PEM Fuel Cell Using Equation-based Modelling

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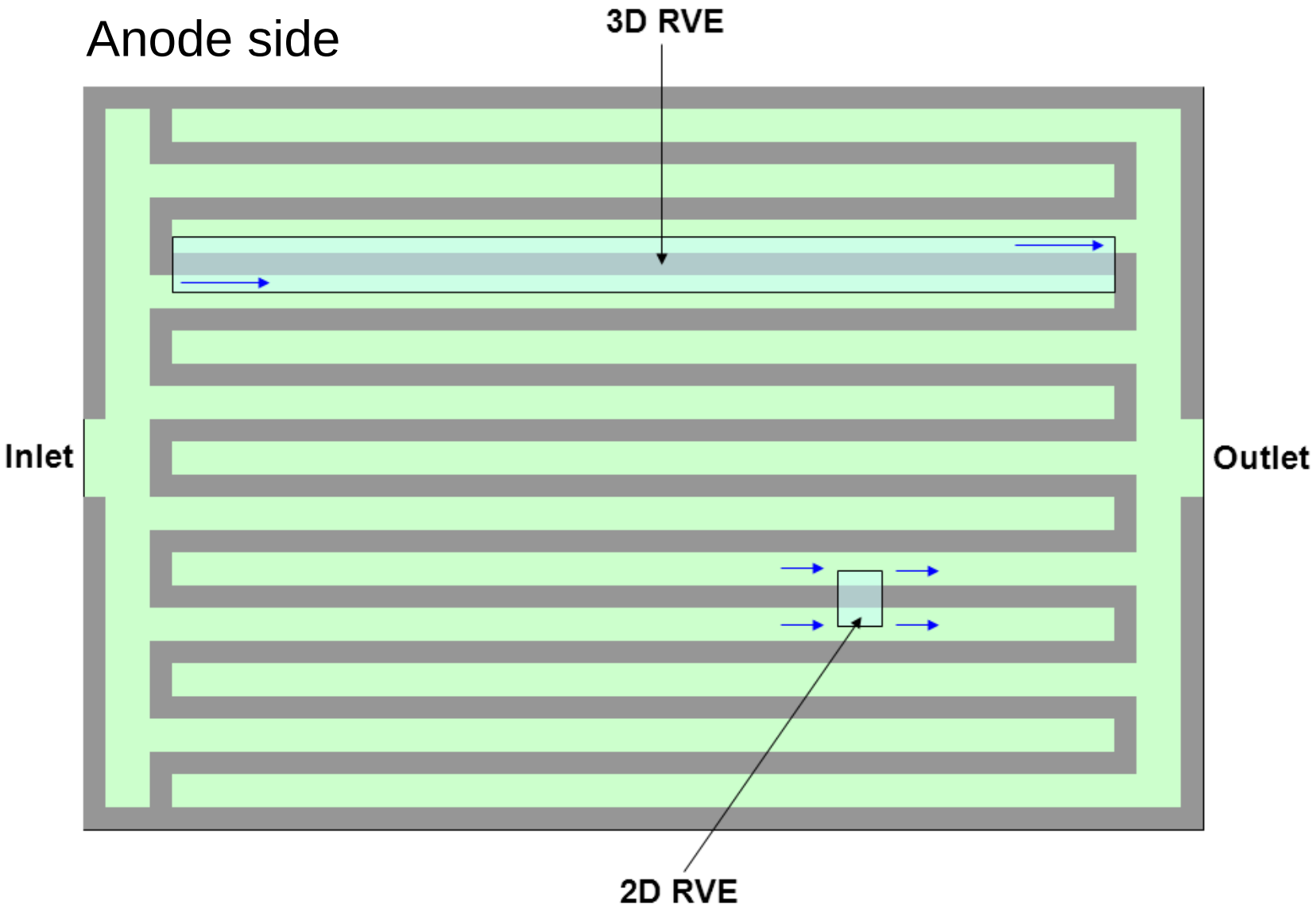
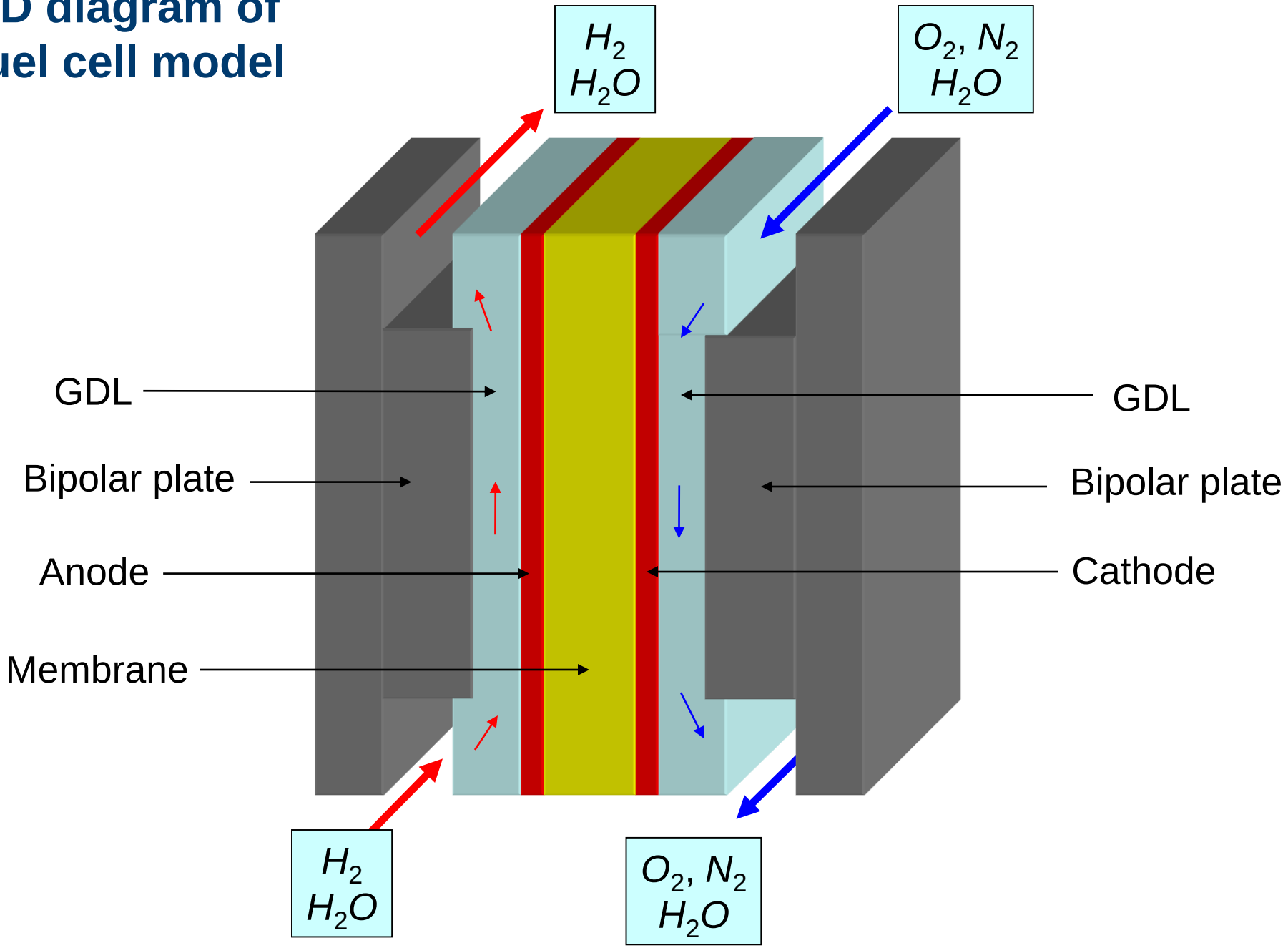
Channels of inter-digitated fuel cell



