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

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

$$\frac{\partial}{\partial t} \quad r^2 \frac{\partial}{\partial r}\left[\quad \frac{\partial}{\partial r} \right]$$

$$s(C(s,r)) =$$

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

$$s(C(s,r)) =$$

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

2 Boundary conditions:

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

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

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

Or

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

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

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

Step 3: PADE Approximation

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, $\frac{\partial c(t,R)}{\partial r} = -mU(t)$

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

$1 + \frac{R}{S} + \ldots \left(\frac{R}{S} - 1\right)r$

$\therefore$

Second Order

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

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

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

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

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

$$m = -1/\ln(R2)$$

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

$$c = \frac{R2}{35D}$$

$$= -\frac{3Dm}{R}\frac{1}{s} + \frac{-\frac{2mR}{7} - \left(\frac{R2}{35D}\right)\left(-\frac{3Dm}{R}\right)}{1 + \frac{R2}{35D}\frac{1}{s}}$$

$$= \frac{-\frac{3Dm}{R}\frac{1}{s} + \frac{-\frac{2mR}{7} + \frac{3Rm}{35}}{1 + \frac{R2}{35D}\frac{1}{s}}}{\frac{\partial R}{\partial t}}$$

Discretization, Finite Differences

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

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

$$= \frac{\pi}{r_2}\left[2r \frac{\partial c}{\partial r} + r^2 \frac{\partial^2 c}{\partial r^2} \right]$$

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

$k=0 \quad r_k = 0$

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

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

$k=3 \quad r_k = R$

$c_{1,2,3,4} = c(r_{1,2,3,4}, t)$

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

$c_0 = c_1$

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

$$\frac{c_3 - c_2}{R/3} = 0$$

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

@ $k = 1$

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

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

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

@ $k = 2$

$$C_2 = D\left[\frac{2}{2/R/3}\frac{C_3 - C_1}{2R/3}\right.$$

$$+\frac{C_3-2C_2+C_1}{(R/3)^2}\Bigg]_{C_3=C_2+\frac{vR}{3}}$$

$$=D\Bigg[\frac{2C_2+\frac{2vR}{3}-2C_1}{4R^2/9}$$

$$+\frac{C_2+\frac{vR}{3}-2C_2+C}{R^2/9}\Bigg]$$

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

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

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

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

$$C_3=C_2+\frac{vR}{3}$$

$$C_3 = C_2 + \frac{v_R}{3}$$

Laplace

$$C_3(s) = C_2(s) + \frac{R}{3} V(s)$$

$$= C_1(s)\left[\frac{R^2}{27D}s + \frac{R}{3}\right] + \frac{R}{3} V(s)$$

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

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

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

$$= C_1(s) + RV(s)$$

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

$$\left[\frac{\ldots}{2430D^2} \quad \left(\frac{\ldots}{9D} \quad \frac{\ldots}{27D}\right)\right]$$

$$C(s) = V(s)$$

$$C_1(s) = \frac{V(s)}{\left[\frac{2R^4}{2430D^2}s^2 + \left(\frac{2R^2}{9D} + \frac{R^2}{27D}\right)s\right]}$$

$$C_3(s) = C_2(s) + \frac{R}{3}V(s)$$

$$= C_1(s)\left[\frac{R^2}{27D}s + 1\right] + \frac{R}{3}V(s)$$

$$= V(s)\left[\frac{R}{3} + \frac{\frac{R^2}{27D}s + 1}{\frac{2R^4}{2430D^2}s^2 + \left(\frac{2R^2}{9D} + \frac{R^2}{27D}\right)s}\right]$$

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

$$\frac{2R_4}{240^2}s^2 + \frac{2R_2 + R_2}{(95\ 270)}s$$

Step 4:

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

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

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

$s=0$

$A = a$

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

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

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

$G(s) =$ "storage" + "RC"

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

$X_1(s) = \frac{a}{s} U(s)$

$X_2(s) = \frac{b-ca}{1+cs} U(s)$

$\dot{Y}_1 = aU(t)$

$\dot{Y}_2 + c\dot{Y}_2 = (b-ca)U(t)$

$\dot{Y}_2 = \frac{(b-ca)}{c} U(t)$

$- \frac{1}{c} Y_2$

For 1 electrode

$\dot{Y}_1 = aU(t)$

$\dot{Y}_2 = \left(\frac{b-ca}{c}\right) U(t) - \frac{1}{c} Y_2$

$C = Y_1 + Y_2$

$$C = Y_1 + Y_2$$

Advanced ☆

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

Let $z_1 = Y_1 C$

Let $z_2 = \frac{Y_2}{\alpha_2}$

Intercalation Current Density $\Rightarrow U(t)$

Surface Concentration $\Rightarrow Y(t)$

Reference Potential $\Rightarrow V(t)$

$\dot{z}_1 = \alpha U(t)$

$\dot{z}_2 = U(t) - \frac{1}{C} z_2$

$Y = z_1 + \alpha z_2$

$V = U_{ref}(Y) + R^{\alpha} U(t)$

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

For Anode + Cathodic

$\dot{z}_1 = \alpha_a U(t)$

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

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

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

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

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

However, eliminate redundancies

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

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

$$\left[-\eta_c - \eta_a - R_{tot} U(t) \right] \quad \text{Discharge Current } U(t)$$

$$\left[+\eta_c + \eta_a + R_{tot} U(t) \right] \quad \text{Charge Current } U(t)$$

