

PEM Fuel Cell Using Equation-based Modelling

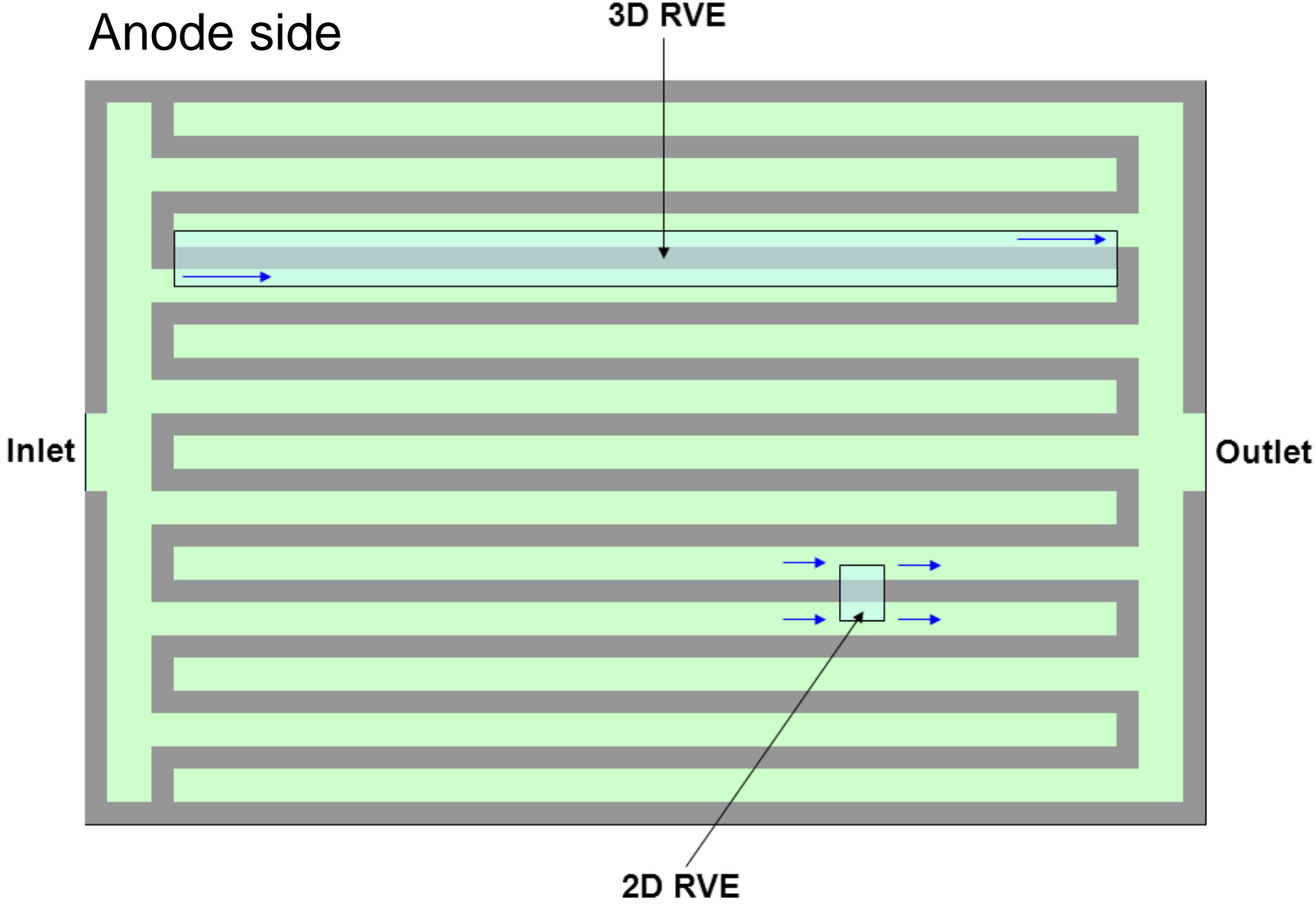
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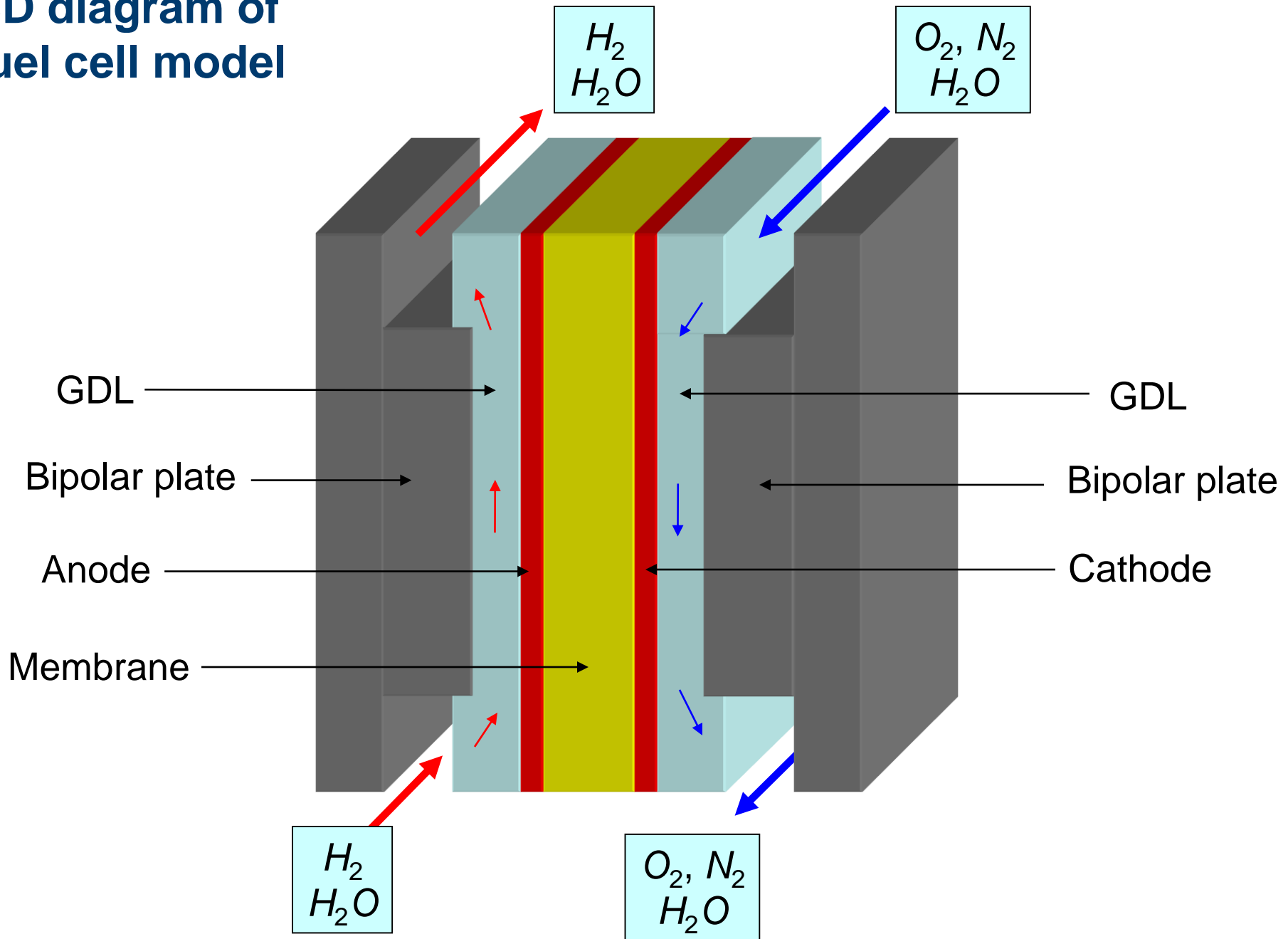
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Channels of inter-digitated fuel cell



