Optimizing fuel cell design with COMSOL Multiphysics

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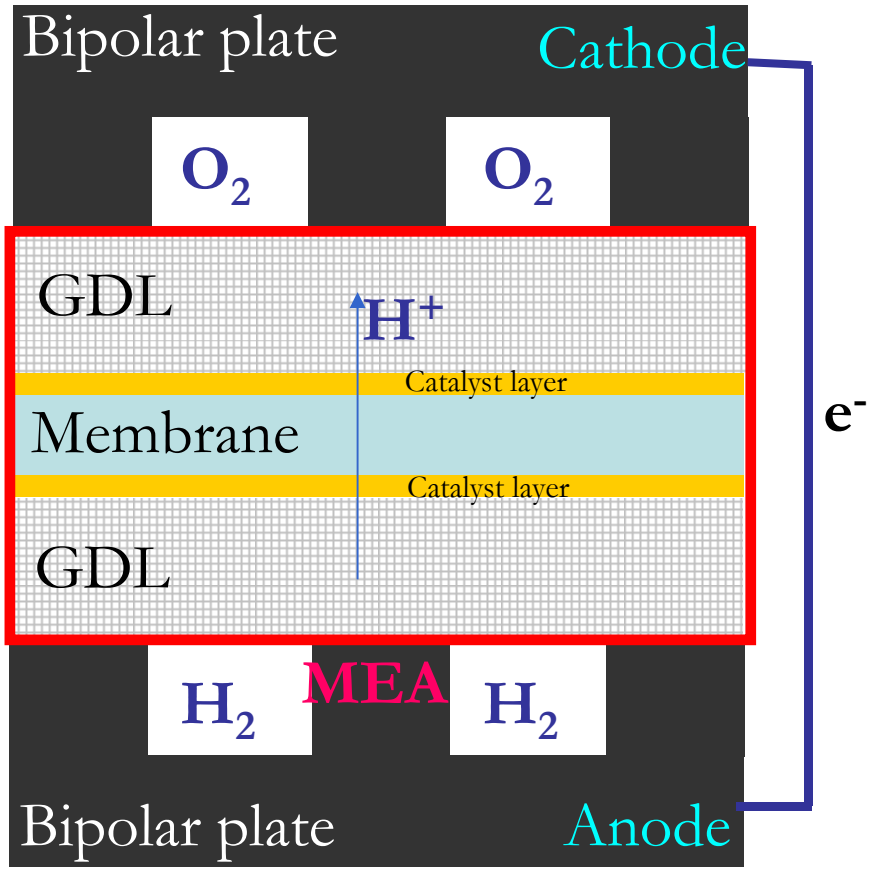
COMSOL User Conference 2012 Nov. 9 2012 Taipei Taiwan

Outline

- Fuel cell introduction
- Simulation detail
- FC applications
  - 2D MEA model (HT-PBI)
  - Multi-scale simulations (conceptual)

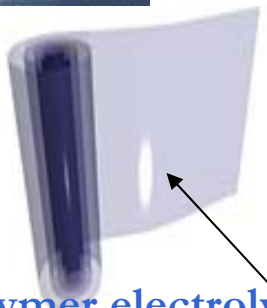
How fuel cell works



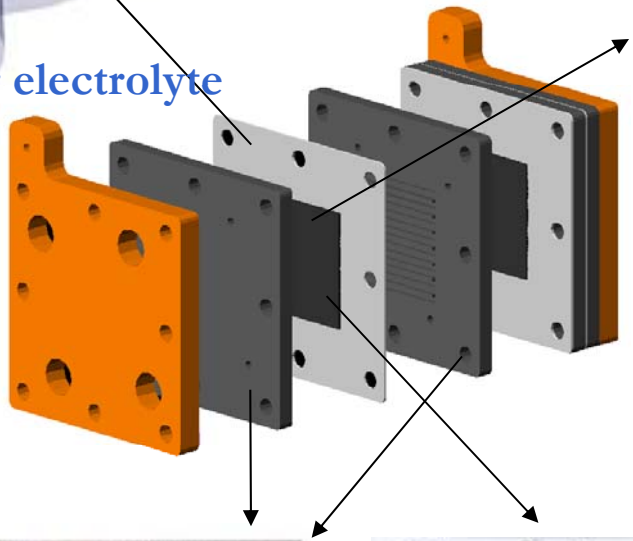
Over all: $H_2+O_2 \rightarrow H_2O$

- **Bipolar plate** (graphite): ~10000 μm
  electron conduction
- **Gas channel** : ~1000 μm
  gas transport
- **GDL** (Carbon cloth/paper): ~250 μm
  electron conduction and gas/water transport
- **CL** (Pt, Carbon, Nafion): ~10 μm
  electron conduction, gas/water transport
  proton conduction and chemical reaction
- **Membrane** (Nafion): ~100 μm
  proton conduction and water transport

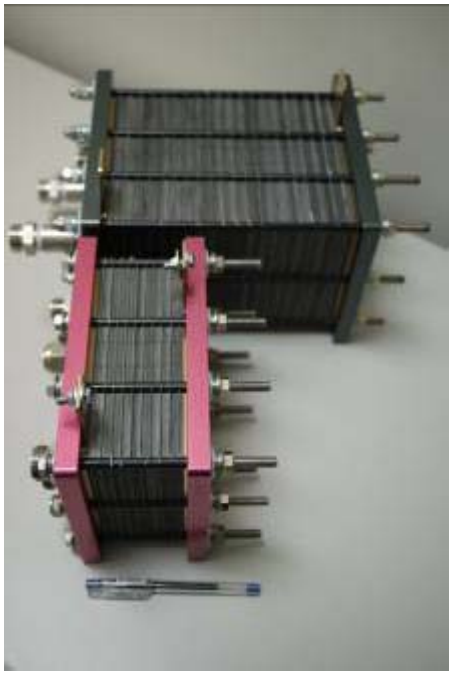
Components, single cell and stack



Polymer electrolyte



Carbon paper



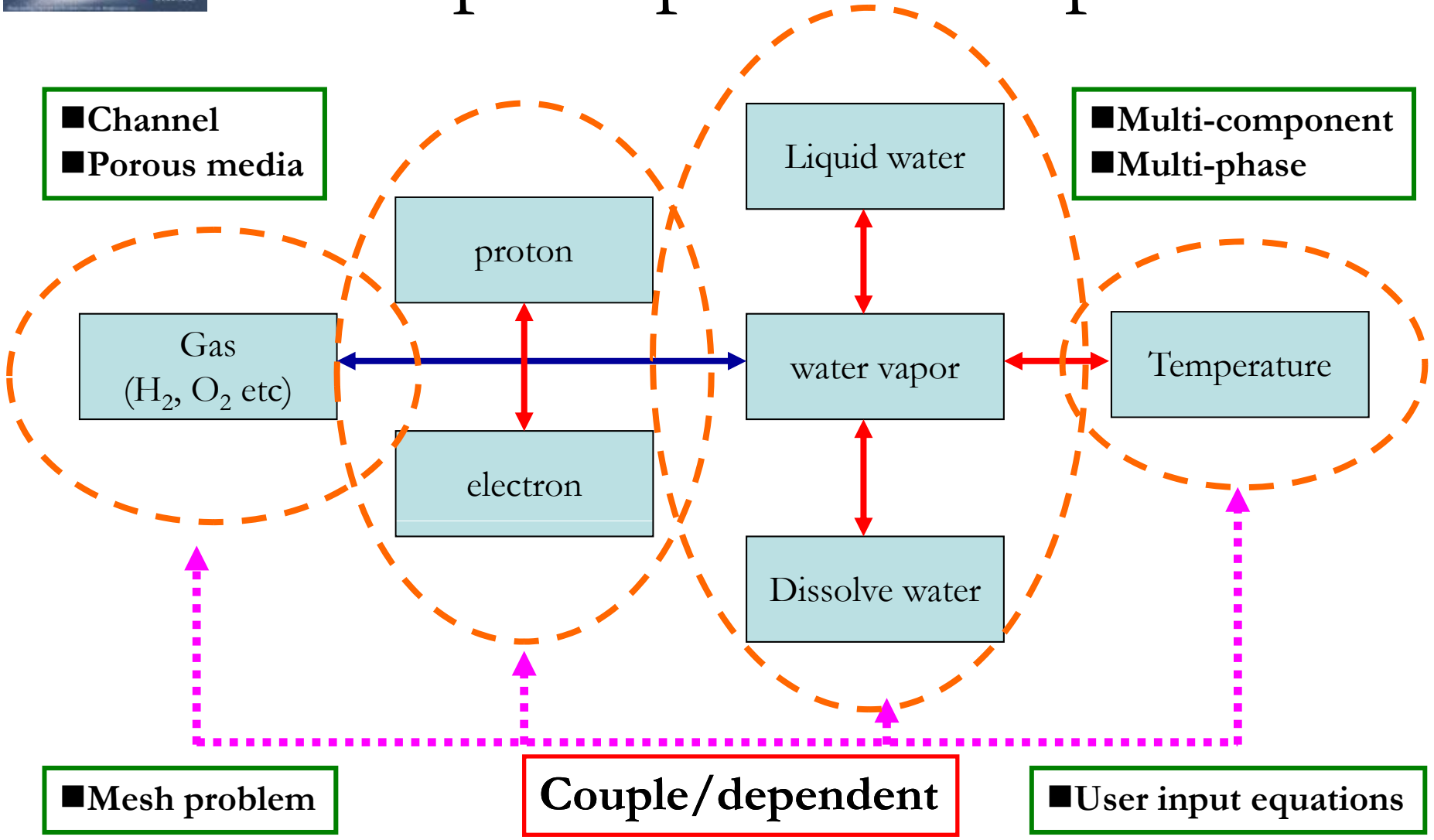
Single cell

FC stack

Bipolar plate

Catalyst layer

Complex species transport



Governing equations

- Conservation of species:

$$\nabla\left(-D_{\text{eff,O2}}\nabla C_{\text{O2}}\right)=S_{\text{O2}}$$

$$\nabla\left(-D_{\text{eff,H2}}\nabla C_{\text{H2}}\right)=S_{\text{H2}}$$

$$\nabla\left(-D_{\text{eff,wv}}\nabla C_{\text{wv}}\right)=S_{\text{wv}}$$

- Conservation of charge:

$$-\nabla\left(\sigma_{\text{e}}^{\text{eff}}\nabla\varphi_{\text{Solid}}\right)=S_{\text{e}}$$

$$-\nabla\left(\sigma_{\text{P}}^{\text{eff}}\nabla\varphi_{\text{electrolyte}}\right)=S_{\text{p}}$$

