# Module 7 and 8

Step 1:

$$4\pi R^2 D \left[\frac{\partial c}{\partial r}\right]_{r=R} = v(t)$$

$$y(t) = c(R, t)$$

$$R = 1, D = 1$$

Step 2:

Fick's Law

$$J = -D \frac{\partial c}{\partial x}$$

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}$$

Fick's Law for ideal spherical medium

$$\frac{\partial c}{\partial t} = \frac{D}{r^2} \frac{\partial}{\partial r}\left[r^2 \frac{\partial c}{\partial r}\right]$$

$$\partial t \qquad r^2\, \partial r \Big[ \qquad \partial r \Big]$$

$$sC(s,r) =$$

$$\frac{D}{r^2}\Big[2r\frac{\partial C(s,r)}{\partial r} + r^2\frac{\partial^2 C(s,r)}{\partial r^2}\Big]$$

$$sC(s,r) =$$

$$D\Big[\frac{2}{r}\frac{\partial C(s,r)}{\partial r} + \frac{\partial^2 C(s,r)}{\partial r^2}\Big]$$

2 Boundary Conditions:

$$\frac{\partial C}{\partial r}(s, r=0) = 0$$

$$\frac{\partial C}{\partial r}(s, r=R)$$

$$= U(t) = 4\pi R^2 D \left[\frac{\partial c}{\partial r}\right]_{r=R}$$

<u>or</u>

$$\frac{\partial c}{\partial r}(t, r=0) = 0$$

$$\frac{\partial c}{\partial r}(t, r=R) = U(t)$$
$$= 4\pi R^2 D \left[\frac{\partial c}{\partial r}\right]_{r=R}$$

Step 3: <u>PADE Approximation</u>

Joel C. Forman et al 2011 J. Electrochem. Soc. 158 A93-
Reduction of an Electrochemistry-Based Li-Ion Battery
Model via Quasi-
Linearization and Padé Approximation

Here, $\frac{\partial c(t,R)}{\partial r} = -m\,u(t)$

$$C(s,r) = \frac{\left(e^{\sqrt{s/D}(R-r)}\left(e^{2\sqrt{s/D}\,r} - 1\right)mR^2\right)}{1 + R\sqrt{\frac{s}{D}} + e^{2R\sqrt{s/D}}\left(R\sqrt{\frac{s}{D}} - 1\right)r}$$

$1 + \frac{R^2 S}{D} + $ [illegible] $\left(\frac{R^2 S}{D} - 1\right)\Big) r$

$\therefore$

## Second Order

$$\frac{Y(s)}{U(s)} = \frac{a_0 + a_1 s}{s(1 + b_2 s)}$$

$$= \frac{-\frac{3Dm}{R} - \frac{2mR}{7} s}{s + \frac{R^2}{35D} s^2}$$

$$U(s) = 4\pi r^2 D\, C(s,r)\, s$$

$$\boxed{\frac{Y(s)}{U(s)} = \frac{-\frac{3Dm}{R} - \frac{2mR}{7} s}{s + \frac{R^2}{35D} s^2}}$$

$$m = -1/(4\pi R^2 D)$$

$m = -1/4\pi(R^2)$

$a = \dfrac{-3Dm}{} \qquad b = -\dfrac{2mR}{7}$

$c = \dfrac{R^2}{35D}R$

$$= \frac{\frac{-3Dm}{R}}{s} + \frac{\frac{-2mR}{7} - \left(\frac{R^2}{35D}\right)\left(\frac{-3Dm}{R}\right)}{1 + \frac{R^2}{35D}s}$$

$$= \frac{\frac{-3Dm}{R}}{s} + \frac{\frac{-2mR}{7} + \frac{3Rm}{35}}{1 + \frac{R^2}{35D}s}$$

OR

Discretization, Finite Differences

$$\frac{\partial c}{\partial t} = \frac{D}{r^2}\frac{\partial}{\partial r}\left[r^2\frac{\partial c}{\partial r}\right]$$

$$= \frac{D}{r^2}\left[2r\frac{\partial c}{\partial r} + r^2\frac{\partial^2 c}{\partial r^2}\right]$$

$$= \frac{D}{r^2}\left[2r\frac{\partial C}{\partial r} + r^2\frac{\partial^2 C}{\partial r^2}\right)$$

$$= D\left[\frac{2}{r}\frac{\partial C}{\partial r} + \frac{\partial^2 C}{\partial r^2}\right]$$

