Electrochemical Impedance Spectroscopy
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Lecture - 43
Two Step Reaction

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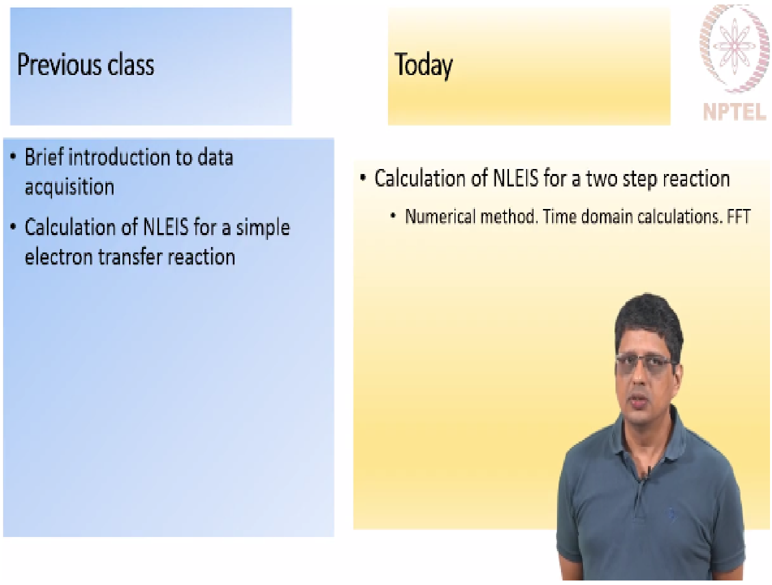

Previous class

- Brief introduction to data acquisition
- Calculation of NLEIS for a simple electron transfer reaction

Today

- Calculation of NLEIS for a two step reaction
  - Numerical method. Time domain calculations. FFT

So earlier we saw that you can handle a simple electron transfer reaction, we can use Fourier series expansion and get the response at fundamental and at higher harmonics. You can also use Taylor series expansion, rearrange it and get an approximation for the Fourier series. You can also use numerical method all of them should give you the same result as long as we use enough number of terms, as long as we have enough accuracy in the numerical calculations.

Now I want to show you how to calculate the NLEIS response for a two-step reaction with an adsorbed intermediate. I am going to illustrate with the numerical method.

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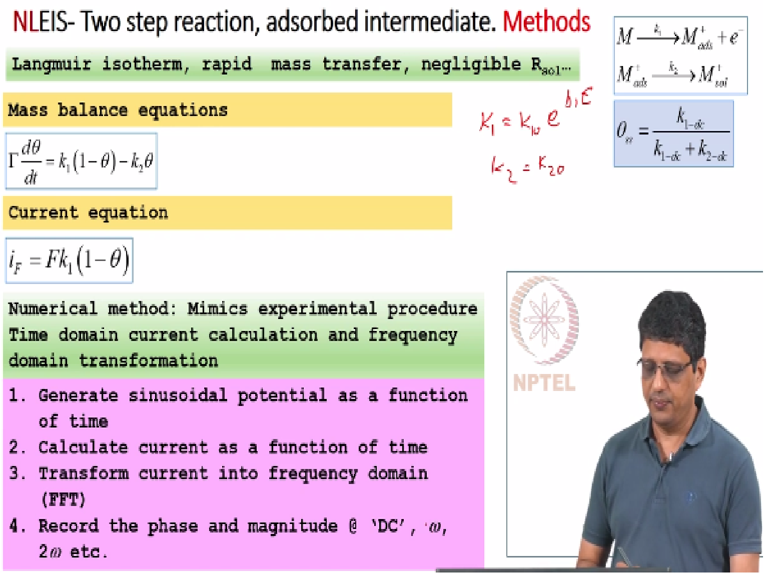

NLEIS- Two step reaction, adsorbed intermediate. Methods

Langmuir isotherm, rapid mass transfer, negligible R_{sol}...

$$M \xrightarrow{k_1} M^{+}_{ads} + e^{-}$$

$$M^{+}_{ads} \xrightarrow{k_2} M^{+}_{sol}$$

Mass balance equations

$$\Gamma \frac{d\theta}{dt} = k_1(1-\theta) - k_2\theta$$

$$K_1 = K_{10} e^{b_1 E}$$

$$K_2 = K_{20}$$

$$\theta_{ss} = \frac{k_{1-dc}}{k_{1-dc} + k_{2-dc}}$$

Current equation

$$i_F = Fk_1(1-\theta)$$

Numerical method: Mimics experimental procedure
Time domain current calculation and frequency domain transformation

1. Generate sinusoidal potential as a function of time
2. Calculate current as a function of time
3. Transform current into frequency domain (FFT)
4. Record the phase and magnitude @ 'DC', ω, 2ω etc.

So we are going to take a reaction where metal is going to dissolve into metal plus solution, but it goes for an intermediate stage we have seen this example before, metal goes to metal plus adsorb and then it goes into solution. So the first reaction rate constant is given by K1, second constant is given by K2. Here also we are assuming that the mass transfer is rapid, we are assuming that the solution resistance is negligible.

So we have written the mass balance equation for this. First step forms theta, the second step consumes theta. So we will rate K1 1 - theta for the rate of formation, K2 theta for the rate of consumption. So gamma D theta by DT is given by K1 1 - theta - K2 theta and a steady state condition we will set it to 0 and we will call the theta as theta SS and the first reaction is electrochemical reaction.

Second reaction there is no charge transfer so it is just a chemical reaction. So the current, Faraday current can be written as Faraday constant multiplied by the rate of the first reaction and the rate of the first reaction is K1 1 – theta. Now if I calculate the steady-state theta value I can set it to 0, rearrange it, K1 value will be K1 at a particular DC potential and K2 of course is independent of potential.

K1 we will write it as K1 0 exponential of b1 e. So DC potential of eDC it is going to be K1 DC. K2 is just constant we can write it as K2 0, but it is basically a constant. Now in the numerical method we are going to mimic the experimental method that means we apply a potential, we measure the current or calculate the current and then subject it to either Fourier transform or say sensitive detection, we are going to go with Fourier transform.