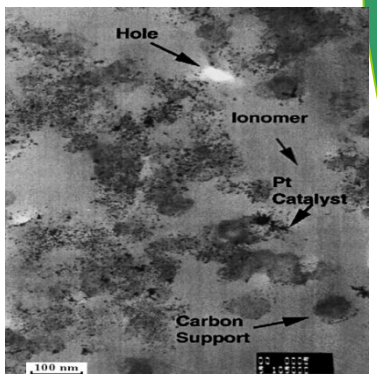
- Conservation of energy:

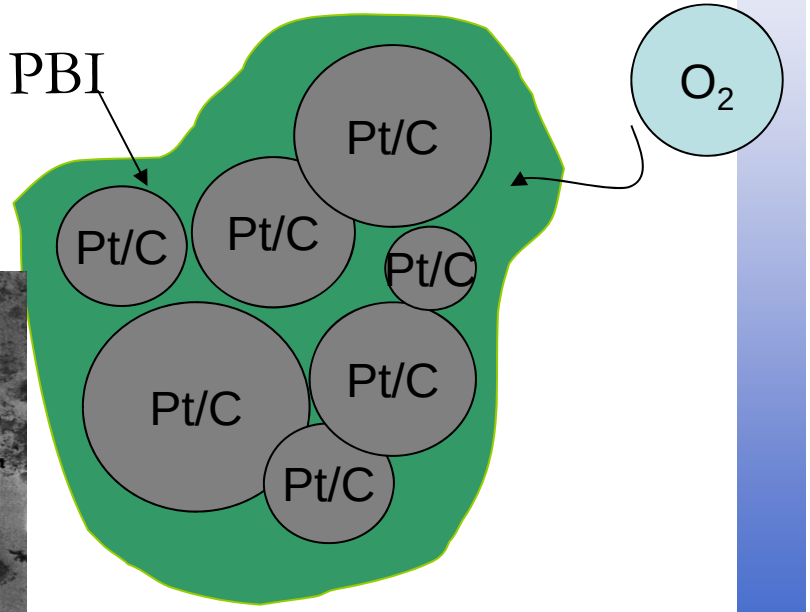
$$\nabla\left(-k_{\text{eff}}\ \nabla T\right)=S_{T}$$

- Bulter-Volmer equation

$$j = j_0\left(\frac{C_i}{C_{ref}}\right)^{\gamma}\left[\exp\left(\frac{\alpha_{a,j}F}{RT}\eta\right)-\exp\left(-\frac{\alpha_{c,j}F}{RT}\eta\right)\right]$$

- Agglomerate model is used





Source terms

Source Terms	AGDL	ACL	PEM	CCL	CGDL
S_{O2} mol/(m^3 s)				$j_c / 4F$	0
S_{H2} mol/(m^3 s)	0	$-j_a / 2F$			
S_{wv} mol/(m^3 s)	$-S_l / M_{H2O}$	$-S_l / M_{H2O} - S_\lambda$		$-S_l / M_{H2O}$	$-S_l / M_{H2O}$
S_λ mol/(m^3 s)		$\xi_a \frac{\rho_M}{EW}(\lambda_{eq} - \lambda)$	0	$\xi_a \frac{\rho_M}{EW}(\lambda_{eq} - \lambda)$	
S_l (kg/m^{3}s)	S_l	S_l		$S_l - S_\lambda M_{H2O} - \frac{j_c}{4F} M_{H2O}$	S_l
S_e (A /m^3)	0	$-j_a$		$-j_c$	0
S_p (A/m^3)		j_a	0	j_c	
S_T (W/m^3)	$\frac{I^2}{\sigma_e^{eff}} + S_l \Delta h_{lg}$	$\lvert j \rvert \lvert \eta \rvert + \frac{I^2}{\sigma_{eff}} + S_l \Delta h_{lg}$	$\frac{I^2}{\sigma_p^{eff}}$	$\lvert j \rvert (\lvert \eta \rvert - \frac{T\Delta S}{nF}) + \frac{I^2}{\sigma_{eff}} + S_l \Delta h_{lg}$	$\frac{I^2}{\sigma_e^{eff}} + S_l \Delta h_{lg}$

Transport parameters

$$D_{H2}^{0} = D_{H2O}^{0} = 1.055\times10^{-4}(T/333)^{1.75}(101325/P)$$

$$D_{H2O}^{0} = 0.2982\times10^{-4}(T/333)^{1.75}(101325/P)$$

$$D_{O2}^{0} = 0.2652\times10^{-4}(T/333)^{1.75}(101325/P)$$

$$D_{O2,nafion}^{0} = 3.1\times10^{-7}\exp(-2768/T))$$

$$D_{H2O,nafion}^{0} = 3.1\times10^{-7}\lambda(e^{0.28\lambda}-1)e^{(-2436/T)} \quad 0<\lambda<3$$

$$D_{H2O,nafion}^{0} = 4.17\times10^{-8}\lambda(161e^{-\lambda}+1)e^{(-2436/T)} \quad 3\le\lambda\le17$$

$$H_{O2}^{Nafion} = 1.33\times10^{5}\exp(-666/T)$$

$$\sigma_{p}^{0} = (0.514\lambda-0.326)\exp(1268(\frac{1}{303}-\frac{1}{T})) \quad \lambda\ge1$$

$$\sigma_{p}^{0} = 0.1879\lambda\exp(1268(\frac{1}{303}-\frac{1}{T})) \quad \lambda<1$$

Kinetic parameters

$$\eta = \varphi_{solid} - \varphi_{electroltye} - \varphi_0$$

$$j_{0,a}^{ref} = i_{0,a}^{ref}\big|_{343K} (S/V)_0 \exp\left[\frac{E_a^{act}}{R}\left(\frac{1}{343} - \frac{1}{T}\right)\right]$$

$$j_{0,c}^{ref} = i_{0,c}^{ref}\big|_{343K} (S/V)_0 \exp\left[\frac{E_c^{act}}{R}\left(\frac{1}{343} - \frac{1}{T}\right)\right]$$

$$j_a = j_{0,a}^{ref}\left(\frac{P_{H2}}{P_{H2}^{ref}}\right)\left[\exp\left(\frac{\alpha\eta F}{RT}\right) - \exp\left(-\frac{\alpha\eta F}{RT}\right)\right]$$

$$j_c = -4F\frac{P_{O2}}{H_{O2}^{Naf}}\xi k_\eta$$

$$\phi = \frac{r_{agg}}{3}\sqrt{k_\eta / \left[D_{O2,eff}^{eff}(1-\varepsilon_{CL})\right]}$$

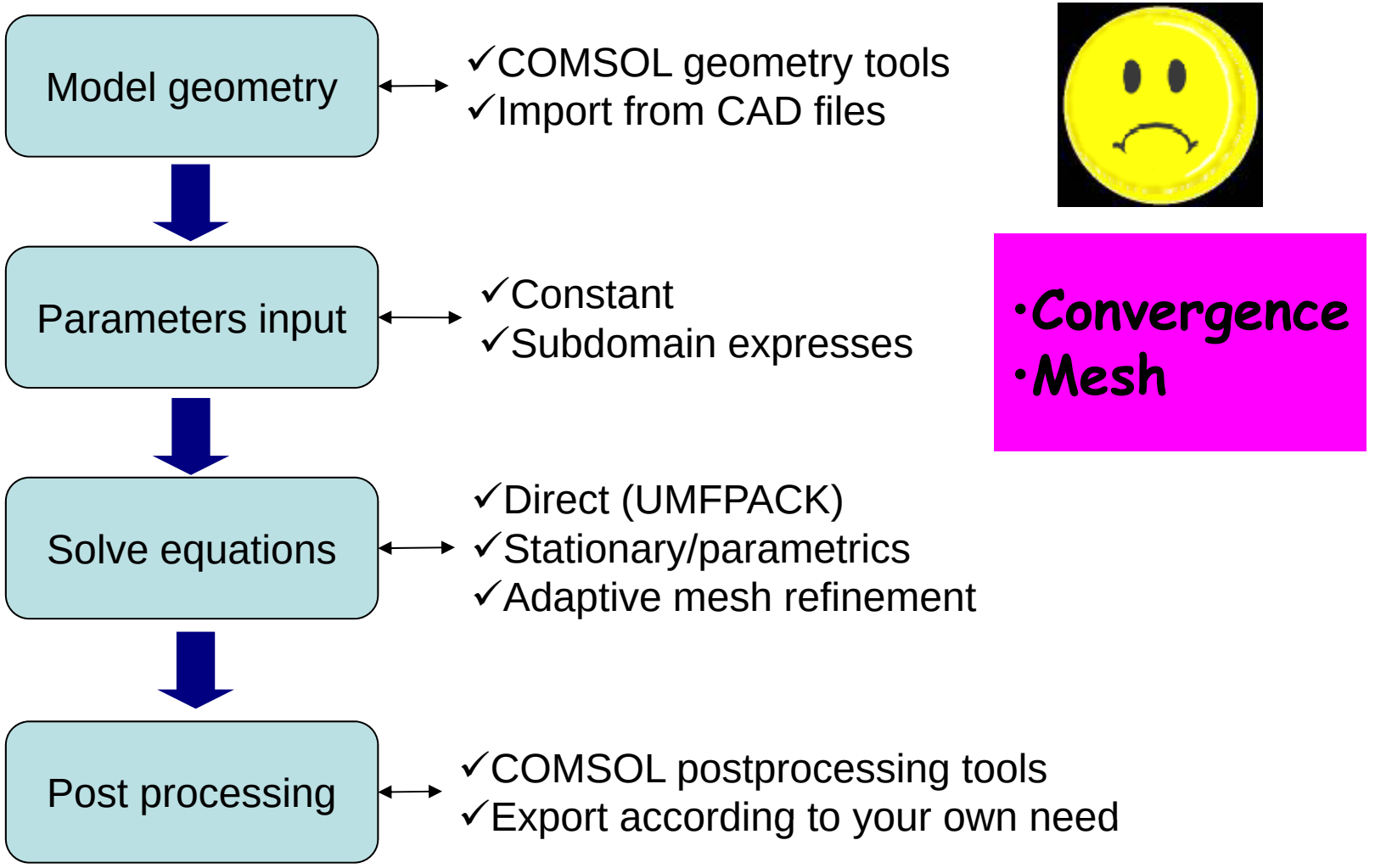
$$\xi = \left[3\phi\coth(3\phi) - 1\right]/(3\phi^2)$$

$$k_\eta = \frac{1}{4FC_{O2}^{ref}} j_{0,c}^{ref} \exp\left[-\frac{\alpha_c \eta F}{RT}\right]$$

$$S_l = K_{cond}\Delta P \varepsilon s \rho_l : \Delta P \langle 0$$

$$S_l = K_{cond}\Delta P \frac{\varepsilon(1-s)X_{wv}M_{H2O}}{RT} : \Delta P \geq 0$$

Simulation flow chart



Challenges & solutions

- Convergence
  - Mainly due to coupled equations (8) and lots of variable dependent parameters.
    - ✓Appropriate value of initial value
    - ✓Using RESTART to solve equations step by step
- Mesh
  - Finer or coarser mesh are both possible to solve the problem (adaptive method can be used)

Great improvement form ver.2.3 → ver.4.2 !!!

