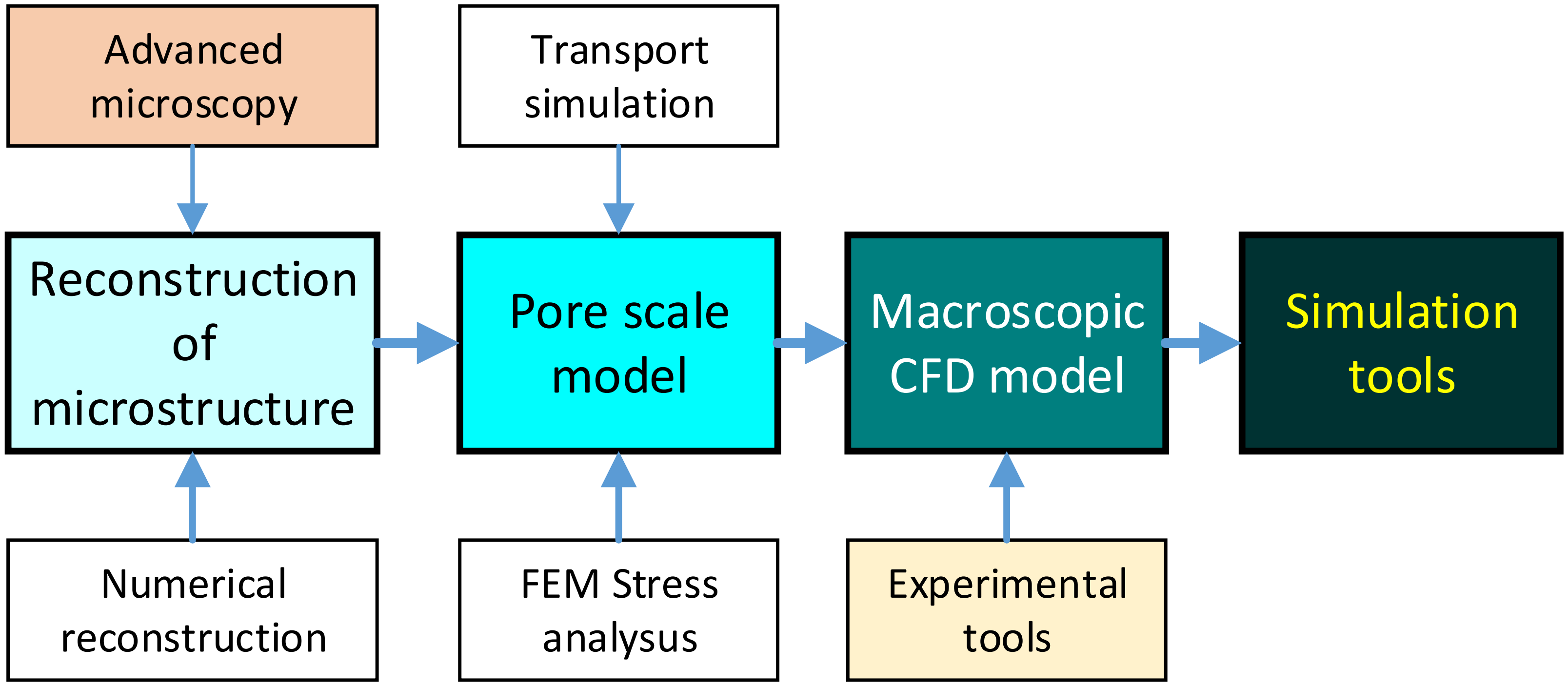
$$2H^{+} + 2e^{-} + \frac{1}{2}O_2 \rightarrow H_2O$$

Multi-scale approach









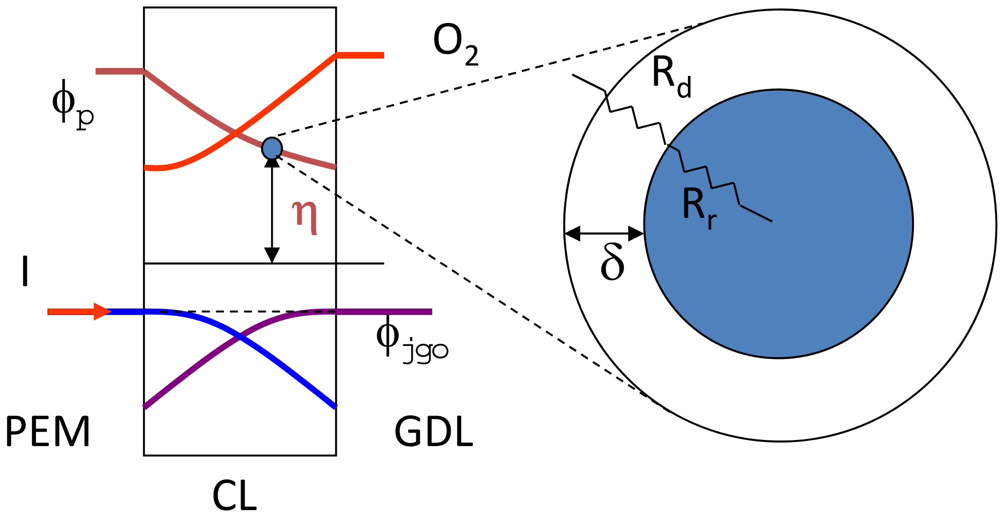
MACROSCOPIC CL MODELS

Macroscopic CL models

- Zero-dimension (interface) model
- Macro-homogeneous model
  - CL flooded and treated as homogeneous medium
- Agglomerate model
  - CPt assumed to form spherical agglomerates
  - Effectively a two-scale model

$$\nabla i = nF\left[\frac{1}{\dfrac{\delta}{aC^{*}_{O_2}D_{eff}} + \dfrac{1}{kE}}\right]$$

None of these models accounts for the true microstructure of CLs



Zero-dimension (interface) model

Molar flow rate:

$$N_{H_2} = \frac{I}{2F}$$

$$N_{O_2} = \frac{I}{4F}$$

$$N_{H_2O} = \frac{I}{2F}$$

Mass flow rate:

$$m_{H_2} = \frac{I}{2F} M_{H_2}$$

$$m_{O_2} = \frac{I}{4F} M_{O_2}$$

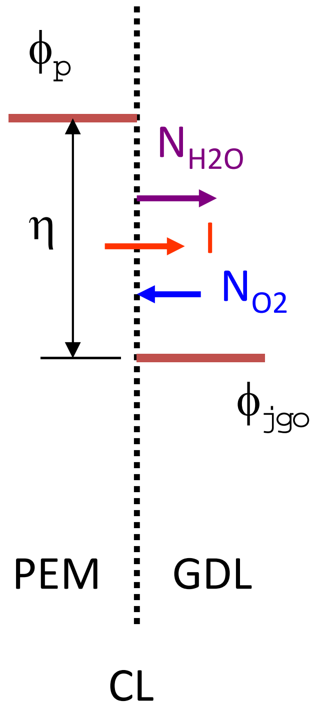
$$m_{H_2O} = \frac{I}{2F} M_{H_2O}$$

$$i_a = i_{0,a}[\exp\frac{-\alpha_a F\eta_a}{RT} - \exp\frac{(1-\alpha_a)F\eta_a}{RT}]$$

$$i_c = i_{0,c}[\exp\frac{-\alpha_c F\eta_c}{RT} - \exp\frac{(1-\alpha_c)F\eta_c}{RT}]$$

$$i_{0,c} = i_{0,c}^{0}(\frac{P_{O_2}}{P_{O_2}^{0}})^{\gamma}[\exp\frac{-E_{A,c}}{RT}(\frac{1}{T} - \frac{1}{T^0})]$$

$$i_{0,a} = i_{0,a}^{0}(\frac{P_{H_2}}{P_{H_2}^{0}})^{\gamma_1}(\frac{P_{H_2O}}{P_{H_2O}^{0}})^{\gamma_2}[\exp\frac{-E_{A,a}}{RT}(\frac{1}{T} - \frac{1}{T^0})]$$

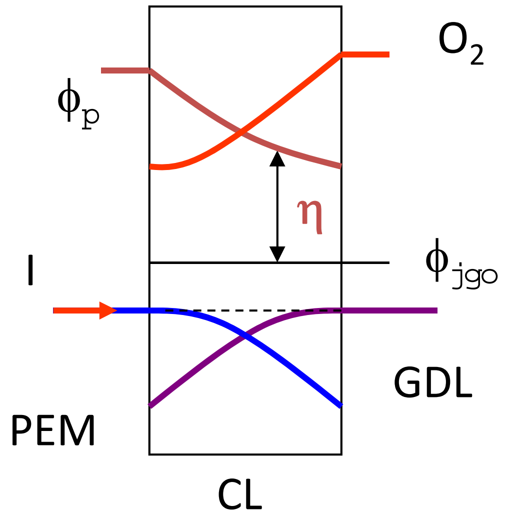


Macro-homogeneous model

- Consider the catalyst layer flooded and transport of species is treated as one homogeneous medium
- Does not reflect the microstructures of the catalyst layer

$$\nabla C = \frac{I - i}{C_{O_2}^{ref} D_{eff} nF} \qquad \nabla \eta = \frac{i}{\sigma_{eff}}$$

