Electrochemical Impedance Spectroscopy
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Lecture - 47
Instabilities

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Previous class

- Modeling Galvanostatic Measurements

Today

- Instabilities
- Effect of Potential drift on impedance spectrum
  - Two step reaction with an intermediate. Example with Matlab ® code

Okay, so yesterday we saw how we can stimulate galvanostatic measurements using numerical method right. Today I want to show you how we can stimulate instabilities in particular potential instabilities. We assume that normally the Dc potential or the open circuit potential does not change with time, but in many cases open circuit potential will drift and it will come to a stable value after sometime.

It may be few seconds, few minutes or in some cases it can take hours to stabilize okay. So what I want to show you here is an example for a two step reaction where the open circuit potential changes with time. It can change linearly; it can change exponentially I want to also show you examples of what I mean by exponential. We will seek quickly how the results will come for a simple electron transfer reaction.

Later I want to show you an example with code of how to handle it when you have potential drift. You can of course use the same concept when you want to stimulate cases where concentration changes with time. All these things basically mean when you do an experiment at the end of the experiment the system has not come back to the original state. So it is not a stable system.

In this case we deliberately introduce a potential ramp or potential change, but what we want to mimic is in real life if potential changes not because we want to change, but because the system itself is not stable. Those cases if we know that this is how the potential changes with time, but still we acquire a data we acquire EIS data. During the time when the potential changes then what should we expect to see that is what we want to see here.

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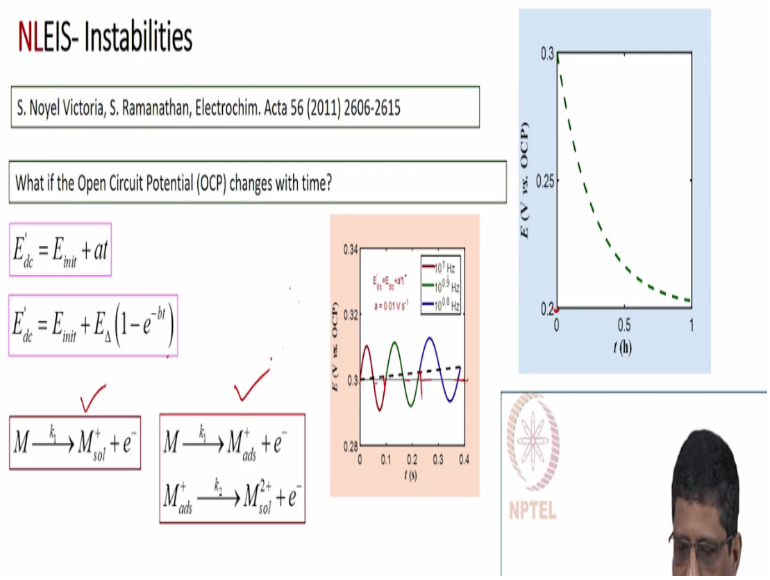

NLEIS- Instabilities

S. Noyel Victoria, S. Ramanathan, Electrochim. Acta 56 (2011) 2606-2615

What if the Open Circuit Potential (OCP) changes with time?

$E'_{dc} = E_{init} + at$

$E'_{dc} = E_{init} + E_{\Delta}\left(1 - e^{-bt}\right)$

✓

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

✓

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

$M^{+}_{ads} \xrightarrow{k_2} M^{2+}_{sol} + e^{-}$

We have done some of this work and publish this in 2011. So the idea is what happens if the open circuit potential changes linearly with time. So in that case our initial potential is given by E whatever we would consider as Dc potential that I call it as Edc prime because it is not really independent of time we denote it as a prime to indicate that it is not normal Edc. So initially let us say that this is our dc potential this is OCP open circuit potential, this is potential with respect to time.

If open circuit potential were independent of time it will be a constant and this may be for example 0.2 volts versus our reference electrode Ag/AgCl or any other reference electrode and then we are at a potential 0.3 volts which is 0.3 volts above the open circuit potential which means it is 0.5 volts versus our reference. Now this is the case if we have open circuit potential that is independent of time.

If the open circuit potential decreases with time then we are maintaining 0.5 volts with respect to the reference electrode, but that is not 0.3 volts versus OCP that is actually changing with time we would call that as 0.3 volts+ at where a tells the rate of change of open circuit potential with respect to time. If that is decreasing, we will say our actual potential where we maintain that is increasing with respect to open circuit potential okay.