Models used in COMSOL

- Chemical Engineering Module
  - Mass Transport → Convection and Diffusion (4)
  - Energy Transport → Convection and Conduction(1)
- AC/DC Module
  - Conductive Media DC (2)
- COMSOL Multiphysics Module
  - PDE, Coefficient Form(1)

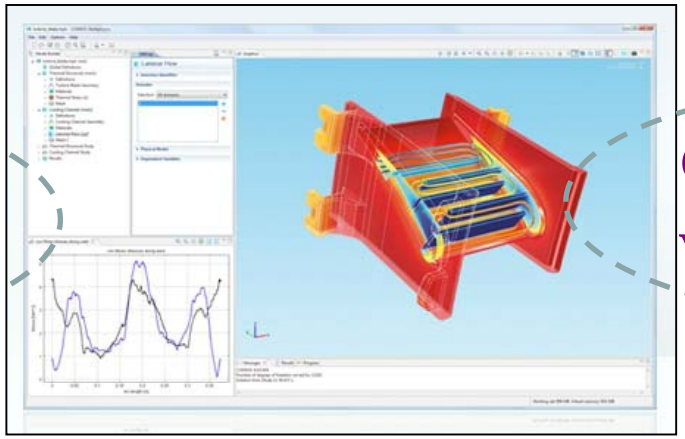
All solved variables are dependent

What we need is…

Flexible mesh generation

User friendly interface

User friendly interface



Couple different variables at will

COMSOL Multiphysics

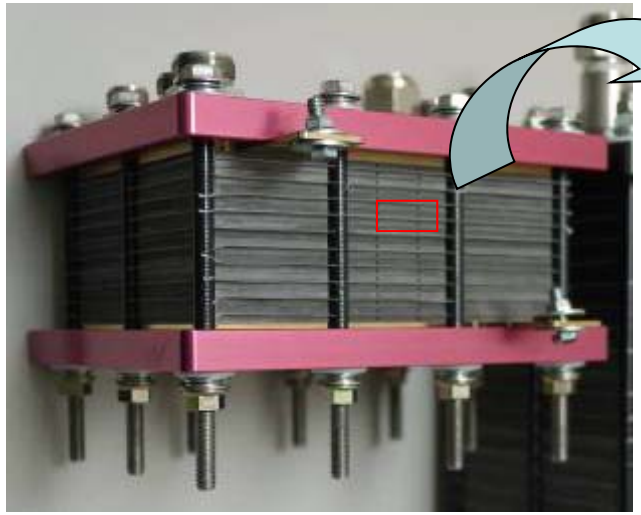
Powerful post-processing

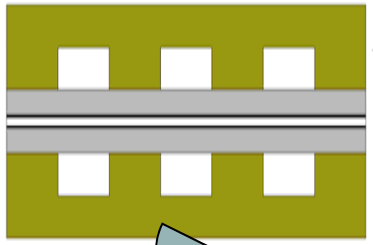
Easy user define function input

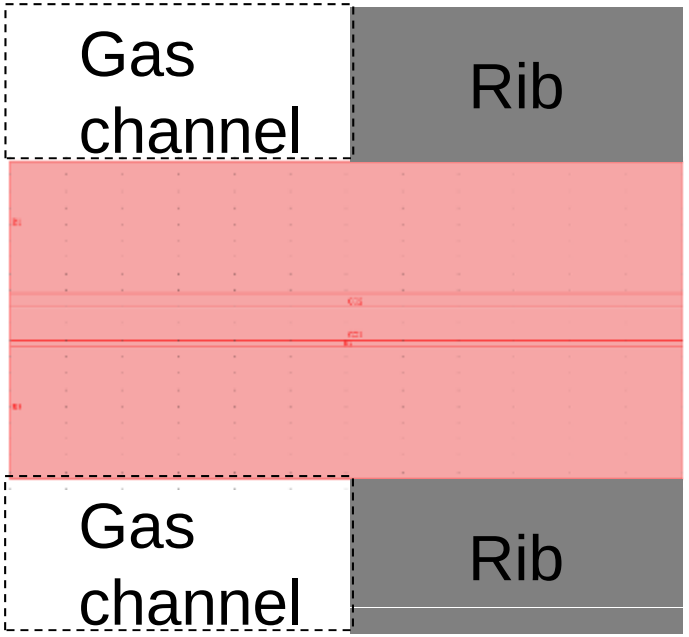
Examples solved by COMSOL
- Proton exchange membrane fuel cell

2D simulations

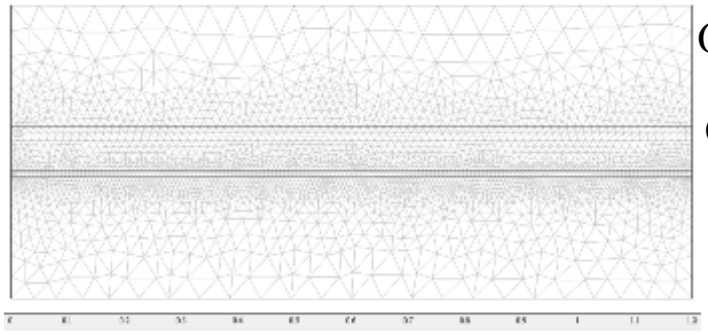
- Simulation domain







Cathode GDL: 200µm
Cathode CL: 20µm
Electrolyte: 50µm
Anode CL: 10µm
Anode GDL 200µm



INCREASE
CL performance

REDUCE
CL cost

- ✓Pt loading
- ✓PBI content
- ✓Pt/C wt%
- ✓Support material
- ✓CL thickness
- ✓Alternative catalyst material

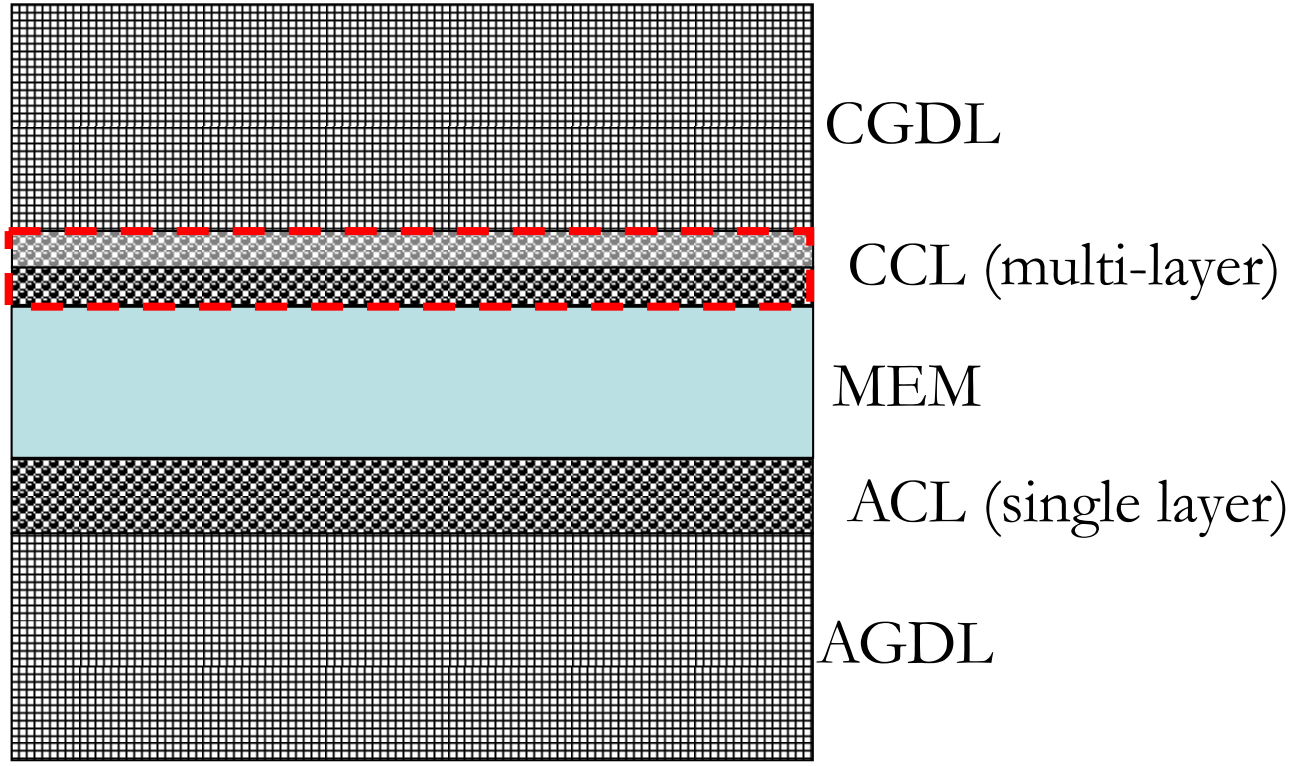
CL with different PBI wt% compositions

Performance can be increased!

Cost can be reduced!

