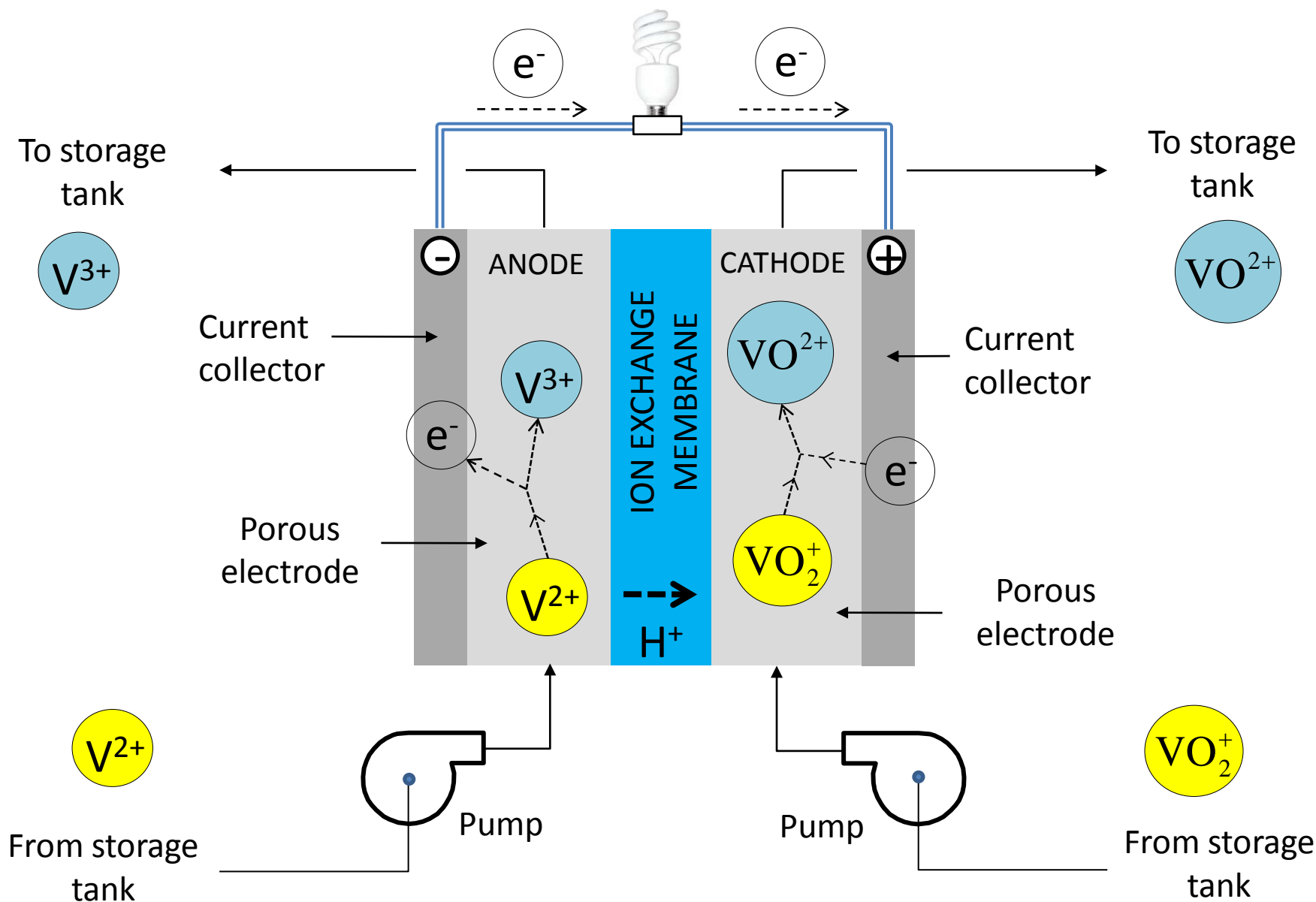
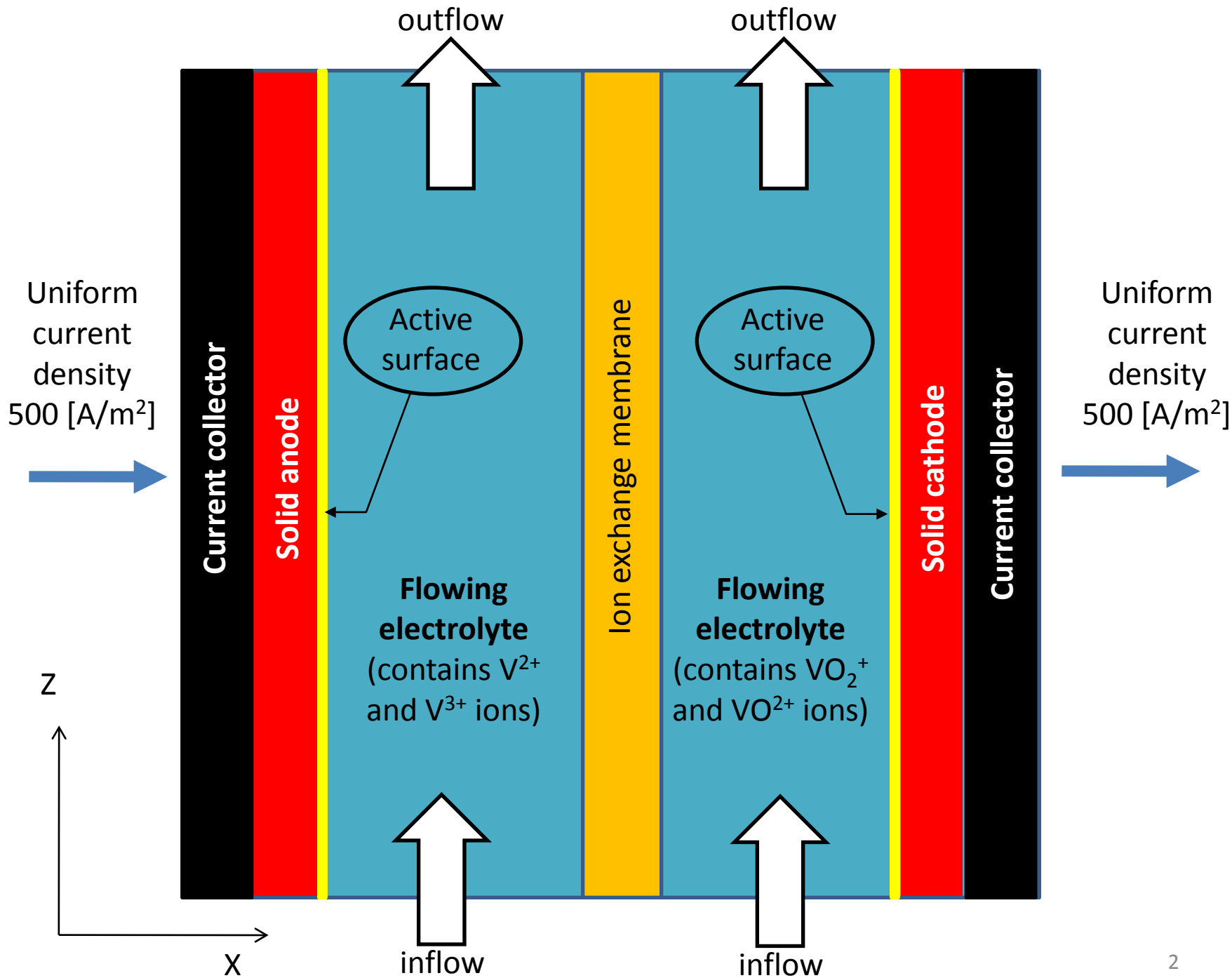
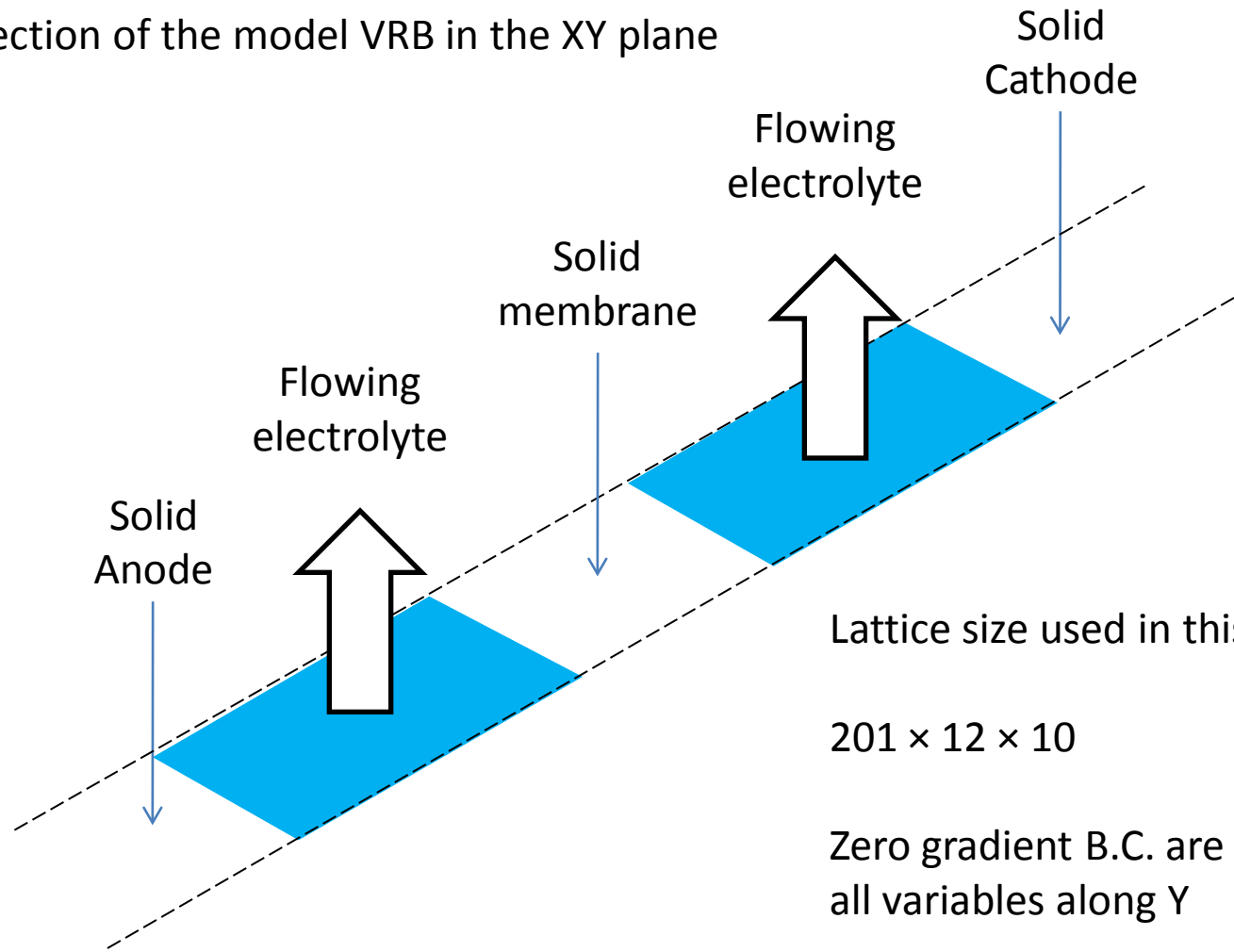


