

# PEM Fuel Cell Using Equation Based Simulation

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**Abstract:** We present computer simulation results for PEM fuel cells using COMSOL Multiphysics. We have developed novel PDE equations at NPL from first principles and these are more realistic than models typically used in literature. The theory includes Maxwell Stephan and Nernst Planck equations for the diffusion and electrochemistry as well as equations governing electrostatic and stress/strain effects. The whole system is a highly coupled multiphysics and non-linear problem with particular complexity arising from the electrochemical source terms which include an agglomerate model. We present these and their derivation equations in this talk and show how we used COMSOL to solve them using two techniques: combining built in modules and using equation based modelling to enter equations explicitly using the "coefficient mode". The latter mode allows us more control over exactly what equations are solved and will help us to generalise the model to include Navier Stokes equations for the stress/strain behaviour. In this paper we compare these different methods of using COMSOL and show preliminary results from our simulations.

**Keywords:** Fuel cell, finite element, hydrogen, proton, exchange, gas, diffusion, equation

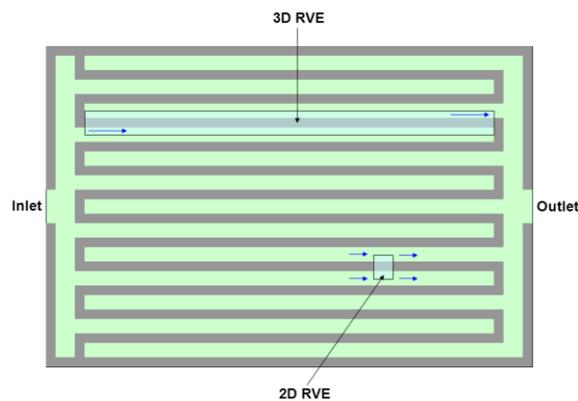
## 1. Introduction

Fuel cell technology promises to be an environmentally friendly power source with broad applications in many industries including transportation as well as portable and stationary power generation. Manufacturing and operating costs can be reduced by optimising the efficiency of fuel cells through detailed analysis of complex electrochemical and mass transport phenomena that occur within the cells.

There are two principal types of fuel cells: the first is known as the proton exchange membrane fuel cell (PEMFC), which has received the most attention for

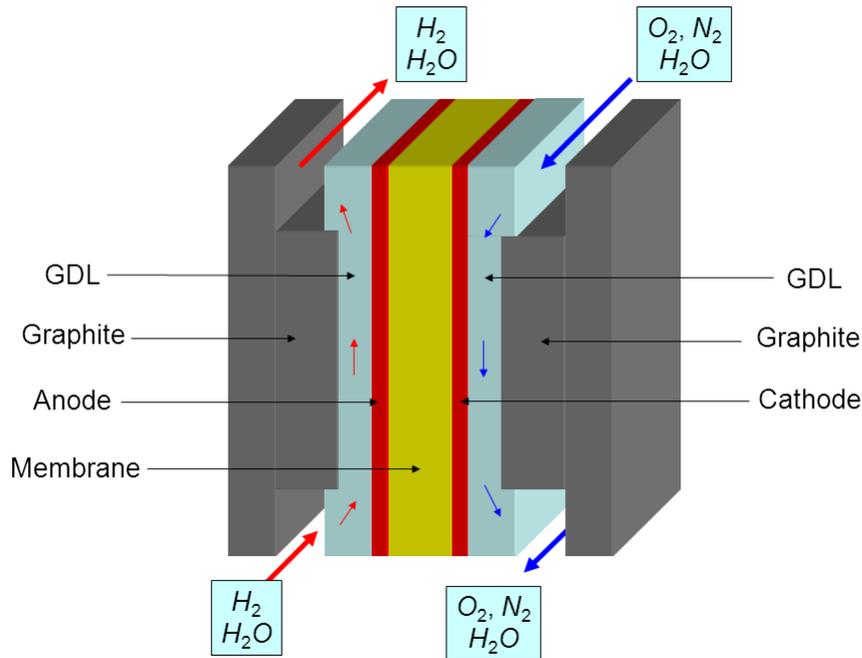
modelling purposes in the literature. The second is known as a solid oxide fuel cell (SOFC), which operates with different chemical systems, and different electrochemical reactions at the electrodes. This paper will focus on developing models for PEMFCs.