Multi-layer CL design

Non-uniform composition of PBI content



MEA structure

Case studied(1/2) – single layer

PBI 含量	5wt%	10wt%	20wt%	30wt%
觸媒層厚度	2e-5m	2.05e-5m	2.3e-5m	2.35e-5m
PBI薄膜厚度	1e-8m	2.4e-8m	5.5e-8m	6e-8m
孔隙率	0.439	0.436	0.404	0.382
Pt/C體積分率	0.510	0.459	0.386	0.267
PBI體積分率	0.0506	0.104	0.209	0.3507
彎曲率	1.3	1.6	2.8	4.5
Pt loading	0.5mg/cm^2	0.5mg/cm^2	0.5mg/cm^2	0.5mg/cm^2

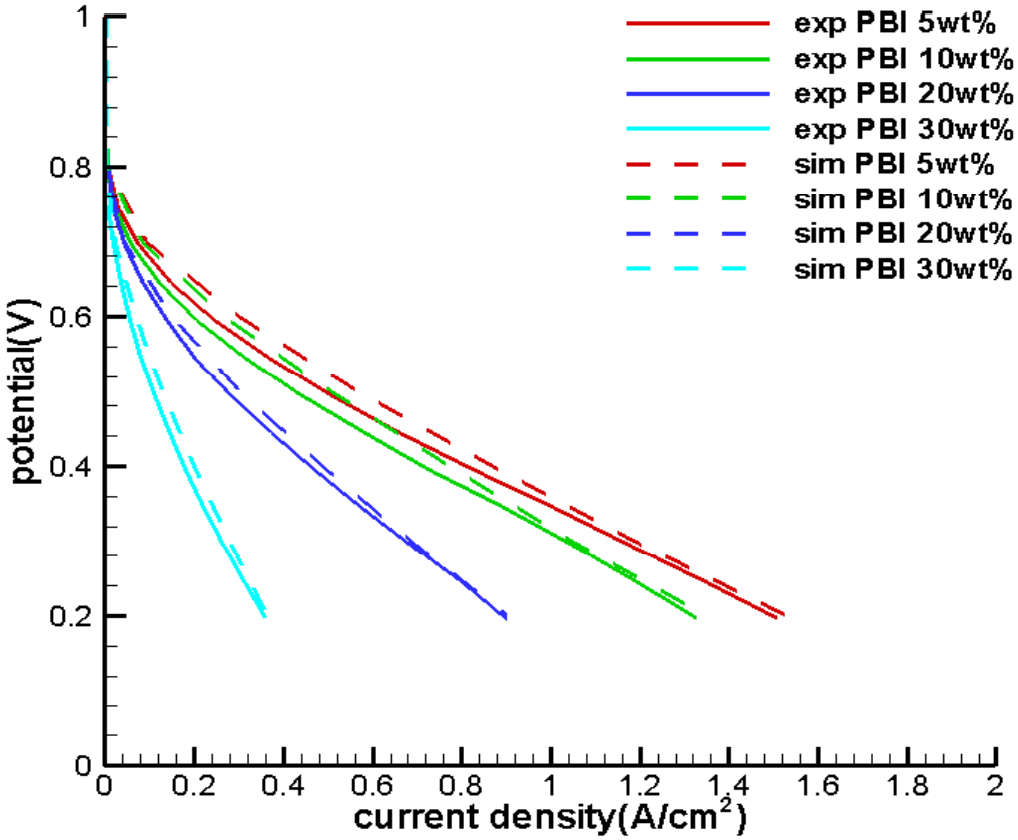
Optimizing PBI content in single CL design

Case studied(2/2) – multi-layer

觸媒層結構		%PBI	Pt loading	觸媒層厚度	PBI薄膜厚度
(a)	cathode	5wt%	0.333mg/cm^2	2e-5/2 m	1e-8m
		30wt%	0.167mg/cm^2	2.35e-5/2m	3e-8m
(b)	cathode	10wt%	0.333mg/cm^2	2.05e-5/2m	2e-8m
		30wt%	0.167mg/cm^2	2.35e-5/2m	3e-8m
(c)	cathode	5wt%	0.167mg/cm^2	2e-5/3m	1e-8m
		10wt%	0.167mg/cm^2	2.05e-5/3m	2e-8m
		20wt%	0.166mg/cm^2	2.3e-5/3m	2.2e-8m

Optimizing PBI content distribution in multi-CL design

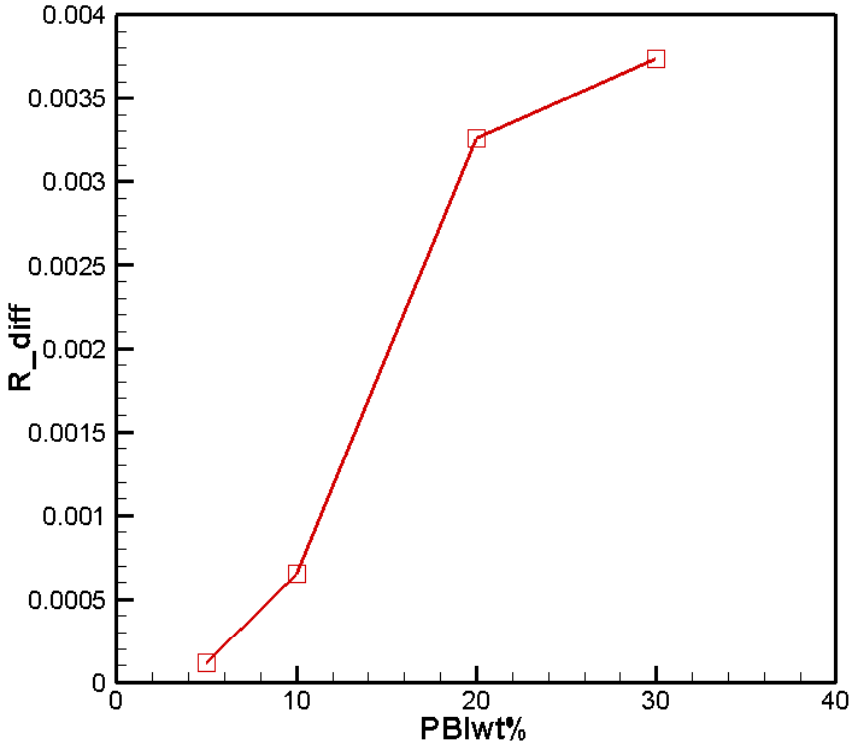
Experimental validation - single layer

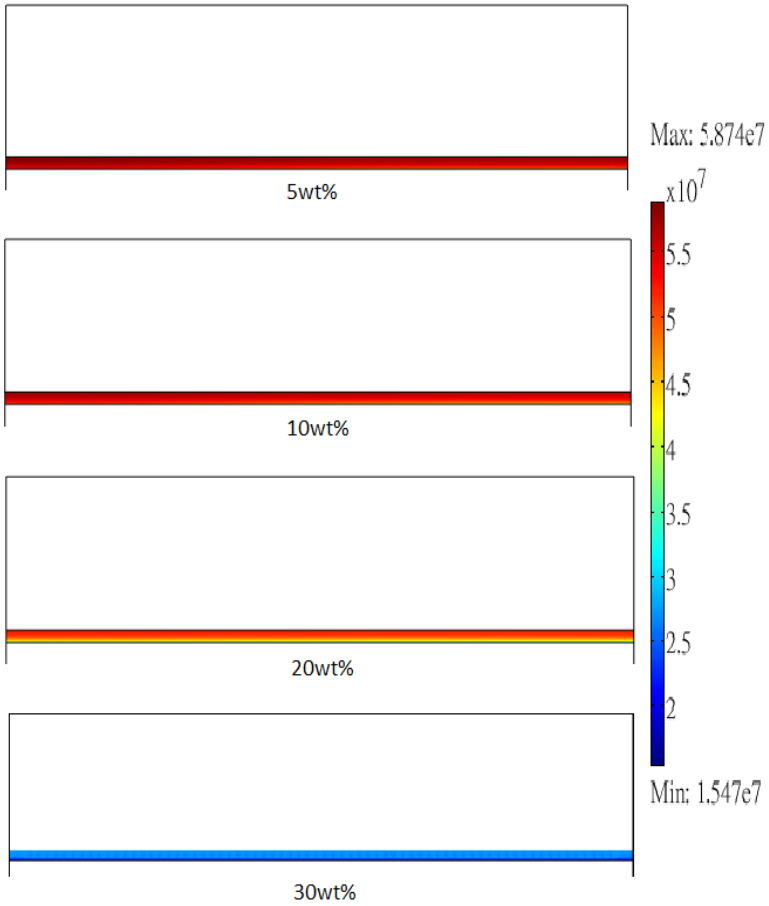


5 wt% of PBI is the best

Good match with experimental data

Detail analysis (single layer)





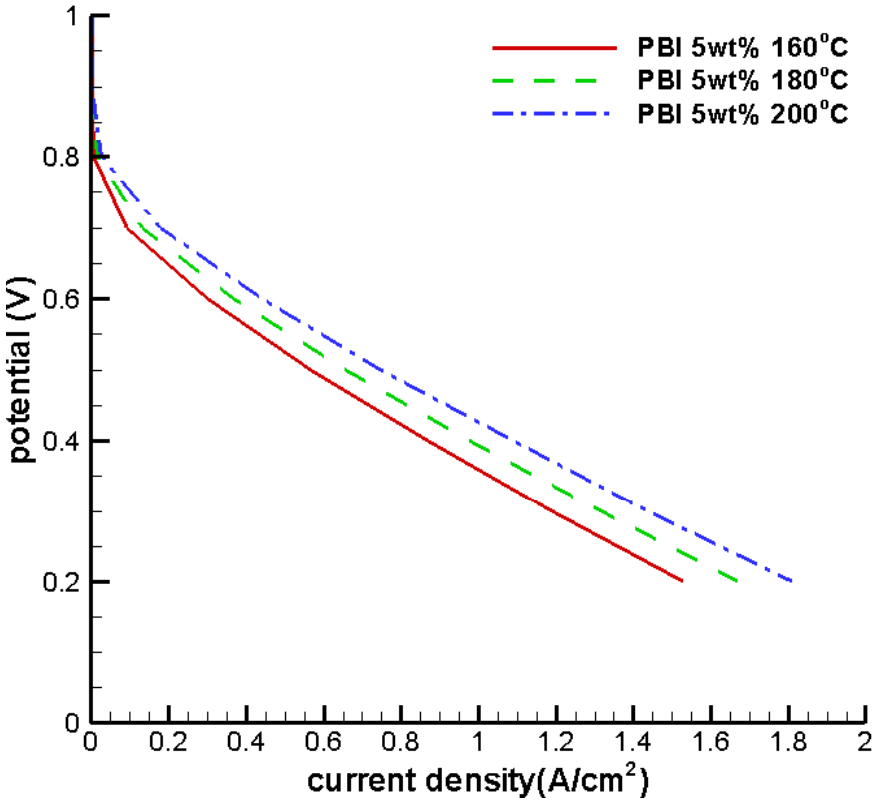
$$R_{diff} = \frac{\delta_{PBI}}{a_{ratio} \times D_{O_2}^{PBI}}$$