3D diagram of fuel cell model



Equations to solve

$$\nabla \cdot \left(\sigma_{ele} \nabla V_{ele} \right) + Q_{ele} = 0$$

Poisson's equation

$$\nabla \cdot \left(-\frac{\rho \kappa}{\eta} \nabla p \right) = F$$

Darcy's Law

Complex Source terms

Maxwell-Stephan equation

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

Nernst-Planck equation

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

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Non-linear source terms (agglomerate model)

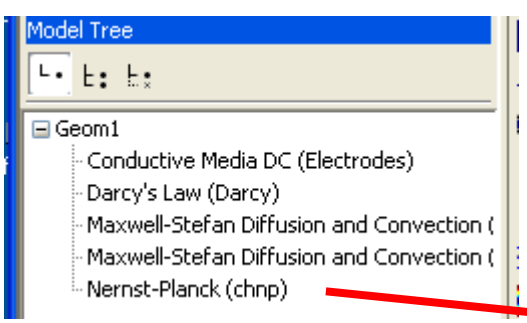
$$R_H = \left(1-\omega_H\right) m_H S_H^{ano} - \omega_H m_{H2O} S_{H2O}^{ano}$$

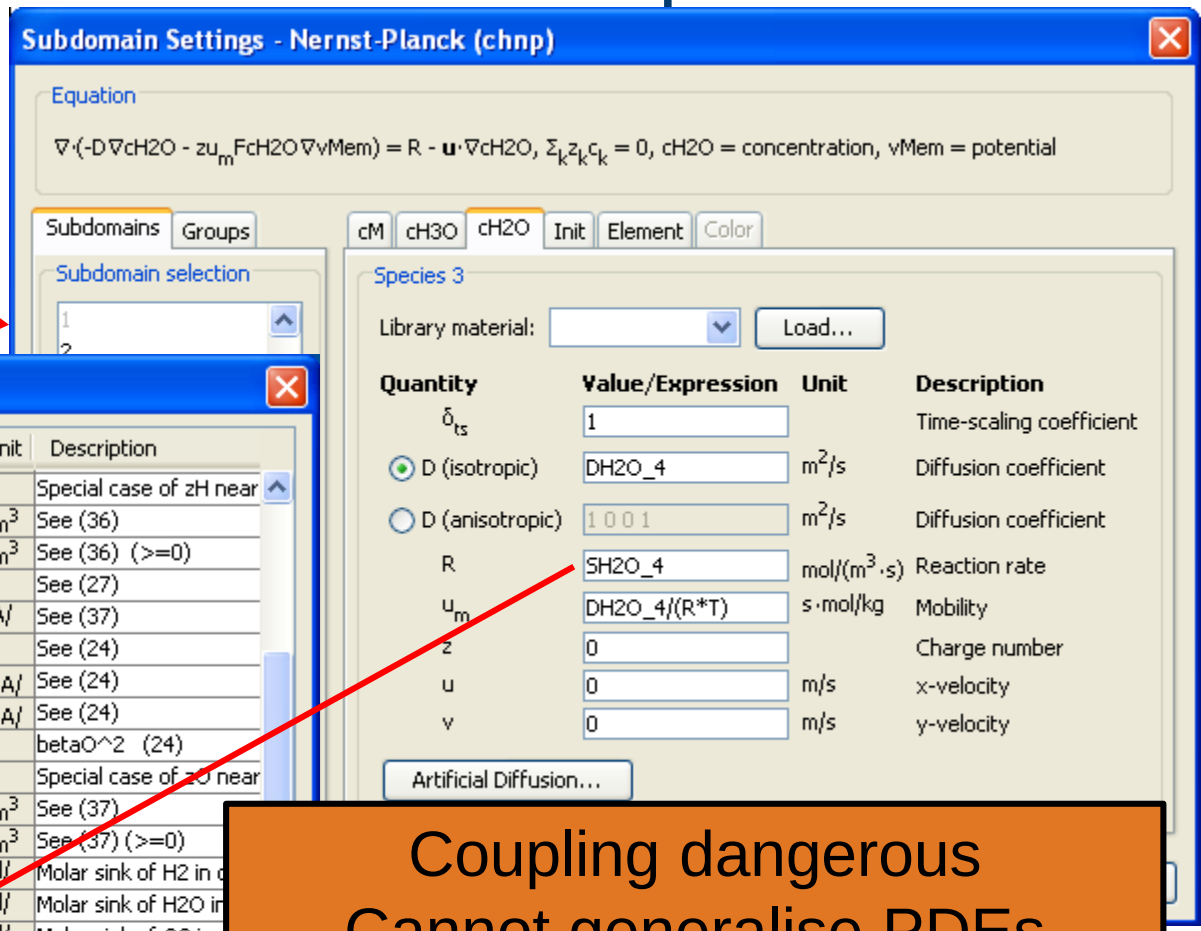
$$S_H^{ano} = -\frac{3 f_{ano}}{r_{ano}^2} D_H^{agg} c_H^{agg} \left[\beta_H \coth\left(\beta_H\right) - 1 \right] \leq 0$$