Figure 1 shows the channels within an interdigitated fuel cell (the type we will discuss in this paper: the alternative is a serpentine system where all the channels line up). Fuel (hydrogen, oxygen) enters the system through the inlet and waste products (water, CO<sub>2</sub>) leave through the outlet: the graphite regions, shown in grey, are impermeable. To cross from inlet to outlet, the chemical products must travel "into the page", underneath the graphite barrier and up again to the plane of the page (see Fig 1) which forces chemicals into contact resulting in reactions.



**Figure 1:** Interdigitated fuel cell.

Since it is impractical to model this entire system, we model a simple "representative volume element" (RVE) shown in the Figure 1. It is hoped that results calculated from the RVE will sufficiently reflect the whole cell's behaviour. A blow-up of the RVE is shown in Fig 2 which has been extracted from Fig 1 and rotated through 90 degrees.

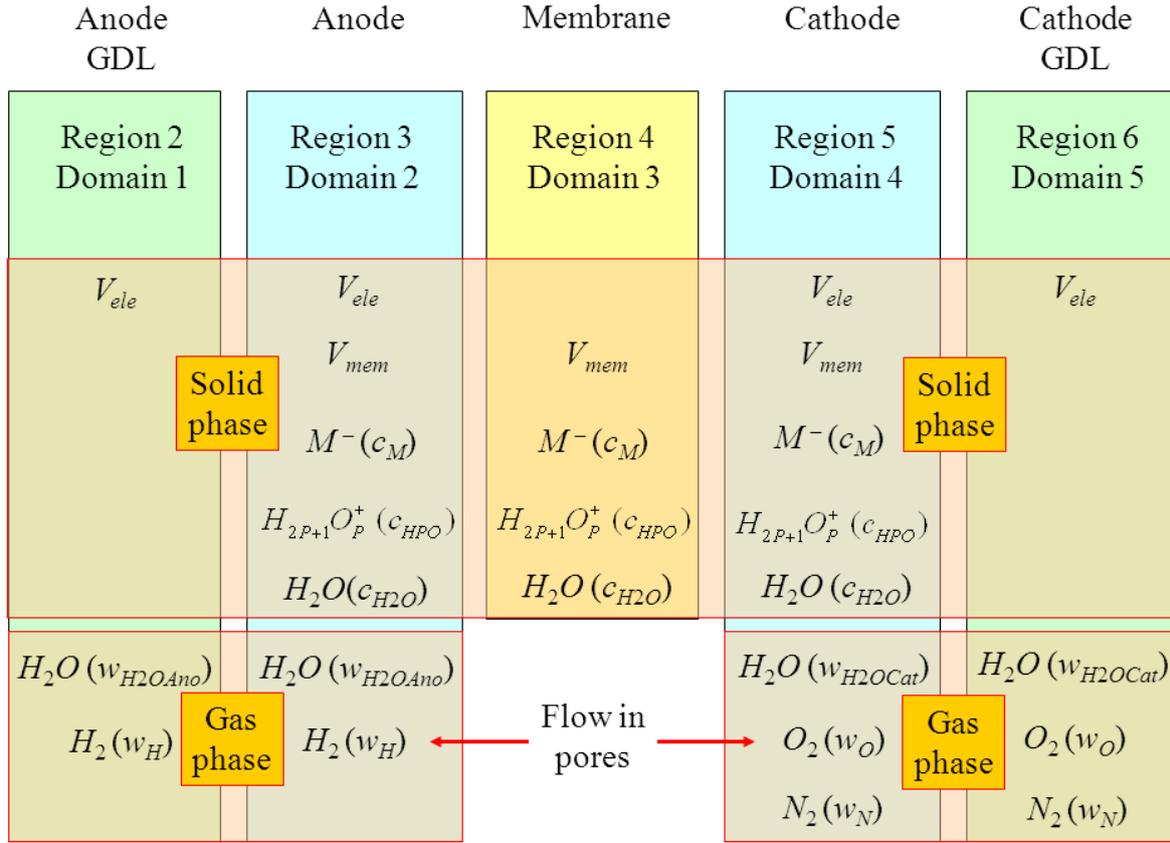


**Figure 2:** Detail of fuel cell representative volume element. The inlet port for  $H_2$  and  $H_2O$  is at the bottom-left and the inlet for  $O_2$ ,  $N_2$  and  $H_2O$  is at the top-right.