So this is one example and this probably works when it changes linearly with time, it changes at a slower rate but over a period of time it continuous to change. It is not likely in practical cases it is not likely that it will change linearly at a fast rate and continue to change linearly okay. So this one possibility another possibility is this. A lot of times we will see that the potential changes quickly for sometimes.

And then it come and stabilize and this would be potential with respect to time. So initially it changes quickly and then later it changes slowly. This one can model using an exponential decay given by an expression like this. This is the change; this is the initial value E delta specifies the maximum possible change if you wait for infinite time or long enough time. This defines how rapidly it decreases or changes okay. So it is given by exponential –bt b is the parameter here and E delta tells the maximum possible change.

So in some cases this is more a realistic representation of what actually happens in a cell. In case I apply a sinusoidal potential when you have a linear change in open circuit potential. Our dc potential is 0.3 volts with respect to open circuit potential. And if the open circuit potential back to remain constant this light gray color line would represent that dc potential with respect to open circuit potential.

When the OCP changes with time and it decreases with time versus OCP the potential dc potential actually increases and if superimpose an ac on top of it right. The way we would do the measurement is initially we would apply a high frequency potential then we will go to little lower frequency and so on. This is typically how the EIS spectrum is measured. This example let us just pretend that we are applying only one sinusoidal wave.

We are acquiring the current and we later do for your transform and calculate their impedance. So if you are applying 10 power 1 hertz then 10 power 0.9 10 power 0.8 this is logarithmically spaced 10 frequencies per decade, but we have a change in the open circuit potential. So that change is given at the rate of 0.01 volts per second just 10 millivolts per second which is actually fairly large change.

But I just want to show you how the potential way will appear and we will continue to apply lower and lower frequencies it will continue to drift like this. So it is not going to be sinusoidal wave at a 0 bias or at a constant bias the bias is changing. In case the actual change in open circuit potential is described better by this exponential change. This is what we would say if I apply a sinusoidal potential that is what we are applying.

And you can change the frequency another frequency and so on. So initially we see a rapid change in that bias and later we see a gradual change in the bias. Now we can consider any mechanism right now I am considering two different mechanism. One is the simple electron transfer reaction second is a reaction with adsorbed intermediate. If you can handle these two you should be able to handle any other reaction okay.

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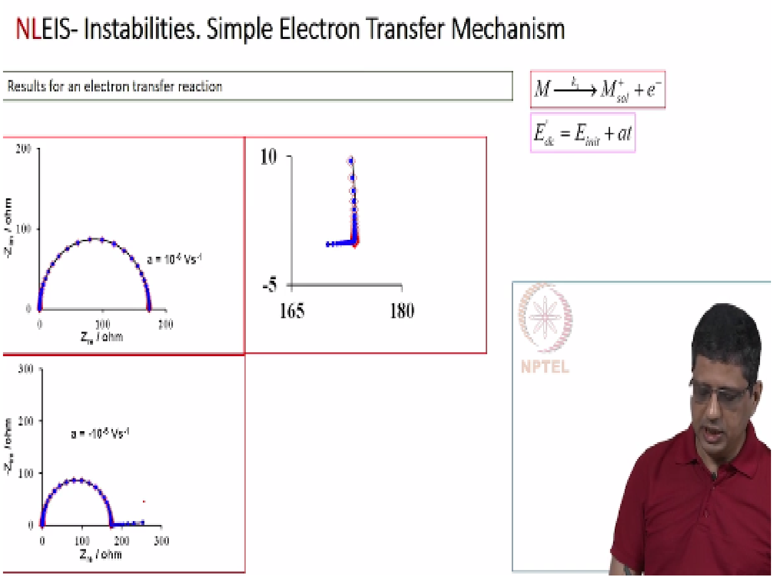

NLEIS- Instabilities. Simple Electron Transfer Mechanism

Results for an electron transfer reaction

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

$E'_{dc} = E_{init} + at$

So if you have an electron transfer reaction and if the dc bias changes linearly with respect to time. I am not going through the full details, but basically what we would do is to apply this, measure the current and remember at the end of this first cycle or n number of cycles the dc potential starting point is different now. And then again apply a sinusoidal potential along with the ramp, measure the current perform FFT calculate the ratio of potential current and call that as impedance.