3D diagram of fuel cell model



Equations to solve

$$\nabla \cdot (\sigma_{ele} \nabla V_{ele}) + Q_{ele} = 0 \quad \text{Poisson's equation}$$

$$\nabla \cdot \left(-\frac{\rho \kappa}{\eta} \nabla p \right) = F \quad \text{Darcy's Law}$$

Complex Source terms

Maxwell-Stephan equation

$$\nabla \cdot \left[-\rho \omega_H \sum_{k=1}^2 \bar{D}_{1k} \left\{ \nabla x_k + (x_k - \omega_k) \frac{\nabla p}{p} \right\} \right] = R_H - \rho \mathbf{u} \cdot \nabla \omega_H$$

Nernst-Planck equation

$$\nabla \cdot \left[-D_k \left(\nabla c_k + \frac{F z_k c_k}{RT} \nabla V_{mem} \right) \right] = \bar{S}_k$$

Non-linear source terms (agglomerate model)

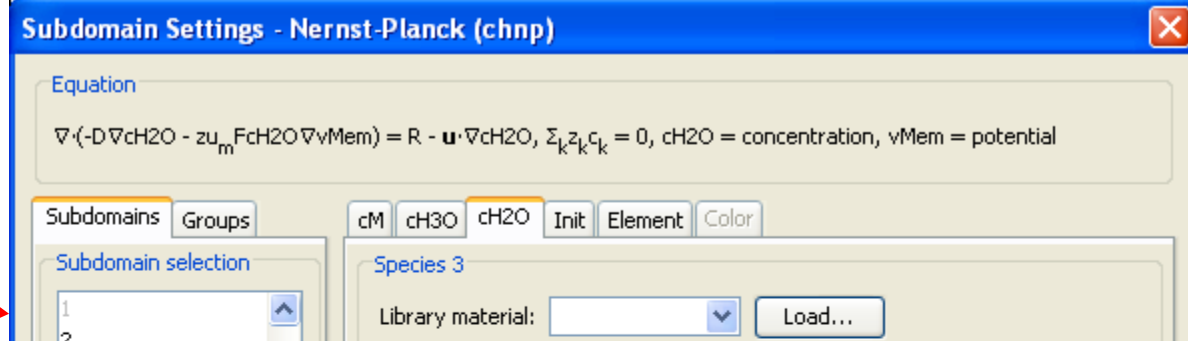
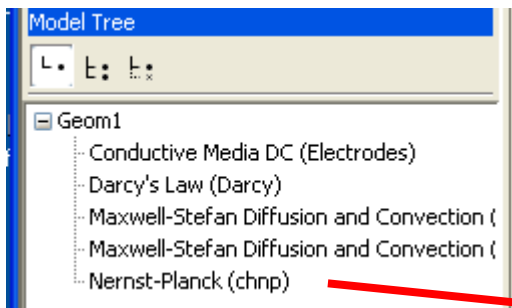
$$R_H = (1 - \omega_H) m_H S_H^{ano} - \omega_H m_{H_2O} S_{H_2O}^{ano}$$

$$S_H^{ano} = -\frac{3 f_{ano}}{r_{ano}^2} D_H^{agg} c_H^{agg} \left[\beta_H \coth(\beta_H) - 1 \right] \leq 0$$