In Fig 2, we see that a concentration of hydrogen, water, oxygen and nitrogen is applied at the inlet ports and these propagate through to the outlet ports in lower concentrations. A pressure difference is also maintained between inlet and outlet ports (the latter being at atmospheric pressure). Furthermore, a different electrostatic potential is applied at each of the graphite electrodes giving a potential difference across the system. The major output of the simulation is the current predicted from the given voltage: running multiple simulations gives an I-V curve.

Figure 3 shows a schematic diagram corresponding to Fig 2. The various symbols shown are the dependent variables that need to be model in space (fields) with the notation used. Notice that some dependent variables are only present in some domains, eg the electrostatic potential,  $V_{ele}$ , is present only in Domains 1, 2, 4 and 5, while the membrane potential,  $V_{mem}$  is only present in the central Domains 2-4. Thus,  $V_{ele}$  must be deactivated

in region 3 etc. The corresponding physics is also only activated where needed, so that the electrostatic physics is only used in Domains 1, 2, 4, 5 etc. When modelling using COMSOL's physics modules, we add the "conductive media" module only within those regions; when using equation based modelling we deactivate rows of the overall matrix accordingly. The "gas phase" (Fig 3) is essentially modelled using Maxwell-Stephan equations while the "solid phase" is modelled using Nernst-Planck, as will be shown. We will prefer to use mass fractions in the outer regions as these naturally occur in Maxwell-Stephan, while concentrations are used in the inner regions for convenience when using Nernst Planck. Naturally, constraints are added to ensure these quantities are mutually consistent. Notice how the system is "staggered" so the electrostatic potential, hydrogen mass-fraction etc in Domain 1 communicates with that in Domain 5 only *indirectly* via the membrane potentials, hydronium concentrations etc, in the inner regions.



**Figure 3:** Schematic diagram showing various species (with notation) that need to be modelled, referred to the phase, region and domain within the fuel cell. The (sub)domain numbers are those used in COMSOL. Here, “c” refers to concentration while “w” is mass-fraction. In our simulations we have  $p=1$  so that the hydronium ( $H_3O$ ) ions are present but  $p > 1$  could also be modelled.

## 2. Theoretical model

Considering now Maxwell-Stephan equations governing hydrogen and water at the anode, we have

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

$$\omega_{H_2O} = 1 - \omega_H \quad (2)$$

where  $k=1 \Rightarrow H$ ,  $k=2 \Rightarrow H_2O$ . Both mass ( $\omega$ ) and molar fractions ( $x$ ) appear in this equation and both vary spatially across the simulation (for solution, either can be eliminated). In practice only one equation need be solved at the anode since mass fractions sum to unity as shown in (2). The pressure,  $p$ , is another dependent variable to solve for giving two remaining dependent variables at the anode:  $\omega_H$  (or  $x_H$ ) and  $p$ . The pressure can be deduced from Darcy’s law as

$$\nabla \cdot \left( -\frac{\rho \kappa}{\eta} \nabla p \right) = F \quad (3)$$

Where  $\kappa$  is the system porosity and  $\eta$  is the viscosity (both spatially uniform). The  $F$  term relates to creates of momentum due to chemical reaction and will be discussed later. The velocity field in (1) is then recovered from  $\mathbf{u} = -\rho \kappa \nabla p / \eta$ . The total density  $\rho$  appearing in (1) and (3) is given by

$$\rho = \frac{p}{RT} (m_H x_H + m_{H_2O} x_{H_2O})$$

where  $m_H$  etc are the molar masses of the constituents.