Resistivity of gas diffusion

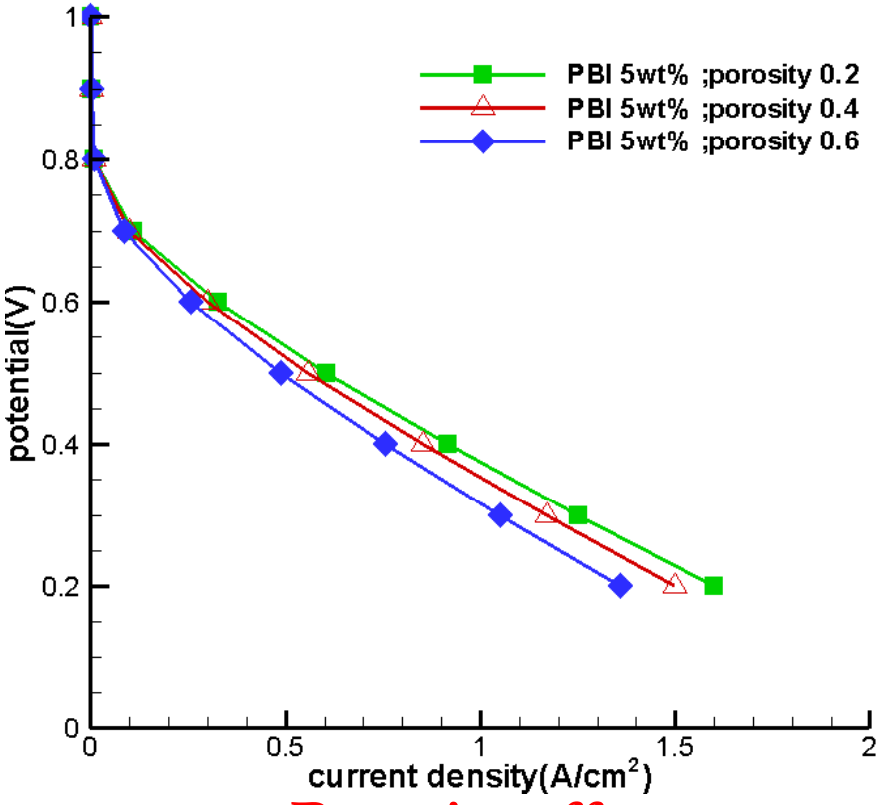
$$a_{ratio} = \frac{6 m_{Pt}}{\rho_{Pt} d_{Pt} L_{cat}} (1-\theta)$$

Effective Pt reaction area

Parametric study (1/2)

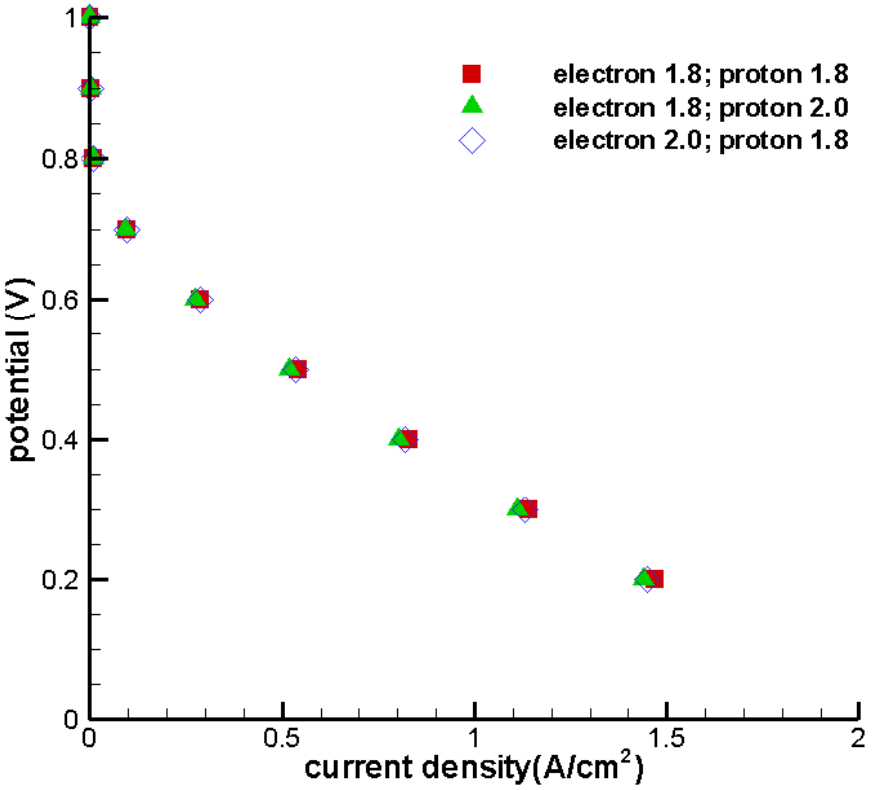


Temperature effect

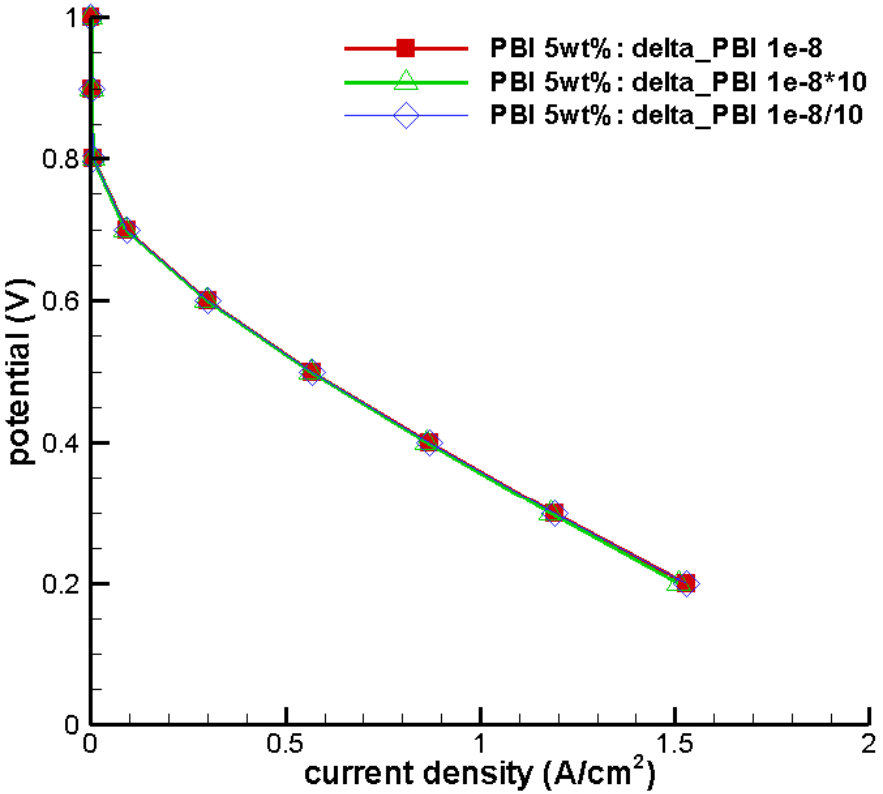


Porosity effect

Parametric study (2/2)