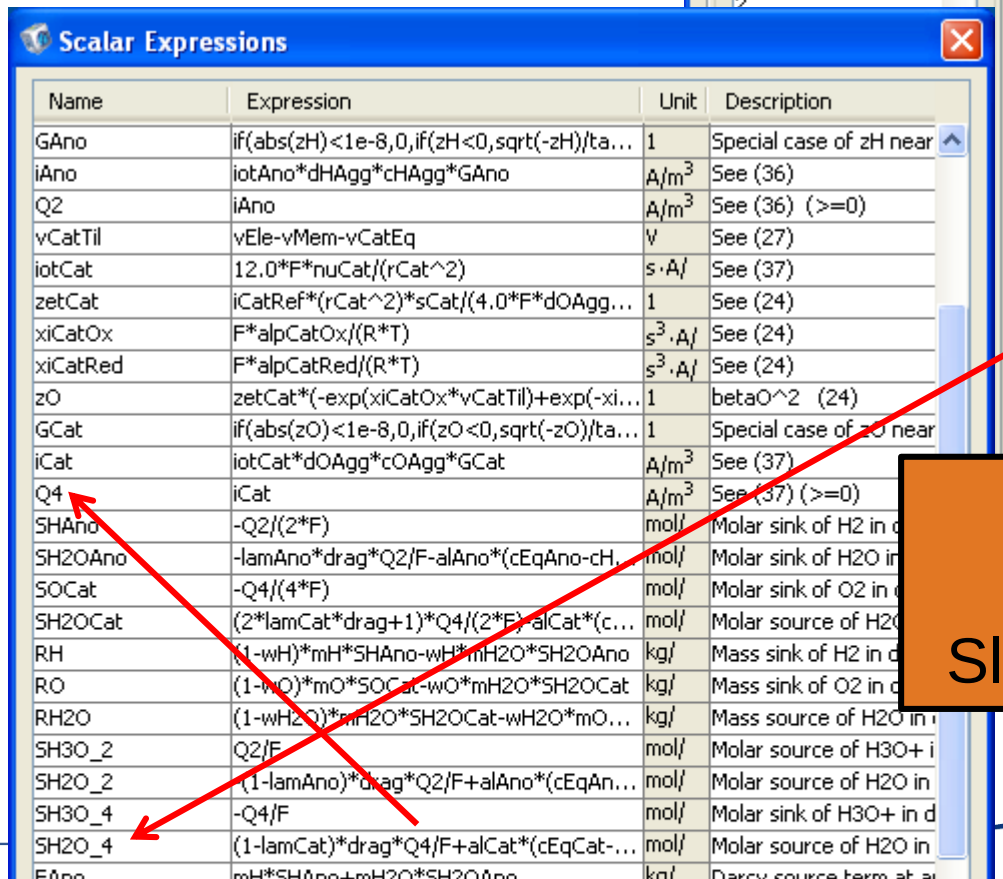
$$\beta_H^2 = \frac{i_{ano}^{ref}}{2F} \frac{s_{ano} r_{ano}^2}{D_H^{agg} c_H^{ref}} \left[\exp\left(\frac{F \alpha_{ox}^{ano} \eta_{ano}}{RT} \right) - \exp\left(-\frac{F \alpha_{red}^{ano} \eta_{ano}}{RT} \right) \right]$$

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

COMSOL Module based FE setup







Coupling dangerous
Cannot generalise PDEs
Slightly inconsistent approach

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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"

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

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)

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

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

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.