Then remember now the potential has shifted again if you do one cycle it has shifted by that period. If you wait for n number of cycles and then perform measurement for n number of cycles or m number of cycles, you had to wait for so long that means the dc potential has shifted by that much. So all these things have to be taken into account. If I have very, very slow change 10 power -6 volts per second that means few hours to get few hundred millivolts then the spectrum will appear more or less same in this scale.

If you go from 0 to 200 Ohms if you really zoom in you would see that the one which is stable settles here, the one which is unstable or drifting or we call it as unstability potential ramp that shows there is a small movement here or small change here. It continuous to move towards the origin so there is a difference, but it is not very, very perceptible and if you have experimental data with (()) (09:40) you may not see the difference clearly.

Now what happens if the ramp rate is little higher that is 10 power -5 10 microvolts per second that is actually quite possible. What you would see is at high frequency and mid frequency you would not see any difference okay, but at low frequencies it increases. It is not a 45 degree line, it increases but at a very low angle it continuous to increase okay. So if you are not careful this is for one set of kinetic parameters right.

If we have another set of kinetic parameter another dc bias another ramp rate it is possible that it will appear somewhat like Warburg impedance okay. One has to be careful at the end of this measurement if you restart and continue this measurement take the spectrum again and compare with the first spectrum do they match that is one way to check for repeatability, that is one way to check for any changes in the system is it stable or not stable.

Here of course the instability it does not arise because we are applying the sinusoidal potential that is systematic instability. It is just that if you are not aware of it and you take measurement and analyze it assuming that the system was stable then you will end up with wrong interpretation. You might in this case end up with the interpretation saying diffusion is contributing to this term or it may be rate limiting.

Of course it is not a 45 degree line so you should not get that interpretation, but just to warn you about this possibility.

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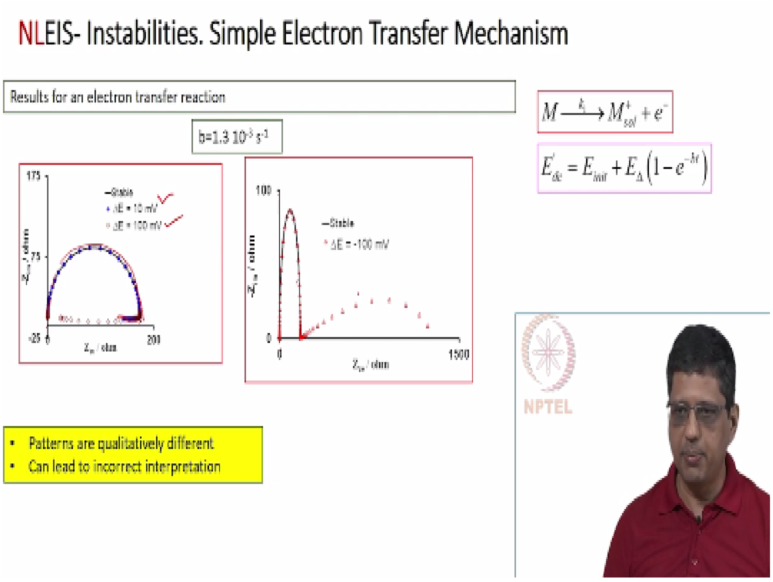

NLEIS- Instabilities. Simple Electron Transfer Mechanism

Results for an electron transfer reaction

b=1.3 10^{-3} s^{-1}

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

$E'_{dc} = E_{init} + E_{\Delta}\left(1 - e^{-bt}\right)$

- Patterns are qualitatively different
- Can lead to incorrect interpretation

What happens if the potential changes actually exponential okay with a maximum change of 10 millivolts and a maximum change of 100 millivolt the 10 millivolts results are given as blue filled circles and 100 millivolts results are given them as diamonds with brown color and the stable results of course will start here and end at this location as a semicircle. In both cases even if there is a 10 millivolt change and there is a rapid change in the beginning.

And slow change later you would see that it is moving towards the origin and if it is 100 millivolt change it is moving to a large extent okay. This tells you the rate at which it changes it is not exactly de/dt, but if the parameter b is large it means it will rapidly come to the final value. If the parameter b is small, it will take long time to come to that final value okay. It can be thought of as inverse of (()) (12:31) constant okay.

Now instead of increasing the dc bias with respect to open circuit potential by 100 millivolts. If it changes in the other direction if it decreases what would you see. Now I have told you that all the time you should plot the abscissa and the ordinate in the complex plane plot in the same scale, but sometimes it is better to plot this with different scale, but clearly mentioned that the scales are not equal.