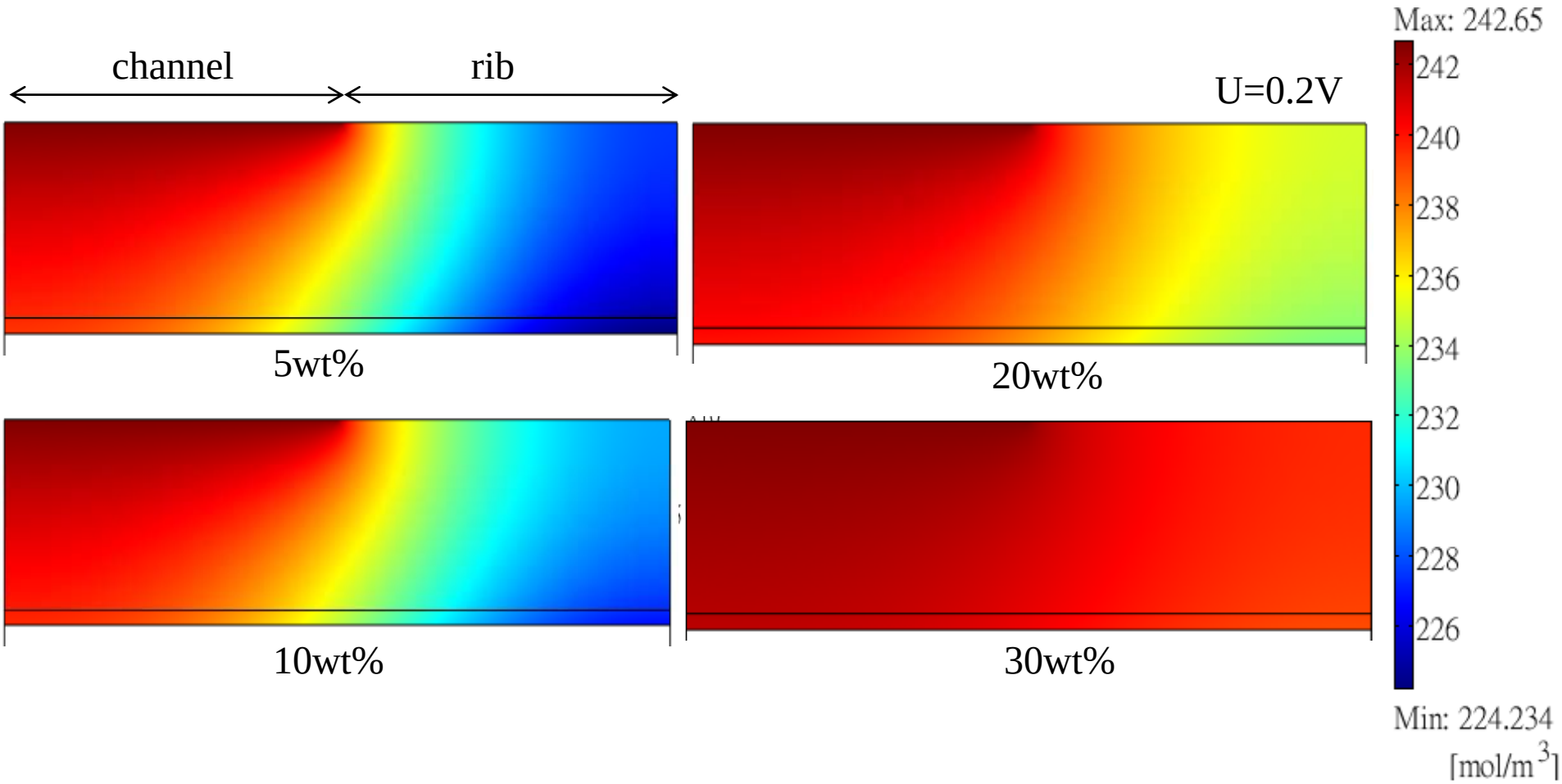


Totuorsity effect

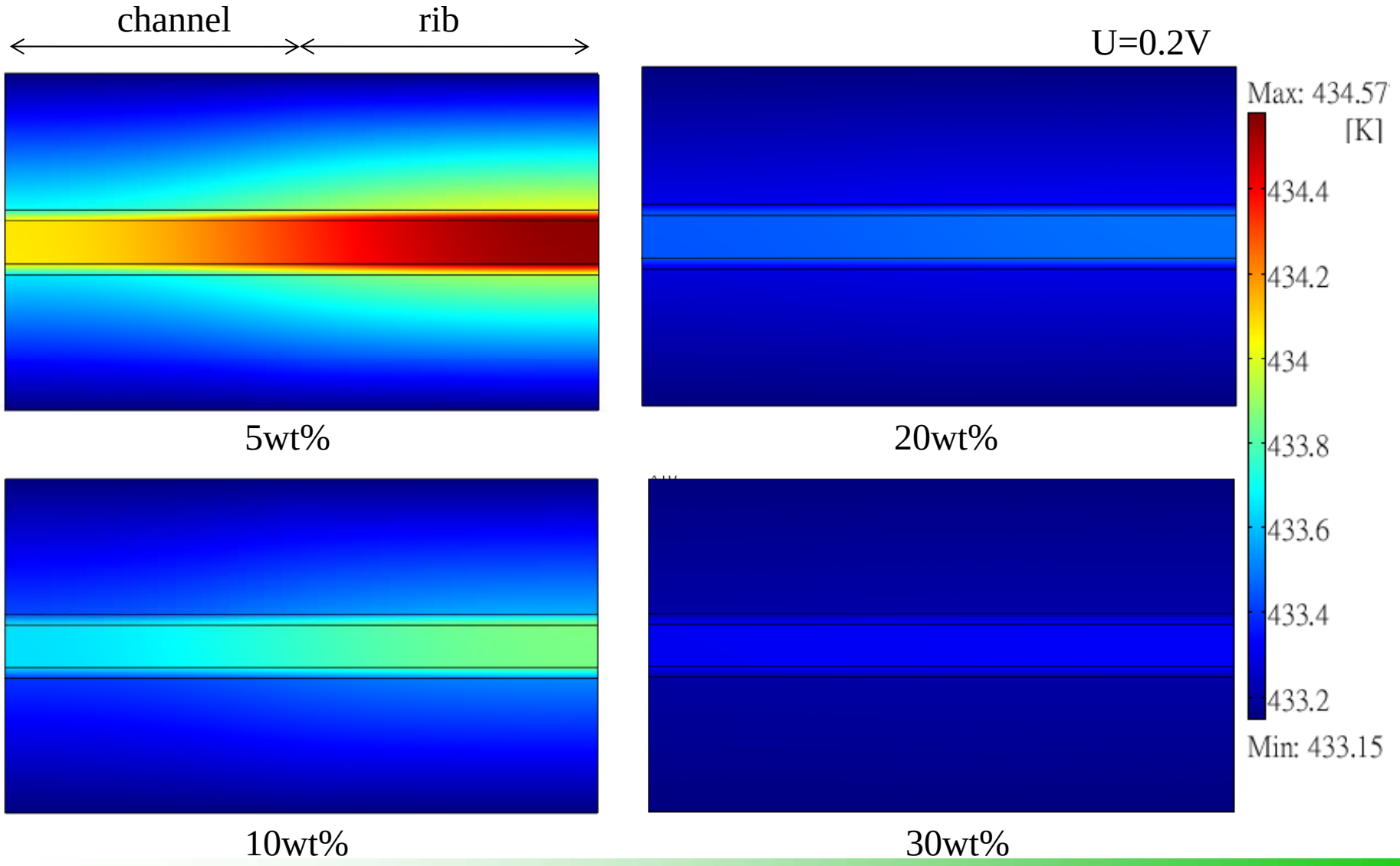


Thickness effect

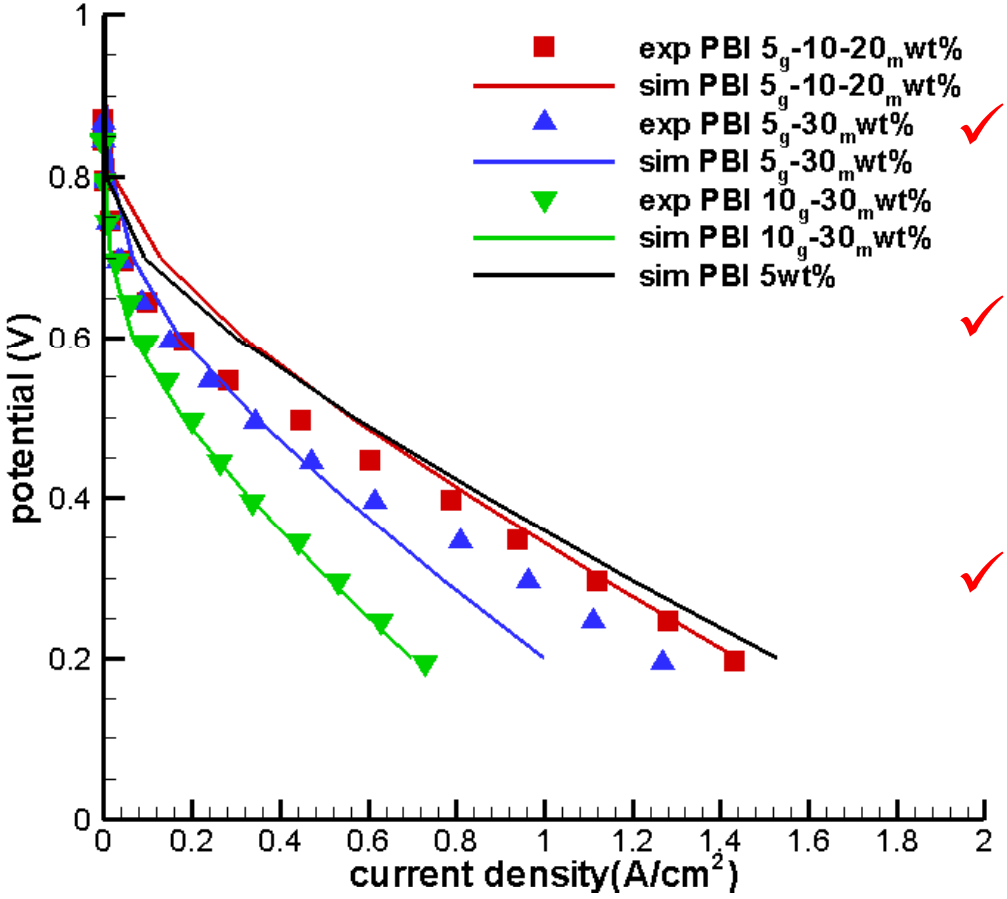
Cathode O_2 distribution



Temperature distribution

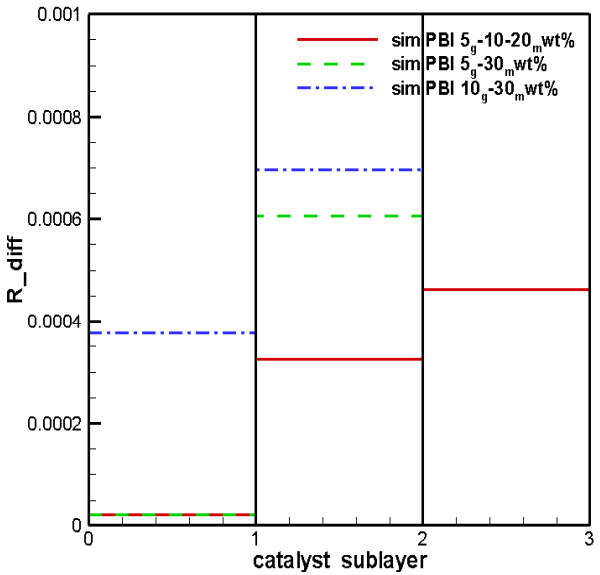


Experimental validation - multi-layer

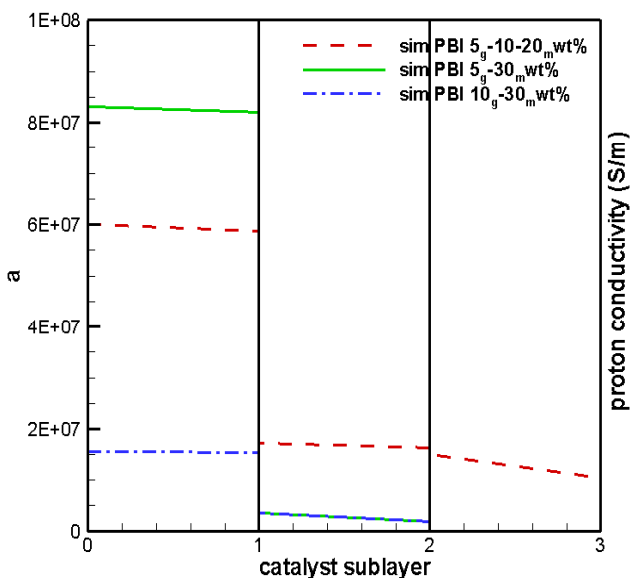


- ✓ **Good match with experimental data**
- ✓ **Higher PBI content is required for sub-layer close to membrane**
  - For increasing proton conductivity
- ✓ **Lower PBI content is required for sub-layer close to GDL**
  - For increasing gas diffusivity

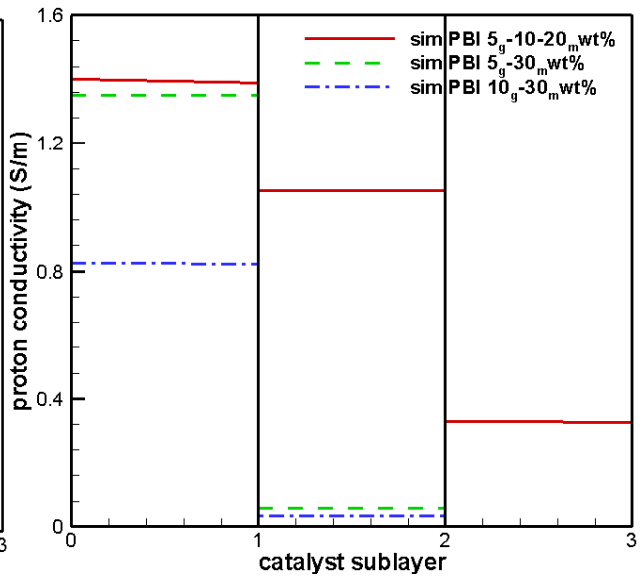
Detail analysis (multi-layer)