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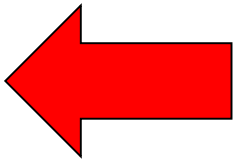
In my opinion…

- 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

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

- 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.

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C-matrix for fuel cell problem

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

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

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

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

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

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

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

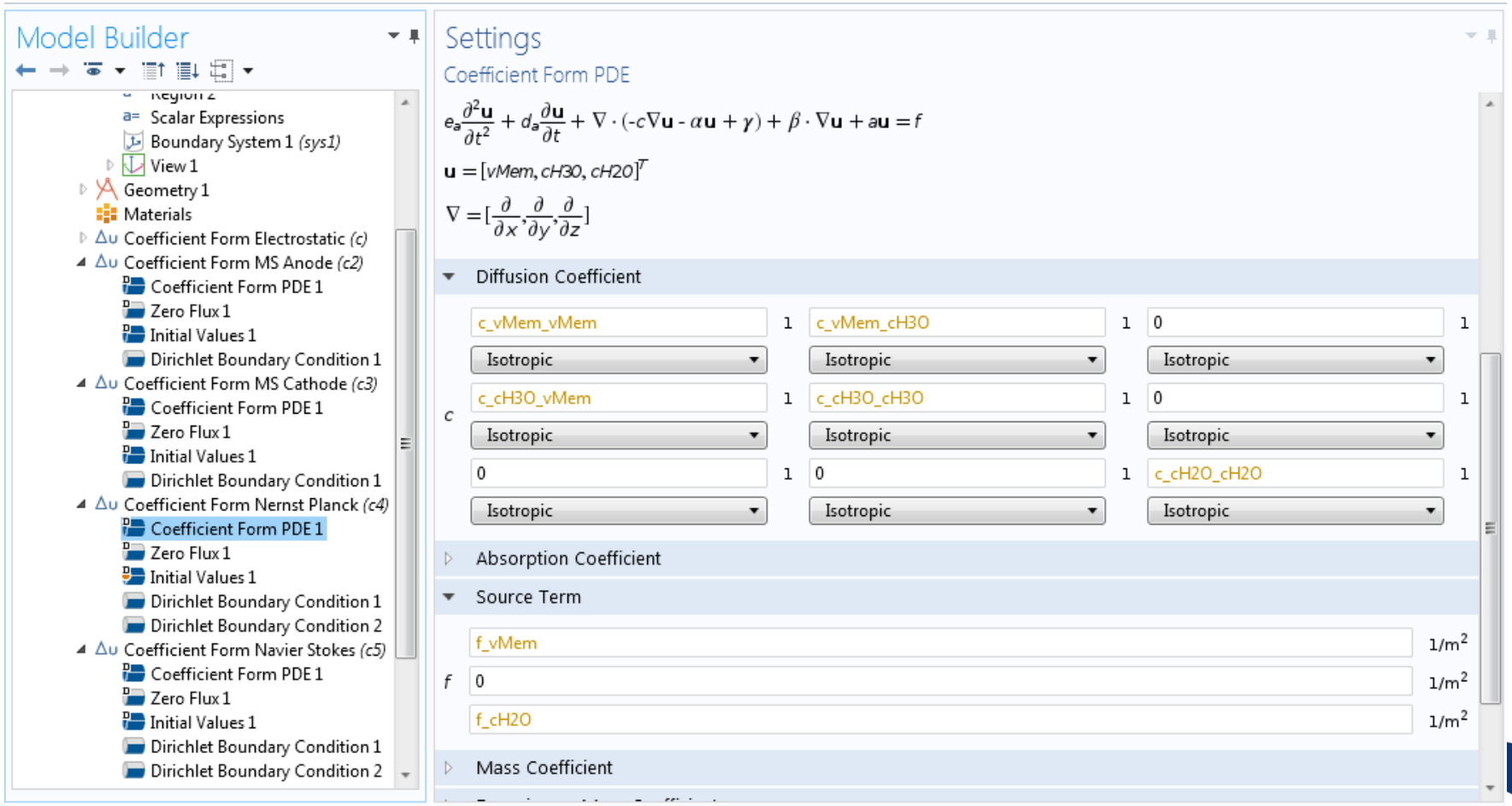
$$-\nabla \cdot (\sigma_{ele} \nabla V_{ele}) = source$$