So here I have plotted 0 to 1500, 0 to 100 in this scale it does not appear as a semicircle although if you really plot with equal scale it will appear more or less like a semicircle here for the first part. The stable results basically show a semicircle and end here. The unstable result if I draw it in the correct scale it will probably look like this a semicircle and as slight change.

I am again exaggerating here very slight change increase and then decrease and settle down. Again somewhat like finite Warburg impedance, but not really going at 45 degree and coming down instead going at a very slight angle and then coming down, but if one is not careful they might come up with the interpretation that there is a (()) (14:06) and this can be model by a finite Warburg impedance.

Of course it will not model correctly if we take finite Warburg impedance and apply it here or use a circuit and fit it, it will not apply correctly, but first thing you need to check is the open circuit potential drift is the concentration the same at the beginning of the experiment and at the end of the experiment okay. Thus the surface looked the same is it the same from the beginning to the end.

If there is a change in the concentration, if there is a change in the surface then open circuit potential can shift or even other otherwise the reaction create constant can change okay. This example may illustrate with a change in dc potential, but you can also incorporate the effect of changes in concentration, effect of changes in rate constant. Effect of changes in area as long as we go with the numerical method.

If you want to use analytical method it is possible only for a simple electron transfer reaction for small changes in this drift, for small Eac0 if I want to apply for large Eac0 I cannot use this method whereas this numerical method can be used for arbitrarily large or small value of amplitude small changes or large changes. So it is lot more general of course it is more time consuming in terms of computational time.

So one of the interpretations says that the patterns that you would get when you have instability they are qualitatively different. It is not just a semi circle which is slightly larger or smaller. It is semi circle with other features okay and which can need to incorrect interpretation.

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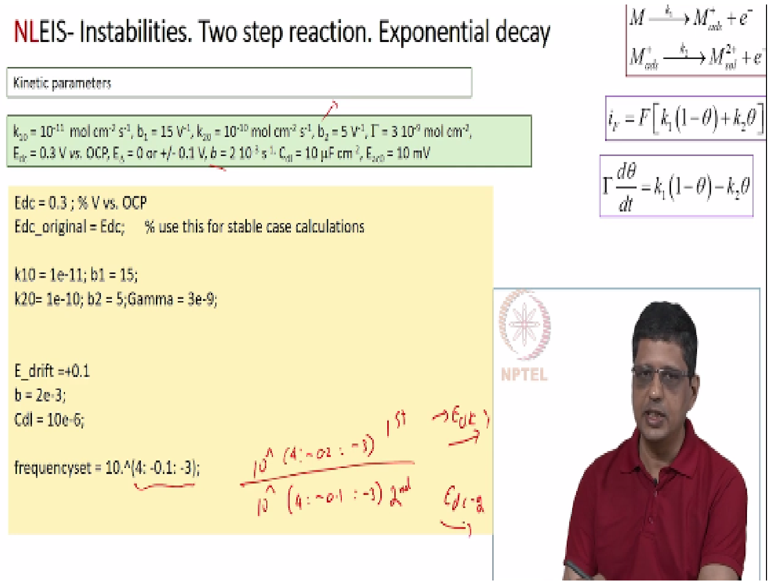

NLEIS- Instabilities. Two step reaction. Exponential decay

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

$M^{+}_{ads} \xrightarrow{k_2} M^{2+}_{sol} + e^{-}$

Kinetic parameters

$k_{10} = 10^{-11}$ mol cm^{-2} s^{-1}, $b_1 = 15$ V^{-1}, $k_{20} = 10^{-10}$ mol cm^{-2} s^{-1}, $b_2 = 5$ V^{-1}, $\Gamma = 3\ 10^{-9}$ mol cm^{-2}, $E_{dc} = 0.3$ V vs. OCP, $E_{\Delta} = 0$ or +/- 0.1 V, $b = 2\ 10^{-3}$ s^{-1}, $C_{dl} = 10$ µF cm^{-2}, $E_{ac0} = 10$ mV

$$i_F = F\left[k_1(1-\theta)+k_2\theta\right]$$

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

```
Edc = 0.3 ; % V vs. OCP
Edc_original = Edc;     % use this for stable case calculations

k10 = 1e-11; b1 = 15;
k20= 1e-10; b2 = 5;Gamma = 3e-9;


E_drift =+0.1
b = 2e-3;
Cdl = 10e-6;

frequencyset = 10.^(4: -0.1: -3);
```

Now I want to show you how we can done this for a two step reaction where you have an exponential decay. The reaction is of course something we have seen many times since we are familiar with this. This is metal going to metal adsorbed and metal adsorbed going to metal 2+ electrodes. So the first and second are electron transfer reactions. Mostly we have seen the reaction where the second reaction is a chemical reaction the first reaction is a electrochemical reaction.