$$\nabla i = j_0 AC \exp\left(\frac{-\alpha F \eta}{RT}\right)$$



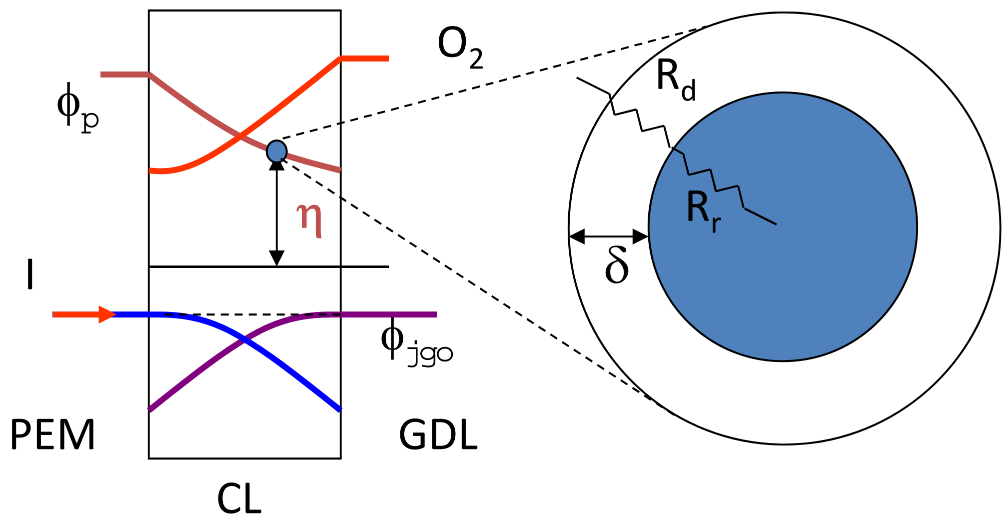
Agglomerate model

- This is equivalent to a two-scale model
- Reflect <u>some</u> microstructures of the catalyst layer
- Need calibration for the model parameters

$$\nabla i = nF\left[\frac{1}{\dfrac{\delta}{aC^*_{O_2}D_{eff}} + \dfrac{1}{kE}}\right]$$

$$E = \frac{\tanh(mL)}{mL};\ mL = L\sqrt{\frac{k}{C^*_{O_2}D_{eff}}}$$

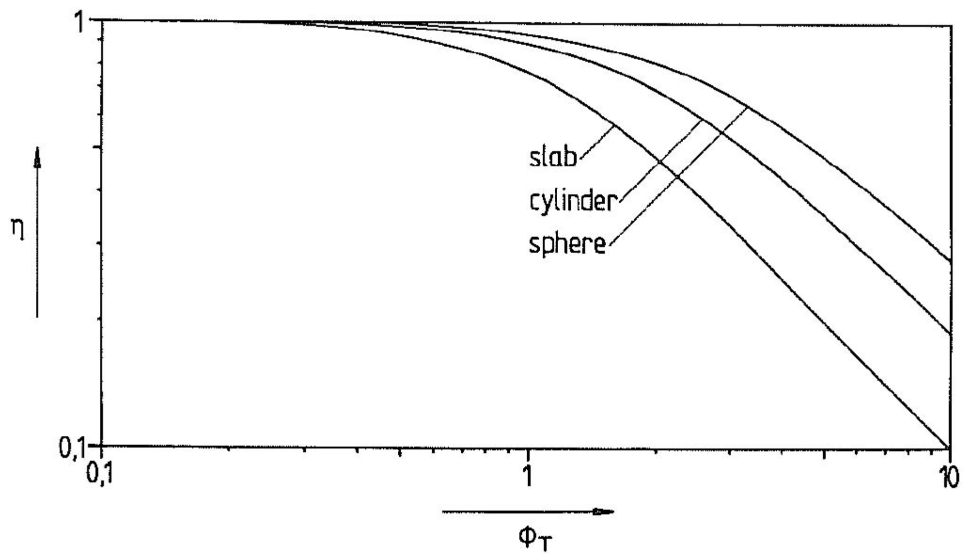
$$k = \frac{Aj_0}{nF}\exp\left(\frac{-\alpha F\eta}{RT}\right)$$

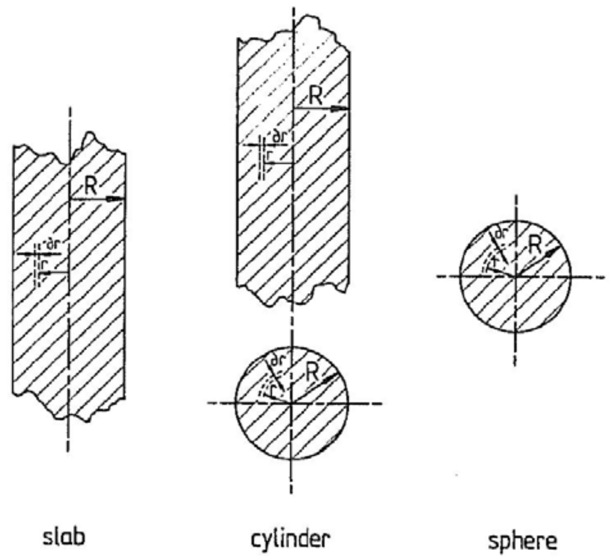


Thiele modulus

- Effectiveness factor of catalyst pellets

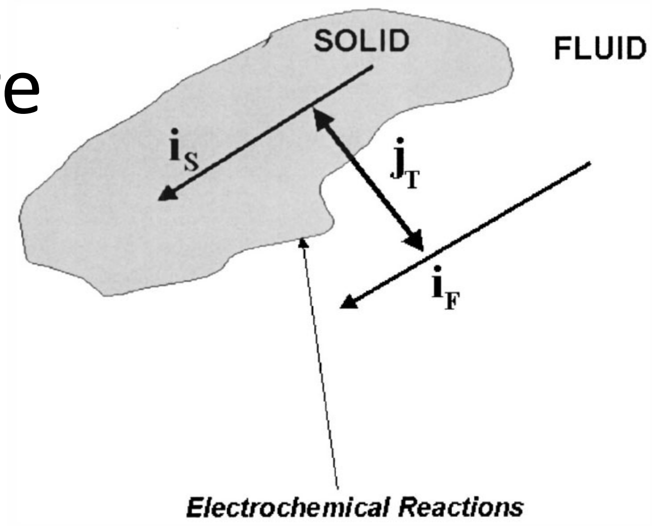
$$\phi_T = R\sqrt{\frac{k'(C)}{DC}}$$





Pore-diffusion limited model

- Assuming mass transport is dictated by diffusion in the pore



$$\sum_{j=1}^{N_{steps}} M_i \frac{j_{T,j}}{F} = \rho D_i \nabla Y_i$$

$$\sum_{j=1}^{N_{steps}} M_i (a_{ij}^{"} - a_{ij}^{'}) \frac{j_{T,j}}{F} = \rho D_i \frac{Y_i - Y_{P,i}}{\delta}$$

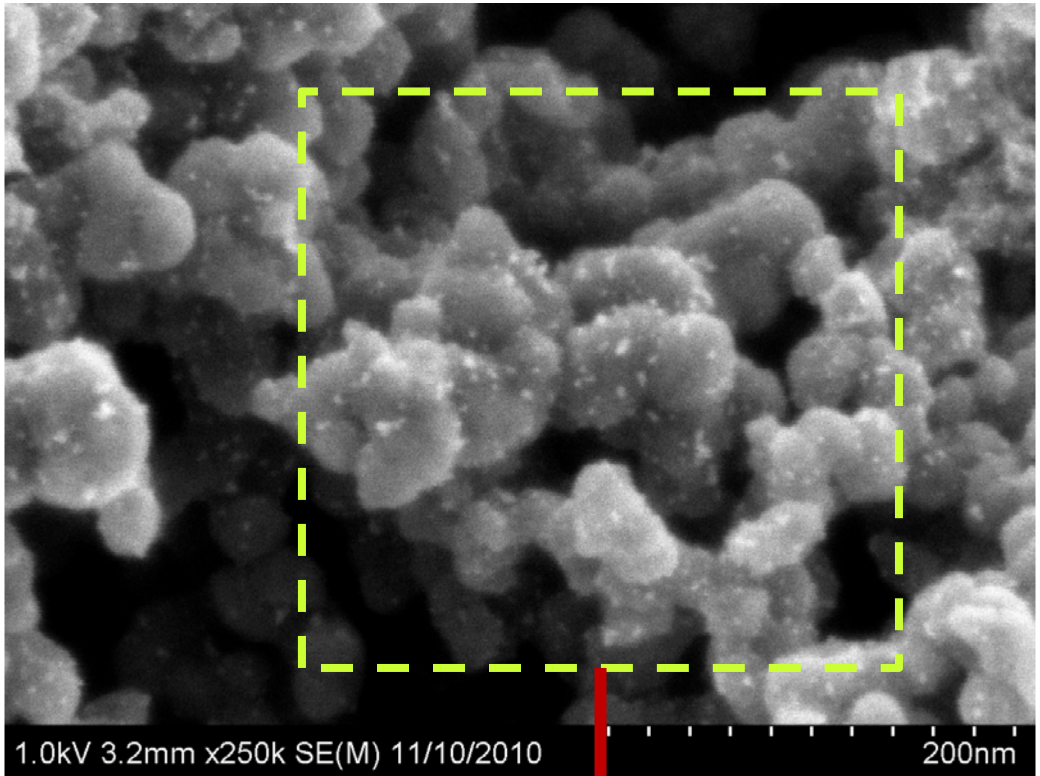
$$\dot{\omega}_i = \rho D_i \frac{Y_i - Y_{P,i}}{\delta} \left(\frac{S}{V} \right)_{eff}$$

$$j_{T,j} = \frac{j_{0,j}}{\prod_{k=1}^{N} [\Lambda_{k,ref}]^{\alpha_{k,j}}} \left[\exp\left(\frac{\alpha_{a,j} F}{RT} \eta \right) - \exp\left(-\frac{\alpha_{c,j} F}{RT} \eta \right) \right] \prod_{k=1}^{N} [\Lambda_k]^{\alpha_{k,j}}$$