Pore-scale simulation of electrolyte flow, charge and species transport in a Vanadium Flow Battery





Cross section of the model VRB in the XY plane



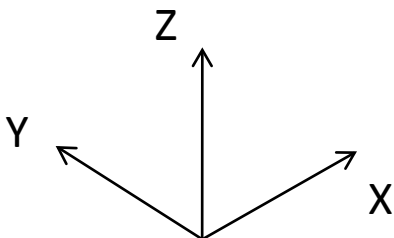
Lattice size used in this simulation

$$201 \times 12 \times 10$$

Zero gradient B.C. are employed for all variables along Y

$$\Delta x = \Delta y = \Delta z = 50 \times 10^{-6} \text{ [m]}$$

$$\Delta t = 10 \text{ [s]}$$



Governing Equations - Flow

$$\nabla \cdot \mathbf{u} = 0$$

Conservation of mass

$$\frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \nabla) \mathbf{u} = \frac{-\nabla p}{\rho} + \nu \nabla^2 \mathbf{u}$$

Conservation of momentum

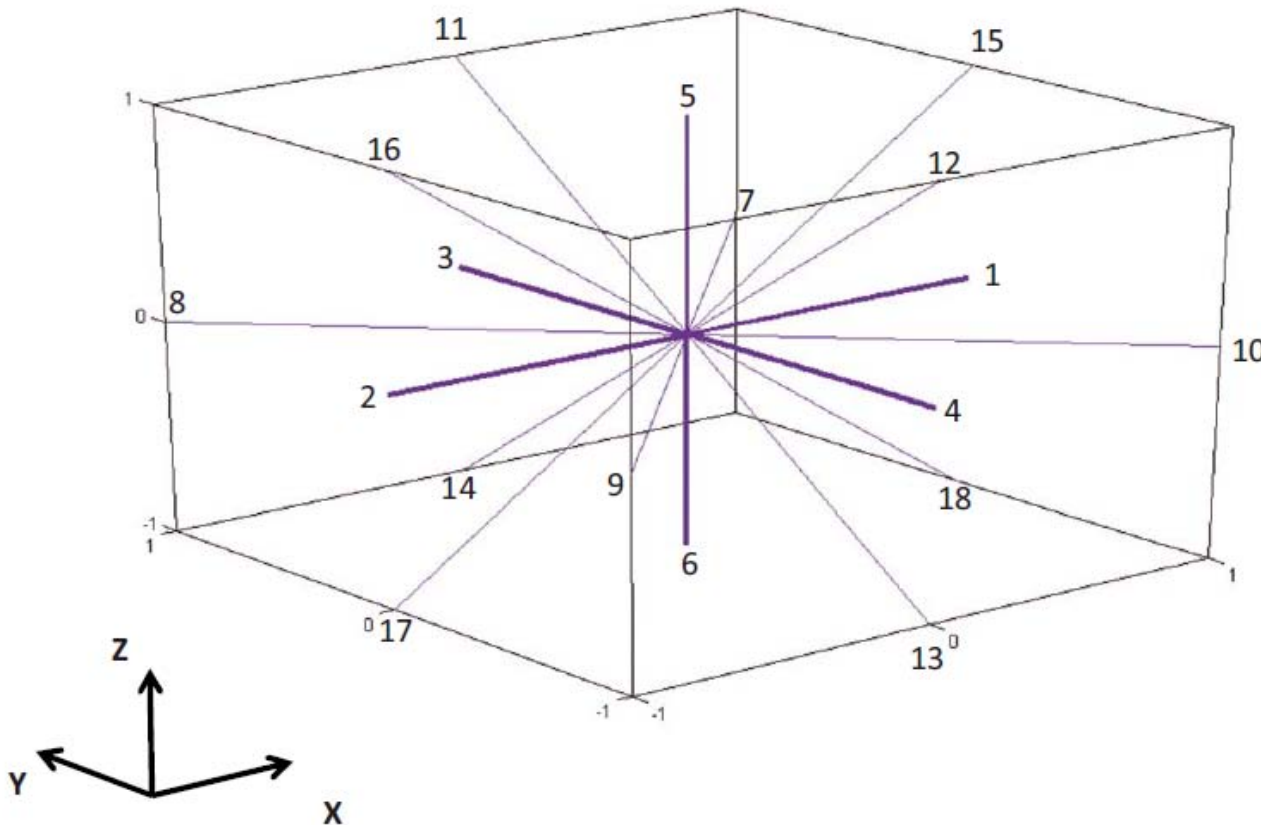
These equations are to be solved for the liquid electrolyte (H_2SO_4) flowing through the pore-space of the electrodes (both anode and cathode side).