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

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

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

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

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

Assume, Overpotential η_c η_a determined by the Butler-Volmer equation is neglected

∴ SPM

Intercalation Current Density → $U(t)$

Surface Concentration → $y(t)$

$\dot{z}_1 = \alpha_a U(t)$

$\dot{z}_2 = U - 1 \; z_2$

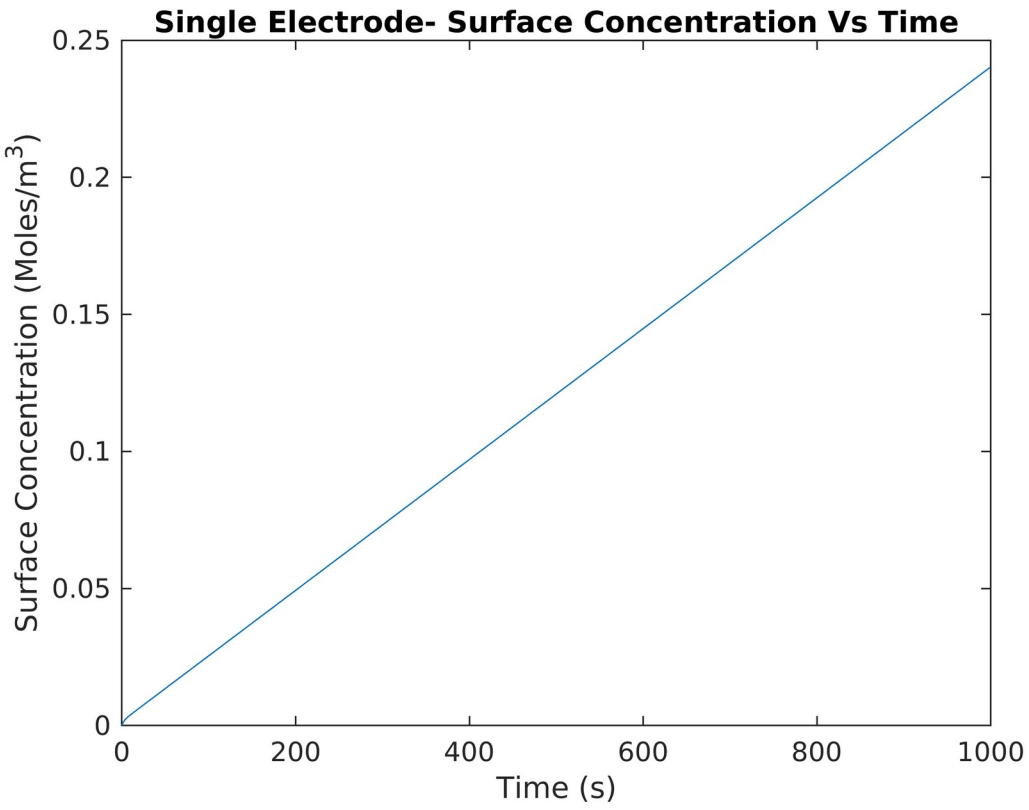
$\dot{z}_3 = -U - \frac{1}{\alpha_c} z_3$

$y(t) = R_{tot} U(t)$

$+ E_{a,c}(\alpha_c z_3 + c_{s,c,initial}$

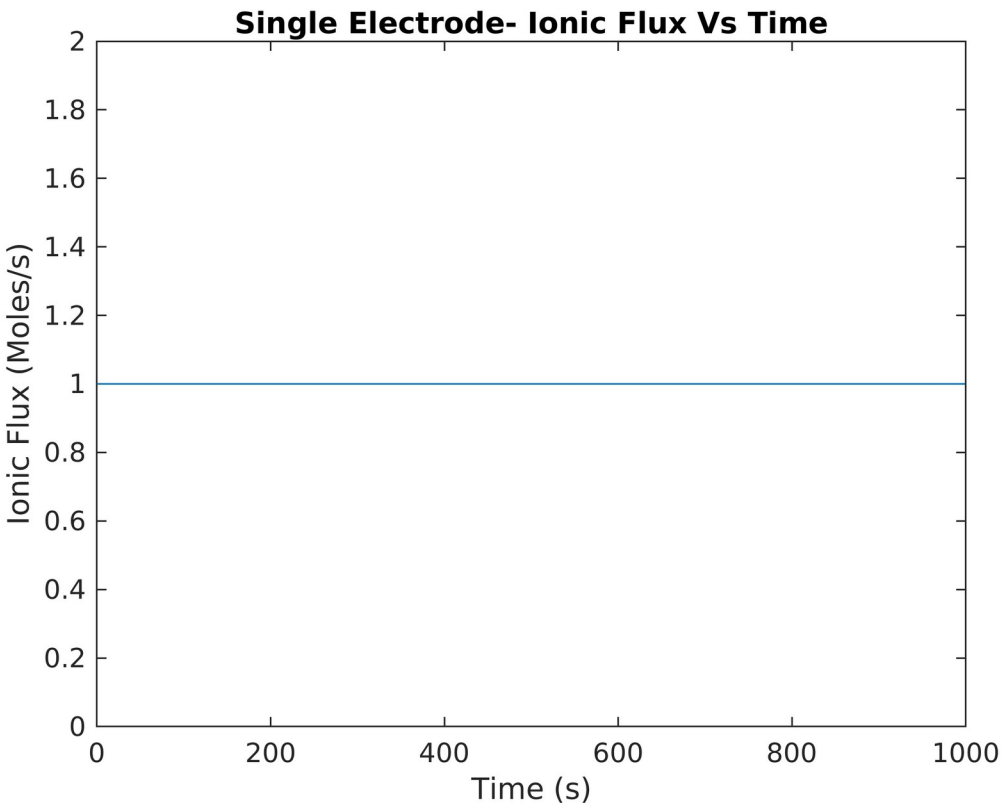
$$+ E_{a,c}(\alpha_c z_3 + \text{Loic}_{\text{initial}}$$
$$- \frac{a_c}{a_a}(z_1(t) - z_1(0))$$
$$- E_{a,a}(\alpha_a z_2 + z_1)$$

```
%Step 5 and 6

%Radius
R=10;
%Diffusivity
D=1;
nSteps=1000;
dt=1;

t=(0:dt:nSteps-1)';
u=ones(nSteps,1);
u_sin=sin(t/(10*pi));

%Initial Conditions
y1_0 = 0;
y2_0 =0;
sigmaY=0;

%Constant Input
y=lithium_model(R, D, u, y1_0, y2_0, dt, sigmaY);
plot(t, y)
title("Single Electrode- Surface Concentration Vs Time")
xlabel("Time (s)")
ylabel("Surface Concentration (Moles/m^3)")
```