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

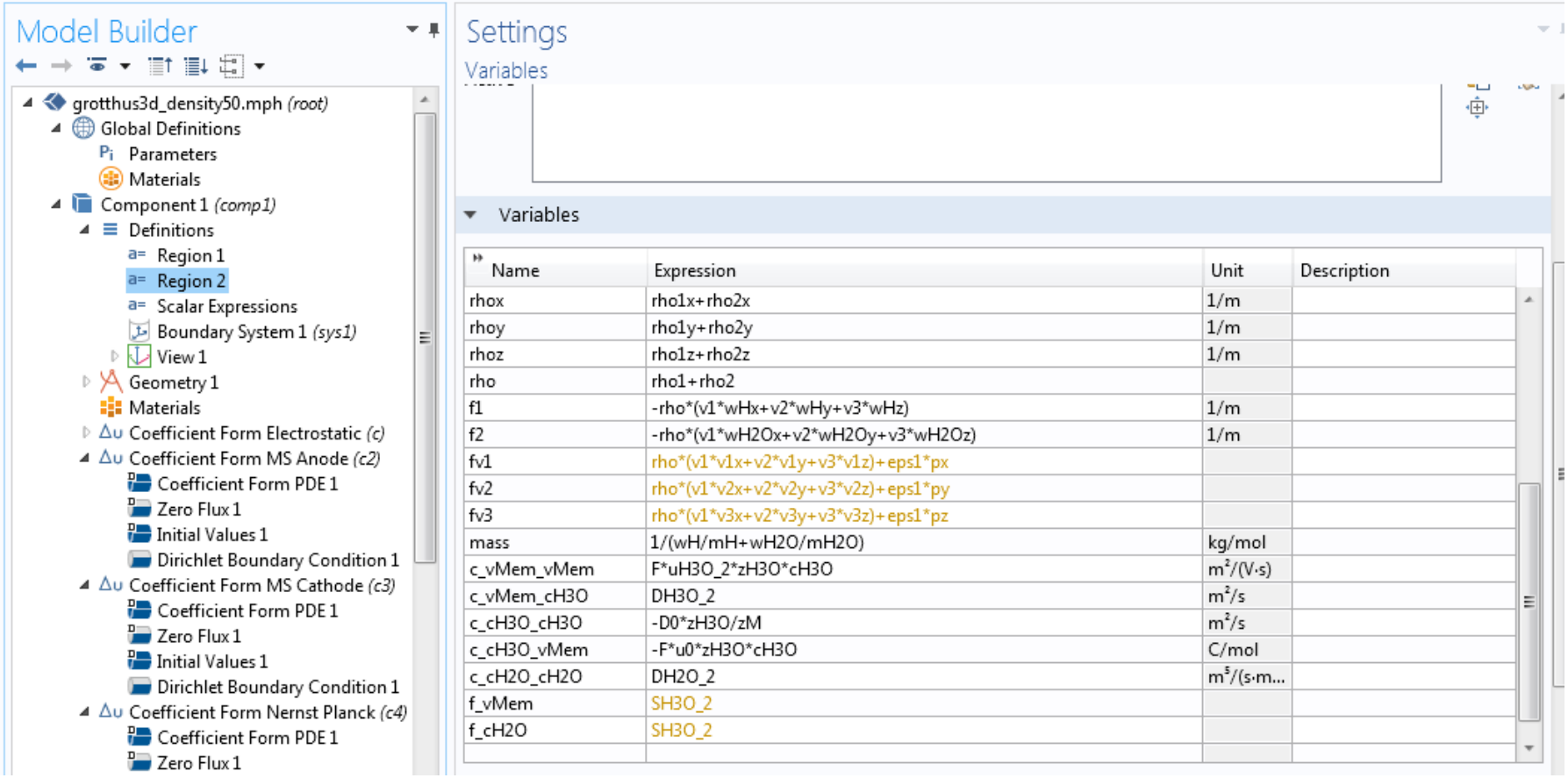
$$-\nabla \cdot [\rho \omega_H (x_H - \omega_H)(D_{1,1} - D_{1,2}) \frac{\nabla p}{p} + \rho \omega_H (D_{1,1} - D_{1,2}) \nabla x_H]$$