The diffusion constants,  $\bar{D}$ , are actually functions of concentrations:

$$\bar{D}_{11} = \frac{\omega_{H_2O}^2}{x_H x_{H_2O}} \hat{D}_{HH_2O}, \quad \bar{D}_{12} = \bar{D}_{21} = -\frac{\omega_H \omega_{H_2O}}{x_H x_{H_2O}} \hat{D}_{HH_2O},$$

where the  $\hat{D}$  expressions are constants. The chemical reaction term  $R_H$  in (1) is given by

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

Where

$$S_H^{ano} = -\frac{3f_{ano}}{r_{ano}^2} D_H^{agg} c_H^{agg} \left[ \beta_H \coth(\beta_H) - 1 \right] \leq 0 \quad (4)$$

$$S_{H_2O}^{ano} = -\frac{6\lambda_{ano} P f_{ano}}{r_{ano}^2} D_H^{agg} c_H^{agg} \left[ \beta_H \coth(\beta_H) - 1 \right] - \alpha_{ano} (c_{ano}^{eq} - c_{H_2O}),$$

The meaning of these terms need not concern us greatly, they are all constants and given as simulation inputs except for the concentrations,  $c$  (which are trivial functions of the mass fractions) and  $\beta_H$ . This is given by,

$$\beta_H^2 = \frac{i_{ano}^{ref}}{2F} \frac{s_{ano} r_{ano}^2}{D_H^{agg} c_H^{ref}} \left[ \exp\left(\frac{F \alpha_{ox}^{ano} \eta_{ano}}{RT}\right) - \exp\left(-\frac{F \alpha_{red}^{ano} \eta_{ano}}{RT}\right) \right] \quad (5)$$

With

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

The remaining parameters are all constants and again need not concern us here (see [1] for a full description). The point to note is that  $\beta_H$  is related to the difference in membrane and electrostatic voltage according to exponential functions and then the reaction rates are given by this  $\beta_H$  via a further coth function in (4). Clearly the system is very non-linear with the strongest (exponential) non-linearity emerging due to the chemical reaction, right-hand-side term  $R_H$ . The complexity of this term arise because we assume reactions can occur only when catalyst particles, membrane material, conducting carbon particles and pores supplying the gas are in mutual contact, and with a film of liquid water, and this often occurs in agglomerate particles which form because of difficulties in dispersing the various types of material. E.g., the term  $r_{ano}$  in (5) refers to the radius of these reacting particles and  $D_H^{agg}$  refers to how material diffuses within them. Introducing this agglomerate system makes our model more complex and realistic than other simulations reported in literature.

On the cathode side, the Maxwell-Stephan equations have a similar form, but now we have 2 equations (plus the constraint that total mass fraction sums to 1):

$$\nabla \cdot \left[ -\rho \omega_O \sum_{k=1}^3 \bar{D}_{1k} \left\{ \nabla x_k + (x_k - \omega_k) \frac{\nabla p}{p} \right\} \right] = R_O - \rho \mathbf{u} \cdot \nabla \omega_O$$

$$\nabla \cdot \left[ -\rho \omega_{H_2O} \sum_{k=1}^3 \bar{D}_{2k} \left\{ \nabla x_k + (x_k - \omega_k) \frac{\nabla p}{p} \right\} \right] = R_{H_2O} - \rho \mathbf{u} \cdot \nabla \omega_{H_2O}$$

$$\omega_N = 1 - \omega_O - \omega_{H_2O}$$

where  $k=1 \Rightarrow O$ ,  $k=2 \Rightarrow H_2O$ ,  $k=3 \Rightarrow N$ . The equations for  $\rho, R_O, R_{H_2O}, \mathbf{u}, \bar{D}$  are similar to those in (1) but rather more complex owing to 3 species rather than 2. We refer the reader to [1] for full details. The dependent variables, which vary in space, are  $\omega_O, \omega_{H_2O}, p$ .