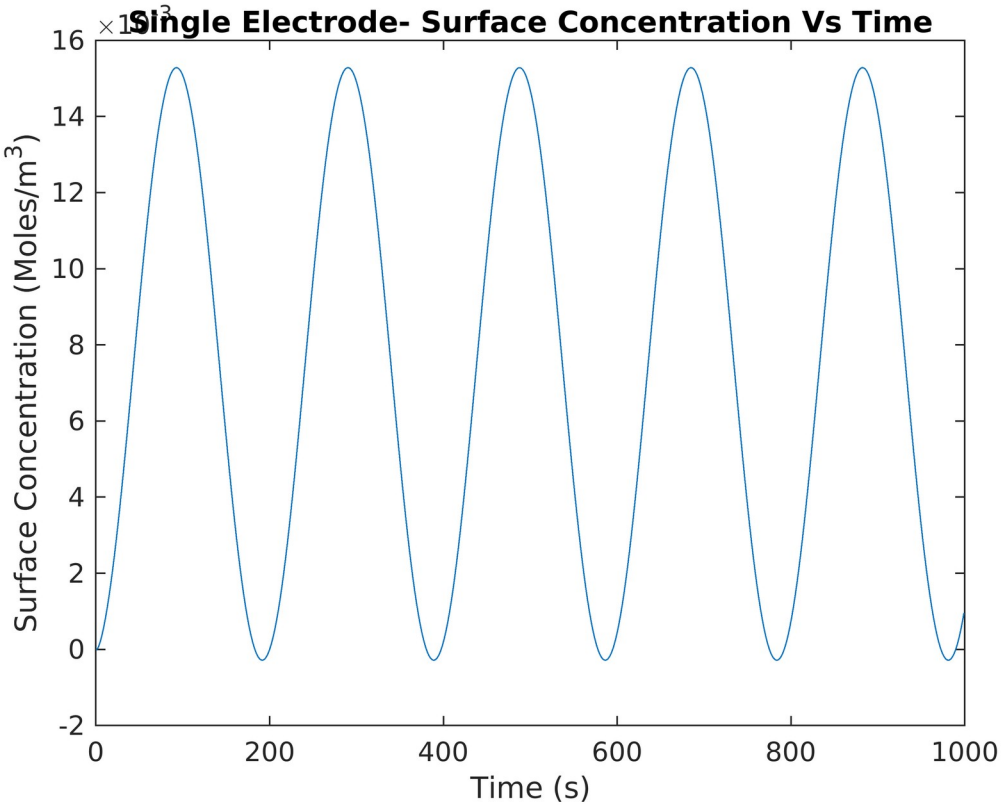



```
plot(t,u)
title("Single Electrode- Ionic Flux Vs Time")
```