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

Nernst Planck in coefficient mode

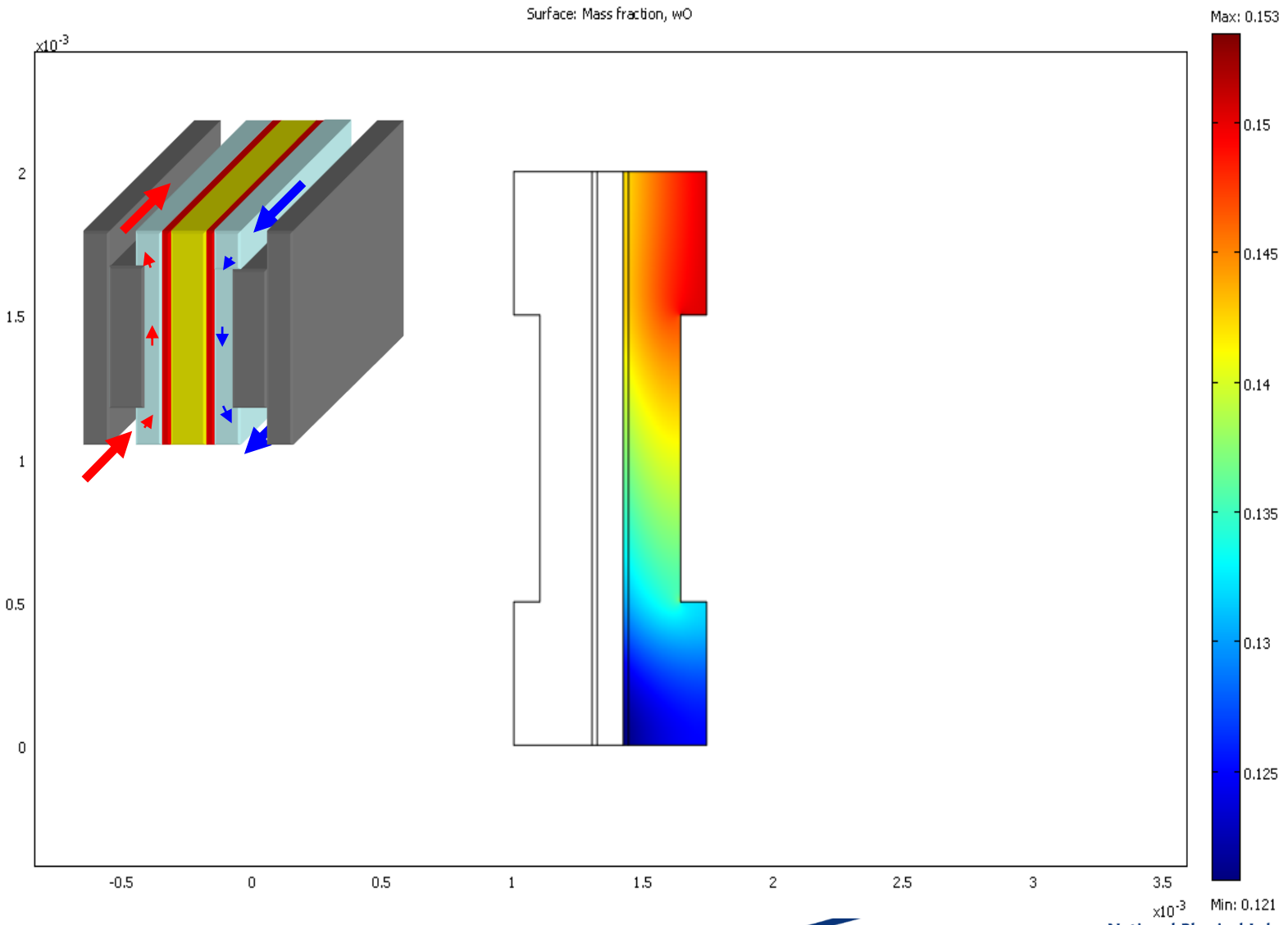


Region dependent variables

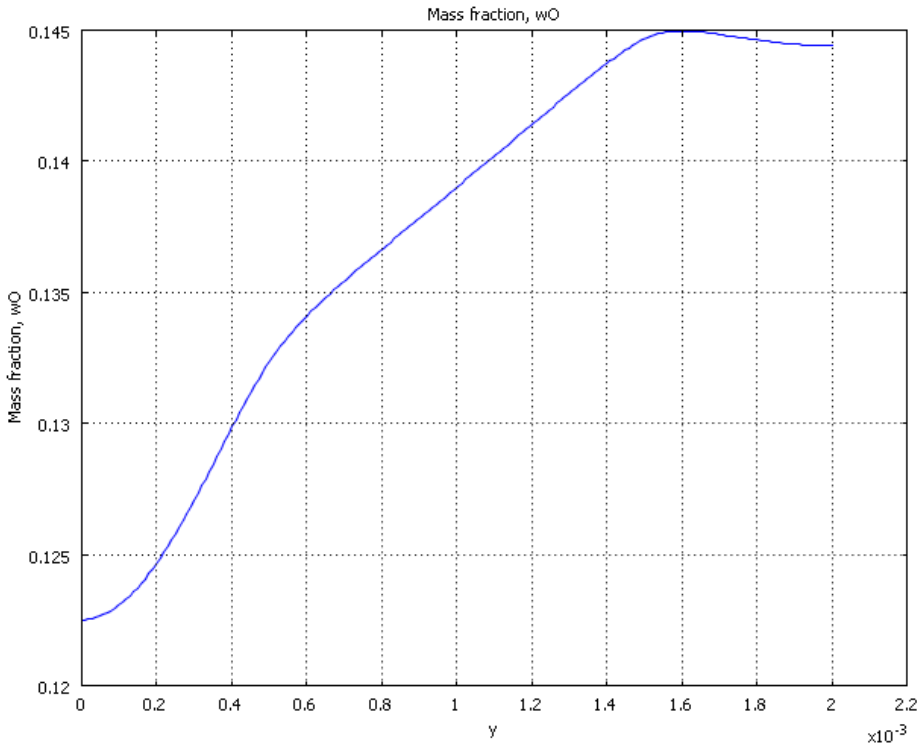


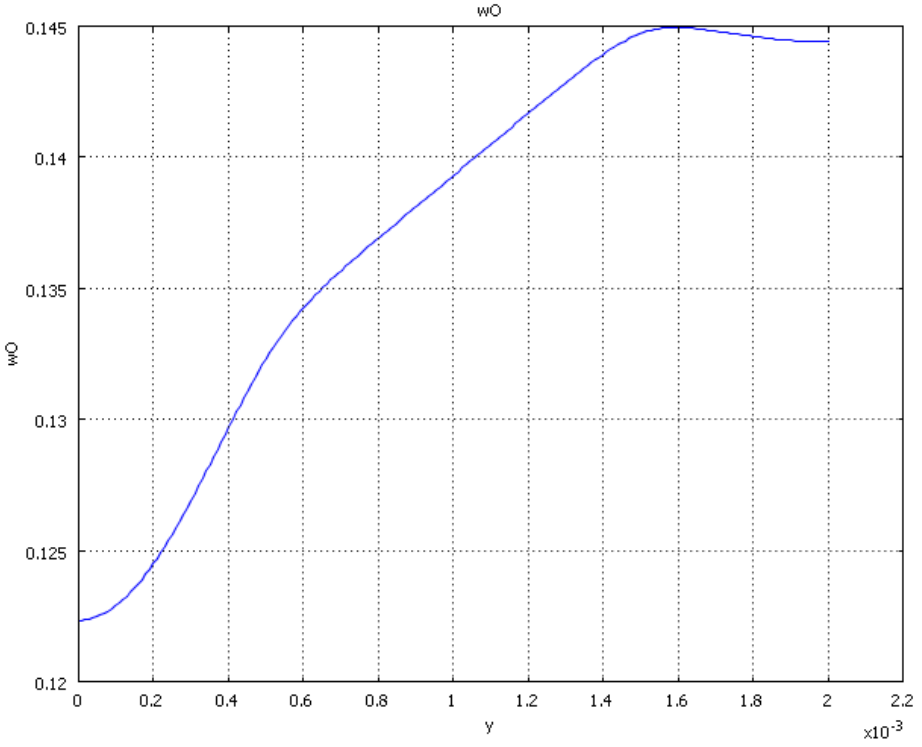
Name	Expression	Unit	Description
rhox	rho1x+rho2x	1/m	
rhoy	rho1y+rho2y	1/m	
rhoz	rho1z+rho2z	1/m	
rho	rho1+rho2		
f1	-rho*(v1*wHx+v2*wHy+v3*wHz)	1/m	
f2	-rho*(v1*wH2Ox+v2*wH2Oy+v3*wH2Oz)	1/m	
fv1	rho*(v1*v1x+v2*v1y+v3*v1z)+eps1*px		