To complete the specification in the outer domains 1,2,4,5, the Poisson equation is used to govern the electrostatic potential

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

Where sigma is the conductivity.  $Q_{ele}$  is a term which creates charge according to the chemical reactions occurring. In fact  $Q_{ele}$  is given by equations similar to (4) as is the F term, already seen in (3). Thus the right hand side terms of all PDEs in the model are roughly the same: an expression in terms of dependent variables with exponential dependence on those variables. All of this arises from the agglomerate model considered. Thus all PDEs are highly non-linear and the simulation is not guaranteed to converge in all cases.

Lastly, consider the inner domains 2-4. The electrolyte membrane of the fuel cell is considered to be a mixture of four species. The abundant solvent is the membrane polymer (usually NAFION) and three solute species are assumed to diffuse within the solvent. They are the negative ions ( $k=1$ ) having concentration  $c_M$ , the positive ions ( $k=2$ ) having concentration  $c_{HPO}$  and the electrically neutral water molecules ( $k=3$ ) having concentration  $c_{H_2O}$ . The equations governing these are given by

$$\nabla \cdot \left[ -D_k \left( \nabla c_k + \frac{F z_k c_k}{RT} \nabla V_{mem} \right) \right] = \bar{S}_k, \quad k=1, 2, 3.$$

Where, again, due to the agglomerate model, the  $\bar{S}$  functions have a similar form to the corresponding S-functions in (4) giving non-linear source behaviour.

### 3. COMSOL implementation using pre-defined modules

COMSOL Multiphysics comes with a great many modules which can be added together to create complex multiphysics systems without the necessity to specify each equation by hand. The disadvantage is that we don't have full control over what equations we wish to solve and could even end up solving a different set of equations

than we intended. Such a mistake might be hard to discover.

In the model we used the following Comsol modules:

- Conductive Media DC (Electrodes)
- Darcy's Law (Darcy)
- Maxwell-Stephan Diffusion and Convection (ms)
- Nernst-Planck (chnp)

As indicated, some of these modules are only active in certain subdomains, see Fig 3.

#### 4. COMSOL implementation using the coefficient mode

The equation-based modelling approach gives us full control over which equations we wish COMSOL to solve. Although the matrices in this section are complex, it should be noted that the greatest complexity in the current work is due to the agglomerate source terms in (4). These must be entered as COMSOL expressions however we model the system. As stated, we can either retain molar or mass fractions in the Maxwell-Stephan equations (eliminating the other one). Here we show the

$$c = \begin{bmatrix} c_{V_{ele}, V_{ele}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & c_{p,p} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & c_{x_H,p} & c_{x_H,x_H} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & c_{x_O,p} & 0 & c_{x_O,x_O} & c_{x_O,x_{H2O}} & 0 & 0 & 0 & 0 \\ 0 & c_{x_{H2O},p} & 0 & c_{x_{H2O},x_O} & c_{x_{H2O},x_{H2O}} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & c_{V_{mem}, V_{mem}} & c_{V_{mem}, c_{H3O}} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & c_{c_{H3O}, V_{mem}} & c_{c_{H3O}, c_{H3O}} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & c_{c_{H2O}, c_{H2O}} & 0 \end{bmatrix} \quad (6)$$

with

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

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

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

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

$$c_{x_O,p} = \frac{\rho \omega_O}{p} [(x_O - \omega_O) (D_{1,1} - D_{1,3}) + (x_{H2O} - \omega_{H2O}) (D_{1,2} - D_{1,3})] I \quad (4,5)$$

$$c_{x_O,x_O} = \rho \omega_O (D_{1,1} - D_{1,3}) I \quad (4,5)$$

$$c_{x_O,x_{H2O}} = \rho \omega_O (D_{1,2} - D_{1,3}) I \quad (4,5)$$

molar fraction approach as the equations are simpler. We first set write down the 8 dependent variables of the model in a vector  $\mathbf{u}$ :

$$\mathbf{u} = \begin{bmatrix} V_{ele} \\ p \\ x_H \\ x_O \\ x_{H2O} \\ V_{mem} \\ c_{H3O} \\ c_{H2O} \end{bmatrix} \quad \nabla \mathbf{u} = \begin{bmatrix} \nabla V_{ele} \\ \nabla p \\ \nabla x_H \\ \nabla x_O \\ \nabla x_{H2O} \\ \nabla V_{mem} \\ \nabla c_{H3O} \\ \nabla c_{H2O} \end{bmatrix} .$$