So we measure the current or we record the current in time domain and then convert that into frequency domain. So here step by step, first step is to generate sinusoidal potential as a function of time, it is pretty straightforward. Second, calculate the current as a function of time and that is where we need to actually use these equations.

Once you calculate the current as a function of time at regular time intervals it is pretty straightforward to subjected to Fourier transform, get the Fourier series expansion and calculate the impedance or calculate the i at any frequency. So we will record the phase and magnitude, of course we record the DC, it has 0 phase, we record the phase and magnitude at omega, 2 omega and so on.

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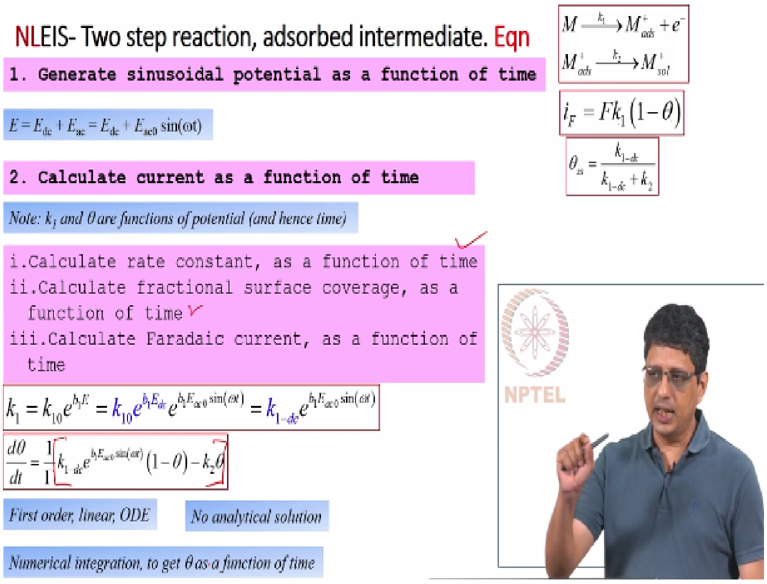

NLEIS- Two step reaction, adsorbed intermediate. Eqn

$M \xrightarrow{k_1} M^+_{ads} + e^-$

$M^+_{ads} \xrightarrow{k_2} M^+_{sol}$

$i_F = Fk_1(1-\theta)$

$\theta_{ss} = \frac{k_{1-dc}}{k_{1-dc} + k_2}$

1. Generate sinusoidal potential as a function of time

$E = E_{dc} + E_{ac} = E_{dc} + E_{ac0}\sin(\omega t)$

2. Calculate current as a function of time

Note: k_1 and θ are functions of potential (and hence time)

i.Calculate rate constant, as a function of time

ii.Calculate fractional surface coverage, as a function of time

iii.Calculate Faradaic current, as a function of time

$k_1 = k_{10}e^{b_1E} = k_{10}e^{b_1E_{dc}}e^{b_1E_{ac0}\sin(\omega t)} = k_{1-dc}e^{b_1E_{ac0}\sin(\omega t)}$

$\frac{d\theta}{dt} = \frac{1}{\Gamma}\left[k_{1-dc}e^{b_1E_{ac0}\sin(\omega t)}(1-\theta) - k_2\theta\right]$

First order, linear, ODE

No analytical solution

Numerical integration, to get θ as a function of time

So the first part is generate the sinusoidal potential E is Edc + Eac0 sin omega t. To calculate the current as a function of time, we first need to calculate theta as a function of time. When we apply sinusoidal potential at some frequency the surface coverage, fractional surface coverage will also change or it will oscillate. So we need to calculate that and in order to calculate that we need to use the mass balance equation.

So we split it as calculate the rate constant in order to calculate the current as a function of time I need to calculate the rate constant as a function of time, I need to calculate theta as a function of time. This is again pretty straightforward; to do this I need to integrate the mass balance equation. Once I have K as a function of time and theta as a function of time it is pretty straightforward to calculate the faraday current as a function of time.

Now K1 as a function of time is easy to write. K1 0 e power b1 E dc e power b1 Eac. The mass balance equation we can rearrange it and write it as with brackets d theta/dt as 1/gamma K1 1- theta – K2 theta, K1 of course we have to expand it and write it as K1 dc e power b1 Eac. This is a first order linear ordinary differential equation. As far as I know there is no analytical solution for this.

For a given initial condition, it does have a unique solution it is guaranteed to have a solution and it is unique, but I am not aware of an analytical solution for this. We can do numerical integration any way and get theta as a function of time. So we assume we apply a DC potential and at certain time where we say this is time t = 0, we will start applying an AC potential.

So at that time just at that time or until at that time the theta value is theta steady state which is calculated here. So we will write at time t = 0 theta is theta steady state and after that we apply a sinusoidal potential and we can calculate the response.

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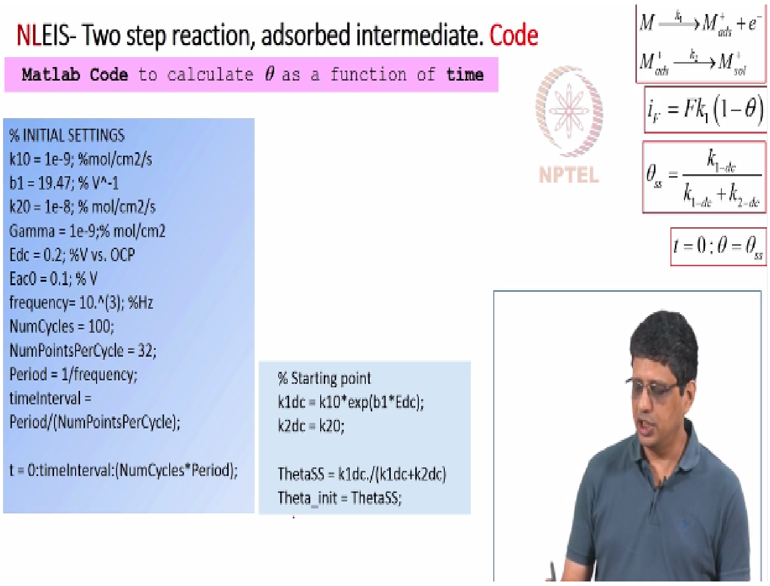