S. Mazumder, J. V Cole, J. Electrochem. Soc. 150 (2003) A1503

TRANSITION BETWEEN MESOSCOPIC AND MACROSCOPIC MODELS

Mesoscopic model for CL



Mesoscopic domain size

Point equation

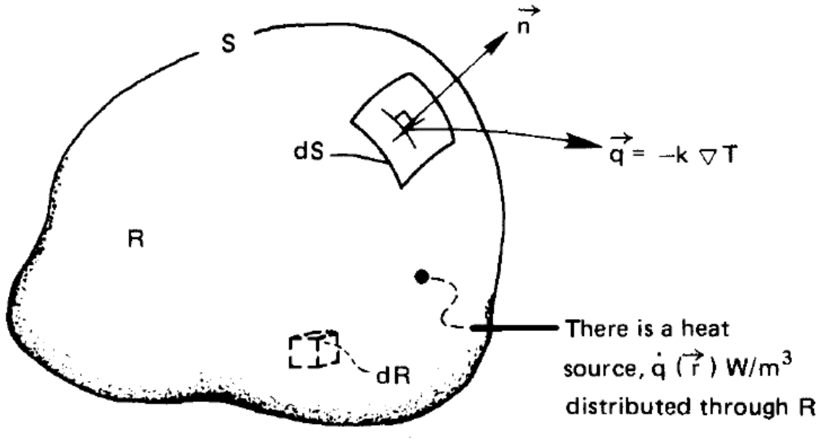
$$Q = -\int_S -k\nabla T \cdot \vec{n}dS + \int_R \dot{q}dR$$

$$\frac{dU}{dt} = \int_R \rho c \frac{\partial T}{\partial t} dR$$

$$\int_S k\nabla T \cdot \vec{n}dS = \int_R (\rho c \frac{\partial T}{\partial t} - \dot{q})dR$$

$$\int_R (\nabla \cdot k\nabla T - \rho c \frac{\partial T}{\partial t} + \dot{q})dR = 0$$

$$-k\nabla T \cdot \vec{n}dS$$



Gauss' theorem

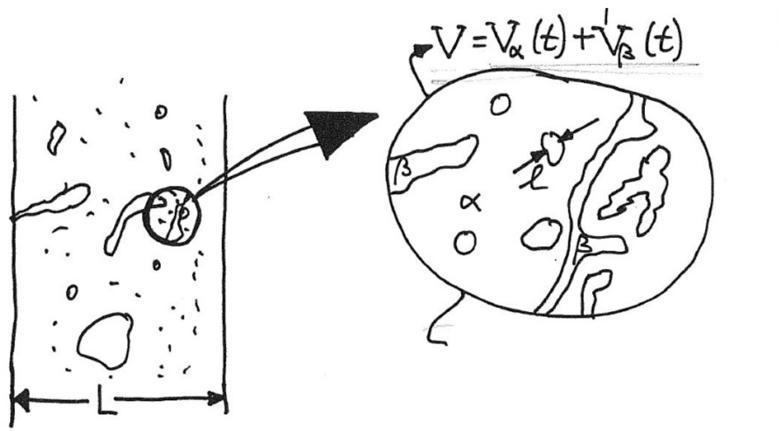
$$\int \vec{A} \cdot \vec{n}dS = -\int \nabla \cdot \vec{A}dR$$

For a porous material, a point equation is only valid within one single phase

Volume averaging

- Governing equations derived using volume average method on conserved physical variables over a *representative element volume* (REV)
- Properties for the transport through bulk material/interface are needed for **model closure**

$$l << r << L$$



The length scale (r) of the REV is chosen that we obtain sufficiently smooth values of the averaged quantity, while the averaged quantity may undergo significant changes over the length of the system L

Volume averaging method

Point equation: Single phase

$$\frac{\partial}{\partial t}(\rho_k \psi_k) + \nabla \cdot (\rho_k \vec{v}_k \psi_k) = -\nabla \cdot (\vec{j}_k) + \rho_k \varphi_k$$

$\psi = 1, \vec{v}, h, Y_i$ (mass, momentum, energy, species)

For PEMFC CL:

$k = carbon, ionomer, gas, liquid$

$$\langle \psi_k \rangle \equiv \frac{1}{V} \int \psi_k dV \qquad \langle \psi_k \rangle^k \equiv \frac{1}{V_k} \int \psi_k dV$$

$$\langle \nabla \psi_k \rangle = \nabla \langle \psi_k \rangle + \frac{1}{V} \int \psi_k \vec{n}_k dA$$

- **Additional terms appear in the volume-averaged equations**
- **Model closure is needed for these terms.**

Advection by the mean flow — **Dispersion** — **Advection across Ai**

$$\frac{\partial}{\partial t}(\rho_k \langle \psi_k \rangle) + \nabla \cdot (\rho_k \langle \vec{v}_k \rangle \langle \psi_k \rangle^k) + \nabla \cdot (\rho_k \langle \tilde{\vec{v}}_k \cdot \tilde{\psi}_k \rangle) + \int_{A_i} \rho_k \langle (\vec{v}_k - \vec{v}_i) \cdot \vec{n}_k \psi_k \rangle dA$$

$$= -\nabla \cdot (\langle \vec{j}_k \rangle) - \frac{1}{V} \int_{A_i} \vec{j}_k \cdot \vec{n}_k dA + \rho_k \langle \varphi_k \rangle$$

Diffusion — **Flux across Ai** — **Production**

$$\frac{\partial}{\partial t}(\rho_k\langle\psi_k\rangle)+\nabla\cdot(\rho_k\langle\vec{v}_k\rangle\langle\psi_k\rangle^k)+\nabla\cdot(\rho_k\langle\tilde{\vec{v}}_k\cdot\tilde{\psi}_k\rangle)+\int_{A_i}\rho_k\langle(\vec{v}_k-\vec{v}_i)\cdot\vec{n}_k\psi_k\rangle dA$$

$$=-\nabla\cdot(\langle\vec{j}_k\rangle)-\frac{1}{V}\int_{A_i}\vec{j}_k\cdot\vec{n}_k dA+\rho_k\langle\varphi_k\rangle$$

S

$$\nabla\cdot(\langle\vec{j}_{O_2}\rangle)+\frac{1}{V}\int_{A_i}(\vec{j}_{O_2}\cdot\vec{n}_{GS,MS})dA=-\rho_{O_2}\langle\varphi_{O_2}\rangle$$

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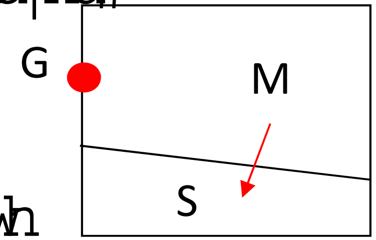


M

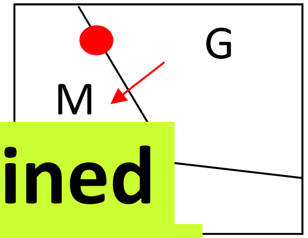
$$\nabla\cdot(\langle\vec{j}_{O_2}\rangle)+\frac{1}{V}\int_{A_i}(\vec{j}_{O_2}\cdot\vec{n}_{MS})dA=0$$

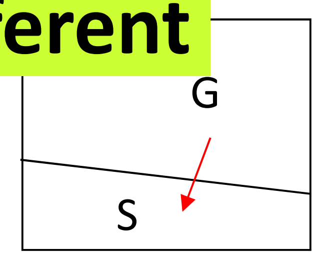
#F0Sw#fryhuhg#e|#hdfwurd|wh

=0

M

$$\nabla\cdot(\langle\vec{j}_{O_2}\rangle)+\frac{1}{V}\int_{A_i}(\vec{j}_{O_2}\cdot\vec{n}_{MG}+\vec{j}_{O_2}\cdot\vec{n}_{MS})dA=0$$





Existing macroscopic models can be explained using volume-average equations with different configurations of phases and interfaces

Interfaces in CL

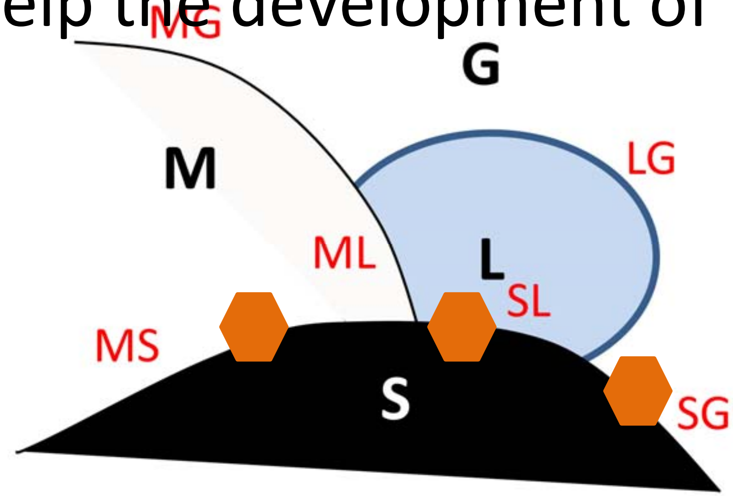
Advection by the mean flow — **Dispersion** — **Advection across Ai**

$$\frac{\partial}{\partial t}(\rho_k\langle\psi_k\rangle)+\nabla\cdot(\rho_k\langle\vec{v}_k\rangle\langle\psi_k\rangle^k)+\nabla\cdot(\rho_k\langle\tilde{v}_k\cdot\tilde{\psi}_k\rangle)+\int_{A_i}\rho_k\langle(\vec{v}_k-\vec{v}_i)\cdot\vec{n}_k\psi_k\rangle dA$$

$$=-\nabla\cdot(\langle\vec{j}_k\rangle)-\frac{1}{V}\int_{A_i}\vec{j}_k\cdot\vec{n}_k dA+\rho_k\langle\varphi_k\rangle$$