We wish to express the PDEs required in the coefficient form  $-\nabla \cdot c \nabla \mathbf{u} = f$  (we set the other COMSOL matrices,  $\alpha, \beta, \gamma, a$  to zero). By substitution, it is easy to check that the following  $c, f$  matrices give the correct set of equations:

$$c_{x_{H2O},p} = \frac{\rho\omega_{H2O}}{p} \left[ (x_O - \omega_O)(D_{2,1} - D_{2,3}) + (x_{H2O} - \omega_{H2O})(D_{2,2} - D_{2,3}) \right] I \quad (4,5)$$

$$c_{x_{H2O},x_O} = \rho\omega_{H2O} (D_{2,1} - D_{2,3}) I \quad (4,5)$$

$$c_{x_{H2O},x_{H2O}} = \rho\omega_{H2O} (D_{2,2} - D_{2,3}) I \quad (4,5)$$

$$c_{V_{mem},V_{mem}} = Fu_{H3O} z_{H3O} c_{H3O} I \quad (2,3,4)$$

$$c_{V_{mem},c_{H3O}} = D_{H3O} I \quad (2,3,4)$$

$$c_{c_{H3O},c_{H3O}} = -D_M \frac{z_{H3O}}{z_M} I \quad (2,3,4)$$

$$c_{c_{H3O},V_{mem}} = -Fu_M z_{H3O} c_{H3O} \quad (2,3,4)$$

$$c_{c_{H2O},c_{H2O}} = D_{H2O} I \quad (2,3,4)$$

where  $I$  is the 3x3 identity matrix. The numbers in brackets after each equation show which domains the component is active in. In other domains, the matrix component should be set to zero.

The  $f$ -vector is given by

$$\mathbf{f} = \begin{bmatrix} f_{V_{ele}} \\ f_p \\ f_{x_H} \\ f_{x_O} \\ f_{x_{H2O}} \\ f_{V_{mem}} \\ 0 \\ f_{c_{H2O}} \end{bmatrix} = \begin{bmatrix} Q_{ele} \\ F \\ R_H - \rho\mathbf{u} \cdot \nabla \omega_H \\ R_O - \rho\mathbf{u} \cdot \nabla \omega_O \\ R_{H2O} - \rho\mathbf{u} \cdot \nabla \omega_{H2O} \\ \bar{S}_{H3O} \\ 0 \\ \bar{S}_{H2O} \end{bmatrix} \begin{matrix} (2,4) \\ (2,4) \\ (1^*,2) \\ (4,5^*) \\ (4,5^*) \\ (2,4) \\ (2,4) \\ (2,4) \end{matrix}$$