ASSUMPTIONS:

Single-phase, constant-properties, laminar ($\text{Re} \sim 0.1$), incompressible flow.

Lattice Boltzmann Method - Flow

The **D3Q19 velocity model** is employed, with bounce-back conditions to enforce no-slip boundaries. The fluid density (pressure) is specified at the inlet and outlets of the flow channels on the anode and cathode side and this pressure difference is the driving force for the flow.



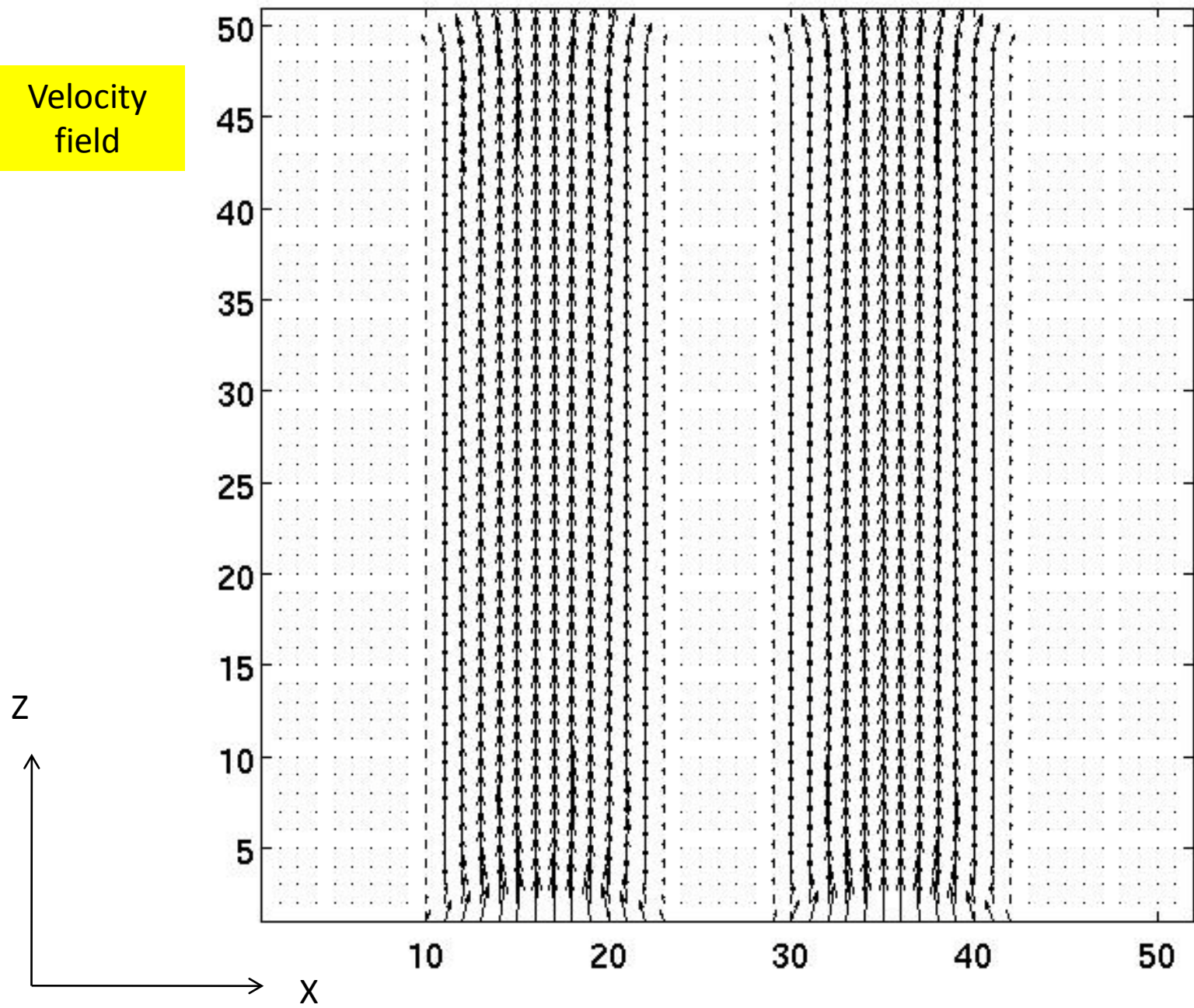
NOTE:

The speed of sound in this model is

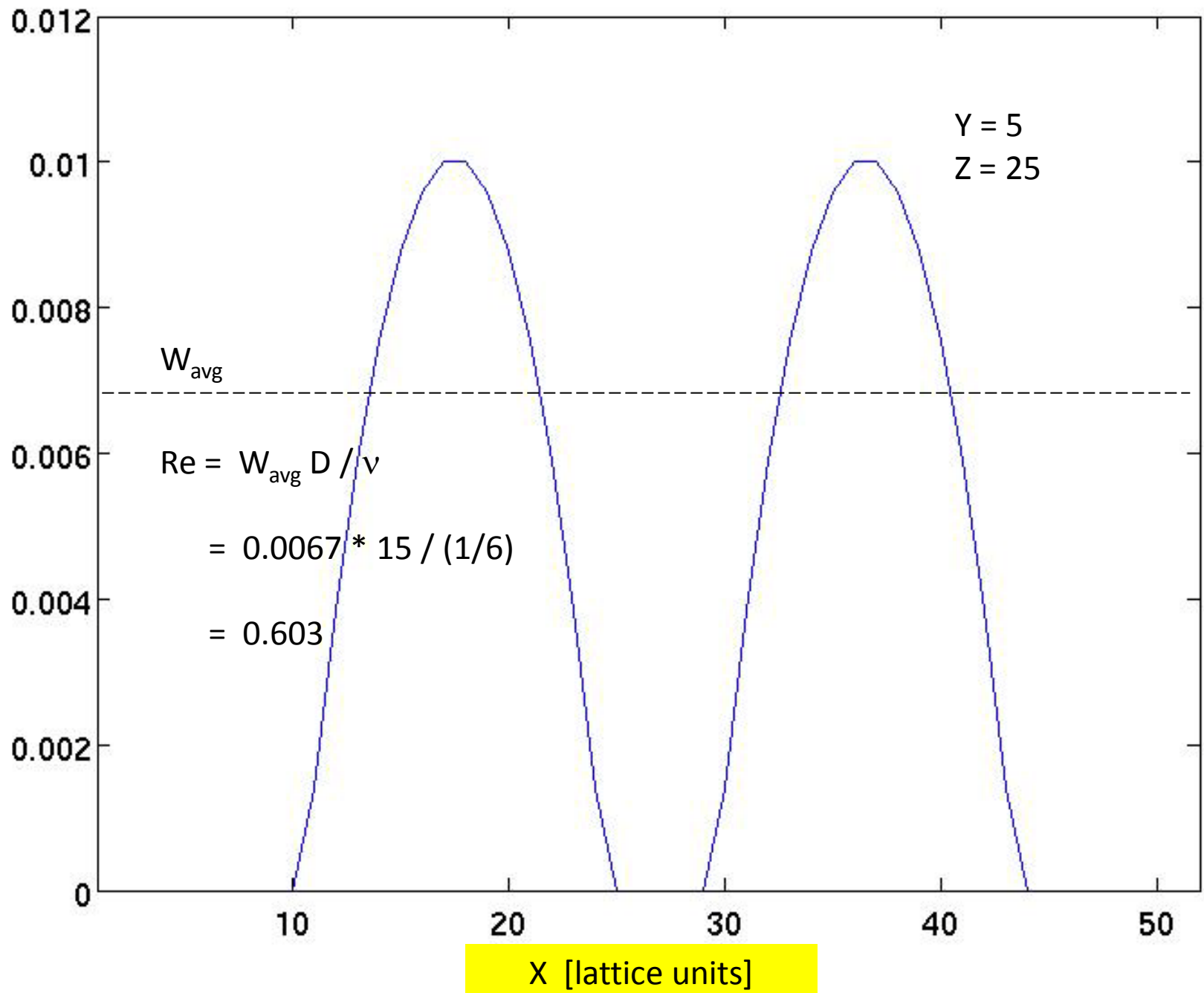
$$c_s = \frac{1}{\sqrt{3}}$$

In order for flow to remain incompressible, the velocity in the channel should be a lot smaller than the speed of sound (low Mach number).

Velocity field



W-component of velocity [lattice units]



Governing Equations – Charge Transport

$$\mathbf{J} = -\lambda \nabla C - \kappa \nabla \phi$$

Definition of current density

$$\nabla \cdot (\lambda \nabla C + \kappa \nabla \phi) = 0$$

Conservation of charge

This equation is to be solved throughout the flow battery (solid + pore phase).

ASSUMPTIONS:

At the anode and cathode current collectors, the current density $\mathbf{J} = -\kappa \nabla \phi$ is known and this boundary condition is the primary input to the model.

The potential is discontinuous across the active surface. The normal flux of charge (current density) is however continuous and given by the Butler-Volmer equation.

It is assumed that the “mass transport” current density is zero $\lambda = 0$

The membrane is assumed to have the same electrical conductivity as the electrolyte.

Governing Equations - Electrochemistry

Butler-Volmer kinetics applied at the active surface

$$\mathbf{J} \cdot \hat{\mathbf{n}} = i_0 \left[\exp\left(\frac{\alpha F}{RT} \eta\right) - \exp\left(\frac{-\alpha F}{RT} \eta\right) \right]$$

Exchange current density = f (local species concentrations)

Electric current density along the local normal to the active surface. This can be converted to species flux \mathbf{N} via dividing by Faraday's constant (F).

ANODE

-0.255 [V]

Open circuit voltage

$$E_a = E_a^0 + \frac{RT}{F} \log_{10} \left(\frac{C_{V^{2+}}}{C_{V^{3+}}} \right)$$

$$\eta_a = \phi_s - \phi_e - E_a$$

1.75×10^{-2}

$$J_1 = -J_2 = \underbrace{k_a (C_{V^{3+}}^s)^{\alpha_{-,c}} (C_{V^{2+}}^s)^{\alpha_{+,c}}}_{i_0} \left[\exp \left(\frac{\alpha_{+,a} F \eta_a}{RT} \right) - \exp \left(-\frac{\alpha_{-,a} F \eta_a}{RT} \right) \right]$$

Exchange current density

i_0

CATHODE

0.991 [V]

Open circuit voltage

$$E_c = E_c^0 + \frac{RT}{F} \log_{10} \left(\frac{C_{VO_2^+}}{C_{VO^{2+}}} \right)$$

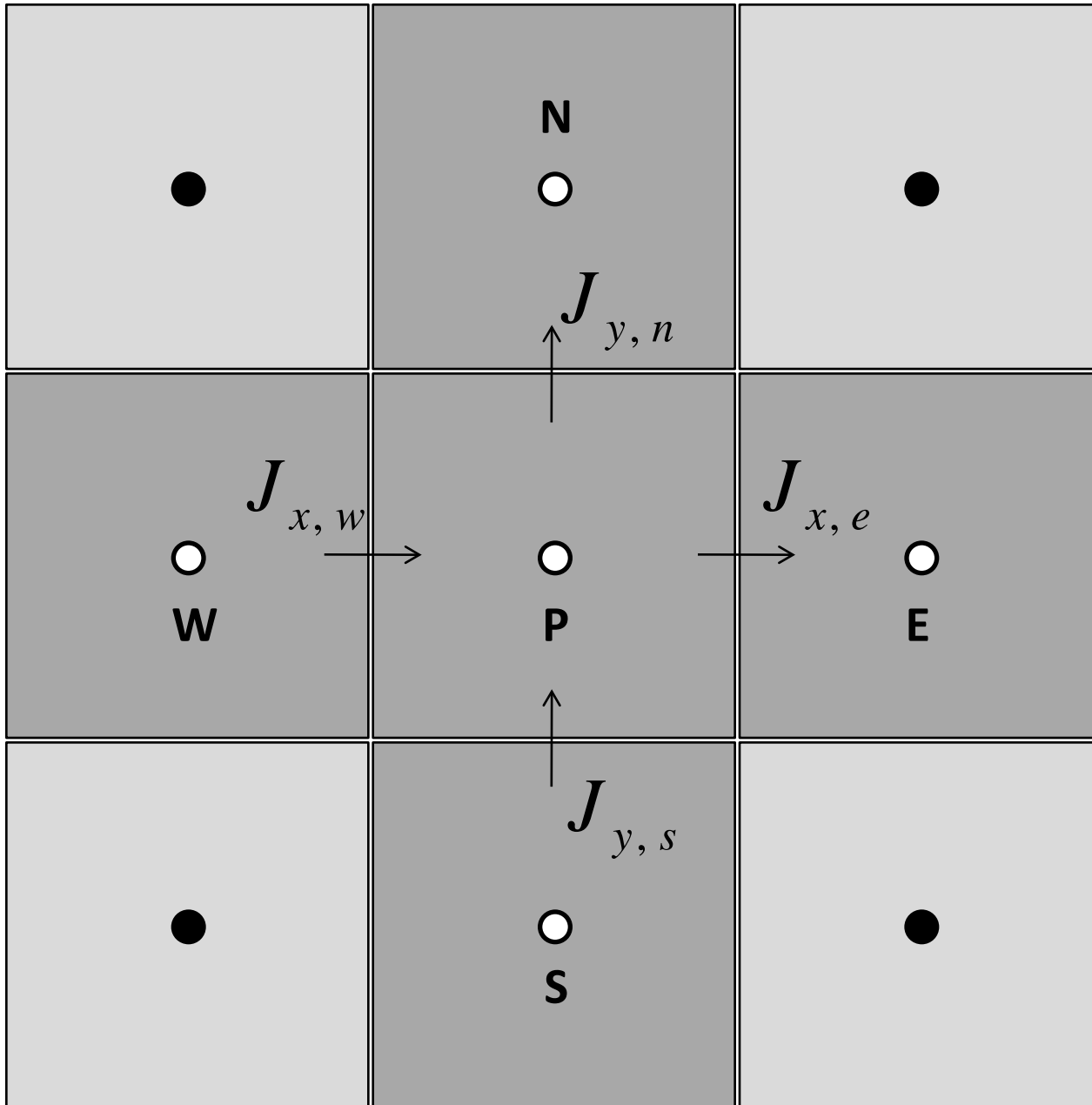
$$\eta_c = \phi_s - \phi_e - E_c$$

3×10^{-6}

$$J_3 = -J_4 = \underbrace{k_c (C_{VO^{2+}}^s)^{\alpha_{-,c}} (C_{VO_2^+}^s)^{\alpha_{+,c}}}_{i_0} \left[\exp \left(\frac{\alpha_{+,c} F \eta_c}{RT} \right) - \exp \left(-\frac{\alpha_{-,c} F \eta_c}{RT} \right) \right]$$

