

Impedance of Symmetric Cell

09/10/2018

Equations:

The governing equation is based on the conservation of electrochemical potential:

$$\kappa_{eff} \nabla^2 \Phi_2 + C_{DL} \frac{\partial \Phi_1 - \Phi_2}{\partial t} = 0$$

where,

κ_{eff} : ionic conductivity in liquid phase (S/m)

Φ_2 : potential of liquid phase (V)

C_{DL} : capacitance of the double-layer (F)

Φ_1 : potential of solid phase (V)

We assume that Φ_1 equals to 0 as reference. Such that,

$$\kappa_{eff} \nabla^2 \Phi_2 - C_{DL} \frac{\partial \Phi_2}{\partial t} = 0$$

Finite Volume Method :

Integral form of conservation equation :

$$\iiint (\kappa_{eff} \nabla^2 \cdot \Phi_2 - C_{DL} \frac{\partial \Phi_2}{\partial t}) dV = 0$$

In 2D case :

$$\iint (\kappa_{eff} \nabla^2 \cdot \Phi_2 - C_{DL} \frac{\partial \Phi_2}{\partial t}) dA = 0$$

1) All of neighbours are liquid phase :

$$\frac{\partial \Phi_{2,P}}{\partial t} = 0$$

then,

$$\iint \kappa_{eff} \nabla^2 \cdot \Phi_2 dA = 0$$

$$\Delta y \left(\frac{d\Phi_2}{dx} \right) (w, e) + \Delta x \left(\frac{d\Phi_2}{dy} \right) (s, n) = 0$$

where

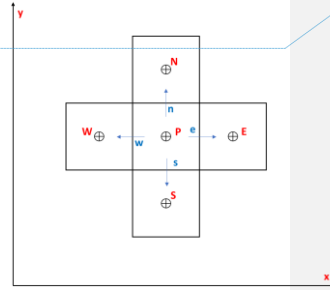
$$\Delta x = \Delta y$$

$$\frac{d\Phi_2}{dx}, e - \frac{d\Phi_2}{dx}, w + \frac{d\Phi_2}{dy}, n - \frac{d\Phi_2}{dy}, s = 0$$

$$\frac{\Phi_{2,E} - \Phi_{2,P}}{\Delta x} + \frac{\Phi_{2,W} - \Phi_{2,P}}{\Delta x} + \frac{\Phi_{2,N} - \Phi_{2,P}}{\Delta y} + \frac{\Phi_{2,S} - \Phi_{2,P}}{\Delta y} = 0$$

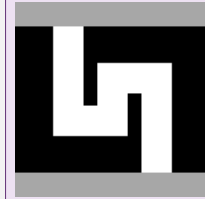
$$\Phi_{2,P} = \frac{\Phi_{2,W} + \Phi_{2,E} + \Phi_{2,N} + \Phi_{2,S}}{NN} \quad (1)$$

NN = number of nearest neighbour which is liquid phase



Commenté [CS1]: This assumption would turn the liquid phase into a pure resistor network, with no time constant, which to my mind is different from both the diffusive case and the migration case.

Commenté [SC2]: Imagine for the following pore that there is a uniform electric field between these two electrodes (i.e. the gradient of the potential field is constant, and the iso-lines are parallel to the two electrodes).



Starting with just a single pair of ions in the middle of the pore (i.e. a near perfectly dilute solution), these two ions would dissociate and follow the electric field in opposite directions. However, if they really start in the middle, then they won't make it to the electrode surface as they'll get stuck in the bend of the pore! If the migration is entirely driven by the field (i.e. photons) of the electrodes, then this only generates a force normal to the electrodes, which means that horizontal motion (and especially backflow) must be diffusion controlled.

2) Neighbours are mix of solid/liquid phase :

$$\iint (\kappa_{eff} \nabla^2 \cdot \Phi_2 - C_{DL} \frac{\partial \Phi_2}{\partial t}) dA = 0$$

$$\kappa_{eff} \left[\Delta y \left(\frac{d\Phi_2}{dx} \right) (w, e) + \Delta x \left(\frac{d\Phi_2}{dy} \right) (s, n) \right] - C_{DL} \iint \frac{\partial \Phi_{2,P}}{\partial t} dA = 0$$

Apply to the case on the right :

$$\kappa_{eff} \left[\Delta y \frac{\Phi_{2,W} - \Phi_{2,P}}{\Delta x} + \Delta x \frac{\Phi_{2,S} - \Phi_{2,P}}{\Delta y} \right] - 2C_{DL} A \frac{\partial \Phi_{2,P}}{\partial t} = 0$$

Apply Laplace transformation :

$$\kappa_{eff} [\Phi_{2,W} - \Phi_{2,P} + \Phi_{2,S} - \Phi_{2,P}] - 2C_{DL} A j\omega \overline{\Phi_{2,P}} = 0$$

where

$$A = \Delta x \Delta y = \Delta x^2$$

$$\Phi_{2,P} = \frac{\kappa_{eff} (\Phi_{2,W} + \Phi_{2,S})}{2\kappa_{eff} + 2C_{DL} j\omega \Delta x^2}$$