Resistivity of gas diffusion



Effective Pt reaction area

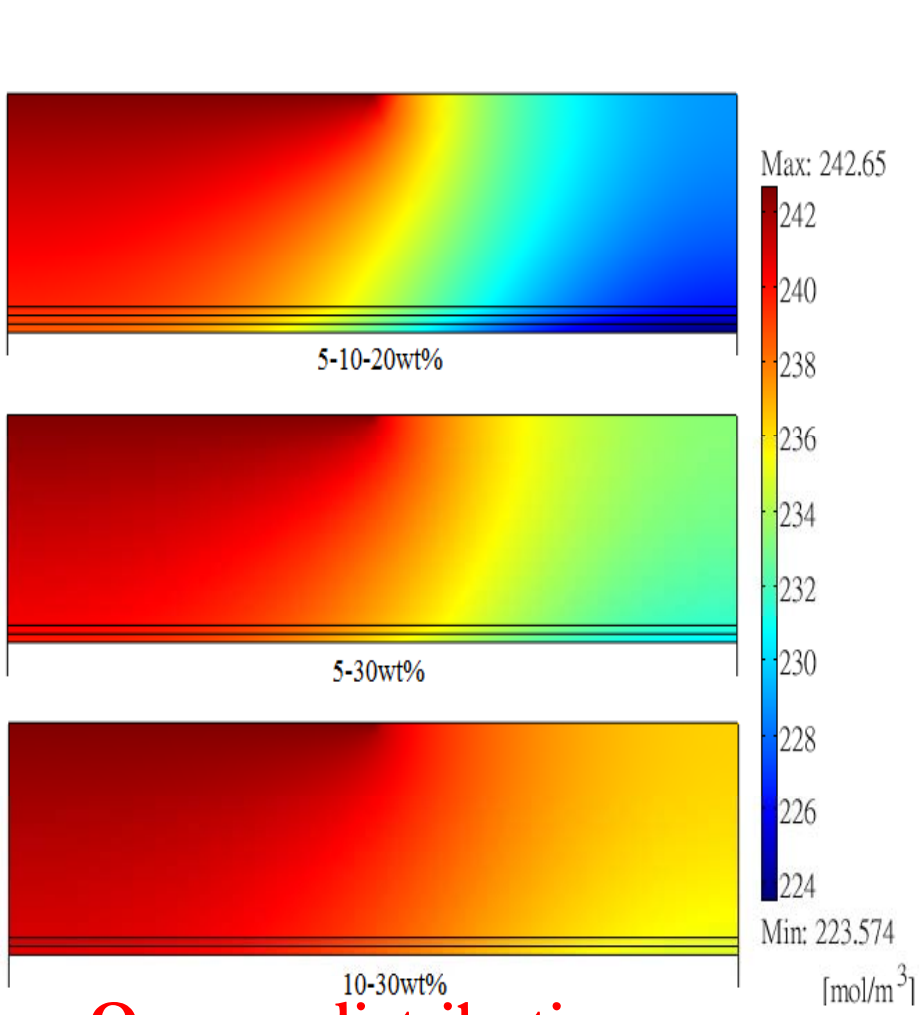


Proton conductivity

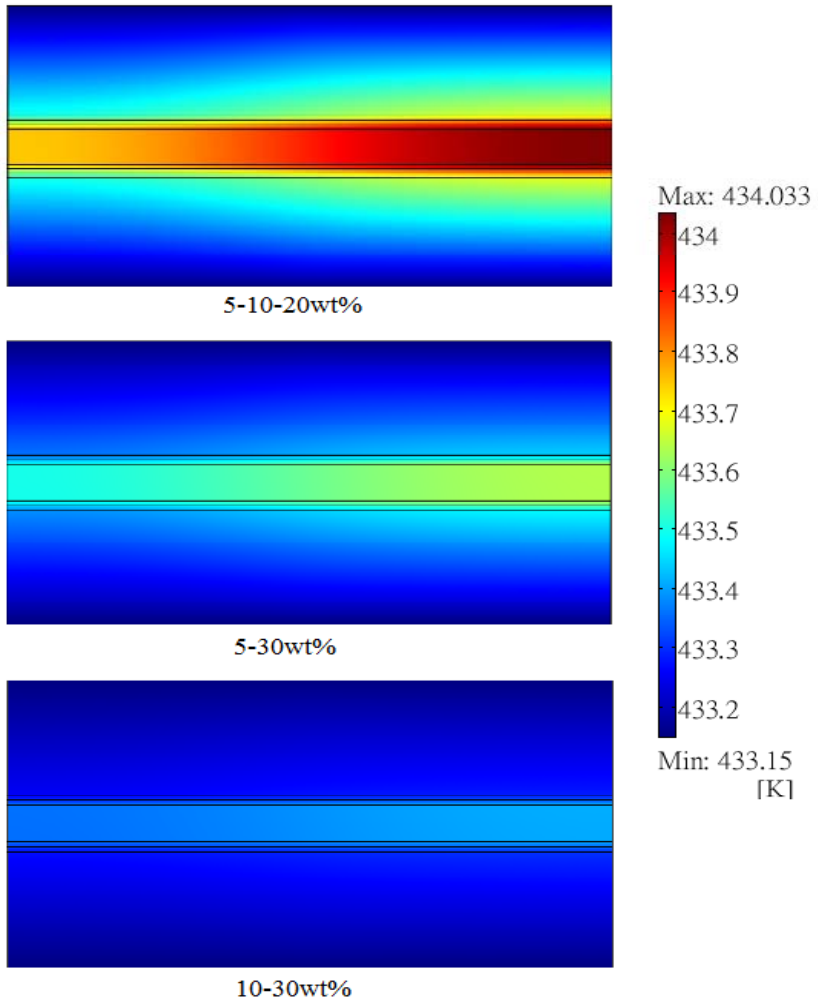
Different effect for different physical properties