NLEIS- Two step reaction, adsorbed intermediate. Code

Matlab Code to calculate θ as a function of **time**

$M \xrightarrow{k_1} M^{+}_{ads} + e^{-}$

$M^{+}_{ads} \xrightarrow{k_2} M^{+}_{sol}$

$i_F = Fk_1(1-\theta)$

$\theta_{ss} = \frac{k_{1-dc}}{k_{1-dc}+k_{2-dc}}$

$t = 0 ; \theta = \theta_{ss}$

```
% INITIAL SETTINGS
k10 = 1e-9; %mol/cm2/s
b1 = 19.47; % V^-1
k20 = 1e-8; % mol/cm2/s
Gamma = 1e-9;% mol/cm2
Edc = 0.2; %V vs. OCP
Eac0 = 0.1; % V
frequency= 10.^(3); %Hz
NumCycles = 100;
NumPointsPerCycle = 32;
Period = 1/frequency;
timeInterval =
Period/(NumPointsPerCycle);

t = 0:timeInterval:(NumCycles*Period);
```

```
% Starting point
k1dc = k10*exp(b1*Edc);
k2dc = k20;

ThetaSS = k1dc./(k1dc+k2dc)
Theta_init = ThetaSS;
```

So just a description of the MATLAB code that we used K1 0 it is 10 power – 9, b1 value is given here, k2 0 gamma value at certain DC potential and AC perturbation 0.1 volt here means 100 millivolt and for 1 frequency we can use certain number of cycles. We do not want to apply 1 sinusoidal potential and look at the response, we want to apply many sinusoidal potentials and look at the response, there is a reason for that, we will see when we see the results okay.

And within 1 cycle I have to collect data at many points. We will use 32 points you want to use 2 power n so that Fourier transform is easy to do and the period of 1 wave is of course inverse of the frequency and I can calculate the time interval based on that period and the number of samples we want to take in a cycle and you can generate a time vector saying starting at 0 at these intervals go for so many cycles or go for this much time.

And to calculate the steady-state value we can calculate K1 at dc K2 of course is independent of potential. You can calculate the steady state theta value and use that as initial value.

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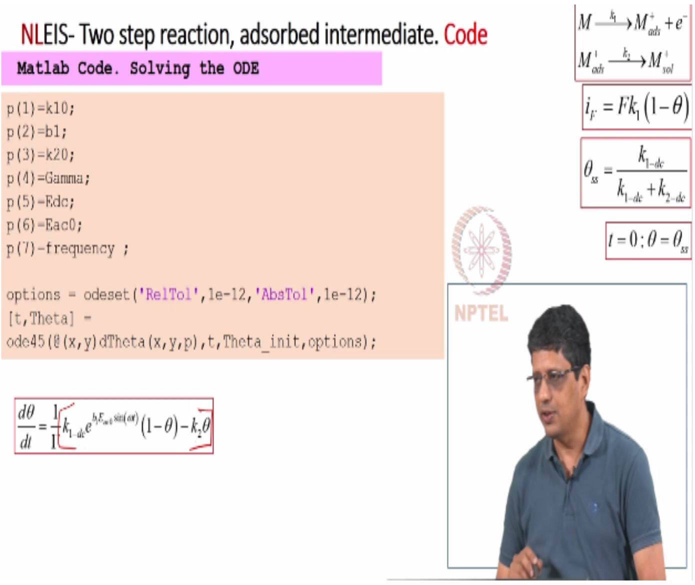

NLEIS- Two step reaction, adsorbed intermediate. Code

Matlab Code. Solving the ODE

```
p(1)=k10;
p(2)=b1;
p(3)=k20;
p(4)=Gamma;
p(5)=Edc;
p(6)=Eac0;
p(7)=frequency ;

options = odeset('RelTol',1e-12,'AbsTol',1e-12);
[t,Theta] =
ode45(@(x,y)dTheta(x,y,p),t,Theta_init,options);
```

$$\frac{d\theta}{dt}=\frac{1}{1}\left\{k_{1-dc}e^{b_1E_{ac0}\sin(\omega t)}(1-\theta)-k_2\theta\right\}$$

$$M \xrightarrow{k_1} M^{+}_{ads} + e^{-}$$

$$M^{+}_{ads} \xrightarrow{k_2} M^{+}_{sol}$$

$$i_F = Fk_1(1-\theta)$$

$$\theta_{ss} = \frac{k_{1-dc}}{k_{1-dc}+k_{2-dc}}$$

$$t=0;\theta=\theta_{ss}$$

And we want to use this equation d theta/dt and integrate. So we use a certain set of parameters. Parameters are given to the program. We need K1 0, b1, K2 0, gamma, dc value, ac value and the frequency of course omega is 2 pi f okay. Now by default if I remember it Matlab uses a tolerance value of 1a - 6 that is 10 power – 6. If you want to get accurate results you can change the tolerance value.

And here we have used ode45 as the numerical solver, we use what is called anonymous function and we create as function called d theta and we pass the parameters to that, t vector is basically going from 0 to so much time with this initial value and with this tolerance values.