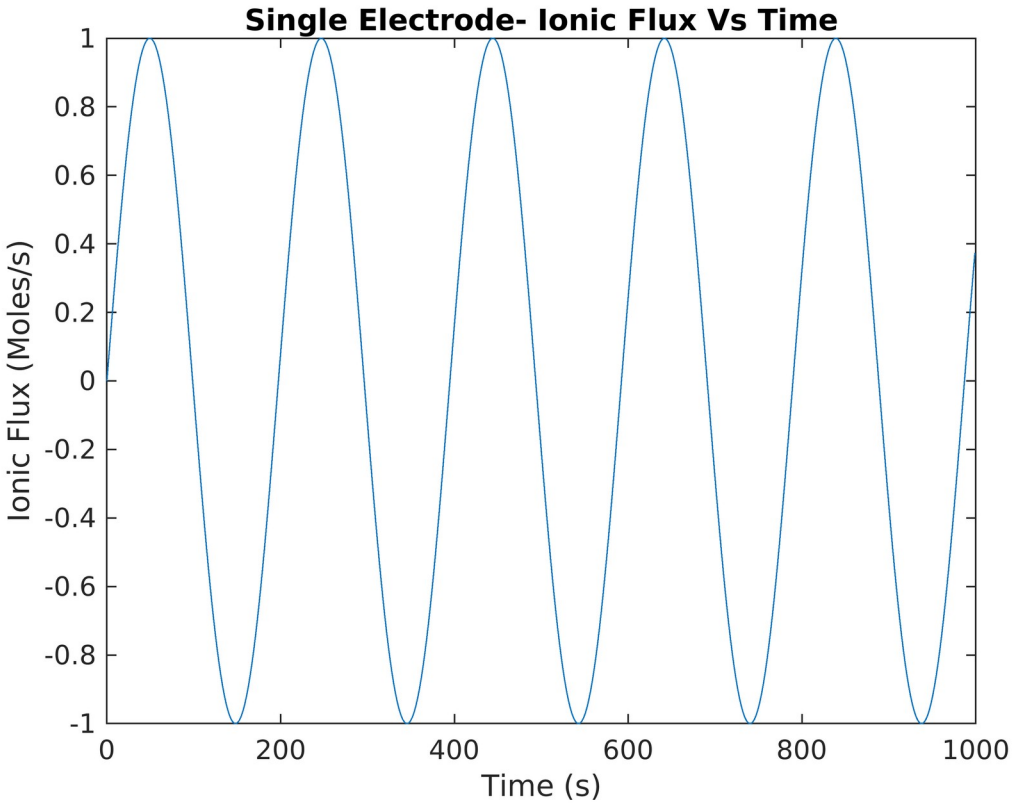
```
xlabel("Time (s)")
ylabel("Ionic Flux (Moles/s)")
```




```
%Sinusoidal Input
y=lithium_model(R, D, u_sin, y1_0, y2_0, dt, sigmaY);
plot(t, y)
title("Single Electrode- Surface Concentration Vs Time")
xlabel("Time (s)")
ylabel("Surface Concentration (Moles/m^3)")
```



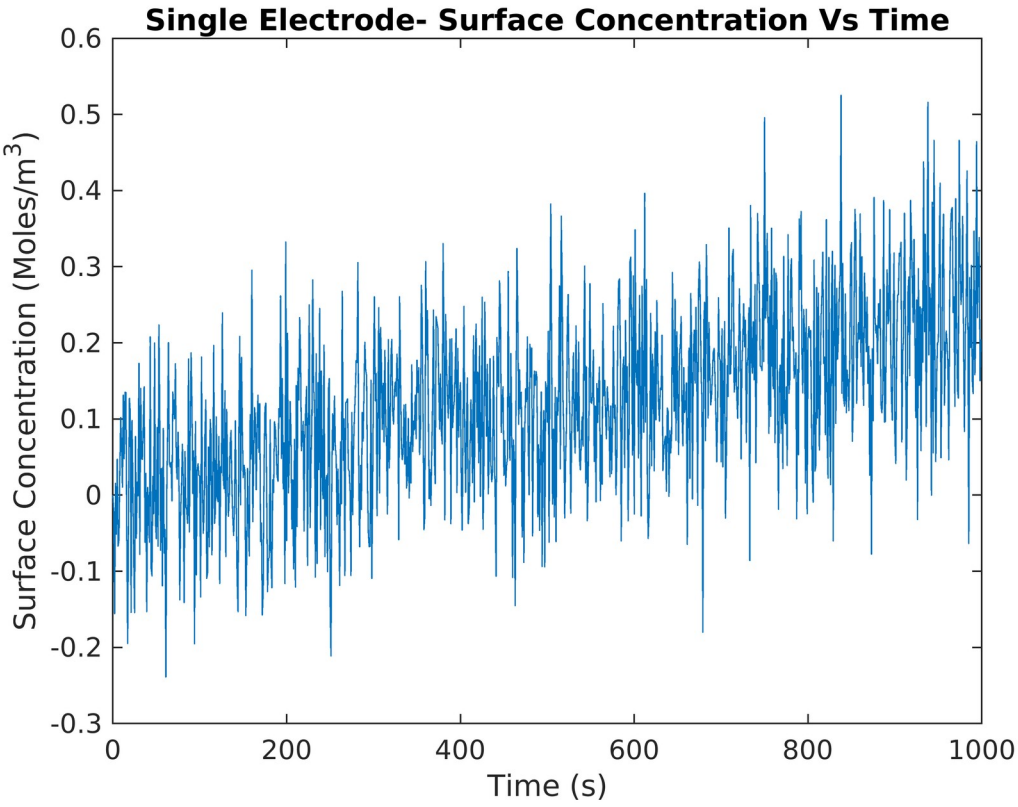

```
plot(t,u_sin)
title("Single Electrode- Ionic Flux Vs Time")
xlabel("Time (s)")
ylabel("Ionic Flux (Moles/s)")
```