Exchange current density

i_0



$$\mathbf{J} = -\kappa \nabla \phi$$

Current density definition

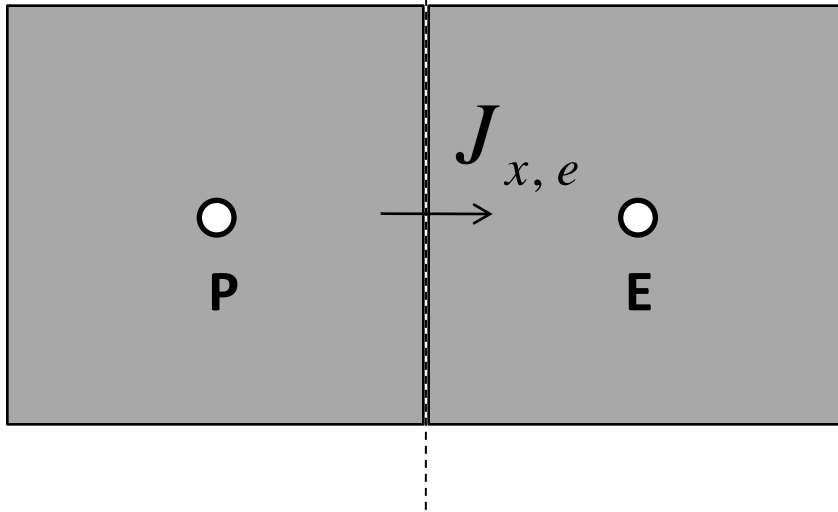
$$\nabla \cdot \mathbf{J} = 0$$

Conservation of charge

Discrete version of the above equation (shown for the 2D case for simplicity):

$$\left[\frac{J_{x,e} - J_{x,w}}{\Delta x} \right] + \left[\frac{J_{y,n} - J_{y,s}}{\Delta y} \right] = 0$$

The EAST face.....

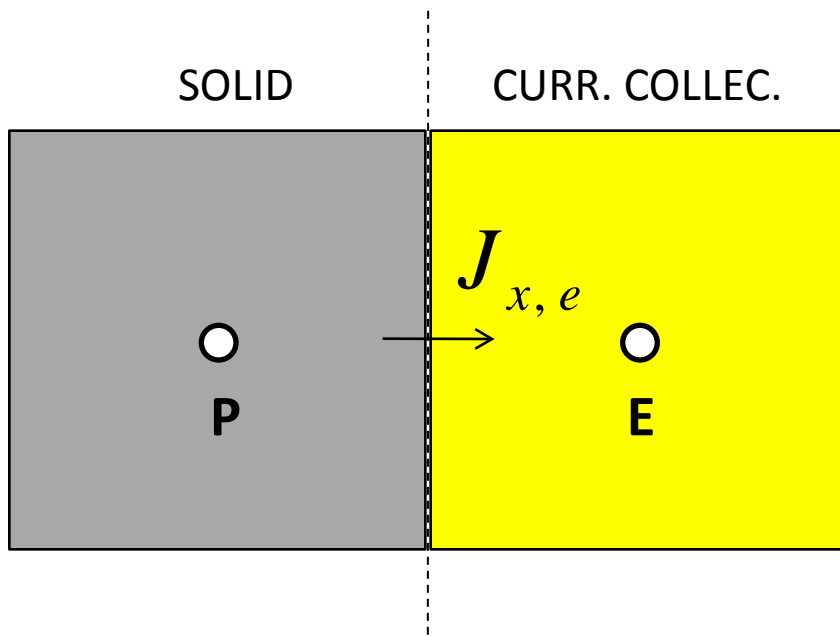


For a “normal” face, i.e. not an active surface or current-collector face

$$J_{x,e} = -\kappa_e \left[\frac{\phi_E - \phi_P}{\Delta x} \right]$$

Face value of conductivity is calculated using “harmonic mean”

$$\kappa_e = \frac{2\kappa_P\kappa_E}{\kappa_P + \kappa_E}$$

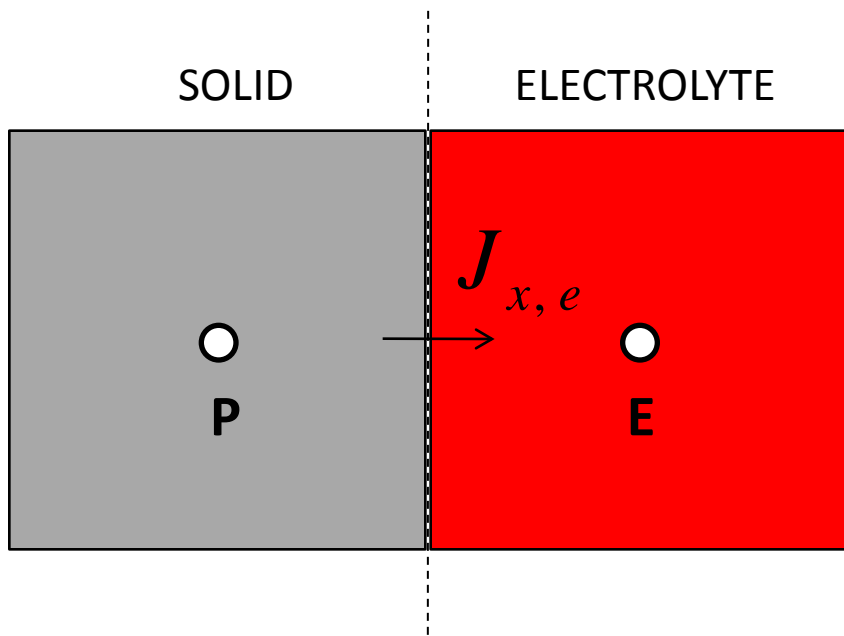


For a “current-collector” face, the current density is known and can be directly used.

$$J_{x,e} = 500 \text{ [A/m}^2\text{]}$$

For “zero gradient” boundaries, the current density can be set directly to zero.

Using the **FINITE VOLUME** approach has advantages compared to using a **FINITE DIFFERENCE** approach for these situations.