In general case :

$$\Phi_{2,P} = \frac{(\Phi_{2,W} + \Phi_{2,S})}{NN + (4 - NN) C_{DL} j\omega \frac{\Delta x^2}{\kappa_{eff}}}$$

NN = number of nearest neighbour which is liquid phase

When a pixel (i) is solid phase, we define :

$$\Phi_{2,i} = 0$$

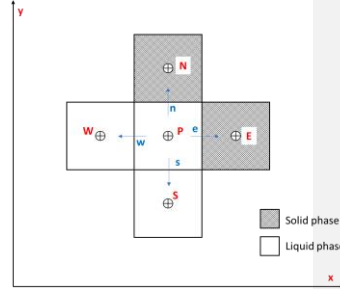
So we can re-write the equation above :

$$\Phi_{2,P} = \frac{\Phi_{2,W} + \Phi_{2,E} + \Phi_{2,N} + \Phi_{2,S}}{NN + (4 - NN) C_{DL} j\omega \frac{\Delta x^2}{\kappa_{eff}}} \quad (2)$$

In 3D case, equation (1) and (2) become respectively :

$$\Phi_{2,P} = \frac{\Phi_{2,W} + \Phi_{2,E} + \Phi_{2,N} + \Phi_{2,S} + \Phi_{2,U} + \Phi_{2,D}}{NN} \quad (3)$$

$$\Phi_{2,P} = \frac{\Phi_{2,W} + \Phi_{2,E} + \Phi_{2,N} + \Phi_{2,S} + \Phi_{2,U} + \Phi_{2,D}}{NN + (6 - NN) C_{DL} j\omega \frac{\Delta x^2}{\kappa_{eff}}} \quad (4)$$



Commenté [SC3]: What are you using the bar notation for here?

The equation (1) and (3) in fact are the equation (2) and (4) in the case $NN = 4$ or 6 respectively.

From the equation above, I think the iteration step to solve the equation by over-relaxation could be the same as present, just to change the denominator (**add the value of double layer capacitance and ionic conductivity**).

And this time, we might need some **initial value** because we don't calculate the steady-state value anymore...

Here, we want to adjust the total neighbours at each voxel. Because this can vary depends on where is the voxel (from 6 to 4 or 3 if the voxel is in the boundary in 3D case)

Then I propose that we can calculate the **total possible neighbours for each voxel** (a new variable called *hand.NN_tot* for ex). The equation become now :

$$\Phi_{2,P} = \frac{\Phi_{2,W} + \Phi_{2,E} + \Phi_{2,N} + \Phi_{2,S} + \Phi_{2,U} + \Phi_{2,D}}{NN + (NN_tot - NN)C_{DL}j\omega \frac{\Delta x^2}{\kappa_{eff}}}$$

The preparation process then maybe need some modifications (at function **preparation2(hand)**)

Boundary Conditions

Here, first, I think the boundary condition will be the current flow at the boundary edge equals to zero, not the potential at the edge.

That means perhaps we don't need the ghost node? Because for me, we impose the flux (not the potential) at the boundary edge. As we're using FV method, the flux at the edge involve directly into the calcul scheme.

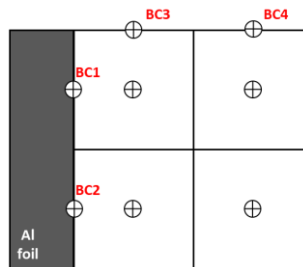
If it's correct, then maybe we don't need to adjust the nearest neighbours at each voxel at the boundaries.

At Current collector side ($x=0$):

We assume that there is no ionic current at the interface between CC/liquid phase → Neumann condition

$$i_{2,BCi(i=1,2)} = \kappa_{eff} \nabla \cdot \Phi_{2,BCi(i=1,2)} = 0$$

$$\nabla \cdot \Phi_{2,BCi(i=1,2)} = 0 \quad (5)$$



At the boundaries of the electrode ($z = Z, y = Y$) :

We assume that there is no ionic current at the boundary of the electrode → Neumann condition

$$\nabla \cdot \Phi_{2,BCi(i=3,4)} = 0 \quad (6)$$

Most recent thoughts:

Since I got back to France, I've had some new thoughts about how we can change the TauFactor code. Here is some of my proposals :

- 1) Perhaps we can add a `hand.symmetric_cell_check` condition (sort of checkbox on the GUI)
=> know when users want to calculate using SC config
- 2) Need to change Boundary conditions (It isn't `Ctop = 0` and `Cbot = 1` anymore but this time it's potential of Solid phase)
- 3) Need to define ionic conductivity k and C double layer
- 4) Check(hand) function need to be modify (the way we calculate the impedance change with the SC config)

Commenté [SC4]: The way the frequency information is given through the system is the added term in frequency domain. If one electrode is 0 and the other is 1, I'm working whether this is the same as -0.5 and +0.5... Certainly for the simulated impedance in `taufactor` now, one boundary is stimulating, while the other is just open or closed...