fv2	rho*(v1*v2x+v2*v2y+v3*v2z)+eps1*py		
fv3	rho*(v1*v3x+v2*v3y+v3*v3z)+eps1*pz		
mass	1/(wH/mH+wH2O/mH2O)	kg/mol	
c_vMem_vMem	F*uH3O_2*zH3O*cH3O	$m^2/(V·s)$	
c_vMem_cH3O	DH3O_2	m^2/s	
c_cH3O_cH3O	-D0*zH3O/zM	m^2/s	
c_cH3O_vMem	-F*u0*zH3O*cH3O	C/mol	
c_cH2O_cH2O	DH2O_2	$m^5/(s·m...$	
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

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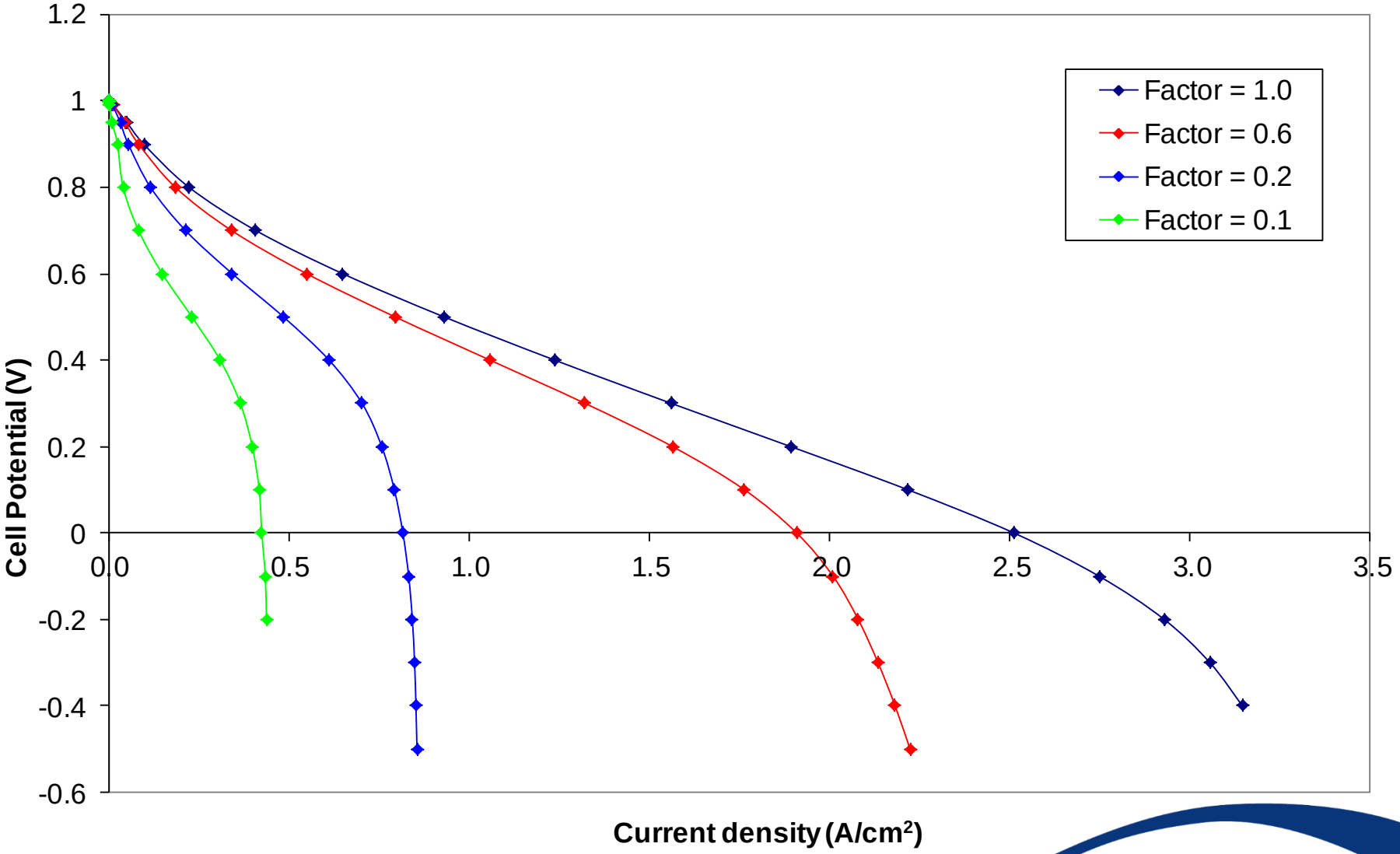
Effect of varying oxygen mass fraction at inlet