For a “active” face, the current density is determined from the Butler-Volmer equation

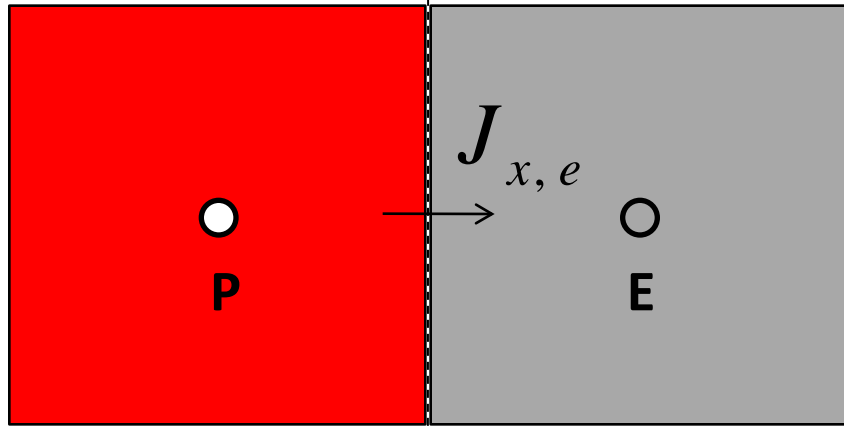
$$J_{x,e} = \frac{k (C_1)^{1/2} (C_2)^{1/2}}{2} \text{SINH} \left\{ \frac{\alpha F}{RT} \left[\phi_P - \phi_E - OCV - \frac{RT}{F} \ln \left(\frac{C_1}{C_2} \right) \right] \right\}$$

Potential in the
solid phase

Potential in the
liquid phase

NOTE: Species concentrations are defined only in the liquid phase, which is node point “E” in this case.

What happens when the CVs are reversed ?



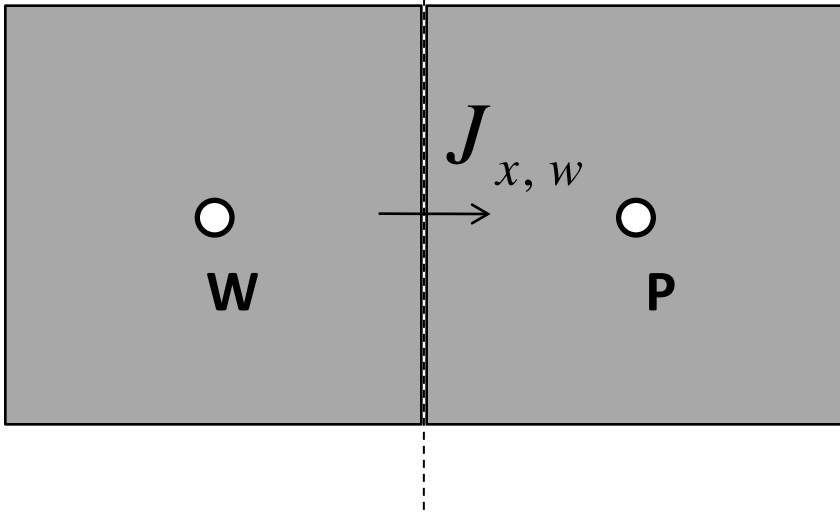
$$J_{x,e} = \frac{-k (C_1)^{1/2} (C_2)^{1/2}}{2} \text{SINH} \left\{ \frac{\alpha F}{RT} \left[\phi_E - \phi_P - OCV - \frac{RT}{F} \ln \left(\frac{C_1}{C_2} \right) \right] \right\}$$

NOTE: Species concentrations are defined only in the liquid phase, which is node point "P" in this case.

Potential in the solid phase

Potential in the liquid phase

The WEST face.....

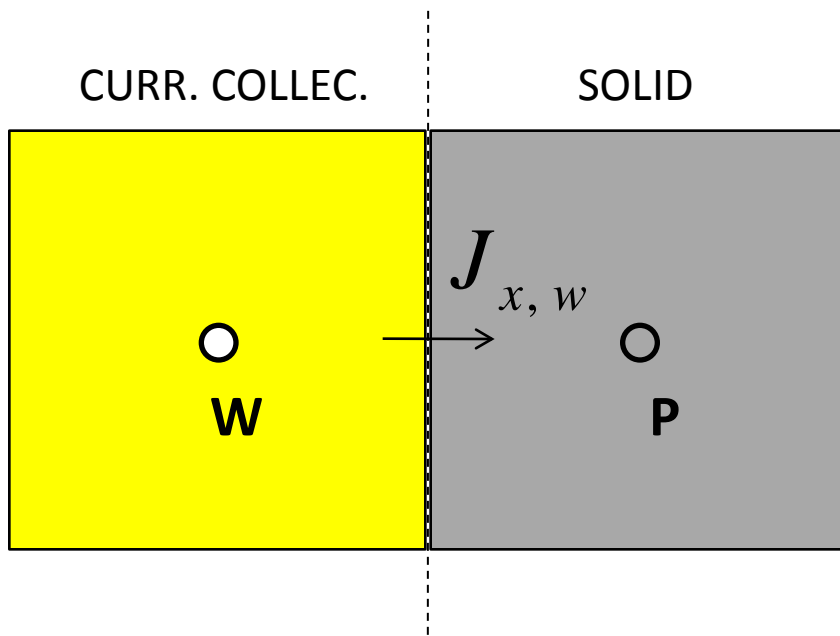


For a “normal” face, i.e. not an active surface or current-collector face

$$J_{x,w} = -K_w \left[\frac{\phi_P - \phi_W}{\Delta x} \right]$$

Face value of conductivity is calculated using “harmonic mean”

$$K_w = \frac{2K_W K_P}{K_W + K_P}$$

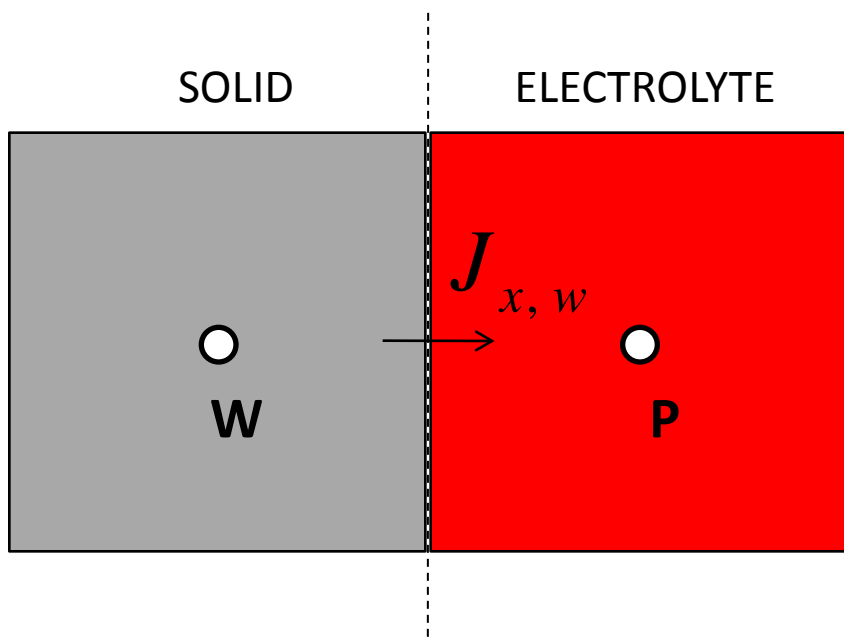


For a “current-collector” face, the current density is known and can be directly used.

$$J_{x, w} = 500 \text{ [A/m}^2\text{]}$$

For “zero gradient” boundaries, the current density can be set directly to zero.

Using the **FINITE VOLUME** approach has advantages compared to using a **FINITE DIFFERENCE** approach for these situations.