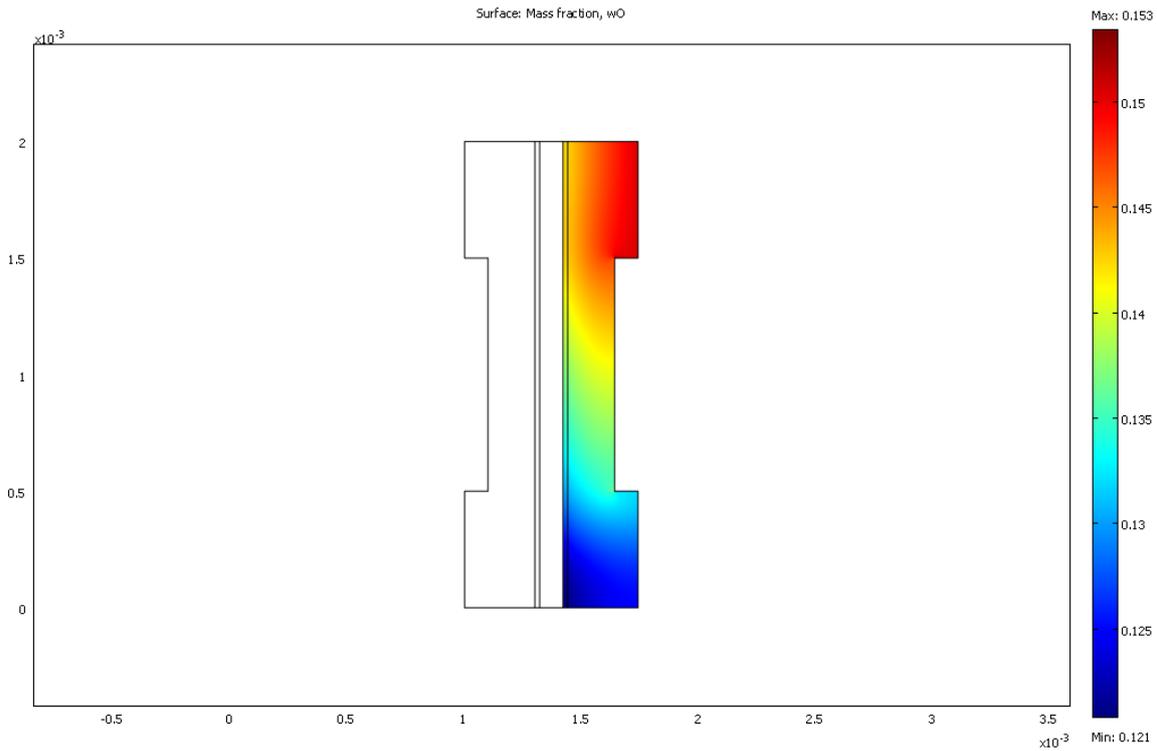
where again the numbers in brackets indicate the domains where the component applies. (Only the  $\text{grad}(\omega)$  term applies in regions marked \*). Due to the fact that some of the matrix components are switched off in different Domains, the system becomes “staggered” as discussed. It is also necessary to deactivate dependent variables in certain Domains. E.g. it would not make sense for  $V_{mem}$  to be active in Domain 5 since COMSOL

would have no way to know how to solve for this. Such mistakes can happen, but COMSOL is good at pointing out when a degree of freedom cannot be determined.

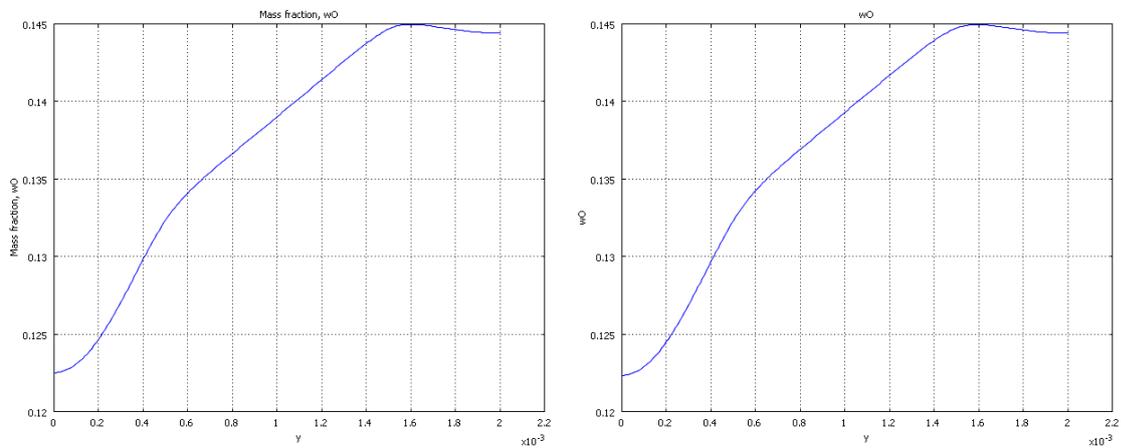
It is interesting to note that the C-matrix in (6) is not block diagonal. This is due to terms in which molar fractions are linked to pressures in (1). In later work we have eliminated molar fractions in terms of densities so that the matrix becomes block diagonal, a situation which seems more satisfactory.