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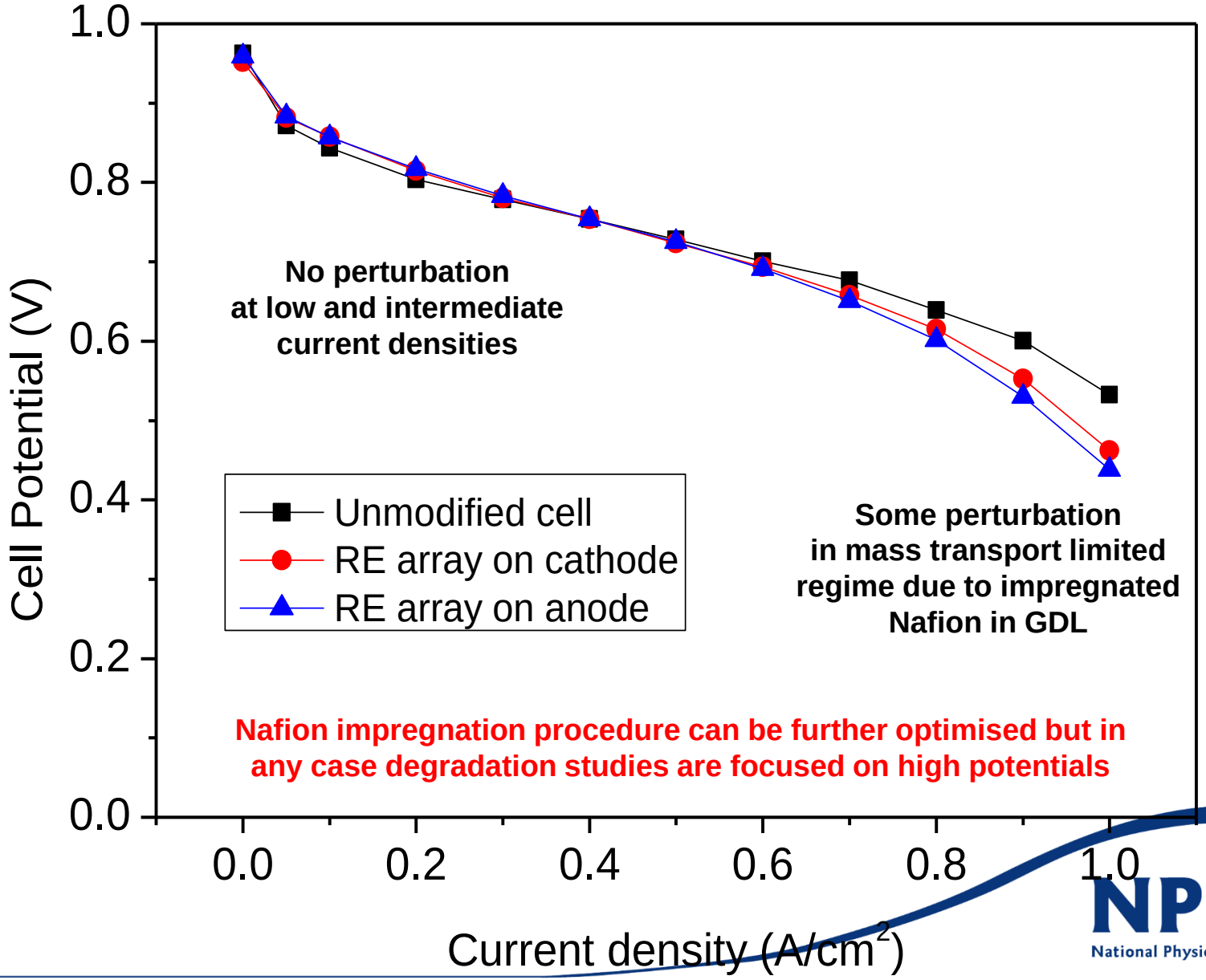
Experimental polarisation curves



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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 traceabilty.

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