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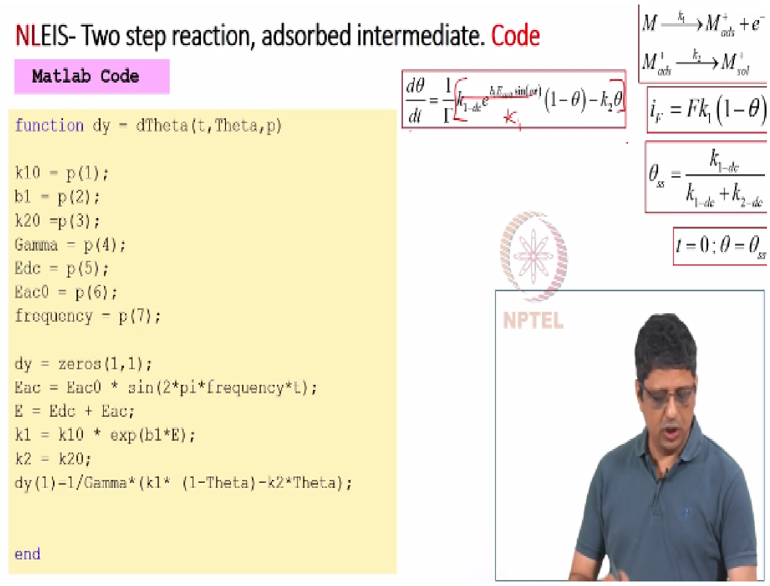

NLEIS- Two step reaction, adsorbed intermediate. Code

Matlab Code

```
function dy = dTheta(t,Theta,p)

k10 = p(1);
b1 = p(2);
k20 =p(3);
Gamma = p(4);
Edc = p(5);
Eac0 = p(6);
frequency = p(7);

dy = zeros(1,1);
Eac = Eac0 * sin(2*pi*frequency*t);
E = Edc + Eac;
k1 = k10 * exp(b1*E);
k2 = k20;
dy(1)=1/Gamma*(k1* (1-Theta)-k2*Theta);


end
```

$$\frac{d\theta}{dt}=\frac{1}{\Gamma}\left[\underbrace{k_{1-dc}e^{b_1E_{ac0}\sin(\omega t)}}_{K_1}(1-\theta)-k_2\theta\right]$$

$$M \xrightarrow{k_1} M^+_{ads}+e^-$$

$$M^+_{ads} \xrightarrow{k_2} M^+_{sol}$$

$$i_F = Fk_1(1-\theta)$$

$$\theta_{ss}=\frac{k_{1-dc}}{k_{1-dc}+k_{2-dc}}$$

$$t=0;\theta=\theta_{ss}$$

The function d theta essentially take this parameters K1 0, b1, K2 0 and so on and this is dy here represents d theta/dt. We first generate Eac as Eac0 sin 2 pi ft or sin omega t and potential is Edc + Eac. K1 is of course K1 0 exponential of b1 multiplied by potential and K2 is K2 0. When d theta by dt is 1/gamma multiplied by within brackets k1. So this entire term I can write it as K1 1 - theta K2 multiplied by theta. So if we do this integration what do I get?

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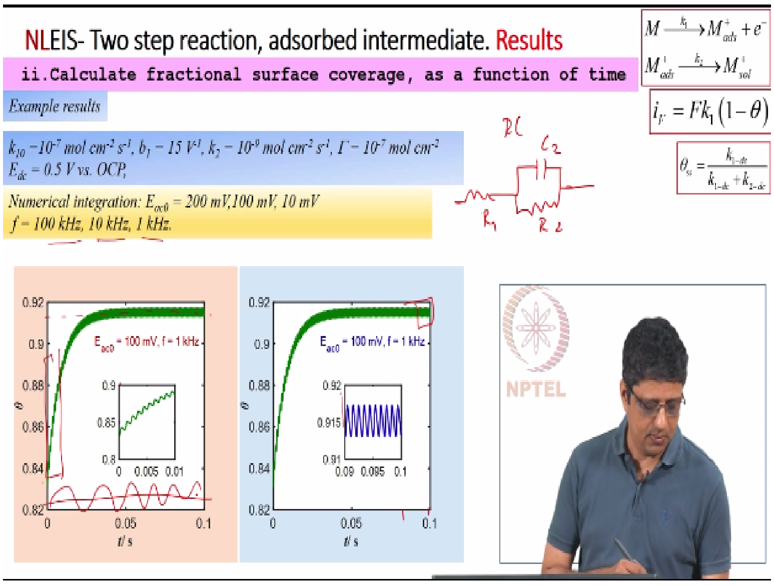

NLEIS- Two step reaction, adsorbed intermediate. Results

ii.Calculate fractional surface coverage, as a function of time

Example results

$k_{10}=10^{-7}$ mol cm^{-2} s^{-1}, $b_1=15$ V^{-1}, $k_2=10^{-9}$ mol cm^{-2} s^{-1}, $\Gamma=10^{-7}$ mol cm^{-2}
$E_{dc}=0.5$ V vs. OCP,

Numerical integration: $E_{ac0}=200$ mV, 100 mV, 10 mV
$f=100$ kHz, 10 kHz, 1 kHz.

$$M \xrightarrow{k_1} M^+_{ads}+e^-$$

$$M^+_{ads} \xrightarrow{k_2} M^+_{sol}$$

$$i_F = Fk_1(1-\theta)$$

$$\theta_{ss}=\frac{k_{1-dc}}{k_{1-dc}+k_{2-dc}}$$

First certain values K1 0 is 10 power - 7 moles per centimeters per second b1 is 15 inverse of voltage K2 0 a certain value gamma with 10 to power - 7 moles per centimeter square and a dc potential of 0.5 volts with respect to open circuit potential. When we are away from open circuit potential significantly far away from the open circuit potential we can neglect the reverse reaction and we have done it for a few frequencies.

Here I am showing you the result for 1 kilohertz and 100 millivolts, later we will see the results for other combinations. Other combinations of perturbation amplitude and frequencies. First thing I want you to notice is the following. When we apply an ac potential the response is not immediately a steady periodic response. This theta value increases and then stabilizes after some time.

We have seen this before when initially we looked at an RC circuit if I just take the Fourier domain and calculate the resistance here, use the resistance here, use the resistance here and use the capacitance here, I can find the impedance, but if I supply a sinusoidal potential it will take some time before it gives me the steady periodic result and if I take the steady periodic result and use Fourier transform I will get the same expression for impedance.

If I take the response in the beginning before it stabilizes I will actually not get the impedance that you would get by adding this as R1 + 1/1/r2 + j omega c2. This is the expression we get when we use Fourier domain or frequency domain. So out here by using numerical method when you integrate you realize that it will come to steady periodic result only after some time, it takes some time to stabilize.