For a “active” face, the current density is determined from the Butler-Volmer equation

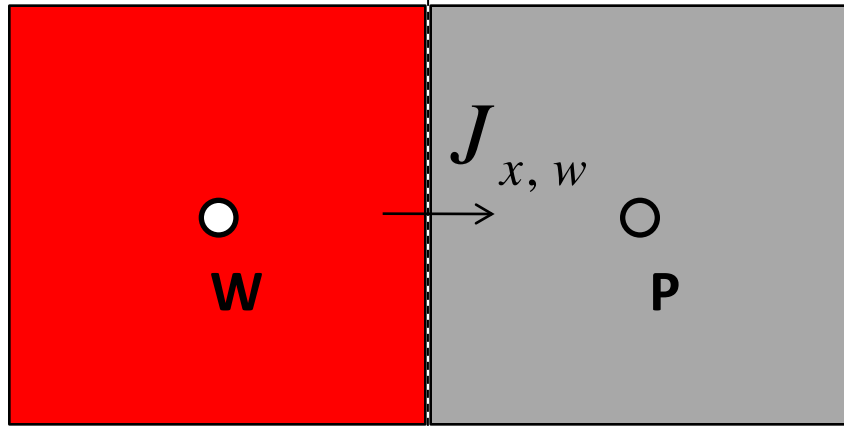
$$J_{x,w} = \frac{k (C_1)^{1/2} (C_2)^{1/2}}{2} \text{SINH} \left\{ \frac{\alpha F}{RT} \left[\phi_W - \phi_P - OCV - \frac{RT}{F} \ln \left(\frac{C_1}{C_2} \right) \right] \right\}$$

Potential in the
solid phase

Potential in the
liquid phase

NOTE: Species concentrations are defined only in the liquid phase, which is node point “P” in this case.

What happens when the CVs are reversed ?



$$J_{x,w} = \frac{-k (C_1)^{1/2} (C_2)^{1/2}}{2} \text{SINH} \left\{ \frac{\alpha F}{RT} \left[\phi_P - \phi_W - OCV - \frac{RT}{F} \ln \left(\frac{C_1}{C_2} \right) \right] \right\}$$

NOTE: Species concentrations are defined only in the liquid phase, which is node point "W" in this case.

Potential in the solid phase

Potential in the liquid phase

Similar expressions can be developed
for the NORTH (N) and SOUTH (S)
faces of the control volume

The final version of the discrete equation for the potential field can be re-arranged into the following format:

$$A_P \phi_P = A_E \phi_E + A_W \phi_W + A_N \phi_N + A_S \phi_S + S_\phi$$

$$A_P \phi_P = \sum_{nb} A_{nb} \phi_{nb} + S_\phi$$

$$A_E = \begin{cases} \frac{\kappa_e}{(\Delta x)^2} & \text{if the "east" face is "normal"} \\ 0 & \text{if current density is known on the "east" face} \end{cases}$$

$$A_W = \begin{cases} \frac{\kappa_w}{(\Delta x)^2} & \text{if the "west" face is "normal"} \\ 0 & \text{if current density is known on the "west" face} \end{cases}$$

Similar expressions can be derived for A_N and A_S

Finally,

$$A_P = \sum_{nb} A_{nb}$$



Note that some of these coefficients can be zero

The source term is calculated using

$$S_{\phi} = - \left\{ \left[\frac{J_{x,e} - J_{x,w}}{\Delta x} \right] + \left[\frac{J_{y,n} - J_{y,s}}{\Delta y} \right] \right\}$$

The current density components along X and Y at the CV faces are

- zero for “normal” faces
- based on the externally specified current density for current collector faces
- based on the Butler-Volmer equation for active faces

JACOBI iteration (a local solution approach)

$$\begin{array}{ccc} \text{new} & & \text{old} \\ \downarrow & & \downarrow \\ A_P \phi_P & = & \sum_{nb} A_{nb} \phi_{nb} + S_\phi \end{array}$$

Use the above equation to update the values of ϕ at each control volume in the solution domain.

Implementation is very straightforward and involves a point-by-point sweep through all the CVs.

Convergence rate is extremely poor because the system is highly non-linear. **The main cause of the non-linearity is the source term, which is a function of ϕ near the active surfaces.**

NEWTON iteration (global solution approach)

$$\Psi_P(\phi_P, \phi_{nb}) = 0 = A_P \phi_P - \sum_{nb} A_{nb} \phi_{nb} - S_\phi$$

| | | | |
|----|----|----|----|
| 1 | 2 | 3 | 4 |
| 5 | 6 | 7 | 8 |
| 9 | 10 | 11 | 12 |
| 13 | 14 | 15 | 16 |

$\phi_1 \phi_2 \phi_3 \dots \phi_{16}$ are the

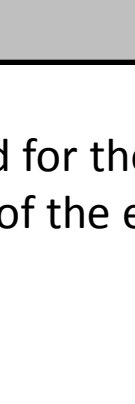
unknown potentials at ALL control volumes in the domain. They are all linked together via the above equation.

There are 16 (non-linear) equations connecting the 16 unknowns.

Governing Equations – Species Transport

| j | Species | z |
|-----|-----------|-----|
| 1 | V^{2+} | +2 |
| 2 | V^{3+} | +3 |
| 3 | VO_2^+ | +1 |
| 4 | VO^{2+} | +2 |

Migration term (motion of ions because of potential gradients in the electrolyte) is not currently considered.