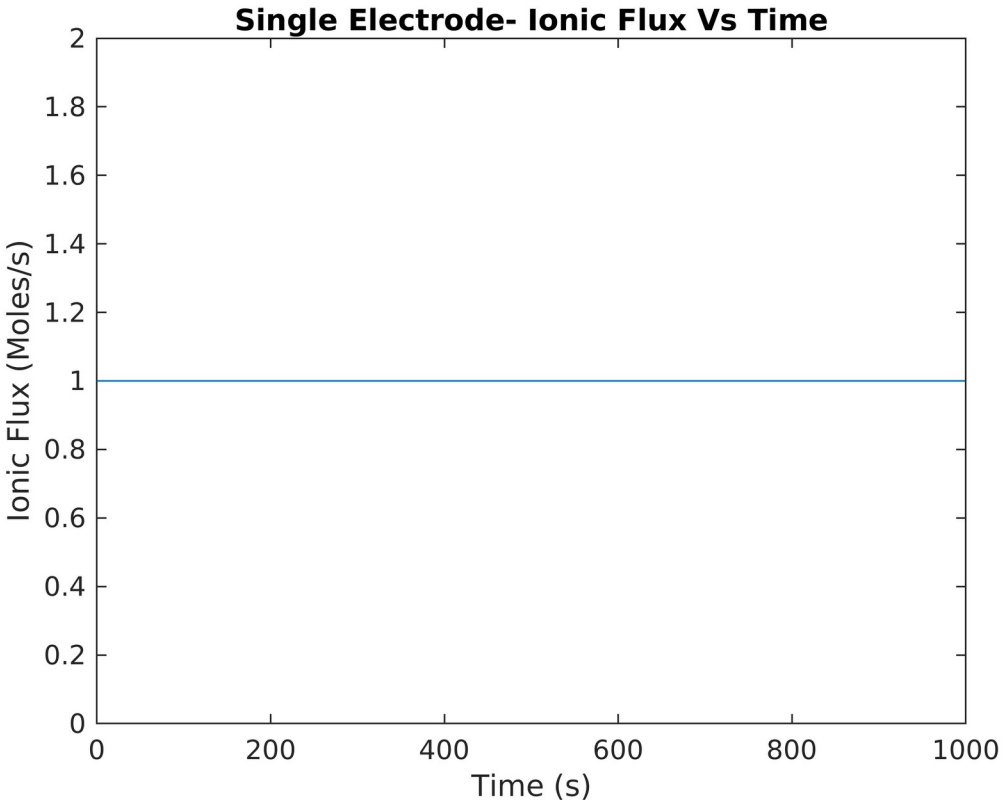

```
%Step 7:
```

As you insert charge into the battery, and electrons leave the anode, Lithium ions will convert to the ionic state an therefore increase the concentration of anode

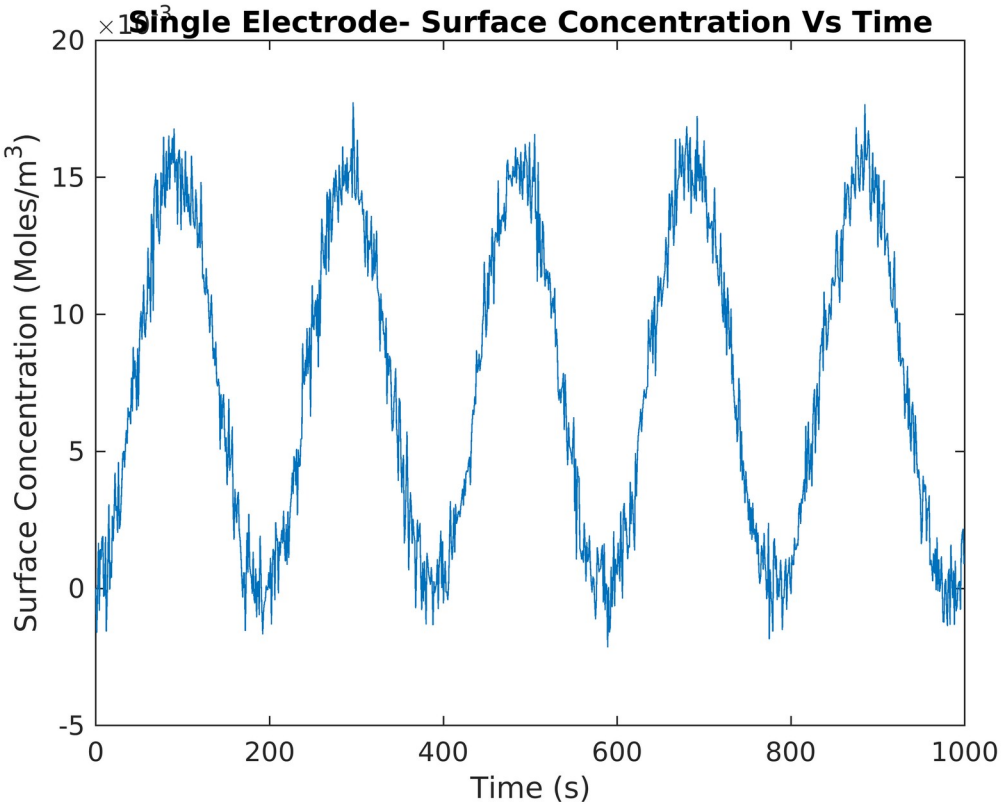
```
%Step 8:

%Independent, Identically Distributed, Zero-mean, Gaussian Noise

%Constant Input
sigmaY = 0.1;
y_noise = lithium_model(R, D, u, y1_0, y2_0, dt, sigmaY);
plot(t,y_noise)
title("Single Electrode- Surface Concentration Vs Time")
xlabel("Time (s)")
ylabel("Surface Concentration (Moles/m^3)")
```