In the beginning it starts it close to 0.8, the fractional surface coverage was close to 0.8, it increases and it oscillates around a value which is probably close to 0.91 or 915, if you just read off the graph you can see that after some time when we are close to 0.09 to 0.1 second that is close to 100 milliseconds, it has stabilized. So this insect shows the result close to this value and this inset shows the result close to this value.

So it takes some time to stabilize and give steady periodic result. Second point is it does not oscillate around the initial value, it oscillates around at different DC bias.

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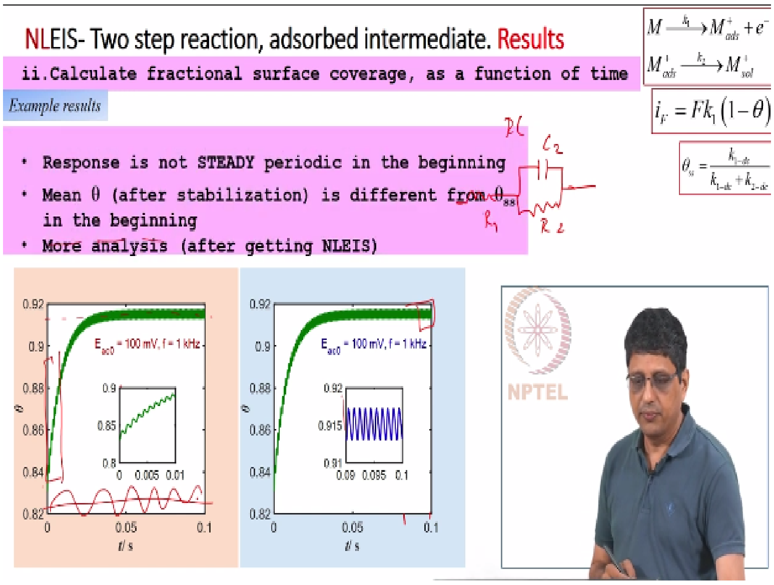

NLEIS- Two step reaction, adsorbed intermediate. Results

ii.Calculate fractional surface coverage, as a function of time

Example results

- Response is not STEADY periodic in the beginning
- Mean θ (after stabilization) is different from θ_{ss} in the beginning
- More analysis (after getting NLEIS)

$M \xrightarrow{k_1} M^+_{ads} + e^-$

$M^+_{ads} \xrightarrow{k_2} M^+_{sol}$

$i_F = Fk_1(1-\theta)$

$\theta_{ss} = \frac{k_{1-dc}}{k_{1-dc} + k_{2-dc}}$

So the summary is the response is not steady periodic in the beginning. The average value of theta after stabilization is different from the steady-state value. If I just apply dc potential, I will get a steady surface coverage value. If I apply AC on top of this average potential is still Edc, but the average surface coverage is not theta ss and how long does it take to stabilize, what will be the average surface coverage when it is oscillating, when it is under steady periodic condition.

This will vary with the applied perturbation, amplitude of the perturbation, it will vary with the frequency, we will do that analysis later. Right now we will say we will wait for sufficient time to get steady periodic response and after that we will subject this to Fourier transform.

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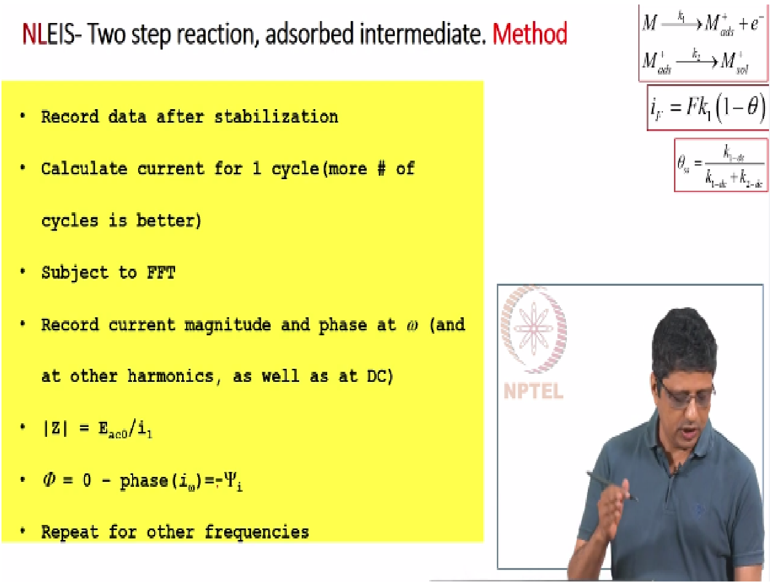

NLEIS- Two step reaction, adsorbed intermediate. Method

- Record data after stabilization
- Calculate current for 1 cycle(more # of cycles is better)
- Subject to FFT
- Record current magnitude and phase at ω (and at other harmonics, as well as at DC)
- $|Z| = E_{ac0}/i_1$
- $\Phi = 0 - \text{phase}(i_\omega) = -\Psi_i$
- Repeat for other frequencies

$M \xrightarrow{k_1} M^+_{ads} + e^-$

$M^+_{ads} \xrightarrow{k_2} M^+_{sol}$

$i_F = Fk_1(1-\theta)$

$\theta_{ss} = \frac{k_{1-dc}}{k_{1-dc} + k_{2-dc}}$

So we will record the data after stabilization, record or save the data. We will calculate the current at least for 1 cycle, it is probably better to do it for many more cycles and then subject the current to Fourier transform. Once you subject the current to Fourier transform you will get Fourier series, constant coefficient, coefficient corresponding to sin omega T and phase, magnitude and phase for a sin omega T.

Magnitude and phase for 2 omega, magnitude and phase for 3 omega and so on. If you want to calculate the impedance, I can calculate the magnitude of the impedance by taking Eac0 and the magnitude at 1 that corresponds to omega. If you want to calculate the phase, phase is 0 for the potential, phase whatever we calculate or get for the current we can subtract that and get the phase of the impedance and once you do it for one frequency, you can do it for other frequencies and then generate the spectrum.