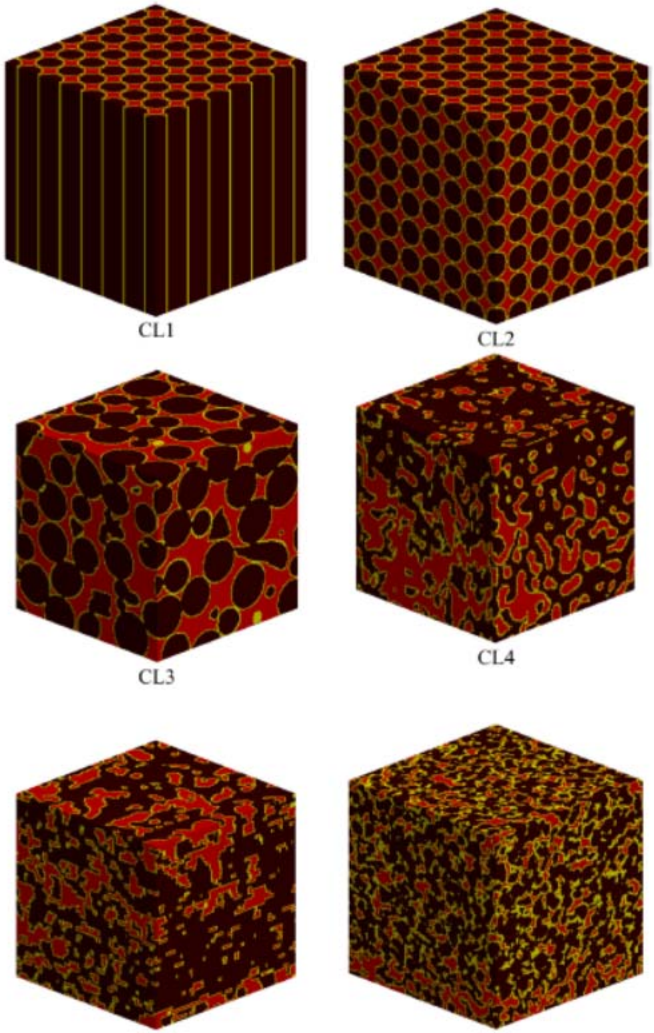
Diffusion — **Flux across Ai** — **Production**

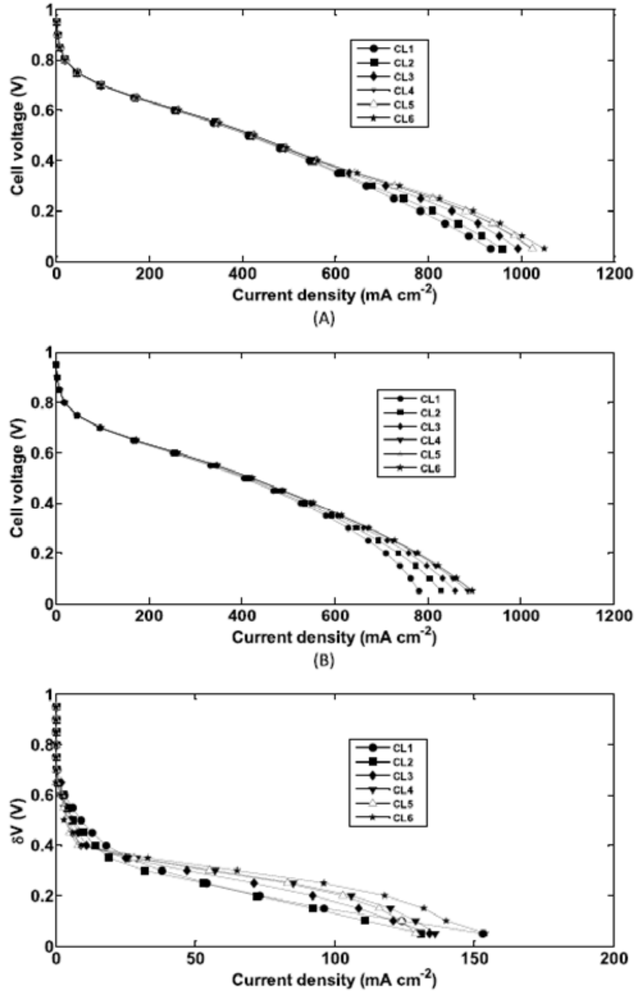
- **Model closure is very involved**
  - Interfacial sub-models needed
  - Microscopic modeling can help the development of sub-models



PORE SCALE MODELLING

Microstructure matters

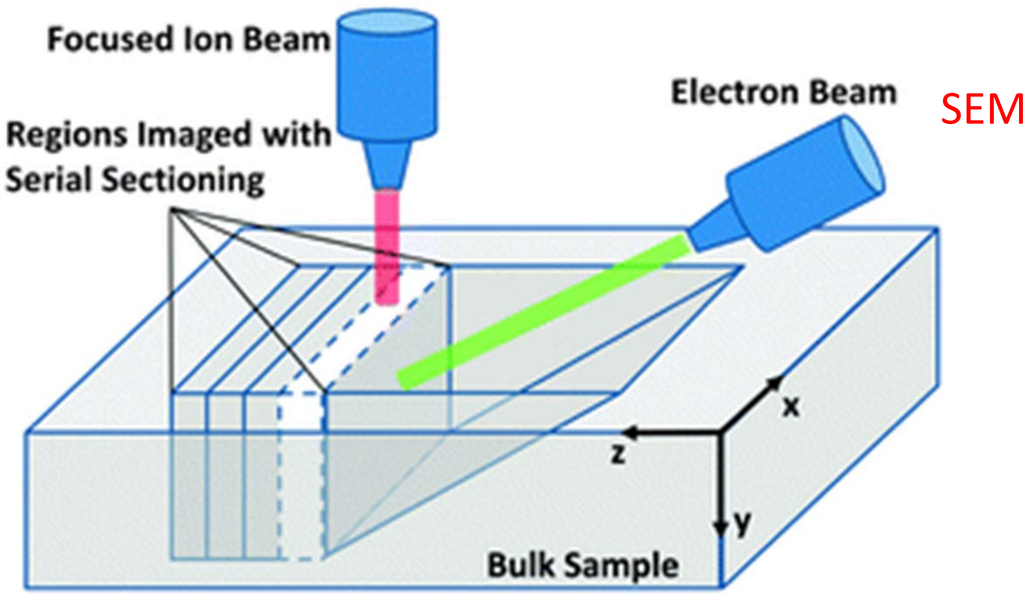




“Geometrical structures of catalyst layer and their impact on oxygen reduction in proton exchange membrane fuel cell”, Y Gao and XX Zhang,, Electrochimica Acta, 218 (2016), 101-109

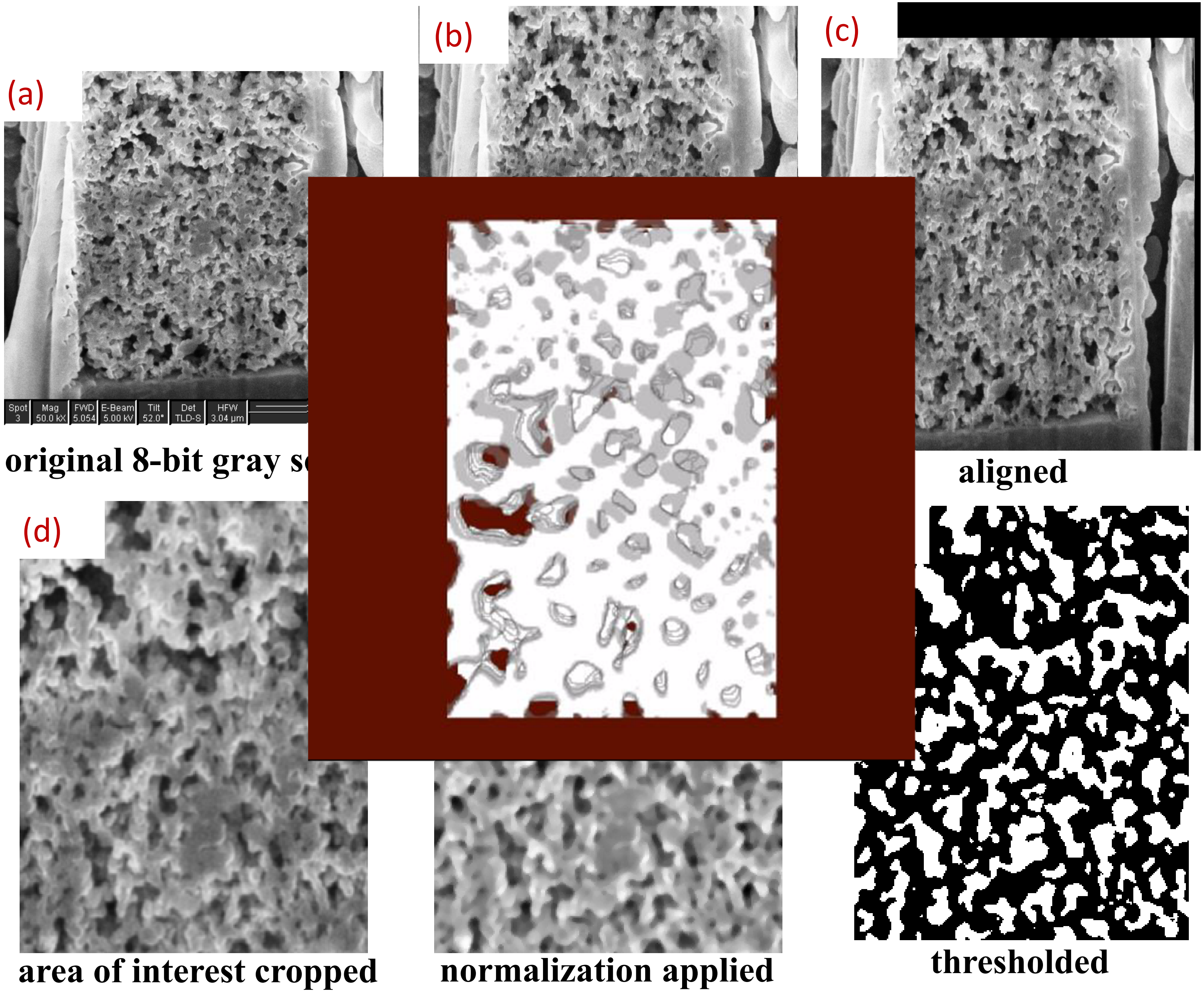
Focused ion beam (FIB) + SEM

- FIB slicing can be done in ~10 nm resolution
- Intrusive method (destroys material)
- Coating of metal (W, Pt) on sample may protect overheat and enhance image acquired (ALD)