And maybe one or two examples we have seen with both steps being electron transfer reaction okay. So what this means is the current faradaic current. It has an expression which is F k11-theta+ k2 theta. Of course the mass balance equation remains the same. Initially we will give the kinetic parameter values we have chosen certain set of kinetic parameter value we may note them down because the second reaction is also electron transfer reaction.

The exponent corresponding to that rate constant is not 0 it can have a positive value. We have gamma dc potential in the beginning is 0.3 volts with respect to open circuit potential and the maximum if I want to find the stable result I can still use the same code and say that the drift is 0 E delta is 0 or I can say it is + or *-0.1 or whatever voltage I want to specify I can put there.

And this b is the drift it is not related to the b1 and b2 that we used in the rate constant. Double layer capacitance of course actually need to be 10, 20 microfarad per centimeter square something that is reasonable and this example I have shown it with 10 millivolt perturbation amplitude, but you can use the same code with a larger perturbation amplitude larger perturbation amplitude and you would get the results anyway.

So we specify the kinetic parameter value. We choose the frequency range, we started 10 power 4 that is 10 kilohertz and ended 1 millihertz at this specified interval. So it is going to go logarithmically spaced or geometric spaced 10 frequency per decay. Now you can understand if I give 10 frequency per decay it is going to make measurements from 10 kilohertz it will take certain time to come to 1 kilohertz then 100 hertz and so on.

If I use 5 frequencies per decay I will come to the 1 kilohertz fast that means where measurement time is less which also means I am definitely not taking so much time to complete this, but at the end the dc potential at the end of this experiment. So if I do one set of experiment with 10 power 4 5 frequencies per day and another set of experiment with 10 power 4 10 frequencies per decay.

It will take longer time for us to complete the second experiment. It will be faster to complete the first experiment and because there is a drift we will end up at 1 dc potential here at the end of this experiment and we will up with another dc potential here at the end of this experiment when I say we will end up at 1 dc potential I mean with respect to open circuit potential with respect to reference electrode the instrument will control and it will come to the original potential with respect to the reference electrode.

When the open circuit potential changes with time with respect to OCP the dc values will be different at the end of this experiment and it is going to be different at the end of this second sort of experiments. So it is not just that how fast does it drift and it is also how long do we take to make the measurement that plays a role in how the spectrum will appear. So that is another way you can have one fine intervals for the frequency and one course intervals for the frequency and fine intervals for the frequencies.

And do two sets of measurements if they are more or less overlapping then you can probably say that yeah drift is not that significant within the experimental level right. If they are quite different then this is one thing you need to consider okay.

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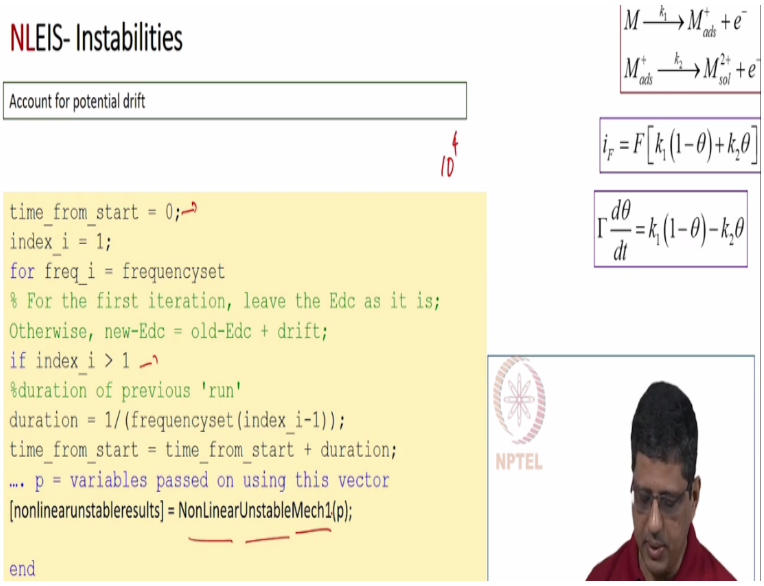