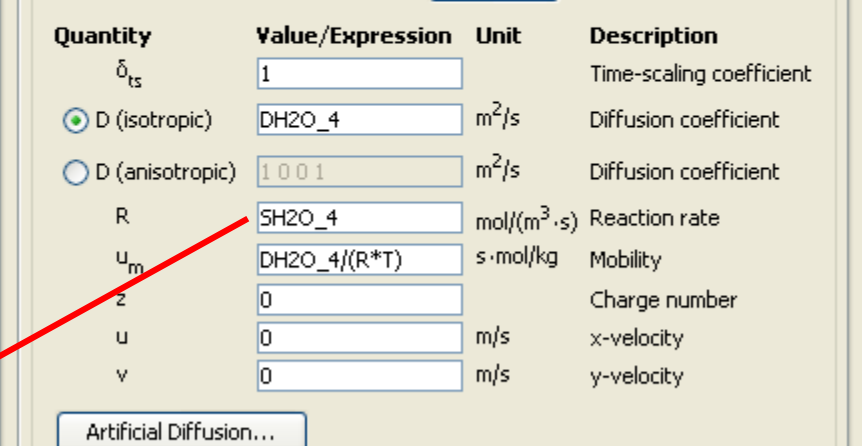
$$\beta_H^2 = \frac{i_{ano}^{ref}}{2F} \frac{s_{ano} r_{ano}^2}{D_H^{agg} c_H^{ref}} \left[\exp\left(\frac{F \alpha_{ox}^{ano} \eta_{ano}}{RT}\right) - \exp\left(-\frac{F \alpha_{red}^{ano} \eta_{ano}}{RT}\right) \right]$$

$$\eta_{ano} = V_{ele} - V_{mem} - V_{ano}^{eq} \geq 0$$

COMSOL Module based FE setup



Name	Expression	Unit	Description
GAno	if(abs(zH)<1e-8,0,if(zH<0,sqrt(-zH)/ta...	1	Special case of zH near
iAno	iotAno*dHAgg*cHAgg*GAno	A/m ³	See (36)
Q2	iAno	A/m ³	See (36) (>=0)
vCatTil	vEle-vMem-vCatEq	v	See (27)
iotCat	12.0*F*nuCat/(rCat^2)	s·A/	See (37)
zetCat	iCatRef*(rCat^2)*sCat/(4.0*F*dOAgg...	1	See (24)
xiCatOx	F*alpCatOx/(R*T)	s ³ ·A/	See (24)
xiCatRed	F*alpCatRed/(R*T)	s ³ ·A/	See (24)
zO	zetCat*(-exp(xiCatOx*vCatTil)+exp(-xi...	1	betaO^2 (24)
GCat	if(abs(zO)<1e-8,0,if(zO<0,sqrt(-zO)/ta...	1	Special case of zO near
iCat	iotCat*dOAgg*cOAgg*GCat	A/m ³	See (37)
Q4	iCat	A/m ³	See (37) (>=0)
SHAno	-Q2/(2*F)	mol/	Molar sink of H2 in d
SH2OAno	-lamAno*drag*Q2/F-alAno*(cEqAno-ch...	mol/	Molar sink of H2O in
SOCat	-Q4/(4*F)	mol/	Molar sink of O2 in d
SH2OCat	(2*lamCat*drag+1)*Q4/(2*F)-alCat*(c...	mol/	Molar source of H2O
RH	(1-wH)*mH*SHAno-wH*mH2O*SH2OAno	kg/	Mass sink of H2 in d
RO	(1-wO)*mO*SOCat-wO*mH2O*SH2OCat	kg/	Mass sink of O2 in d
RH2O	(1-wH2O)*mH2O*SH2OCat-wH2O*mO...	kg/	Mass source of H2O in
SH3O_2	Q2/F	mol/	Molar source of H3O+ i
SH2O_2	(1-lamAno)*drag*Q2/F+alAno*(cEqAn...	mol/	Molar source of H2O in
SH3O_4	-Q4/F	mol/	Molar sink of H3O+ in d
SH2O_4	(1-lamCat)*drag*Q4/F+alCat*(cEqCat-...	mol/	Molar source of H2O in
EAno	mH*SHAno+mH2O*SH2OAno	kg/	Darcy source term at



Coupling dangerous
Cannot generalise PDEs
Slightly inconsistent approach

Specifying a finite element problem

- Pick from a list of predefined systems
 - Good for standard systems like electrostatic, elastic, basic heat flow problems
 - Solver optimised for particular physics system
 - User shielded from mathematics details
 - Not so good for bespoke problems or complex multiphysics systems and non-linearity.
- Enter equations yourself
 - Good for unusual, bespoke equation sets. Can have multiphysics and/or non-linearity
 - General purpose solver: convergence not guaranteed
 - Good if you like mathematics!
 - Total control over system you are solving
 - Traceability back to fundamental physics

McCartney's "Theory of Everything"

$$\frac{\partial \rho_k}{\partial t} + \nabla \cdot \left[m_k \hat{\mathbf{J}}_k - \omega_k \sum_{i=1}^{n-1} (m_i \hat{\mathbf{J}}_i) + \rho_k \mathbf{v} \right] = \rho_k \gamma_k \quad k = 1, 2, \dots, n$$

Mass conservation
(n or n-1 issue...)
(chemical potentials assume ideal gas)

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0$$

$$\frac{\partial (\rho \mathbf{v})}{\partial t} + \nabla \cdot (\rho \mathbf{v} \mathbf{v}) = \nabla \cdot \boldsymbol{\sigma} + \sum_{k=1}^n \rho_k \mathbf{b}_k$$