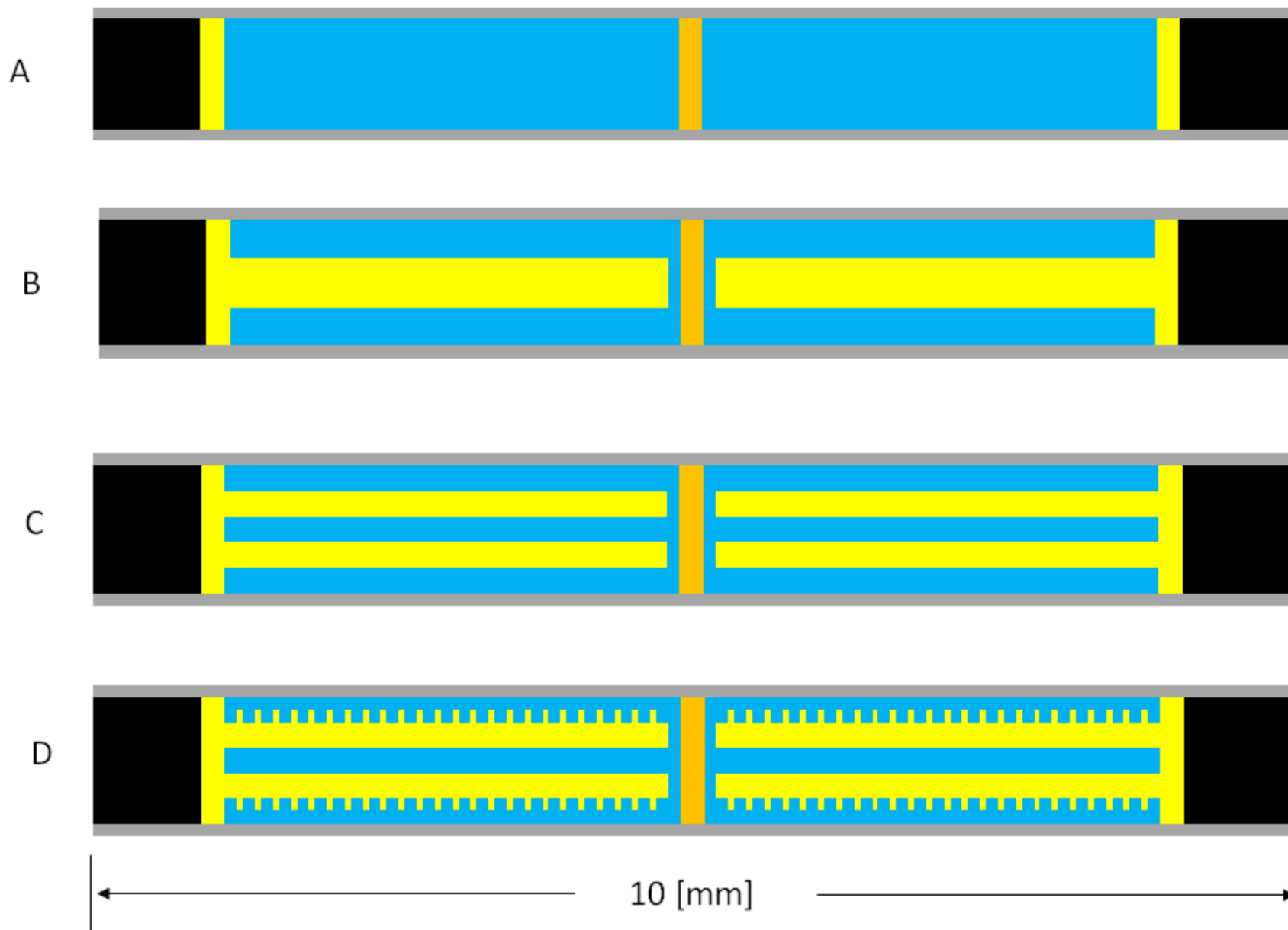

$$\frac{\partial C_j}{\partial t} + (\mathbf{u} \cdot \nabla) C_j = D_j \nabla^2 C_j + \nabla \cdot \left(\frac{z_j C_j D_j}{RT} \nabla \phi \right)$$

These equations are to be solved for the various ionic species present in the liquid electrolyte flowing through the pore-space of the electrodes (both anode and cathode side).

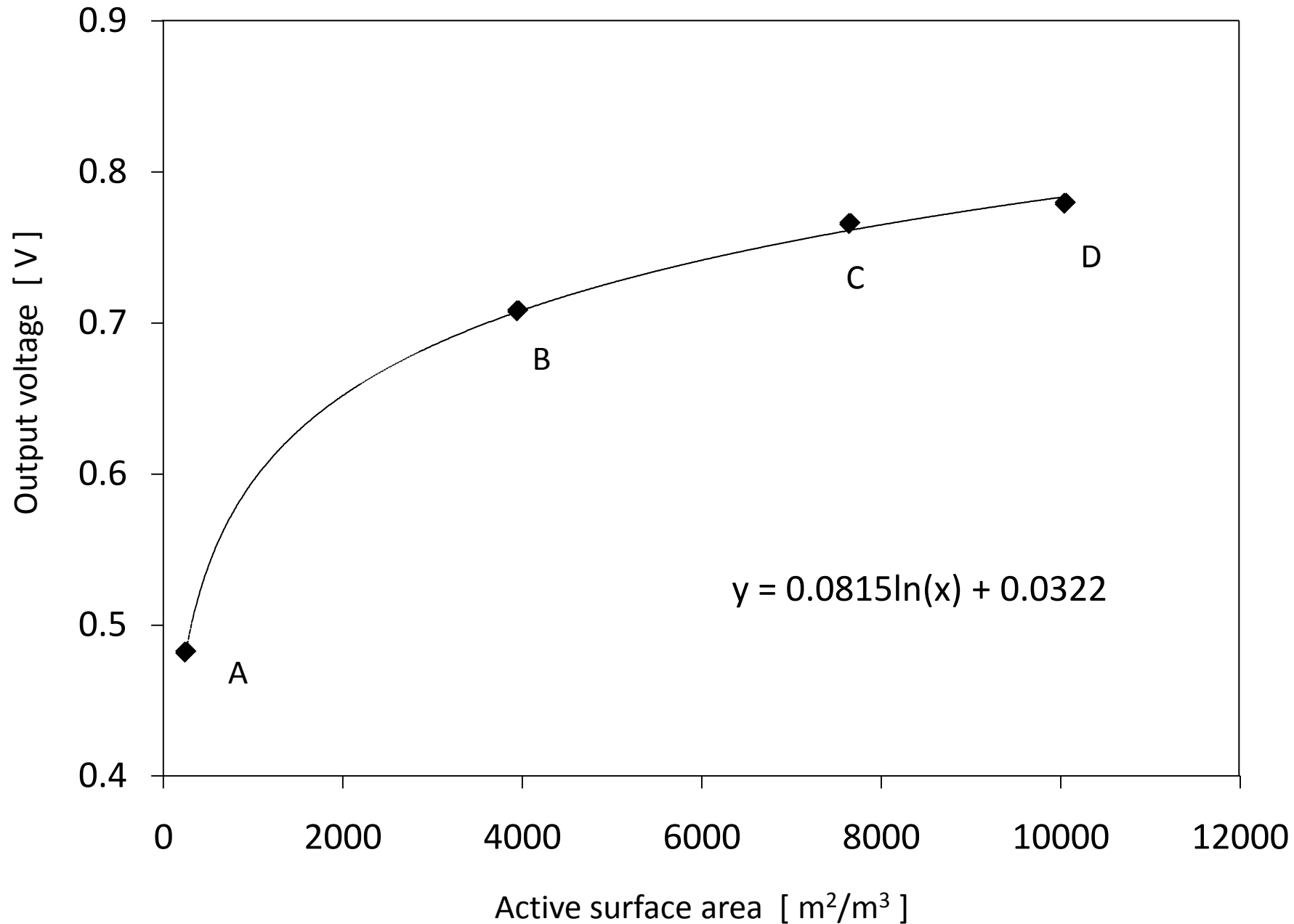
ASSUMPTIONS:

The presence of reacting species does not affect the flow because species concentration is very dilute (passive advection).

Investigating different cross-sectional geometries of the electrode to examine the effect of active surface area on the output voltage



Effect of Active Surface Area on Power Density



Electro-neutrality Condition for the Electrolyte

$$\sum_j z_j C_j = 0$$

If V^{2+} and V^{3+} are the only species considered on the anode side, it is hard to see how this condition can be satisfied in the present framework.....

Similar considerations hold for the species on the cathode side.

DO I NEED ADDITIONAL SPECIES IN MY MODEL?

Conclusions

1.

Inlet SOC (both anode and cathode) is fixed. This leads to a “steady-state” situation. In reality, the inlet SOC should reduce with time (during discharging) because the “fuel” in the external storage tanks keeps reducing with time.

2.

Species concentration change inside the flow channel is negligibly small and the SOC remains identical to that at the inlet (50%).

3.

The cell voltage increases in a logarithmic fashion with the active surface area. For a current density of 500 [A/m²], the estimated voltage for an active area of 50,000 [m²/m³] is 0.91 [V].

4.

The calculations are extremely slow. For a realistic aspect ratio, we need to run a 200 x 50 x 2000 grid. The current grid size is 200 x 12 x 10.

5.

The current grid resolution is 50 [micron]. If this is reduced to accommodate the XCT data, the required grid resolution will be 1[micron] – 5[micron]. This will increase the system size by several orders of magnitude.

Future Work

1.

Solve the potential equation using Newton's method instead of "point-by-point" Jacobi iteration.

2.

Add in the migration term in the species transport equation.

3.

Check if "electroneutrality" is relevant to the calculations. In other words, do we need to include more species ?

4.

Include the external storage tanks in the model. Essentially, this enables a calculation of how the inlet species concentration changes with time during charge / discharge.

5.

Use the actual XCT geometry.