## 5. Results

Figure 4 shows the oxygen mass fraction result on the cathode side of the RVE. The oxygen is input at the top right of the figure so the oxygen concentration naturally decreases as we move to the other port. Note that oxygen is only present in the cathode area: this dependent variable is deactivated at the membrane and anode region. Figure 5 is equivalent to Fig 4 except we are scanning along the line  $x=1.6$  mm to produce a line graph. The figure shows the same result for the module and equation-based simulation proving that the two simulations solve the same physics and validating both models. Figure 6 shows the I-V curve obtained from the model. The result agrees well with experiment (not shown).



**Figure 4:** Plot of oxygen mass fraction at the cathode side of the cell.



**Figure 5:** Plot of oxygen mass fraction through the cathode side of the cell for: built-in module based modelling (left) and equation based modelling with the coefficient mode (right)

## 6. Conclusions

We have shown that a fuel cell can be modelled using both COMSOL's built-in modules and by directly specifying the equations needed using the coefficient mode. The latter approach, while more complex, allows us total control over which equations we are solving and will allow us to generalise the model in future, e.g., extending it to

3D, replacing the Darcy physics with Navier Stokes equations, and using densities in place of mass fractions in the Maxwell Stephan formulation. In this paper we have described a sophisticated and highly non-linear fuel cell system based on a novel agglomerate model for the electrochemical reactions.

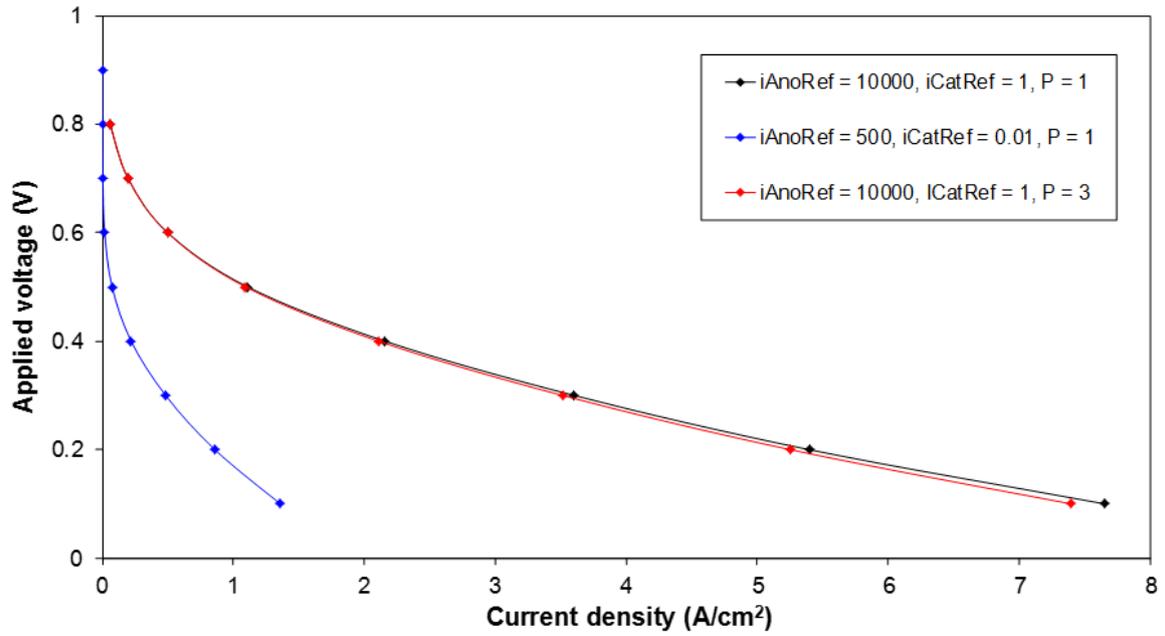


Figure 6: Current-voltage curve obtained for fuel cell with a variety of agglomerate parameters.

## 7. References

[1] NPL Technical Note: Modelling of PEM Fuel cell using COMSOL Multiphysics, L N McCartney, X-S Yang, J Urquart, December 2013