for different regions is observed

Internal distributions

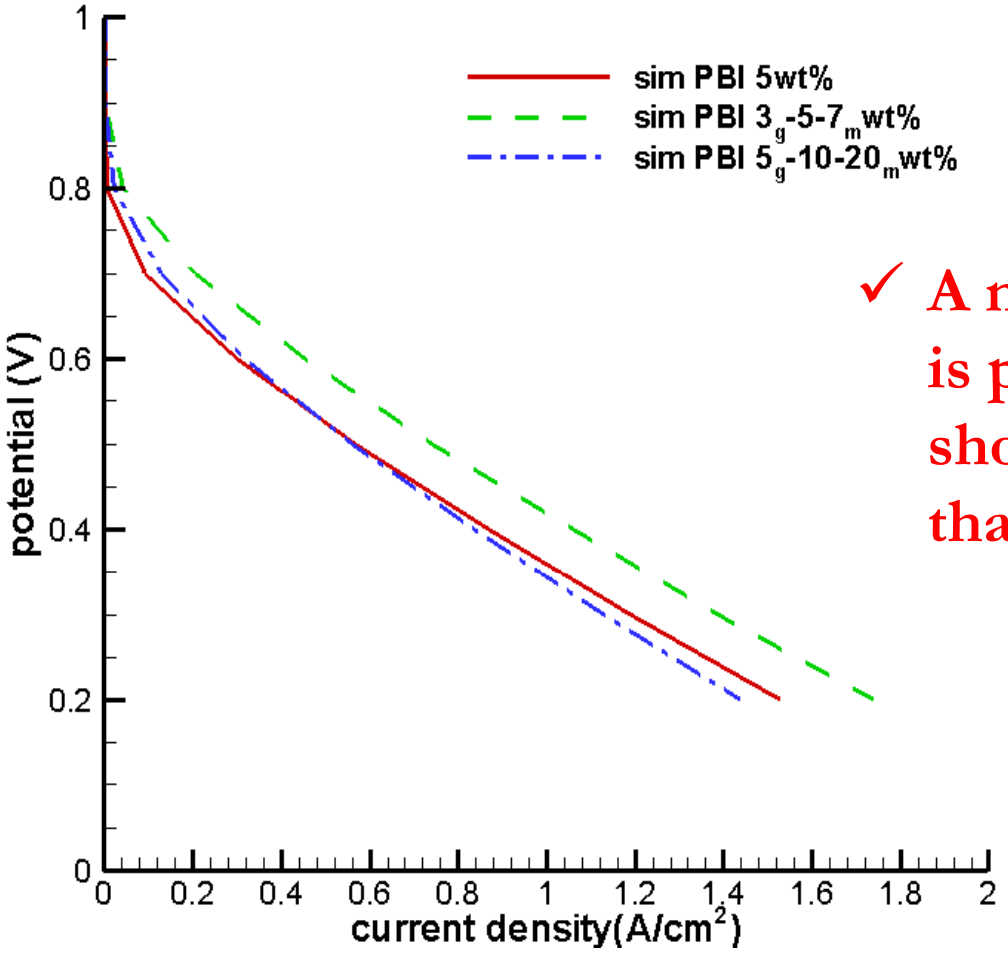


Oxygen distribution



Temperature distribution

New multi-layer CL design



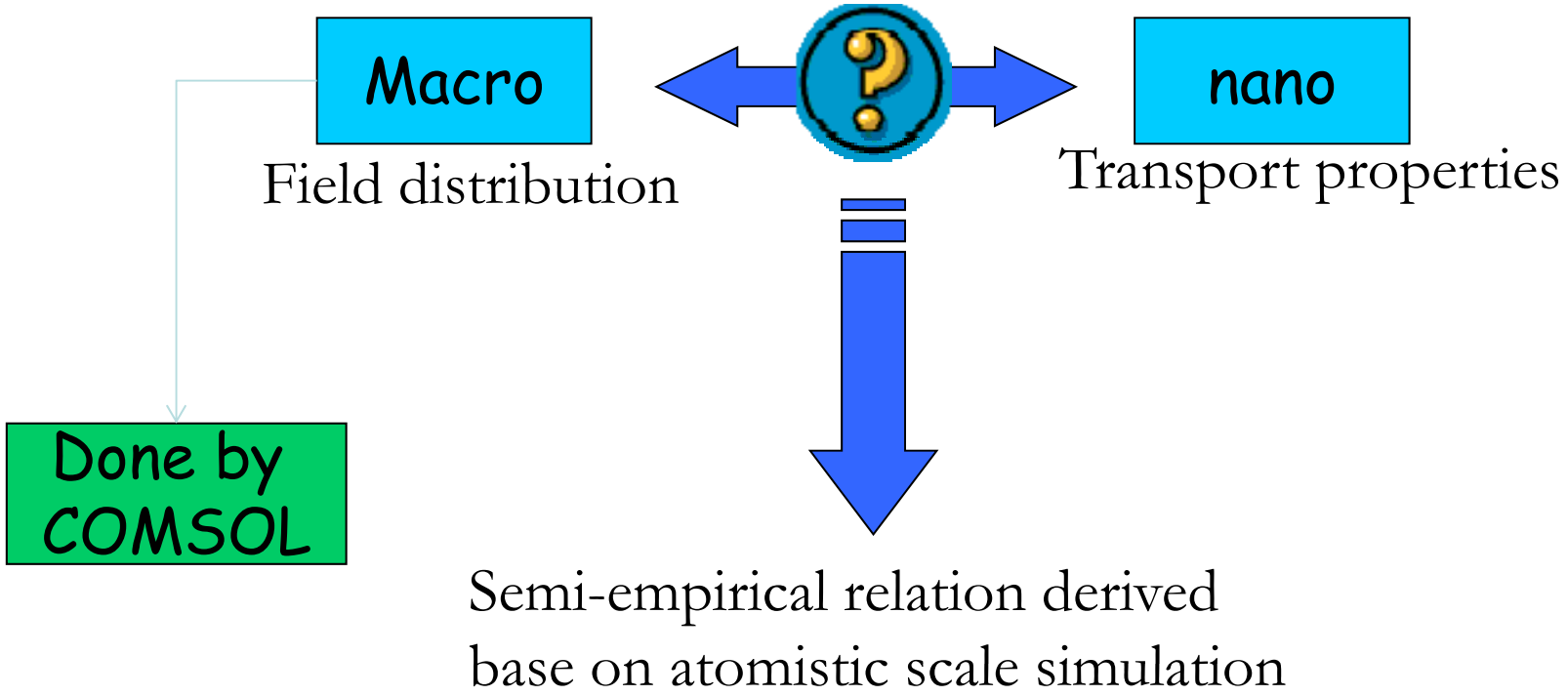
- ✓ **A new <u>triple-layer</u> CL design is proposed (3-5-7wt%) and is shown to have better performance than single layer design**

Examples solved by COMSOL
- Conceptual multi-scale simulation

Why multi-scale simulation?

- From fundamental point of view…
  - All macroscopic transport properties (eg. diffusivity) are ensemble average of microscopic transport phenomena
  - Traditional correlations is inadequate to describe what really happen
- Challenges…
  - No real couple multi-scale simulation package can be found
  - Alternative way to do this is necessary

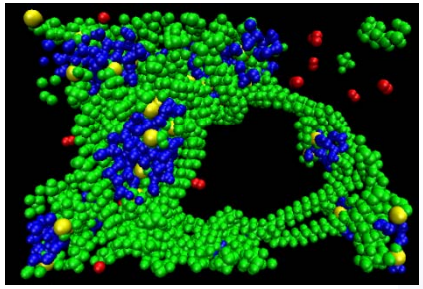
Concept of multi-scale



Take advantage of COMSOL's very flexible and user friendly interface/functions!

Simulation procedures

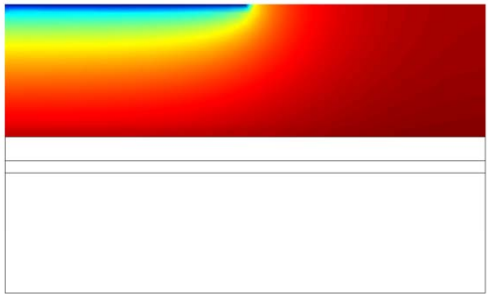
$$D_{O_2,Nafion} = 5.438\times10^{-9}\lambda - 2.4589\times10^{-9}(m^2s^{-1})$$
$$D_{H_2O,Nafion} = 2.8814\times10^{-9}\lambda + 3.4678\times10^{-10}(m^2s^{-1})$$

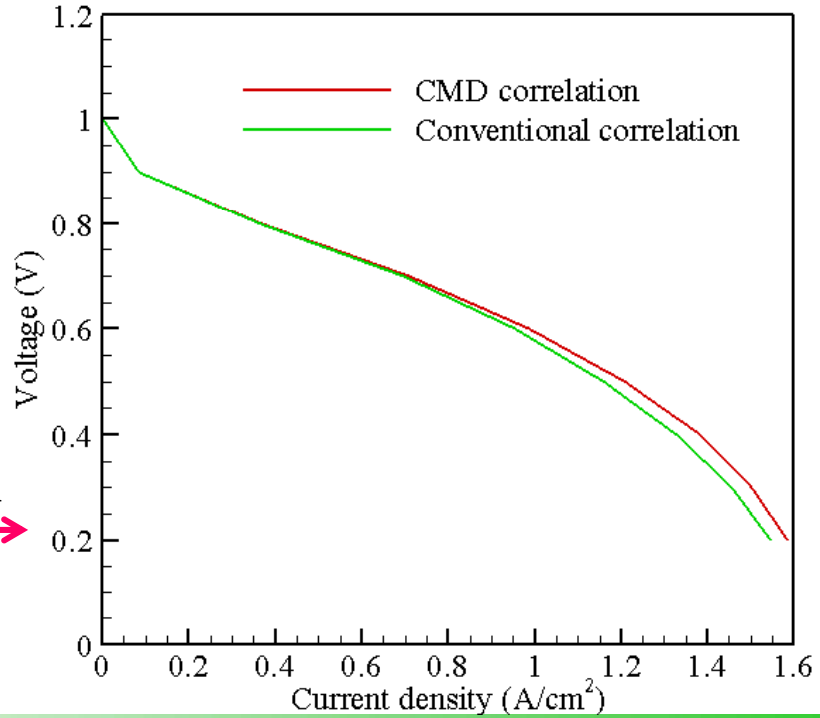


Estimated by molecular dynamics simulations

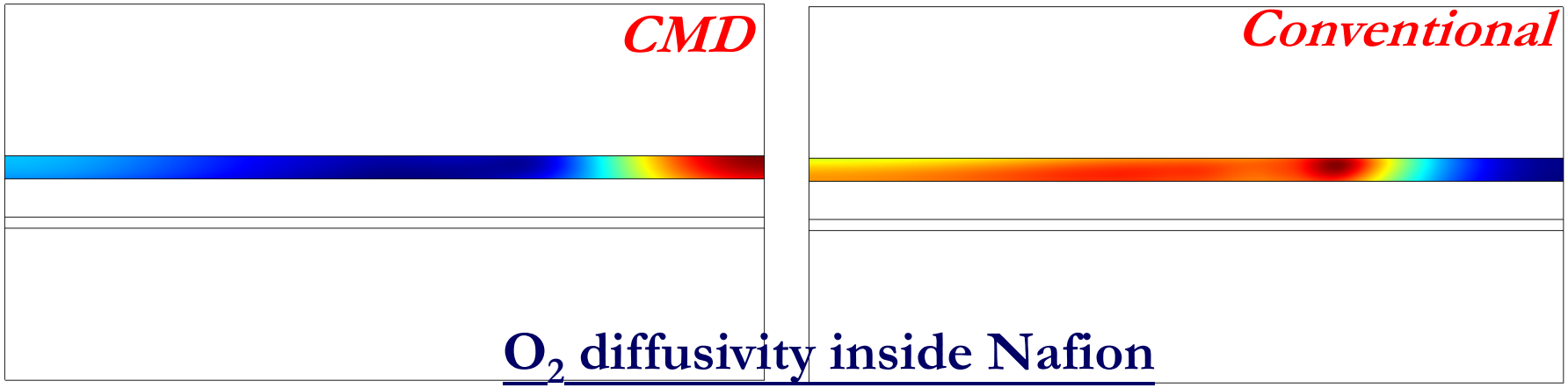
Input into **COMSOL**

simulation

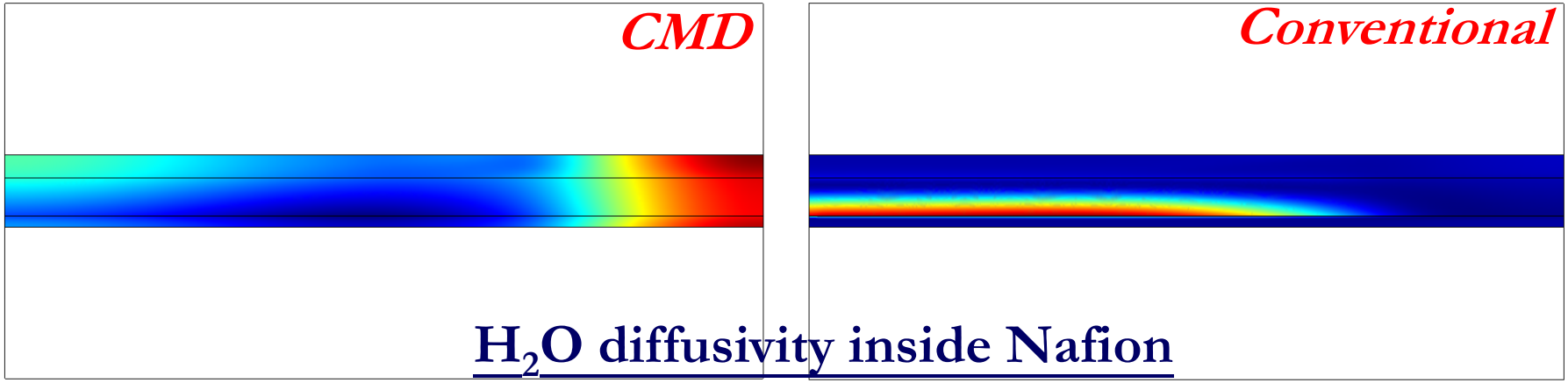




Diffusivity distribution



O_2 diffusivity inside Nafion



H_2O diffusivity inside Nafion

- ✓ Similar performance but different internal distribution
- ✓ Different optimization design will be proposed !!!

Thanks for your attention!