NLEIS- Instabilities

Account for potential drift

10^4

```
time_from_start = 0;
index_i = 1;
for freq_i = frequencyset
% For the first iteration, leave the Edc as it is;
Otherwise, new-Edc = old-Edc + drift;
if index_i > 1
%duration of previous 'run'
duration = 1/(frequencyset(index_i-1));
time_from_start = time_from_start + duration;
…. p = variables passed on using this vector
[nonlinearunstableresults] = NonLinearUnstableMech1(p);

end
```

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

$$M^{+}_{ads} \xrightarrow{k_2} M^{2+}_{sol} + e^{-}$$

$$i_F = F\left[k_1(1-\theta)+k_2\theta\right]$$

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

When you want to account for the potential drift you have to have a variable saying how long is it from the beginning of the experiment. So we call it time from start stated to 0. First when you apply a sinusoidal potential in the very beginning there is no drift meaning we are starting at the right potential whatever you want to start at you are starting at that potential and then second frequency onwards you will have to remember that with respect to time the dc potential has changed because the time has changed from 0 the dc potential has changed.

So we say duration, duration is the period for that particular frequency okay. So initially we apply 10 power 4 hertz that means 10 kilohertz. So we have waited for sometimes to complete at least one cycle. So now the time from start is whatever time we have waited before+ the period of last perturbation. If I apply n number of cycles, I need to multiply this by n.

If I am applying only one cycle in this example I am assuming that I am applying only one cycle, I am not at all waiting as well as I apply one cycle. I take the data go to the next cycle okay which is probably not what the instrument does. If you had to wait for sometime in the simulation also you have to say wait for that time that means you apply sinusoidal potential the dc potential keeps changing during this time.

And then you apply sinusoidal potential few more cycles hoping that these are steady periodic because we do not know we assume that dc potential is stable. We assume that the response has come to steady periodic although in the simulation we had to recognize that it has not come to steady periodic and then at the end of it the dc potential has changed so much and then we had to start and then new dc potential.

We say this as variables pass it as a vector and then supply it to a function which we call as nonlinear and stable and this is denoted as (()) (22:35).

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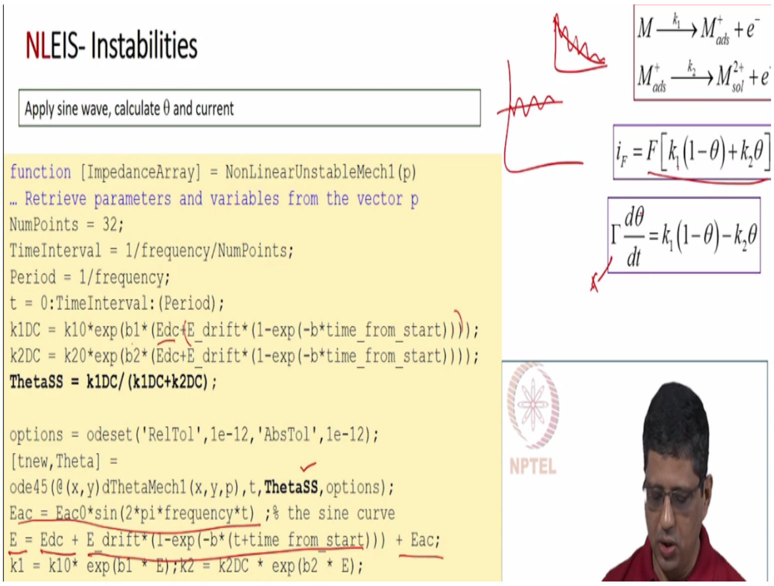

NLEIS- Instabilities

Apply sine wave, calculate θ and current

```
function [ImpedanceArray] = NonLinearUnstableMech1(p)
… Retrieve parameters and variables from the vector p
NumPoints = 32;
TimeInterval = 1/frequency/NumPoints;
Period = 1/frequency;
t = 0:TimeInterval:(Period);
k1DC = k10*exp(b1*(Edc+E_drift*(1-exp(-b*time_from_start))));
k2DC = k20*exp(b2*(Edc+E_drift*(1-exp(-b*time_from_start))));
ThetaSS = k1DC/(k1DC+k2DC);

options = odeset('RelTol',1e-12,'AbsTol',1e-12);
[tnew,Theta] =
ode45(@(x,y)dThetaMech1(x,y,p),t,ThetaSS,options);
Eac = Eac0*sin(2*pi*frequency*t) ;% the sine curve
E = Edc + E_drift*(1-exp(-b*(t+time_from_start))) + Eac;
k1 = k10* exp(b1 * E);k2 = k2DC * exp(b2 * E);
```