$k=0 \quad r_k = 0$

$k=1 \quad r_k = R/3$

$k=2 \quad r_k = 2R/3$

$k=3 \quad r_k = R$

$C_{1,2,3,4} = C(r_{1,2,3,4}, t)$

$$\left.\frac{\partial C}{\partial r}\right|_{r=0} = 0$$

$C_0 = C_1$

$$\left.\frac{\partial C}{\partial r}\right|_{r=R} = 0$$

$$\frac{C_3 - C_2}{R/3} = 0$$

$$C_3 = C_2 + U\frac{R}{3}$$

@ $k=1$

$$\dot{C}_1 = D\left[\frac{2}{R/3}\,\frac{C_2 - C_0}{2R/3} + \frac{C_2 - 2C_1 + C_0}{(R/3)^2}\right] \Rightarrow C_0 = C_1$$

$$= D\left[\frac{2}{R/3}\,\frac{C_2 - C_1}{R/3} + \frac{C_2 - 2C_1 + C_1}{R^2/9}\right]$$

$$= \frac{D}{R^2}\left[27(C_2 - C_1)\right]$$

@ $k=2$

$$\dot{C}_2 = D\left[\frac{2}{2R/3}\,\frac{C_3 - C_1}{2R/3}\right.$$

$$+ \frac{C_3 - 2C_2 + C_1}{(R/3)^2} \Big] \quad C_3 = C_2 + \frac{UR}{3}$$

$$= D\left[ \frac{2C_2 + \frac{2UR}{3} - 2C_1}{4R^2/9} + \frac{C_2 + \frac{UR}{3} - 2C_2 + C_1}{R^2/9} \right]$$

$$= \frac{9D}{R^2}\left[-0.5C_2 + 0.5UR + 0.5C_1\right]$$

$$= \frac{9D}{2R^2}\left[C_1 - C_2 + UR\right]$$

$$\dot{C}_1 = \frac{27D}{R^2}\left[C_2 - C_1\right]$$

$$\dot{C}_2 = \frac{9D}{2R^2}\left[C_1 - C_2 + UR\right]$$

$$C_3 = C_2 + \frac{UR}{}$$

$$C_3 = C_2 + U\frac{R}{3}$$

Laplace

$$C_3(s) = C_2(s) + \underline{R}\,U(s)$$

$$= C_1(s)\left[\frac{R^2}{27D}s + 1\right]$$

$$+ \frac{R}{3}U(s)$$

$$\left[\frac{R^2}{27D}s + 1\right]C_1(s) = C_2(s)$$

$$\left[s\frac{2R^2}{9D} + 1\right]C_2(s) = C_1(s) + RU(s)$$

$$\left[\frac{2R^2}{9D}s + 1\right]\left[\frac{R^2}{27D}s + 1\right]C_1(s)$$

$$= C_1(s) + RU(s)$$

$$\left[\frac{2R^4}{243D^2}s^2 + \left(\frac{2R^2}{9D} + \frac{R^2}{27}\right)s + \cancel{1}\right]^*$$

$$\left.\frac{}{243D^2} \qquad \left(\frac{}{9D} \quad \frac{}{27D}\right) \quad \right]$$

$$C(s) = U(s)$$

$$C_1(s) = \frac{U(s)}{\left[\frac{2R^4}{243D^2}s^2 + \left(\frac{2R^2}{9D} + \frac{R^2}{27D}\right)s\right]}$$

$$C_3(s) = C_2(s) + \underline{R}\,U(s)$$

$$= C_1(s)\left[\frac{R^2}{27D}s + 1\right]$$

$$+ \frac{R}{3}U(s)$$

$$= U(s)\left[\frac{R}{3} + \frac{\frac{R^2}{27D}s + 1}{\frac{2R^4}{243D^2}s^2 + \left(\frac{2R^2}{9D} + \frac{R^2}{27D}\right)s}\right]$$

$$\frac{C_3(s)}{U(s)} = \left[\frac{R}{3} + \frac{\frac{R^2}{27D}s + 1}{\ldots}\right.$$

$$\left[ \frac{s}{\frac{2R^4}{243D^2}s^2 + \left(\frac{2R^2}{9D} + \frac{R^2}{27D}\right)s} \right]$$