2166 nm

FIB-SEM: Image processing

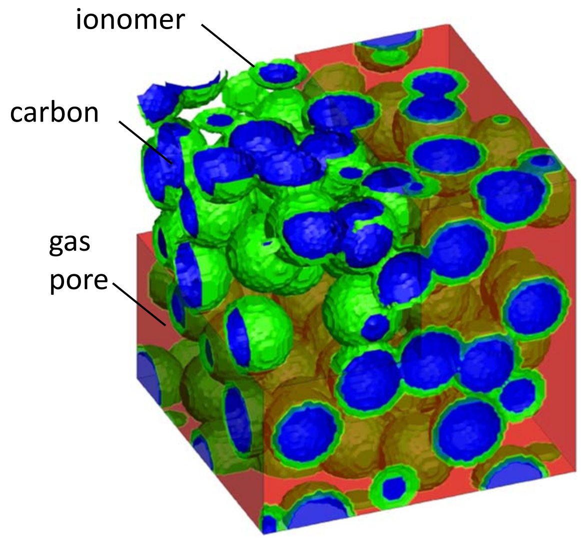


Pore scale modeling (PSM)

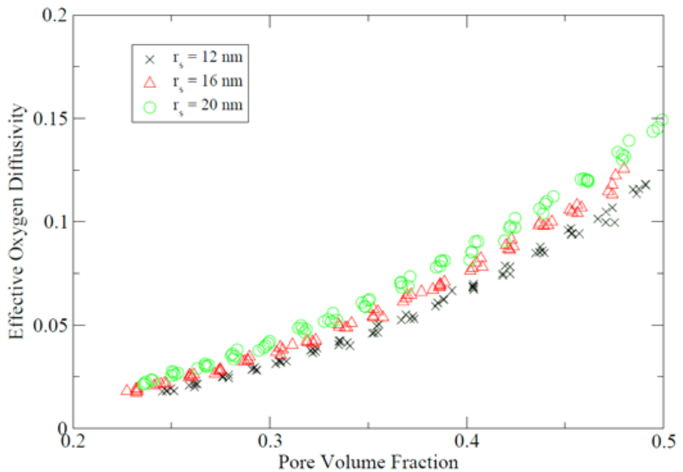
- Direct solution of conservation equations on microscopic geometry

$$0 = -\nabla \cdot (\vec{j}_k) + \rho_k \varphi_k$$

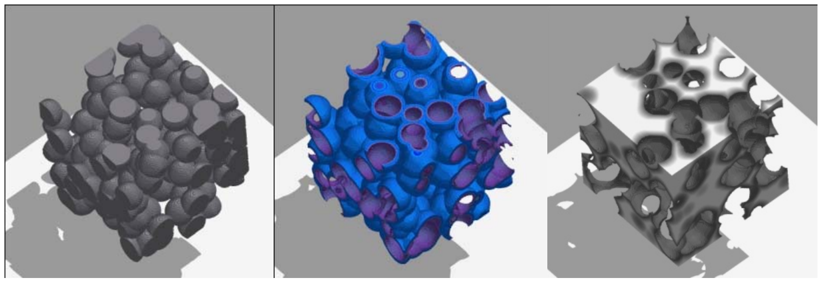
- Stochastically generated or actual microstructure
- Macroscopic properties computed



$$2H^{+} + 2e^{-} + \frac{1}{2}O_2 \rightarrow H_2O$$



e^{-} H^{+} O_2,H_2O



Porous medium reconstruction

A

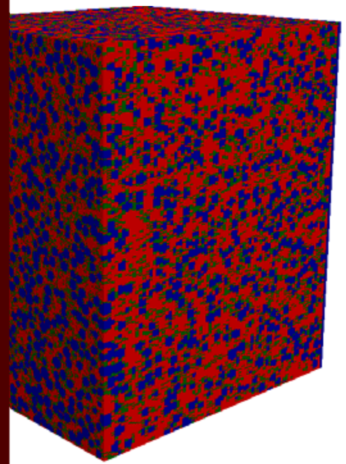
FIB/SEM
3D, 2 phase data

B

Porosity

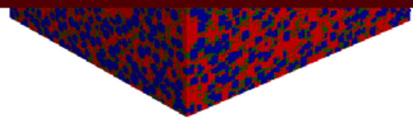
R1

Stochastic
), 3 phase data

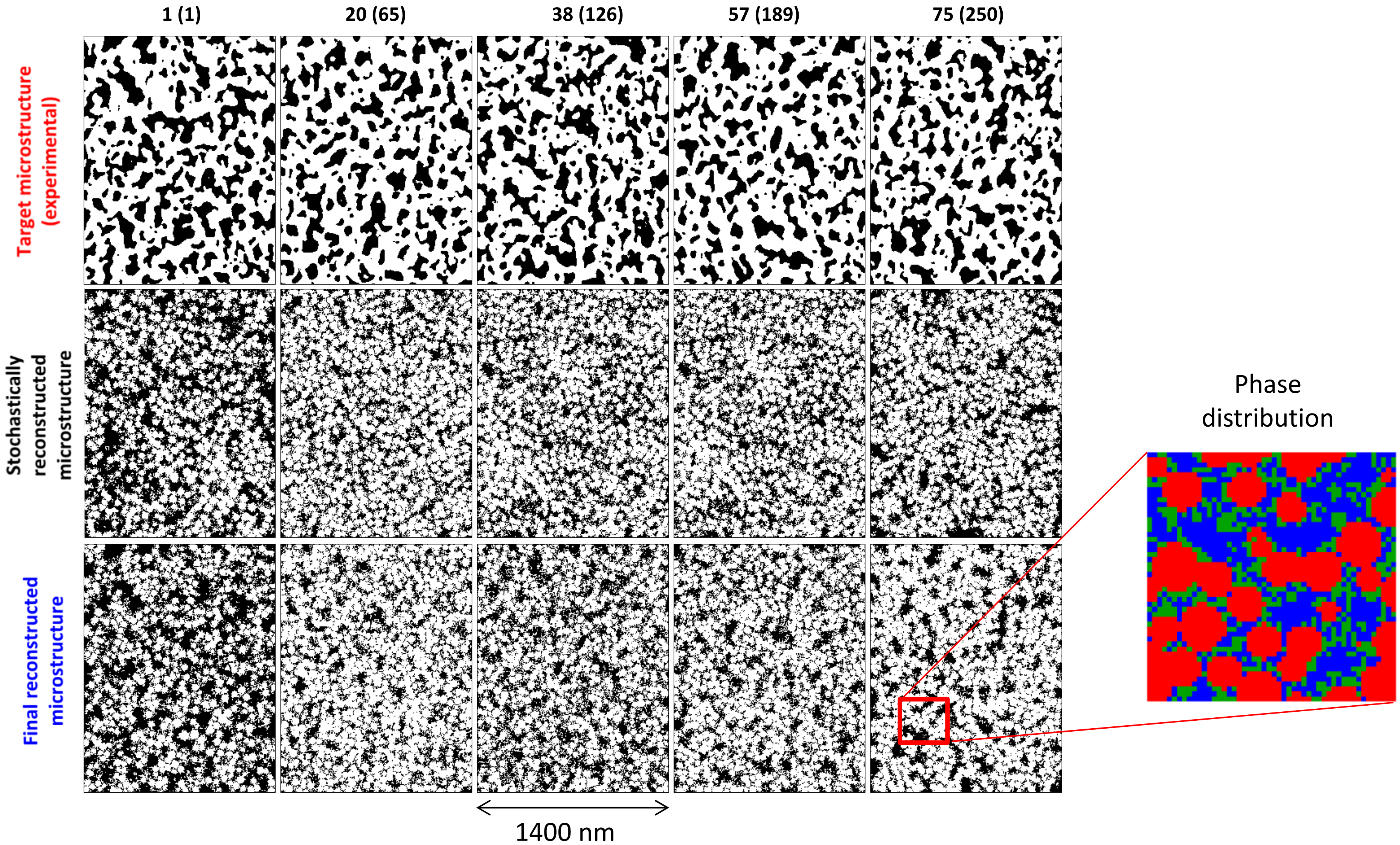


Red=pore (34%)
Blue=C (44%)
Green=ionomer (22%)