Momentum conservation
(Darcy law may be inadequate => Navier Stokes)

$$\frac{\partial}{\partial t} \left(\rho \varepsilon + \frac{1}{2} \rho v^2 \right) + \nabla \cdot \left(\rho \varepsilon \mathbf{v} + \frac{1}{2} \rho v^2 \mathbf{v} \right) = -\nabla \cdot \left[\mathbf{e} + \sum_{k=1}^n (\mu_k + T s_k) \left(\hat{\mathbf{J}}_k - x_k \sum_{i=1}^{n-1} \hat{\mathbf{J}}_i \right) + \left(\frac{\boldsymbol{\Sigma}_0}{\rho} - \varepsilon \mathbf{I} \right) \cdot \sum_{i=1}^{n-1} (m_i - m) \hat{\mathbf{J}}_i - \boldsymbol{\sigma} \cdot \mathbf{v} \right]$$

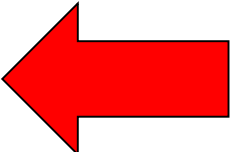
$$+ \sum_{k=1}^n \left(m_k \hat{\mathbf{J}}_k - \omega_k \sum_{i=1}^{n-1} (m_i \hat{\mathbf{J}}_i) + \rho_k \mathbf{v} \right) \cdot \mathbf{b}_k$$

Energy conservation
(ignored!)

Our current simulation comes from simplified mass and momentum conservation laws. Energy balance not even considered yet and this is the most complex eq'n.

Unlikely any packaged FE does justice to this theory.

In my opinion...

- Either go for fully packaged system (then you are restricted to basic problems) or set up system completely by hand.
- Comsol allows PDEs to be input manually in three different ways
 - Coefficient mode: specify coefficients of generalised PDE. 
 - Weak mode: use variational principles. Not PDE. (very general purpose but hard to use)
 - General form. Note sure: coefficient mode on steroids...

Coefficient mode

$$\sum_{jkl} \frac{\partial}{\partial x_j} \left(C_{ijkl} \frac{\partial u_k}{\partial x_l} \right) - \sum_j a_{ij} u_i + f_i = \frac{\partial u_i}{\partial t} \quad i = 1, 2, \dots, N$$

- Some terms omitted. C-matrix is most important, corresponds to diffusion (permittivity, stiffness etc)
- f-matrix encodes source terms.
- Pattern in C_{ijkl} tensor describes simulation. Only difference between quantum transistor and fuel cell is this tensor
- Like DNA of simulation.

C-matrix for fuel cell problem

$$C = \begin{bmatrix} c_{V_{ele}, V_{ele}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & c_{p,p} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & c_{x_H,p} & c_{x_H,x_H} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & c_{x_O,p} & 0 & c_{x_O,x_O} & c_{x_O,x_{H2O}} & 0 & 0 & 0 & 0 \\ 0 & c_{x_{H2O},p} & 0 & c_{x_{H2O},x_O} & c_{x_{H2O},x_{H2O}} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & c_{V_{mem}, V_{mem}} & c_{V_{mem}, c_{H3O}} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & c_{c_{H3O}, V_{mem}} & c_{c_{H3O}, c_{H3O}} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & c_{c_{H2O}, c_{H2O}} \end{bmatrix}$$

$$c_{V_{ele}, V_{ele}} = \sigma_{ele} I \quad (1, 2, 4, 5)$$

$$c_{p,p} = \frac{\rho \kappa}{\eta} I \quad (1, 2, 4, 5)$$

$$c_{x_H,p} = \frac{\rho \omega_H}{p} (x_H - \omega_H) (D_{1,1} - D_{1,2}) I \quad (1, 2)$$

$$c_{x_H,x_H} = \rho \omega_H (D_{1,1} - D_{1,2}) I \quad (1, 2)$$

$$-\nabla \cdot \mathbf{c} \nabla \mathbf{u} = f$$

$$\begin{bmatrix}
 c_{V_{ele}, V_{ele}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
 0 & c_{p,p} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
 0 & c_{x_H,p} & c_{x_H,x_H} & 0 & 0 & 0 & 0 & 0 & 0 \\
 0 & c_{x_O,p} & 0 & c_{x_O,x_O} & c_{x_O,x_{H_2O}} & 0 & 0 & 0 & 0 \\
 0 & c_{x_{H_2O},p} & 0 & c_{x_{H_2O},x_O} & c_{x_{H_2O},x_{H_2O}} & 0 & 0 & 0 & 0 \\
 0 & 0 & 0 & 0 & 0 & c_{V_{mem},V_{mem}} & c_{V_{mem},c_{H_3O}} & 0 & 0 \\
 0 & 0 & 0 & 0 & 0 & c_{c_{H_3O},V_{mem}} & c_{c_{H_3O},c_{H_3O}} & 0 & 0 \\
 0 & 0 & 0 & 0 & 0 & 0 & 0 & c_{c_{H_2O},c_{H_2O}} & 0
 \end{bmatrix}
 \begin{bmatrix}
 \nabla V_{ele} \\
 \nabla p \\
 \nabla x_H \\
 \nabla x_O \\
 \nabla x_{H_2O} \\
 \nabla V_{mem} \\
 \nabla c_{H_3O} \\
 \nabla c_{H_2O}
 \end{bmatrix}$$

$$-\nabla \cdot (\sigma_{ele} \nabla V_{ele}) = source$$

$$-\nabla \cdot (\rho \kappa \nabla p / \eta) = source$$

$$-\nabla \cdot [\rho \omega_H (x_H - \omega_H) (D_{1,1} - D_{1,2}) \frac{\nabla p}{p} + \rho \omega_H (D_{1,1} - D_{1,2}) \nabla x_H]$$