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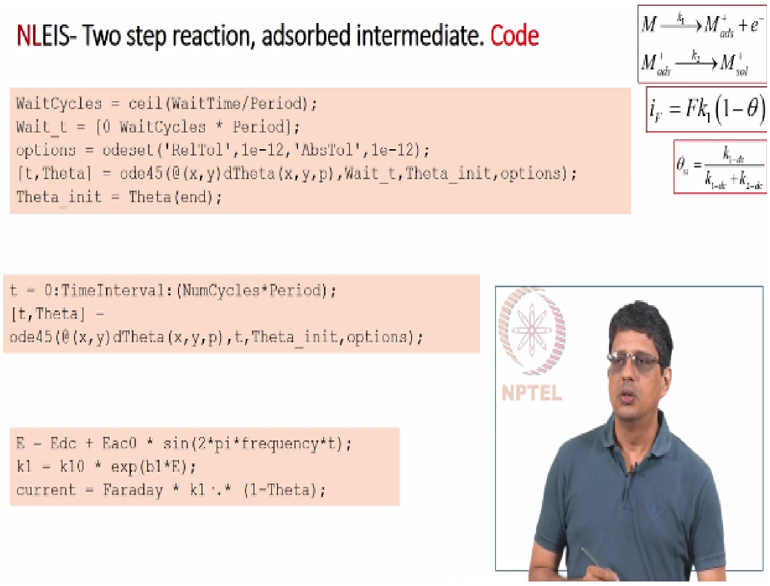

NLEIS- Two step reaction, adsorbed intermediate. Code

$M \xrightarrow{k_1} M^{+}_{ads} + e^{-}$

$M^{'}_{ads} \xrightarrow{k_2} M^{'}_{sol}$

$i_F = Fk_1\left(1-\theta\right)$

$\theta_{ss} = \frac{k_{1-dc}}{k_{1-dc}+k_{2-dc}}$

```
WaitCycles = ceil(WaitTime/Period);
Wait_t = [0 WaitCycles * Period];
options = odeset('RelTol',1e-12,'AbsTol',1e-12);
[t,Theta] = ode45(@(x,y)dTheta(x,y,p),Wait_t,Theta_init,options);
Theta_init = Theta(end);
```

```
t = 0:TimeInterval:(NumCycles*Period);
[t,Theta] -
ode45(@(x,y)dTheta(x,y,p),t,Theta_init,options);
```

```
E - Edc + Eac0 * sin(2*pi*frequency*t);
k1 - k10 * exp(b1*E);
current = Faraday * k1 .* (1-Theta);
```

So in order to implement it we can give the parameter values. Previously we have seen how to calculate the theta. In order to implement it correctly we have to wait for some time. So we have to say wait for in this case I would say wait for 100 millisecond or wait for 0.1 second and then take results or at least wait for 0.05 seconds and then take the cycles. So in order to do it correctly it is good to wait till a complete cycle is done.

So we calculate the number of cycles that one needs to wait so that the response has stabilized and then we have to integrate it and whatever value of theta where it ends that should be the initial value for the subsequent integration that is you apply sinusoidal potential wait for some time and then take the data. So the theta value and the current value should be at that end.

So we calculate the theta values and then the last value of that theta should be the initial value for the next integration. So until now we have been waiting, now we are going to record the data. So this num cycles tells how many cycles we want to use to record this, at certain time interval you can do the integration and once you get the theta values you can calculate the rate constant, you can calculate the current using this expression.

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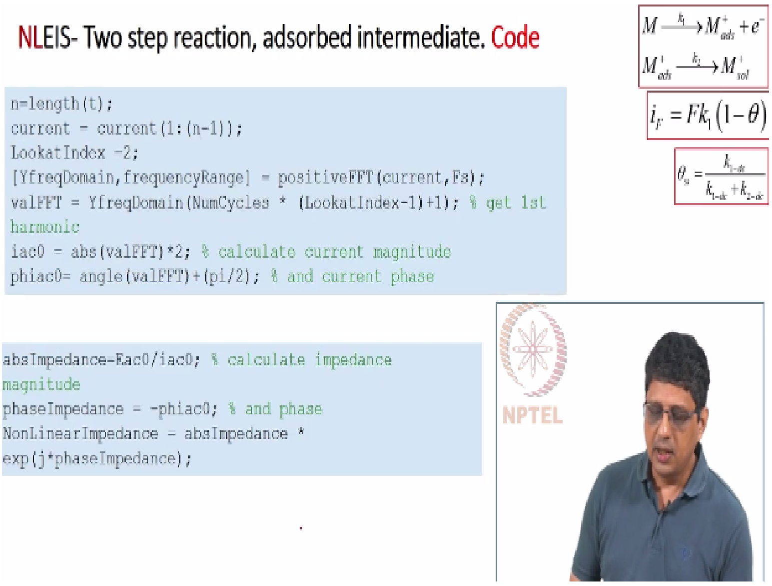

NLEIS- Two step reaction, adsorbed intermediate. Code

$$M \xrightarrow{k_1} M_{ads}^{+} + e^{-}$$

$$M_{ads}^{+} \xrightarrow{k_2} M_{sol}^{+}$$

$$i_F = Fk_1\left(1-\theta\right)$$

$$\theta_{ss} = \frac{k_{1-dc}}{k_{1-dc}+k_{2-dc}}$$

```
n=length(t);
current - current(1:(n-1));
LookatIndex -2;
[YfreqDomain,frequencyRange] = positiveFFT(current,Fs);
valFFT = YfreqDomain(NumCycles * (LookatIndex-1)+1); % get 1st
harmonic
iac0 = abs(valFFT)*2; % calculate current magnitude
phiac0= angle(valFFT)+(pi/2); % and current phase
```

```
absImpedance-Eac0/iac0; % calculate impedance
magnitude
phaseImpedance = -phiac0; % and phase
NonLinearImpedance - absImpedance *
exp(j*phaseImpedance);
```

And then you will remember that if I give a sin wave like this I of course give discrete points here. For this implementation in the Matlab, I should not give all the way until this, I should actually give one point less, so I can give up to this and then Matlab will assume that we are going to replicate it and then do this Fourier transform. So I find the length of this current and then give one point less.