Step 4:

$$\frac{Y(s)}{U(s)} = \frac{a+bs}{s(1+cs)}$$

$$\frac{a+bs}{s(1+cs)} = \frac{A}{s} + \frac{B}{1+cs}$$

$$a+bs = A(1+cs) + Bs$$

$s=0$

$A = a$

$s = -\frac{1}{c}$ $\quad -\frac{B}{c} = a - \frac{b}{c}$

$$B = -c\left(a - \frac{b}{c}\right) = b - ca$$

$$\frac{Y(s)}{U(s)} = \frac{a}{s} + \frac{b-ca}{1+cs}$$

$C_s(s) = \text{"Storage"} + \text{"RC"}$

$= Y_1(s) + Y_2(s)$

$$Y_1(s) = \frac{a}{s} U(s)$$

$$Y_2(s) = \frac{b-ca}{1+cs} U(s)$$

$$\dot{y}_1 = a u(t)$$

$$y_2 + c\dot{y}_2 = (b-ca) u(t)$$

$$\dot{y}_2 = \frac{(b-ca)}{c} u(t)$$

$$- \frac{1}{c} y_2$$

For 1 electrode

$$\boxed{\begin{aligned} \dot{y}_1 &= a u(t) \\ \dot{y}_2 &= \left(\frac{b-ca}{c}\right) u(t) - \frac{1}{c} y_2 \\ C &= \dot{y}_1 + \dot{y}_2 \end{aligned}}$$

$$\boxed{C = Y_1 + Y_2}$$

Advanced ☆

Let $\alpha = \underline{b-ca}$

Let $z_1 = y_1 c$

Let $z_2 = \frac{y_2}{\alpha_2}$

Intercalation Current Density → $u(t)$

Surface Concentration → $y(t)$

Reference Potential → $V(t)$

$$\dot{z}_1 = a\,u(t)$$

$$\dot{z}_2 = u(t) - \frac{1}{c} z_2$$

$$y = z_1 + \alpha z_2$$

$$V = U_{ref}(y) + R^* u(t)$$

$$= U_{ref}(z_1 + \alpha z_2) + R^* u(t)$$

For Anode + Cathode

$$\dot{z}_1 = Q_a u(t)$$

$$\dot{z}_2 = u - \frac{1}{C_a} z_2$$

$$c_{s,a} = z_1 + \alpha_a z_2$$

$$\dot{z}_3 = -Q_c u(t)$$

$$\dot{z}_4 = -u - \frac{1}{C_c} z_4$$

$$c_{s,c} = z_3 + \alpha_c z_4$$

However, eliminate redundancies

$$R_{tot} = R_c + R_a + R_{sol}$$

$$V(t) = E_{eq,c} - E_{eq,a}$$

$$\left[ -\eta_c - \eta_a - R_{tot}\, u(t) \right]$$ Discharge current $u(t)$

$$\left[ +\eta_c + \eta_a + R_{tot}\, u(t) \right]$$ Charge current $u(t)$

$$\dot{z}_1 = Q_a u(t)$$

$$\dot{z}_2 = u - \frac{1}{C_a} z_2$$

$$c_{s,a} = z_1 + \alpha_a z_2$$

$$\dot{z}_3 = -u - \frac{1}{C_c} z_3$$

$c_{s,c} = \alpha_c z_3 +$
$c_{s,c,initial} - \frac{\alpha_c}{\alpha_a}(z_1(t)$
$- z_1(0)))$

Assume, Overpotential
$\eta_c, \eta_a$, determined by
the Butler-Volmer
equation is negleted
$\therefore$ SPM

Intercalation Current
Density $\to u(t)$
Surface Concentration $\to y(t)$

$\dot{z}_1 = Q_a u(t)$

$\dot{z}_2 = u - \frac{1}{\phantom{x}} z_2$

$\dot{z}_3 = - u - \frac{\varphi_a}{c_c} z_3$

$y(t) = R_{tot} u(t)$
$+ E_{a,c}(\alpha_c z_3 + c_{s,c,initial}$

$+ F_{a,c}(\alpha_c z_3 + c_{0,c,\text{initial}}$

$- \frac{a_c}{a_a}(z_1(t) - z_1(0)))$

$- F_{a,a}(\alpha_a z_2 + z_1)$