$$= R_H - \rho \mathbf{u} \cdot \nabla \omega_H$$

Nernst Planck in coefficient mode

Model Builder

- region z
 - Scalar Expressions
 - Boundary System 1 (sys1)
 - View 1
 - Geometry 1
 - Materials
 - Coefficient Form Electrostatic (c)
 - Coefficient Form MS Anode (c2)**
 - Coefficient Form PDE 1
 - Zero Flux 1
 - Initial Values 1
 - Dirichlet Boundary Condition 1
 - Coefficient Form MS Cathode (c3)
 - Coefficient Form PDE 1
 - Zero Flux 1
 - Initial Values 1
 - Dirichlet Boundary Condition 1
 - Coefficient Form Nernst Planck (c4)**
 - Coefficient Form PDE 1**
 - Zero Flux 1
 - Initial Values 1
 - Dirichlet Boundary Condition 1
 - Dirichlet Boundary Condition 2
 - Coefficient Form Navier Stokes (c5)
 - Coefficient Form PDE 1
 - Zero Flux 1
 - Initial Values 1
 - Dirichlet Boundary Condition 1
 - Dirichlet Boundary Condition 2

Settings

Coefficient Form PDE

$$e_a \frac{\partial^2 \mathbf{u}}{\partial t^2} + d_a \frac{\partial \mathbf{u}}{\partial t} + \nabla \cdot (-c \nabla \mathbf{u} - a \mathbf{u} + \gamma) + \beta \cdot \nabla \mathbf{u} + a \mathbf{u} = f$$

$$\mathbf{u} = [vMem, cH3O, cH2O]^T$$

$$\nabla = \left[\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right]$$

Diffusion Coefficient

c_vMem_vMem	1	c_vMem_cH3O	1	0	1
Isotropic		Isotropic		Isotropic	
c_cH3O_vMem	1	c_cH3O_cH3O	1	0	1
Isotropic		Isotropic		Isotropic	
0	1	0	1	c_cH2O_cH2O	1
Isotropic		Isotropic		Isotropic	

Absorption Coefficient

Source Term

f_vMem	1/m ²
f	1/m ²
f_cH2O	1/m ²

Mass Coefficient

Region dependent variables

Model Builder

- grotthus3d_density50.mph (root)
 - Global Definitions
 - Parameters
 - Materials
 - Component 1 (comp1)
 - Definitions
 - a= Region 1
 - a= Region 2**
 - a= Scalar Expressions
 - Boundary System 1 (sys1)
 - View 1
 - Geometry 1
 - Materials
 - Coefficient Form Electrostatic (c)
 - Coefficient Form PDE 1
 - Zero Flux 1
 - Initial Values 1
 - Dirichlet Boundary Condition 1
 - Coefficient Form MS Anode (c2)
 - Coefficient Form PDE 1
 - Zero Flux 1
 - Initial Values 1
 - Dirichlet Boundary Condition 1
 - Coefficient Form MS Cathode (c3)
 - Coefficient Form PDE 1
 - Zero Flux 1
 - Initial Values 1
 - Dirichlet Boundary Condition 1
 - Coefficient Form Nernst Planck (c4)
 - Coefficient Form PDE 1
 - Zero Flux 1