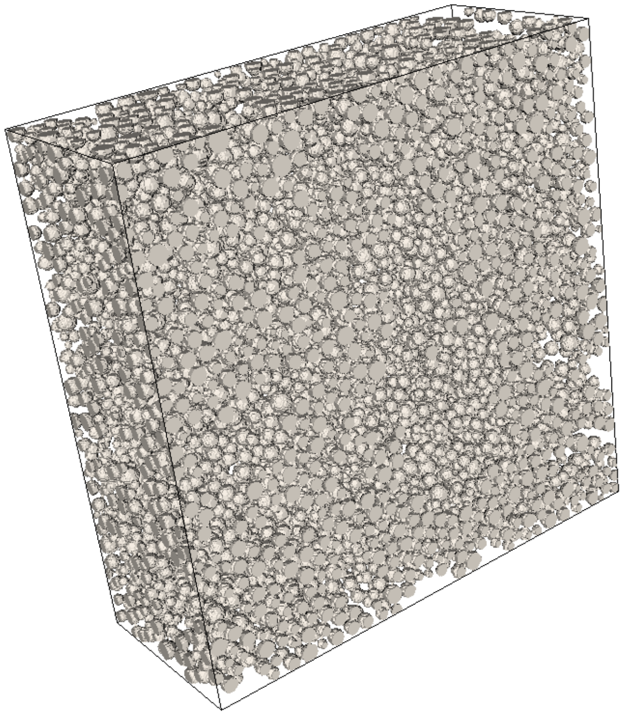
Constrai



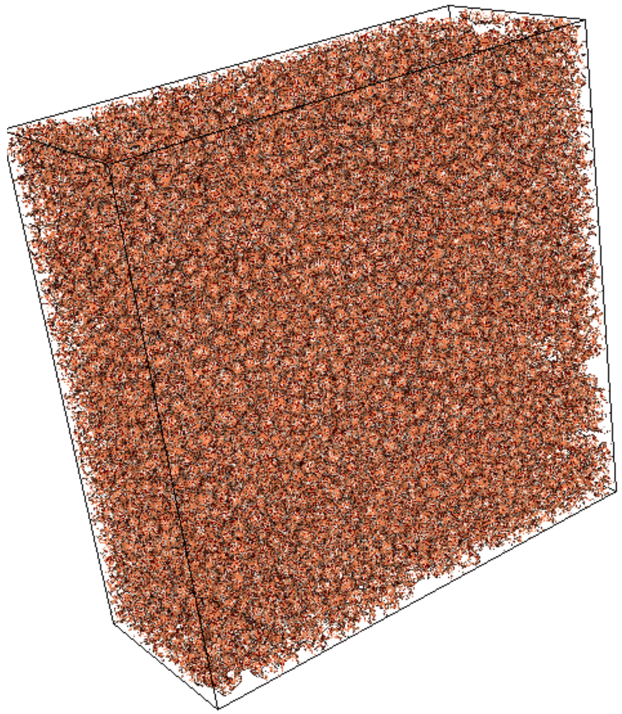
Comparison: FIB-SEM vs. Reconstruction



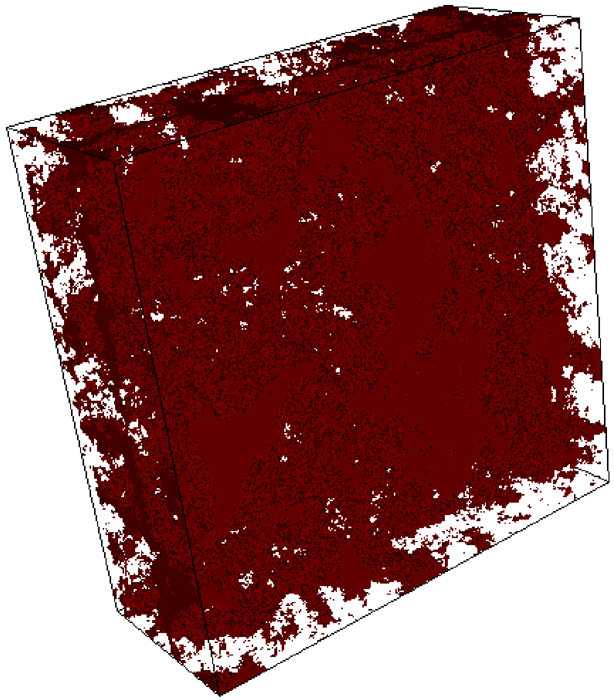
Reconstructed catalyst layer



C-Pt



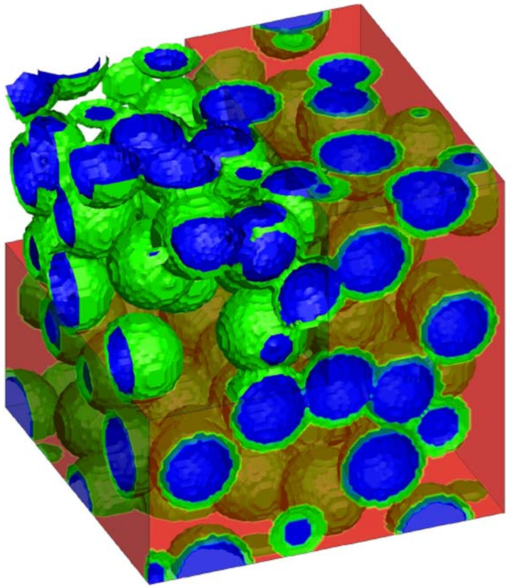
Ionomer



Pores

Lange, Carlsson, Stewart, Sui, Djilali, Electrochem. Acta 2012

Coupled transport processes in CL



Transport fluxes

$$\widehat{\boldsymbol{\Gamma}}_t = \begin{bmatrix} \widehat{\Gamma}_{O_2,t} \\ \widehat{\Gamma}_{H_2O,t} \\ \widehat{\Gamma}_{H^+,t} \\ \widehat{\Gamma}_{e,t} \end{bmatrix} = \begin{bmatrix} -\widehat{D}_{O_2}\hat{\nabla}\widehat{C}_{O_2} \\ -\widehat{D}_{H_2O}\hat{\nabla}\widehat{C}_{H_2O} - \frac{n_d\sigma_{m,ref}\phi_{m,ref}}{C_{H_2O,ref}D_{H_2O,ref}F}\hat{\sigma}_m\hat{\nabla}\hat{\phi}_m \\ -\hat{\sigma}_m\hat{\nabla}\hat{\phi}_m \\ \hat{\sigma}_s\hat{\nabla}\hat{\phi}_s \end{bmatrix}$$

Reaction fluxes

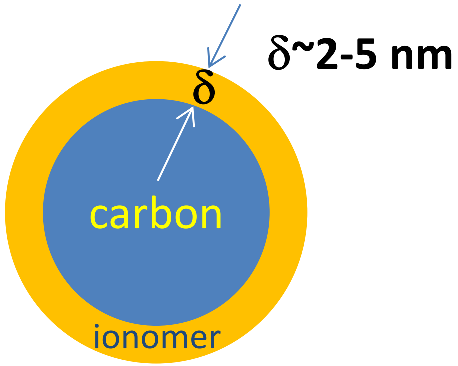
$$\widehat{\boldsymbol{\Gamma}}_r = \begin{bmatrix} \widehat{\Gamma}_{O_2,r} \\ \widehat{\Gamma}_{H_2O,r} \\ \widehat{\Gamma}_{H^+,r} \\ \widehat{\Gamma}_{e,r} \end{bmatrix} = \begin{bmatrix} \frac{i_0 l_{ref}}{4FD_{O_2,ref}C_{O_2,ref}}\widehat{C}_{O_2}\exp\left(\frac{-\alpha_c F}{RT}\eta\right) \\ -\frac{i_0 l_{ref}}{2FD_{H_2O,ref}C_{H_2O,ref}}\widehat{C}_{O_2}\exp\left(\frac{-\alpha_c F}{RT}\eta\right) \\ \frac{i_0 l_{ref}}{\sigma_{m,ref}\phi_{m,ref}}\widehat{C}_{O_2}\exp\left(\frac{-\alpha_c F}{RT}\eta\right) \\ \frac{i_0 l_{ref}}{\sigma_{s,ref}\phi_{s,ref}}\widehat{C}_{O_2}\exp\left(\frac{-\alpha_c F}{RT}\eta\right) \end{bmatrix}.$$

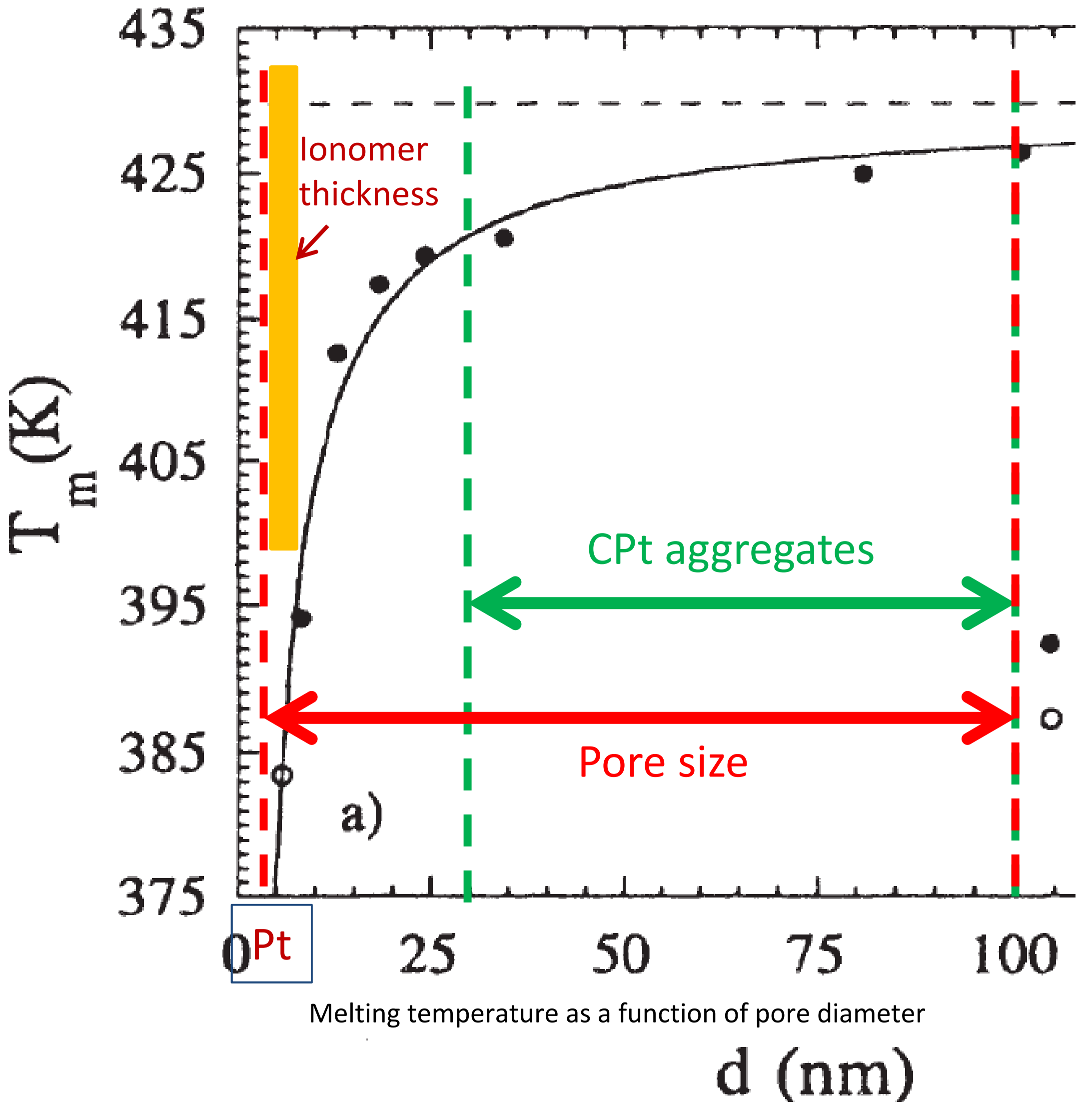
Limitations

- FIB/SEM provides only morphological information of solid materials
- MD/CGMD are limited to small length/time scales
- PSM considers nano-material as continuum
- LBM does not consider thermodynamic behavior at nano-scale