If you want to look at the response at fundamental I should look at this second term in the series. If you want to look at the response at second harmonic I should look at the third term because in Matlab first term corresponds to the dc, second term corresponds to omega, third term corresponds to 2 omega and so on if you are using one cycle. If we use many cycles the Fourier transform will give you response like this 0.

Let us say we used 10 cycles, 0.1 frequency, 0.2 frequency and so on and then 1 frequency, 1.1 frequency and so on because the more number of cycles we give the better resolution meaning instead of going from 0 to 1 in one step it will go in 10 steps or n steps, n number of cycle will give you n steps. So correspondingly we should look at the right coefficient based on number of cycles and then take the value for the first harmonic.

And because of the way it works you have to multiply by 2 to get the magnitude, you have to add pi/2 to the phase. Now we get the current magnitude and phase and to calculate the magnitude of the impedance Eac0/iac0 will give you the magnitude of the impedance. Phase of the impedance is basically 0 – the phase of the current and the nonlinear impedance ZF nonlinear is nothing but Z e power j phi where phi is the phase of the impedance and magnitude of course is mod Z.

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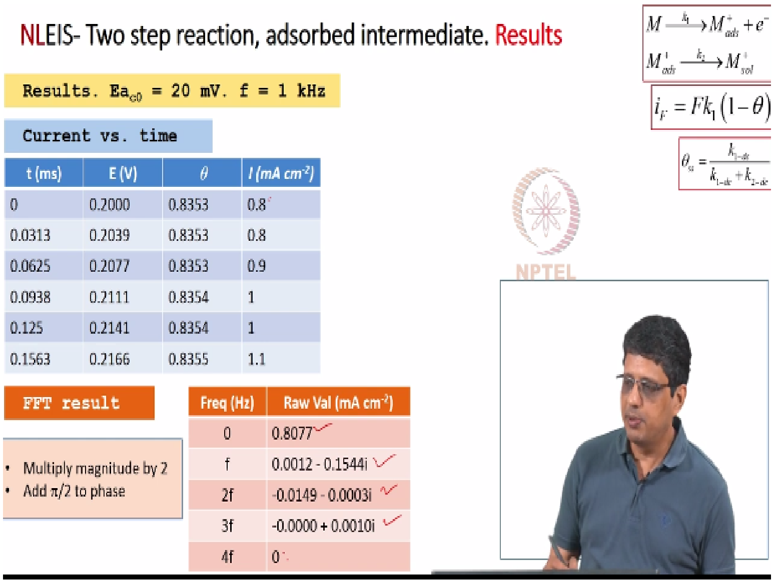

NLEIS- Two step reaction, adsorbed intermediate. Results

$$M \xrightarrow{k_1} M^{+}_{ads} + e^{-}$$

$$M^{+}_{ads} \xrightarrow{k_2} M^{+}_{sol}$$

$$i_F = Fk_1(1-\theta)$$

$$\theta_{ss} = \frac{k_{1-dc}}{k_{1-dc}+k_{2-dc}}$$

`Results. Ea`$_{G0}$ `= 20 mV. f = 1 kHz`

`Current vs. time`

t (ms)	E (V)	θ	I (mA cm^{-2})
0	0.2000	0.8353	0.8
0.0313	0.2039	0.8353	0.8
0.0625	0.2077	0.8353	0.9
0.0938	0.2111	0.8354	1
0.125	0.2141	0.8354	1
0.1563	0.2166	0.8355	1.1

`FFT result`

- Multiply magnitude by 2
- Add π/2 to phase

Freq (Hz)	Raw Val (mA cm^{-2})
0	0.8077 ✓
f	0.0012 - 0.1544i ✓
2f	-0.0149 - 0.0003i ✓
3f	-0.0000 + 0.0010i ✓
4f	0

That is an example, if I give 20 millivolt at 1 kilohertz few time intervals here right, 1 millisecond I would get one cycle, few time intervals I got some numbers correspondingly dc potential of 0.2 + 20 millivolt sinusoidal will give me a value like this after waiting for sufficient time when we continue with the integration these are the theta values and correspondingly I will get current value.

Of course I have truncated it would give many more decimals, I have truncated it so that we can see it easily. These numbers are not identical 0.8 and 0.8, these are actually slightly different, but you get the idea. Now take this current and the time interval, this is the sampling interval and subject it to Fourier transform. Once we subject it to Fourier transform I will get results like 0 f 2f and so on.

This is the raw value it is dc, this is a complex number, this is also a complex number, this is also complex number. After 4f it is going to be 0, here I have used only 1 cycle. Therefore, after the first dc bias next term is the response at fundamental. I had to multiply the magnitude by 2 and add pi/2, what I also want you to note is even though I am applying 20 millivolts it is actually fairly small perturbation.

There is some response, a small value at second f, there is even a smaller value, but nonzero value at the third frequency only for fourth and fifth harmonic we see it is pretty much 0.

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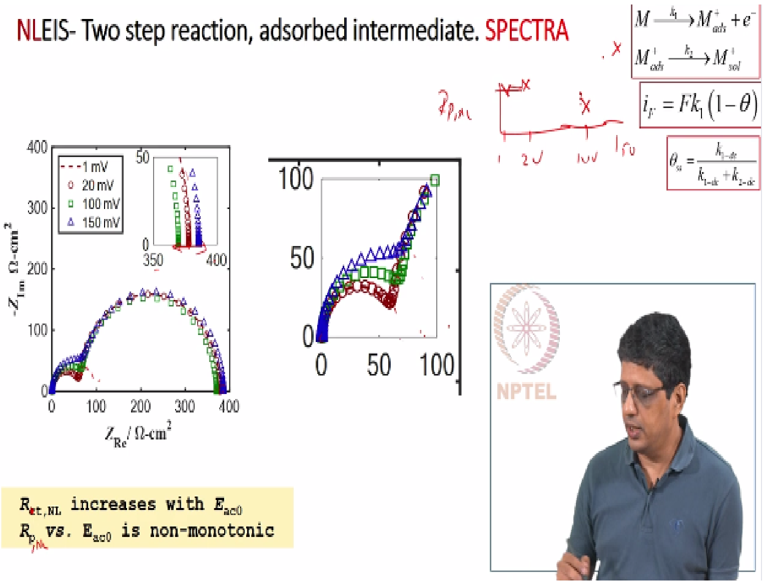