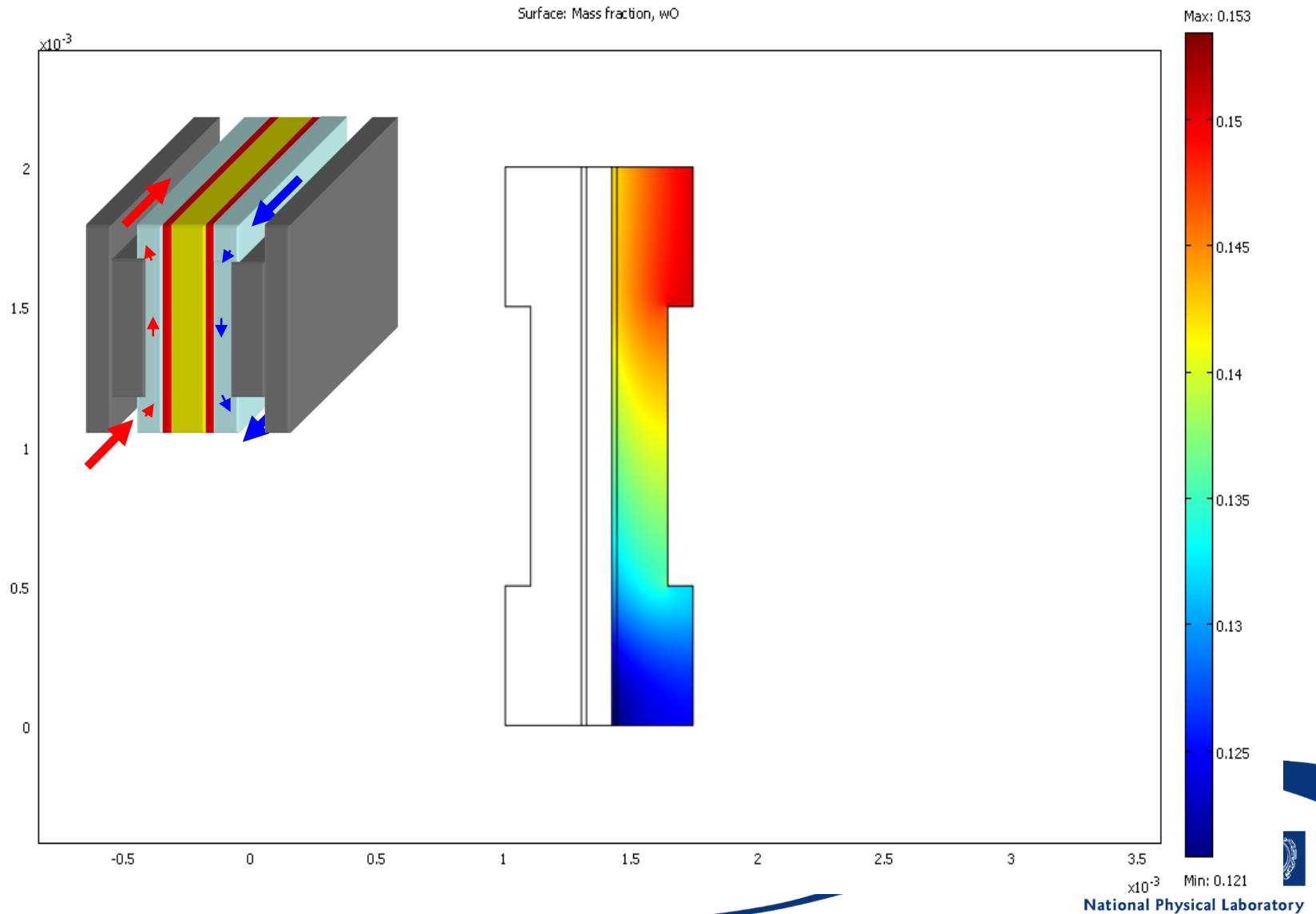
Settings

Variables

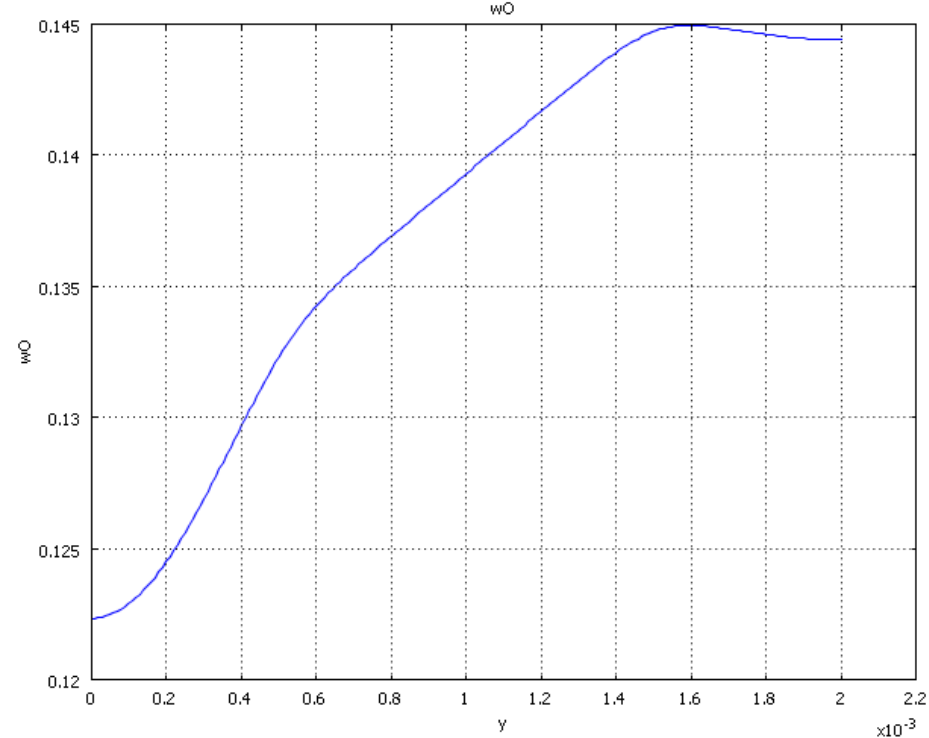
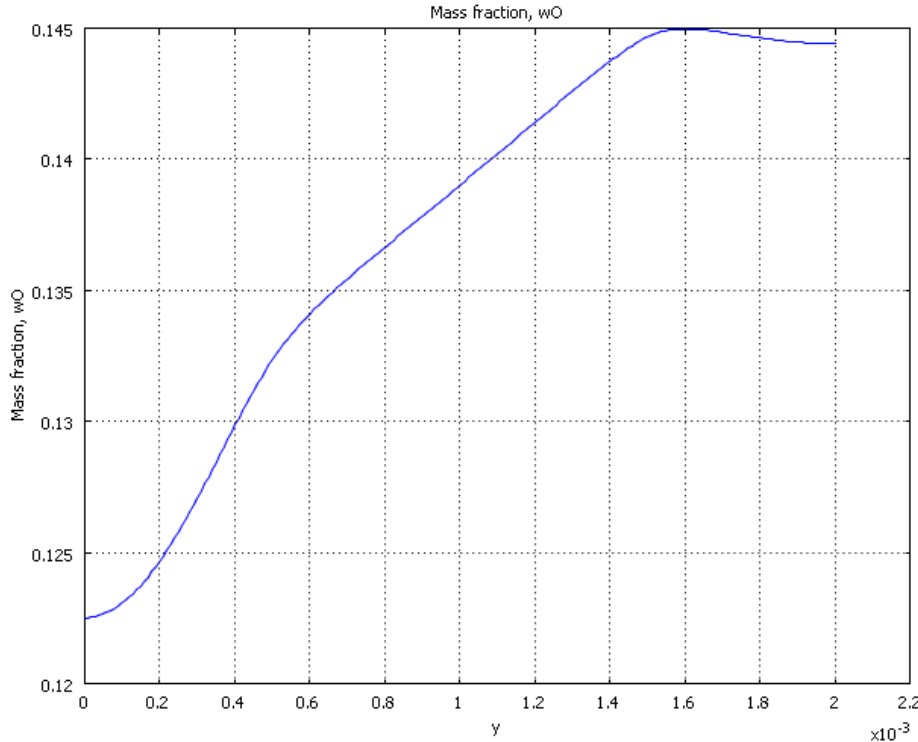
Variables