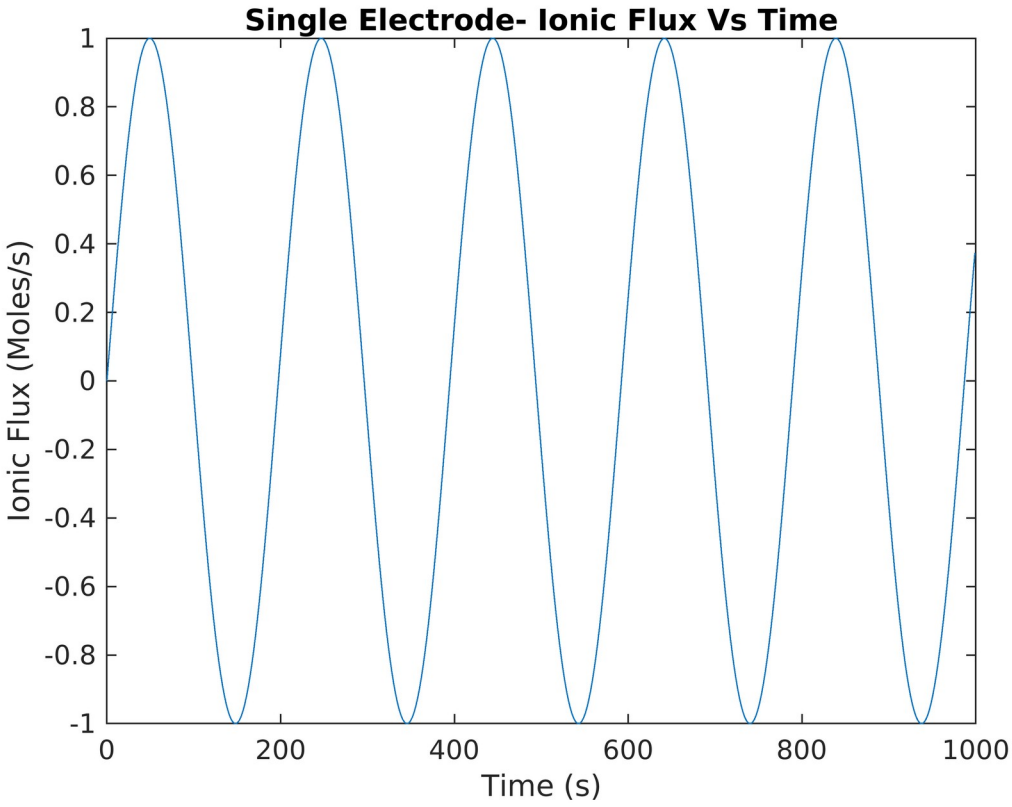

```
plot(t,u)
title("Single Electrode- Ionic Flux Vs Time")
xlabel("Time (s)")
ylabel("Ionic Flux (Moles/s)")
```




```
%Sinusoidal Input
sigmaY = 0.001;
y_noise = lithium_model(R, D, u_sin, y1_0, y2_0, dt, sigmaY);
plot(t,y_noise)
title("Single Electrode- Surface Concentration Vs Time")
xlabel("Time (s)")
ylabel("Surface Concentration (Moles/m^3)")
```




```
plot(t,u_sin)
title("Single Electrode- Ionic Flux Vs Time")
xlabel("Time (s)")
ylabel("Ionic Flux (Moles/s)")
```




```
%Step 9:
```

The fminsearch is able to converge to a resonable value of R reliably, but D is unable to converge to the correct value.

```
clear all

Rtrue = 10;
Dtrue = 1;
N = 1000;
deltaT= 1;
sigmaY = 0.0005;
u = ones(N,1);
y1_0 = 0;
y2_0 = 0;

yhat = lithium_model(Rtrue, Dtrue, u, y1_0, y2_0, deltaT, sigmaY);

Rguess = 30;
Dguess = 8;
thetaGuess(1) = Rguess;
thetaGuess(2) = Dguess;

options = optimset('MaxFunEvals',100000,'TolX',1E-6,'TolFun',1E-6);
optimFunction = @(theta)(LSP(theta, Rtrue, Dtrue, u, N, deltaT, yhat, y1_0, y2_0, sigma
```

```
varEstimation=fminsearch(optimFunction,thetaGuess,options)
```

```
Exiting: Maximum number of iterations has been exceeded
         - increase MaxIter option.
         Current function value: 0.000561
varEstimation = 1×2
    9.9730    4.5852
```