NLEIS- Two step reaction, adsorbed intermediate. SPECTRA

$M \xrightarrow{k_1} M^{+}_{ads} + e^{-}$

$M^{+}_{ads} \xrightarrow{k_2} M^{+}_{sol}$

$i_F = Fk_1(1-\theta)$

$\theta_{ss} = \frac{k_{1-dc}}{k_{1-dc}+k_{2-dc}}$

$R_{ct,NL}$ increases with E_{ac0}

R_p vs. E_{ac0} is non-monotonic

And if we do it for a set of frequencies we can get the results and plot it in complex plane plot, 1 millivolt and 20 millivolts, you get 2 semicircles for a set of kinetic parameters, 1 millivolt is given as a dashed line, 20 millivolts given as a circle and you can see they pretty much overlap, they show 2 semicircles. This is the value at low frequency and this is just an expanded version at the high frequency and mid frequencies.

The response at 100 millivolts is given by their green color square. The response at 150 millivolts is given by blue triangles. I want you to see this. This will correspond to charge transfer resistance and this values correspond to polarization resistance. When I increase the ac potential this is going to settle somewhere here. So 1 millivolt to 20 millivolt there is not much of a difference, 20 to 50 the nonlinear charge transfer resistance increases.

So at 20 to 100 it increases, 100 to 150 it again increases. So Rt nl increases with Eac0 for this case. Earlier example where we have looked at simple electron transfer reaction, when we increase the perturbation amplitude Rt actually decreased, but that is not universal or T can increase, it may increase or it may decrease. Next I want to look at polarization, nonlinear polarization resistance, there is a low frequency value.

1 and 20 twenty millivolts it is pretty much the same 20 to 100 it decreases, 100 to 150 it actually increases that means if I plot Rpnl with 120, 100, 150, not necessarily drawn to scale it is constant, constant, it shows an decrease here and then an increase here. We do not know whether it is the minimum here, it is just to say it is not monotonic.

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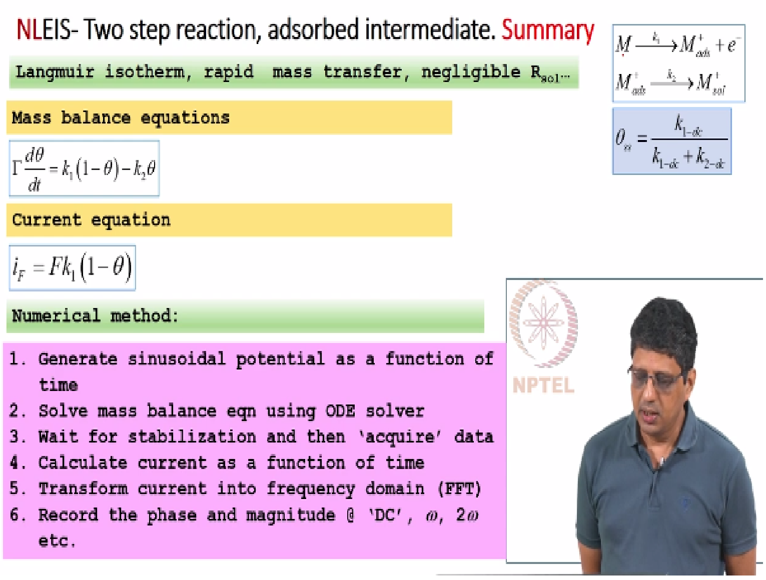

NLEIS- Two step reaction, adsorbed intermediate. Summary

$M \xrightarrow{k_1} M^{+}_{ads} + e^{-}$

$M^{+}_{ads} \xrightarrow{k_2} M^{+}_{sol}$

$\theta_{ss} = \frac{k_{1-dc}}{k_{1-dc} + k_{2-dc}}$

Langmuir isotherm, rapid mass transfer, negligible R_{sol}...

Mass balance equations

$\Gamma \frac{d\theta}{dt} = k_1(1-\theta) - k_2\theta$

Current equation

$i_F = Fk_1(1-\theta)$

Numerical method:

1. Generate sinusoidal potential as a function of time
2. Solve mass balance eqn using ODE solver
3. Wait for stabilization and then 'acquire' data
4. Calculate current as a function of time
5. Transform current into frequency domain (FFT)
6. Record the phase and magnitude @ 'DC', ω, 2ω etc.

So to summarize for this reaction two-step reaction with adsorbed intermediate we have to take the mass balance equation and the current equation. We do not have to expand this in Taylor series or Fourier series, just integrate the mass balance equation, first find the steady state values, use that as the initial point and use numerical integration, take the mass balance equation and integrate it.

So generate sinusoidal potential, solve mass balance equation using a ODE solver. We have used Matlab and ODE 45 or ODE 15S, you can use any similar software, you should be able to do the integration. Recognize that it takes some time for the response to stabilize, wait for certain time and then start recording the data and this is true even when you do experiments because the system takes certain time to stabilize.

Once you have waited for sufficient time and start recording the data save the current data as a function of time, subject that to Fourier transform and record the values that dc record the response at, fundamental response at higher harmonics, both the magnitude and phase and then you can calculate the impedance, you can plot the current response at any harmonic as a function of frequency in Bode plots.

So we saw that they take some time to stabilize what we would do in the next class is to look at the effect of changing perturbation amplitude look at the effect of changing frequency and then get an idea of how these things affect stabilization time, how these parameters affect the average value or mean value around which this stabilizes. After that I also want to discuss how to estimate the charge transfer resistance and the polarization resistance for any perturbation amplitude.

For small perturbation amplitude we know we can linearize the equation and get an expression for RP and RT in fact for the entire impedance spectrum. For large amplitude perturbation it is not possible to get an analytical expression for any reaction in general, but for many of these cases we should be able to estimate the charge transfer resistance and we will be able to calculate the polarization resistance without going through the integration. We will stop here today.