What's missing

- **Transitions**
  - Thermodynamics
  - Transport regimes



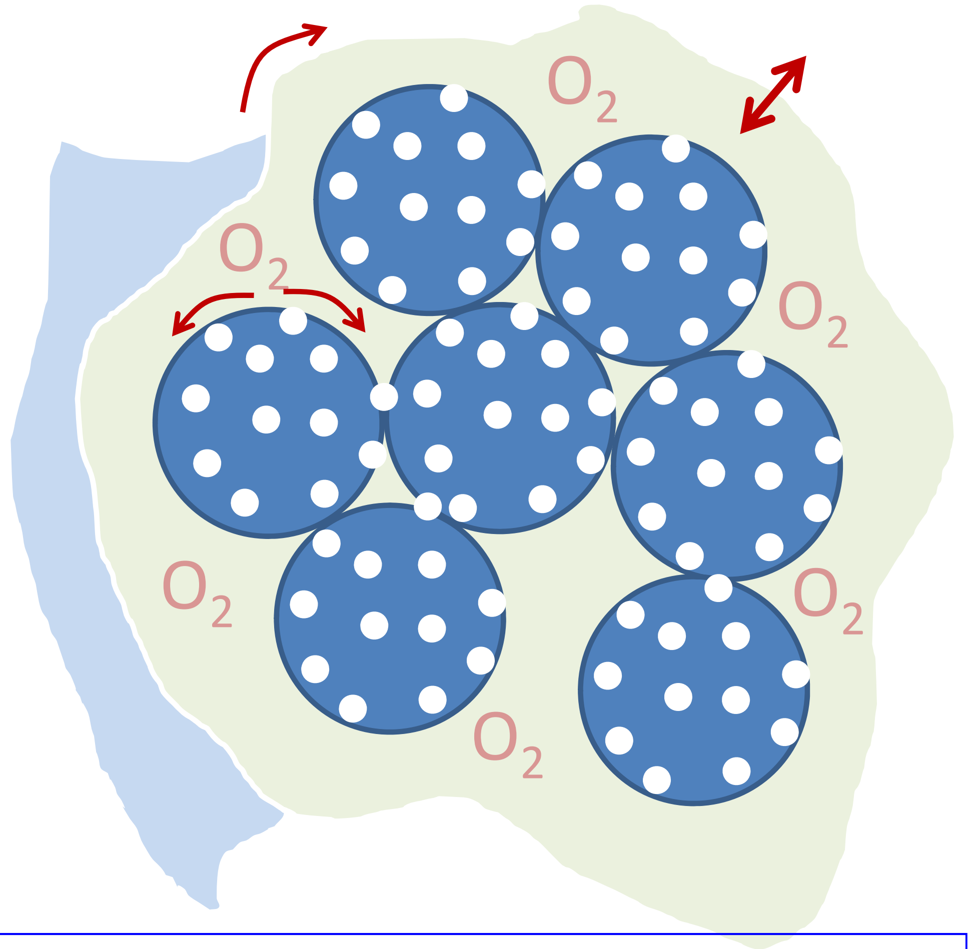


Melting temperature as a function of pore diameter

E. Roduner, "Size matters: why nanomaterials are different" Chem. Soc. Rev., 2006, 35, 583–592

What's missing

- **Interfacial transport**
  - Adsorption
  - Surface diffusion
  - Wettability



Advection by the mean flow **Dispersion** **Advection across Ai**

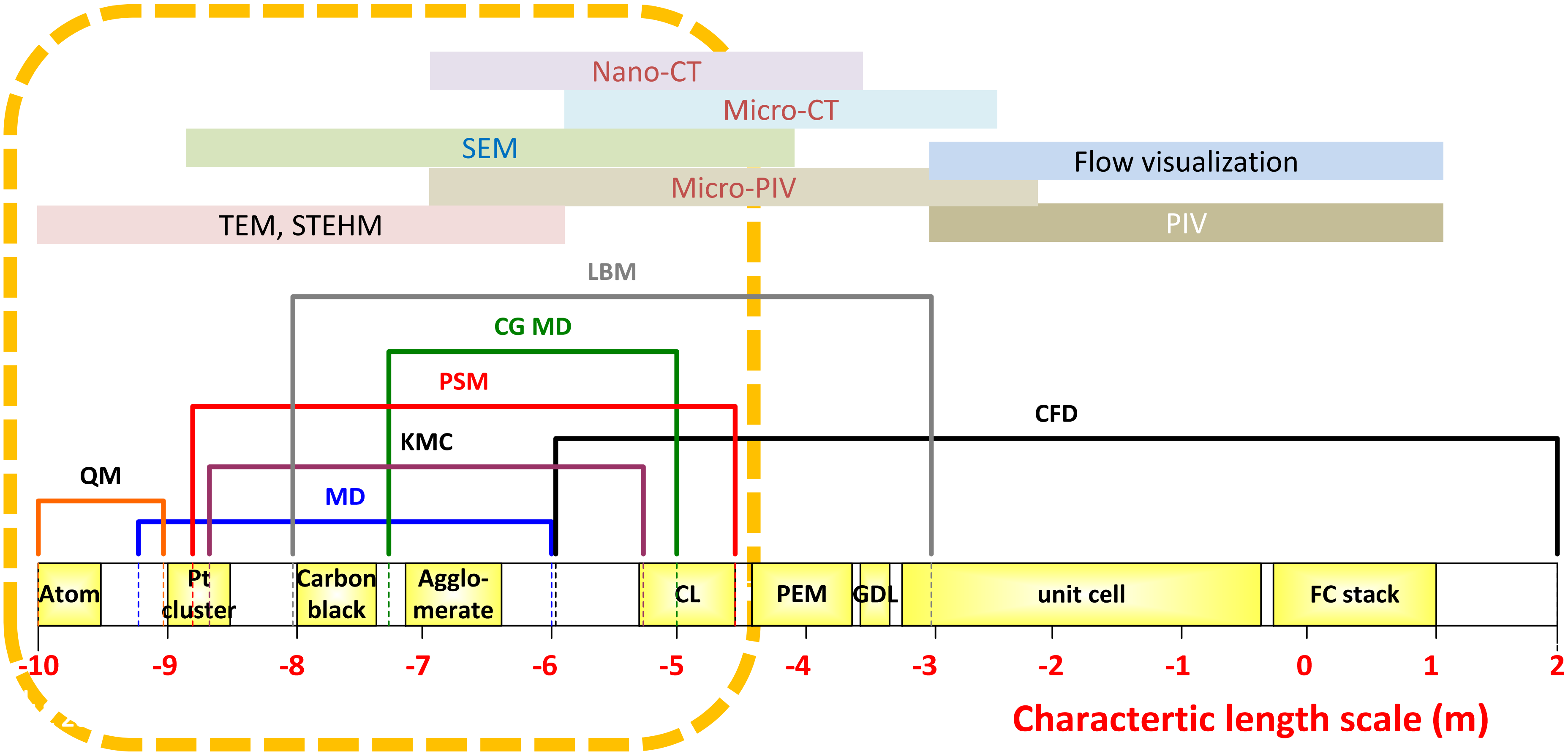
$$\frac{\partial}{\partial t}(\rho_k\langle\psi_k\rangle)+\nabla\cdot(\rho_k\langle\vec{v}_k\rangle\langle\psi_k\rangle^k)+\nabla\cdot(\rho_k\langle\tilde{\vec{v}}_k\cdot\tilde{\psi}_k\rangle)+\int_{A_i}\rho_k\langle(\vec{v}_k-\vec{v}_i)\cdot\vec{n}_k\psi_k\rangle dA$$

$$=-\nabla\cdot(\langle\vec{j}_k\rangle)-\frac{1}{V}\int_{A_i}\vec{j}_k\cdot\vec{n}_k dA+\rho_k\langle\varphi_k\rangle$$

Diffusion **Flux across Ai** **Production**

OUTLOOK

PSM + experiment/simulation tools



PSM model can play a central role in CL research and development

Research opportunities

- **In situ and operando SEM/TEM observation**
  - True validation for mesoscopic models
- **Measurement of physical properties of material at its actual length scale in CL**
  - Surface properties
  - Diffusivity
- **Multiscale simulation technique**
  - Mesoscopic model to bridge both ends
- **Establish links between fabrication processes and BOL**

Pine soot + ‘goo’