Name	Expression	Unit	Description
rhox	rho1x+rho2x	1/m	
rhoy	rho1y+rho2y	1/m	
rhoz	rho1z+rho2z	1/m	
rho	rho1+rho2		
f1	$-\rho \cdot (v_1 \cdot w_{Hx} + v_2 \cdot w_{Hy} + v_3 \cdot w_{Hz})$	1/m	
f2	$-\rho \cdot (v_1 \cdot w_{H2Ox} + v_2 \cdot w_{H2Oy} + v_3 \cdot w_{H2Oz})$	1/m	
fv1	$\rho \cdot (v_1 \cdot v_{1x} + v_2 \cdot v_{1y} + v_3 \cdot v_{1z}) + \epsilon_{s1} \cdot p_x$		
fv2	$\rho \cdot (v_1 \cdot v_{2x} + v_2 \cdot v_{2y} + v_3 \cdot v_{2z}) + \epsilon_{s1} \cdot p_y$		
fv3	$\rho \cdot (v_1 \cdot v_{3x} + v_2 \cdot v_{3y} + v_3 \cdot v_{3z}) + \epsilon_{s1} \cdot p_z$		
mass	$1 / (w_H / m_H + w_{H2O} / m_{H2O})$	kg/mol	
c_vMem_vMem	$F \cdot u_{H3O_2} \cdot z_{H3O} \cdot c_{H3O}$	$m^2 / (V \cdot s)$	
c_vMem_cH3O	DH3O_2	m^2 / s	
c_cH3O_cH3O	$-D_0 \cdot z_{H3O} / z_M$	m^2 / s	
c_cH3O_vMem	$-F \cdot u_0 \cdot z_{H3O} \cdot c_{H3O}$	C/mol	
c_cH2O_cH2O	DH2O_2	$m^2 / (s \cdot m \dots)$	
f_vMem	SH3O_2		
f_cH2O	SH3O_2		