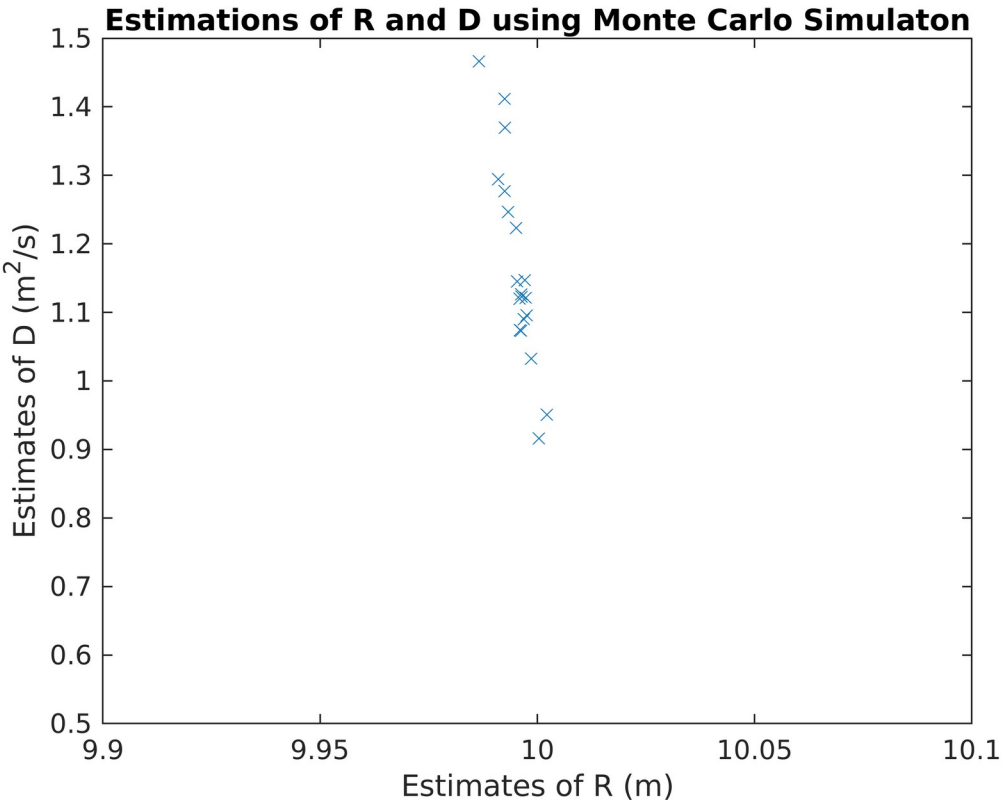
The fminsearch is able to converge to a resonable value of R reliably, but D is unable to converge to the correct value. My parameter esimates appear to be biased as sigmaY is small I am unsatisfied with the estimated accuracy because D does not conververge to the correct value

```
%Step 10:

nMonteCarlo= 500;

parfor i=1:nMonteCarlo
    optimFunction = @(theta)(LSP(theta, Rtrue, Dtrue, u, N, deltaT, yhat, y1_0, y2_0, s
    bestTheta=fminsearch(optimFunction,thetaGuess,options);
    RMonteCarlo(i) = bestTheta(1);
    DMonteCarlo(i) = bestTheta(2);
end
```

```
Exiting: Maximum number of iterations has been exceeded
         - increase MaxIter option.
         Current function value: 8.170867

Exiting: Maximum number of iterations has been exceeded
         - increase MaxIter option.
         Current function value: 3.974066

Exiting: Maximum number of iterations has been exceeded
         - increase MaxIter option.
         Current function value: 0.000584

Exiting: Maximum number of iterations has been exceeded
         - increase MaxIter option.
         Current function value: 6.846169

Exiting: Maximum number of iterations has been exceeded
         - increase MaxIter option.
         Current function value: 0.000521

Exiting: Maximum number of iterations has been exceeded
         - increase MaxIter option.
         Current function value: 0.000572

Exiting: Maximum number of iterations has been exceeded
         - increase MaxIter option.
```