184 *J.R. Swider et al. / Journal of Cultural Heritage 4 (2003) 175–186*

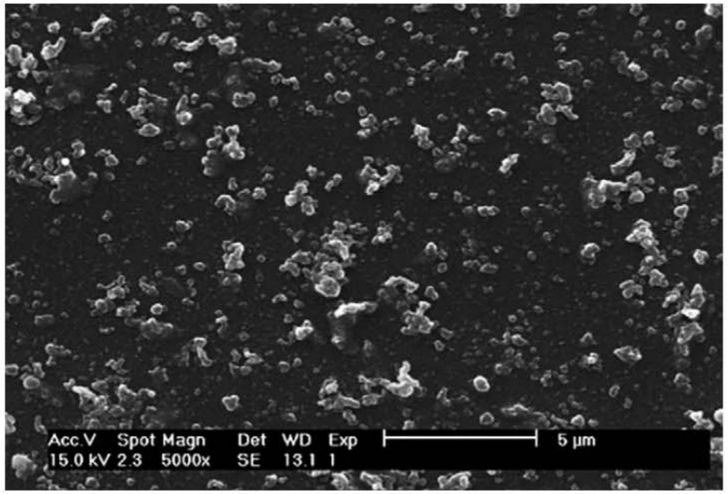
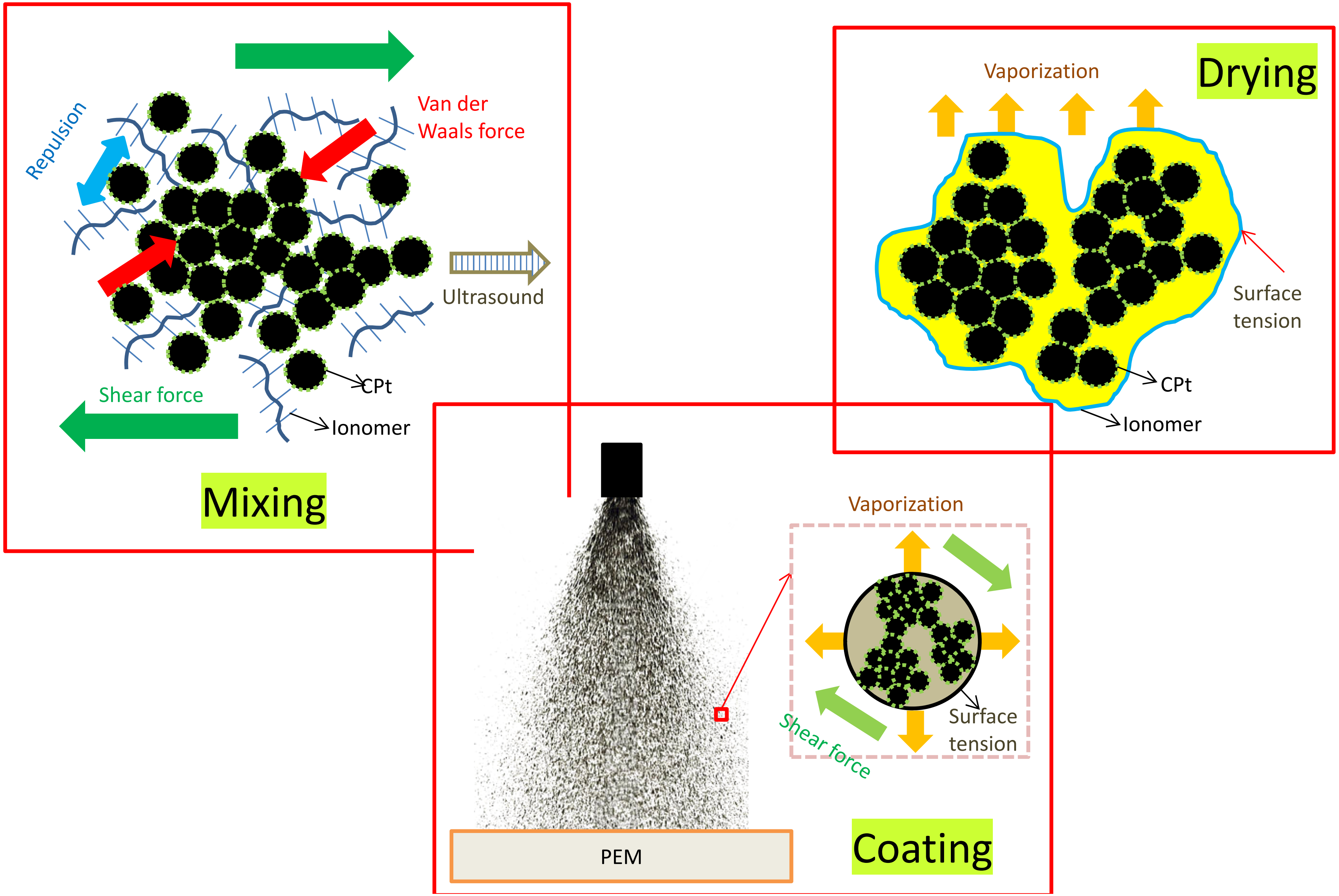


Fig. 7. SEM image of Chinese Shanghai pine soot ink.

Model & simulation of CL fabrication



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- Hubei 100-Talent program, China
- Prof. Ned Djilali, UVic
- Hanse-Wissenschaftskolleg, Germany
- Pacific Institute for the Mathematical Sciences (PIMS)

International Collaboration

- **Long term collaboration with Canadian universities**
  – UVic, SFU, UBC
  – U of Toronto, U of Alberta, UQTR
- **In contact with research organizations**
  – Canada： Ballard Power Systems, NRC
  – Japan: Yamanashi University, Doshisha University, Honda R&D Tochigi
  – Germany: NEXT ENERGY (DLR), Helmholtz Inst. Ulm
  – USA: UC Merced
  – Iran: SBUK
  – India: IIT
- **Bi-annual EEST conference for IAOEES**

Additional activities

- **PEM-based electrolyzer** (Profs. MJ Luo and Chen of WUT)
- **Membrane desalination** (MD) and MD-FC hybrid systems (PhD student Hesam Harandi)
- **HT-PEM** fuel cell + methanol reformer (Beihang University)
- **AEMFC** (NCU, ITRI)
- **Hydrogen infrastructure**: regulations and planning (Dr. SX Li of WUT)

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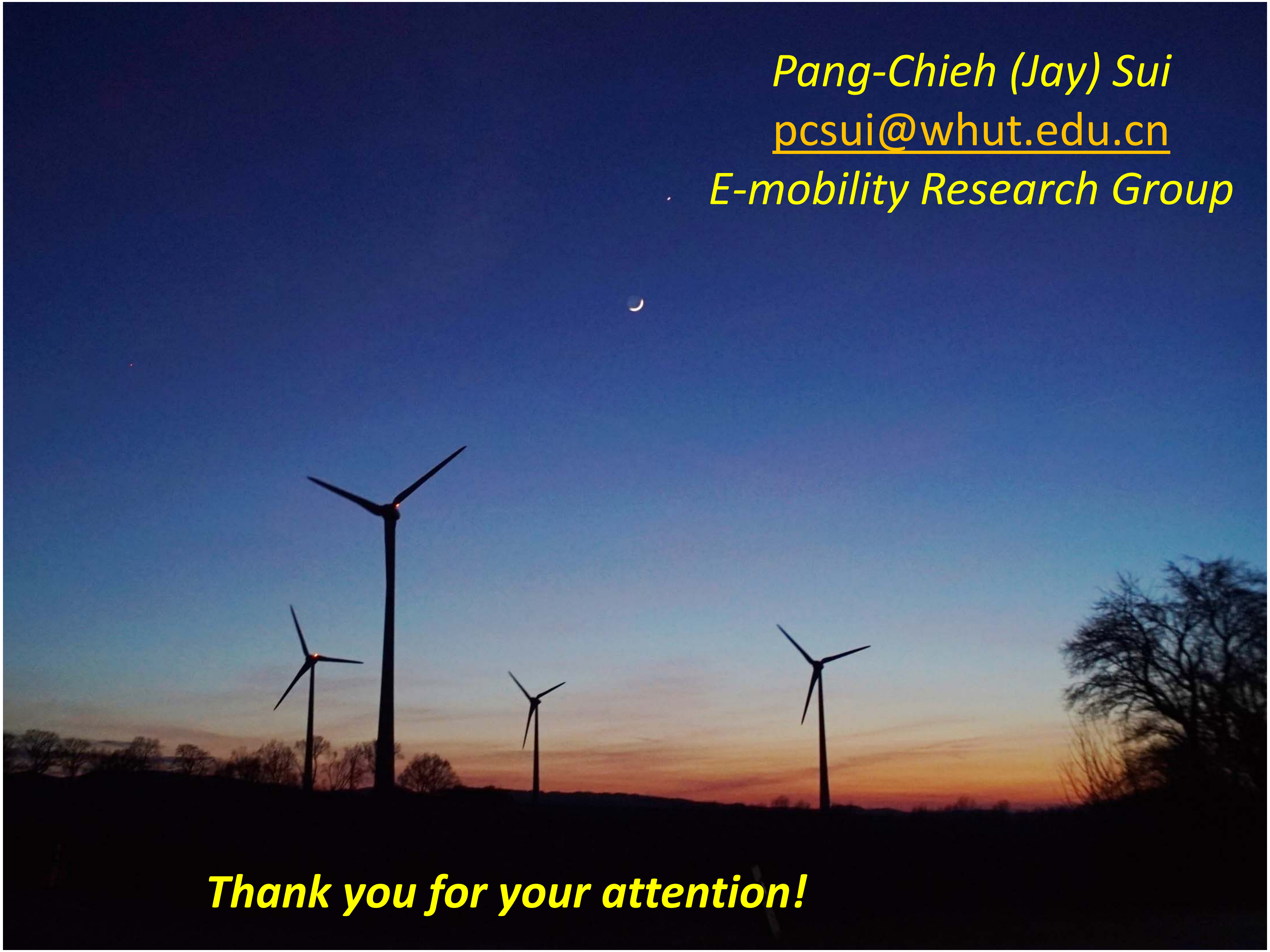
International Conference on Electrochemical Energy Science & Technology (EEST)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E-mobility Research Group
Thank you for your attention!