Oxygen mass fraction variation

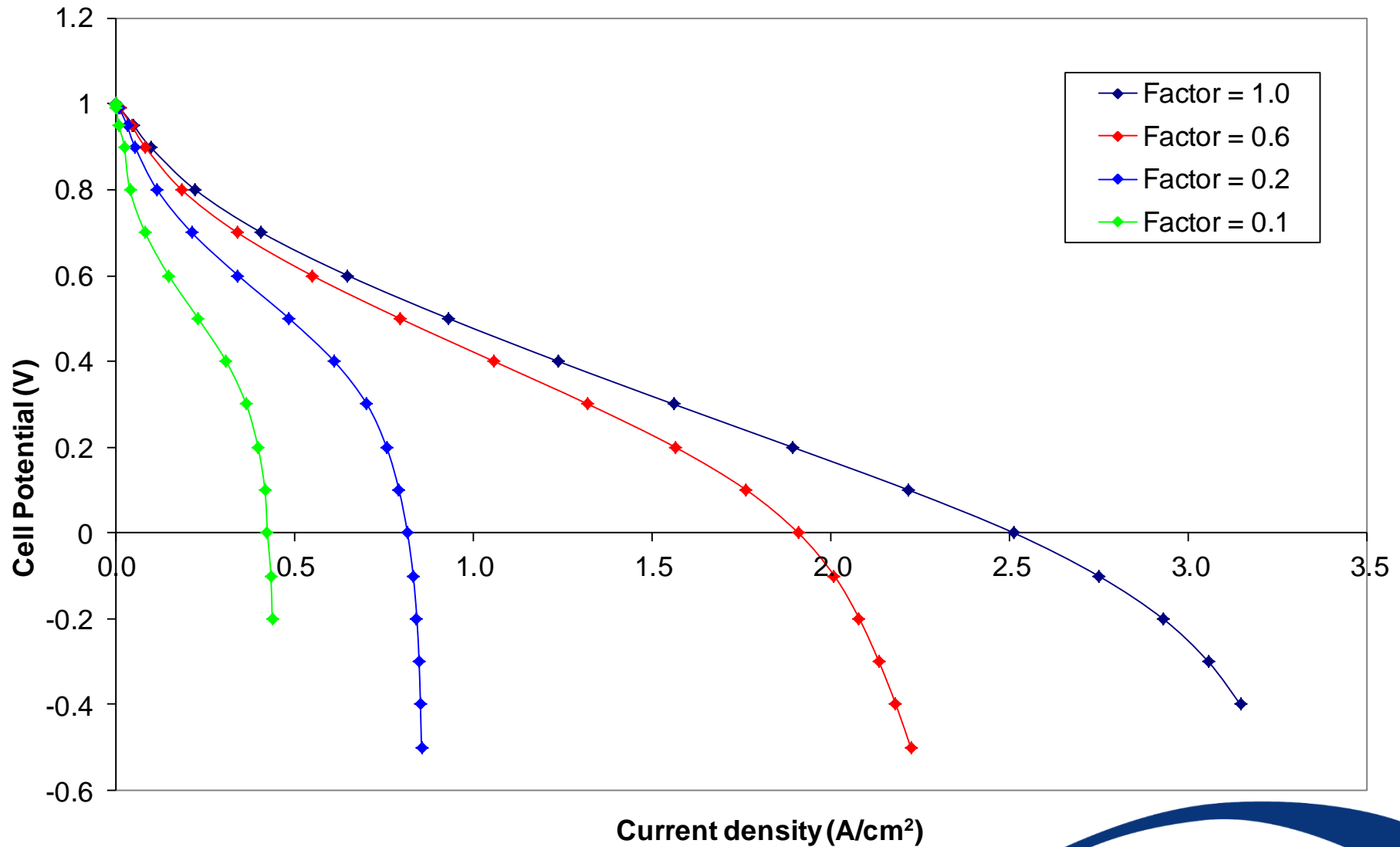


Built-in module vs. PDE coefficient mode

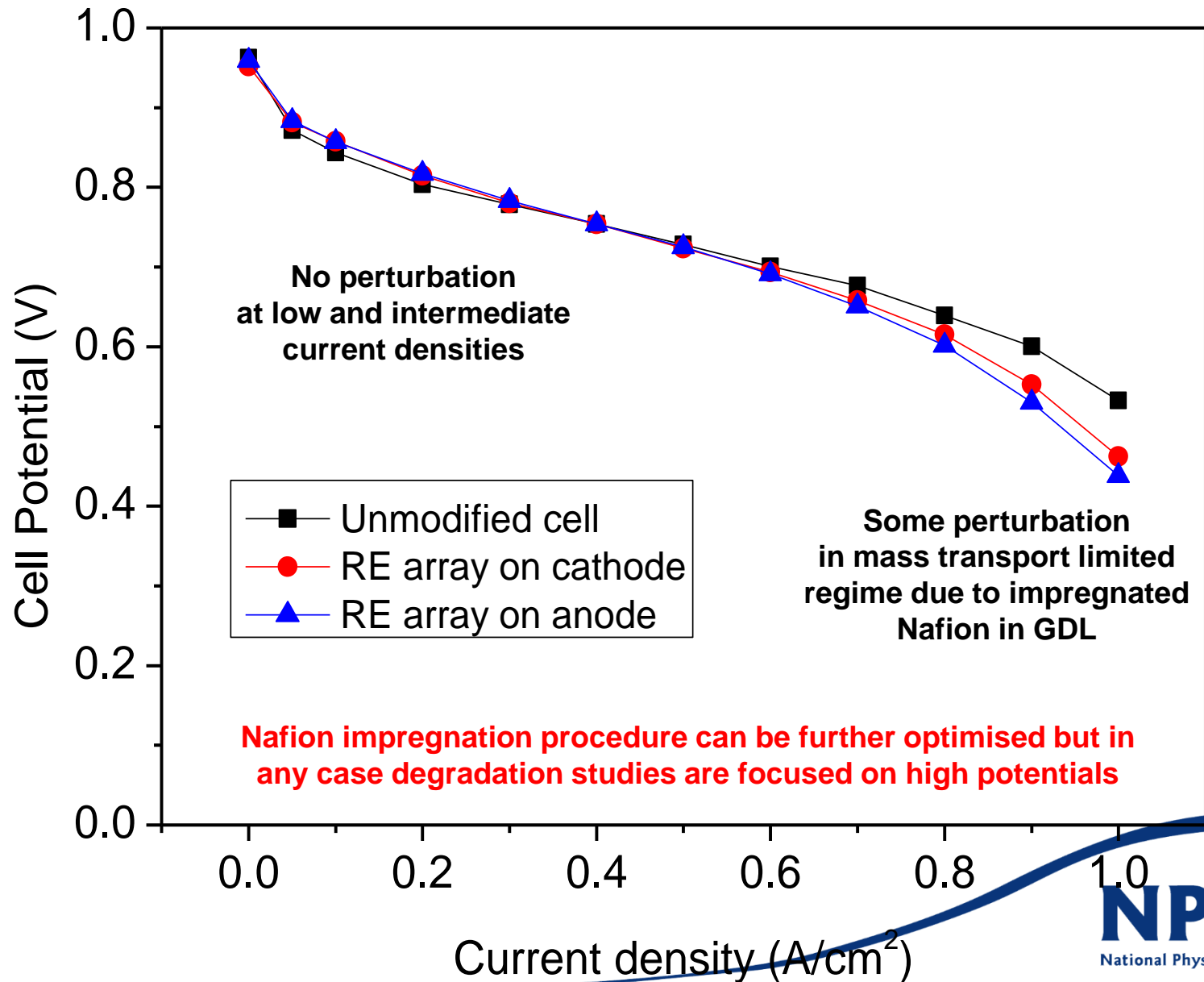


- Good agreement after some effort
- Here $V=0.7$ V,
- $I=0.3716$ A/m (coeff), $I=0.406$ A/m original
- Careful! E-field not defined on boundary

Effect of varying oxygen mass fraction at inlet



Experimental polarisation curves



The tip of the iceberg...

- Now extended to 3D (previously 2D model)
- Added additional fluid layers outside of the GDL layers for channel flow
- Replaced Darcy with more realistic Navier Stokes
- Unfortunately the last does not converge yet. Equation based modelling allows any equations to be specified but no guarantee you can solve them!
- Work is ongoing.

Summary

- Derived PDEs for fuel cells which are more advanced than in normal literature
- Solved these equations using Comsol's coefficient mode (equation based modelling)
- Good initial agreement with experimental results (but theory very simple cf experiment)
- Eq'n based modelling is better for complex, multiphysics, non-linear systems. Allows new equations to be solved without waiting for built-in module
- Gives better traceability.