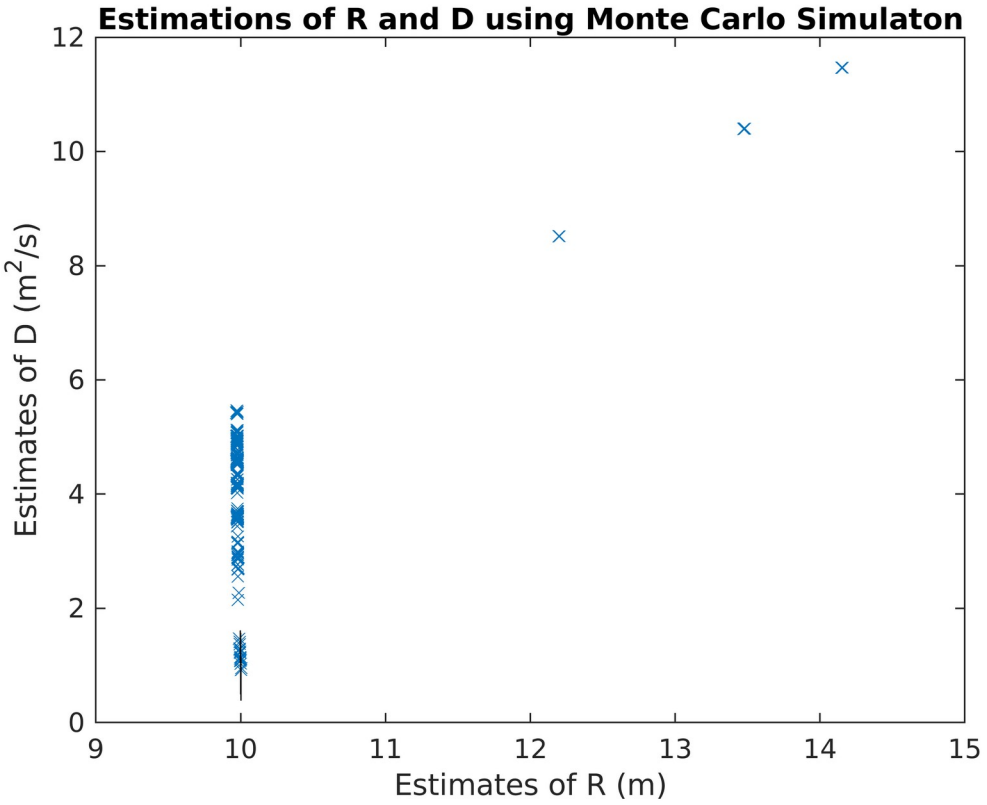
```
Exiting: Maximum number of iterations has been exceeded
         - increase MaxIter option.
         Current function value: 6.841349


Exiting: Maximum number of iterations has been exceeded
         - increase MaxIter option.
         Current function value: 6.842117


Exiting: Maximum number of iterations has been exceeded
         - increase MaxIter option.
         Current function value: 0.000578


Exiting: Maximum number of iterations has been exceeded
         - increase MaxIter option.
         Current function value: 0.000240


Exiting: Maximum number of iterations has been exceeded
         - increase MaxIter option.
         Current function value: 0.000568


Exiting: Maximum number of iterations has been exceeded
         - increase MaxIter option.
         C...
```

```
plot(RMonteCarlo, DMonteCarlo, 'x')
title("Estimations of R and D using Monte Carlo Simulaton")
ylabel('Estimates of D (m^2/s)')
xlabel('Estimates of R (m)')
deltaD=.5;
deltaR=.1;
ylim([Dtrue-deltaD,Dtrue+deltaD]);
xlim([Rtrue-deltaR,Rtrue+deltaR]);
hold off
```




```
plot(RMonteCarlo, DMonteCarlo, 'x')
title("Estimations of R and D using Monte Carlo Simulaton")
xlabel('Estimates of R (m)')
ylabel('Estimates of D (m^2/s)')
hold on
yNominal = lithium_model(Rtrue, Dtrue ,u, y1_0, y2_0, deltaT, 0);
epsilon = 1e-3;

y1 = lithium_model(Rtrue*(1+epsilon), Dtrue, u, y1_0, y2_0, deltaT, 0);
y2 = lithium_model(Rtrue, Dtrue*(1+epsilon), u, y1_0, y2_0, deltaT, 0);

s1 = (y1-yNominal)/(Rtrue*epsilon);
s2 = (y2-yNominal)/(Rtrue*epsilon);

S= zeros(length(s1), 2);
S(:,1) = s1;
S(:,2) = s2;

F = (1/(sigmaY^2))*(S')*S;
CRLB = inv(F);
[V, D] = eig(CRLB);
lambda1 = D(1,1);
lambda2 = D(2,2);
v1 = V(:,1);
v2 = V(:,2);

xprime = linspace(-sqrt(lambda1),sqrt(lambda1));
```

```
yprime = sqrt((1-(xprime.^2)/lambda1)*lambda2);

xypoints = [Rtrue;Dtrue]+v1*xprime+v2*yprime;
xypointsRef = [Rtrue;Dtrue]+v1*xprime-v2*yprime;
xy2points = [Rtrue;Dtrue]+2*v1*xprime+2*v2*yprime;
xy2pointsRef = [Rtrue;Dtrue]+2*v1*xprime-2*v2*yprime;
xy3points = [Rtrue;Dtrue]+3*v1*xprime+3*v2*yprime;
xy3pointsRef = [Rtrue;Dtrue]+3*v1*xprime-3*v2*yprime;

hold on

plot(xypoints(1,:), xypoints(2,:), 'k')
plot(xypointsRef(1,:), xypointsRef(2,:), 'k')
plot(xy2points(1,:), xy2points(2,:), 'k')
plot(xy2pointsRef(1,:), xy2pointsRef(2,:), 'k')
plot(xy3points(1,:), xy3points(2,:), 'k')
plot(xy3pointsRef(1,:), xy3pointsRef(2,:), 'k')
```



I am not satisfied with the results of the fisher information anylisis, as can be seen above, there is a portion of the estimations of R and D that converge to the correct value, and a portion that don't converge, then another portion that converge to arroneous values. the ellipisies that are produced are unable to account for the outliers and the two distinct clusters of points.

```
function y = lithium_model(R, D, u, y1_0, y2_0, dt, sigmaY)
%Pre-Allocation
```

```
nSteps = length(u);
y1=zeros(nSteps,1);
y2=zeros(nSteps,1);
y=zeros(nSteps,1);

%Initial Conditions
y1(1)=y1_0;
y2(1)=y2_0;

%PADE Second Order Approximation
%Transfer Function Coefficients

m=-1/(4*pi*R^2*D);
a=(-3*D*m)/R;
b=-(2*m*R)/7;
c=R^2/(35*D);

%Foward Euler
for i=2:nSteps
    y1(i)=y1(i-1)+a*u(i-1)*dt;
    y2(i)=y2(i-1)+((b-c*a)/c)*u(i-1)*dt-(1/c)*y2(i-1)*dt;
    y(i)=(y1(i)+y2(i))+sigmaY*randn(1);
end
return
end

function error = LSP(theta, Rexact, Dexact, u, nSteps, dt, yhat, y1_0, y2_0, sigmaY)

nSteps = 1000;
R = theta(1);
D = theta(2);

yhat = lithium_model(Rexact, Dexact, u, y1_0, y2_0, dt, sigmaY);
y = lithium_model(R, D, u, y1_0, y2_0, dt, 0);

error = 0;

for i=1:nSteps
    error = error + (yhat(i)-y(i))^2;
end

end
```