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

$$M^+_{ads} \xrightarrow{k_2} M^{2+}_{sol} + e^-$$

$$i_F = F\left[k_1(1-\theta)+k_2\theta\right]$$

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

We need to integrate this equation we need to specify what is the theta steady state and that theta steady state is going to change because the Edc is changing. So every time you need to calculate the new theta steady state and then send it as initial value. If dc potential is slowly changing we assume theta is also slowly changing and we can call it as pseudo steady state right now we are calling it as steady state.

So we get the k10 exponential b1 E, but the E is different compared to the initial value E depends on the Edc and then it is specified by E delta 1- exponential b time from start how long we will waited and likewise for k2 and this can be integrated after we integrate we get the value of theta and then you can calculate the current by using this expression. If you have theta as a function of time you can generate anyway E as a function of time.

Just remember you have Eac, but E is Edc+ drift+ Eac. So it is not just dc+ sin it is actually dc that is changing+ sin and then once you know the E as a function of time you can calculate k1 and k2 as a function of time the integration has given as theta as a function of time. So we can calculate the current and then perform the FFT.

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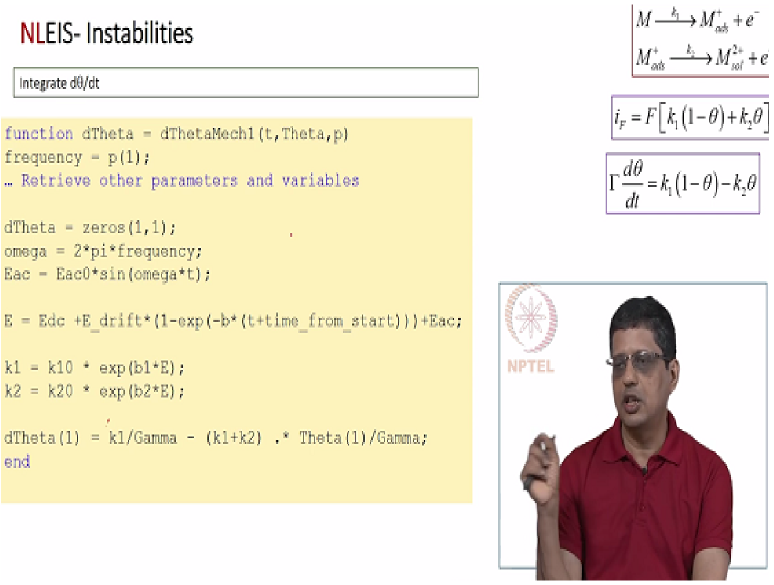

NLEIS- Instabilities

Integrate dθ/dt

```
function dTheta = dThetaMech1(t,Theta,p)
frequency = p(1);
… Retrieve other parameters and variables

dTheta = zeros(1,1);
omega = 2*pi*frequency;
Eac = Eac0*sin(omega*t);

E = Edc +E_drift*(1-exp(-b*(t+time_from_start)))+Eac;

k1 = k10 * exp(b1*E);
k2 = k20 * exp(b2*E);

dTheta(1) = k1/Gamma - (k1+k2) .* Theta(1)/Gamma;
end
```

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

$$M_{ads}^{+} \xrightarrow{k_2} M_{sol}^{2+} + e$$

$$\boxed{i_F = F\left[k_1(1-\theta)+k_2\theta\right]}$$

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

So for the integration we have passed on this parameter. We calculate the theta using this equation d theta/dt is given by k1-k1+k2 theta yeah this is correct okay and this has be divided by gamma value. Only thing we need to remember is E value do not write it as Edc+ Eac instead remember to write that this is a function of time given by E drift E delta 1- E power bt.

But this here the t is time from start and time from start+ whatever time we are using in the integration. So if you want you can note this down. So it is not just taking the formula and applying directly and using E power – bt you had to recognize that when you are applying some perturbation you might have applied some perturbations before and that would have taken time.

So the dc potential has changed and in addition you are changing when you are applying the sinusoidal potential and measuring that time also that dc baseline is not constant it is changing.

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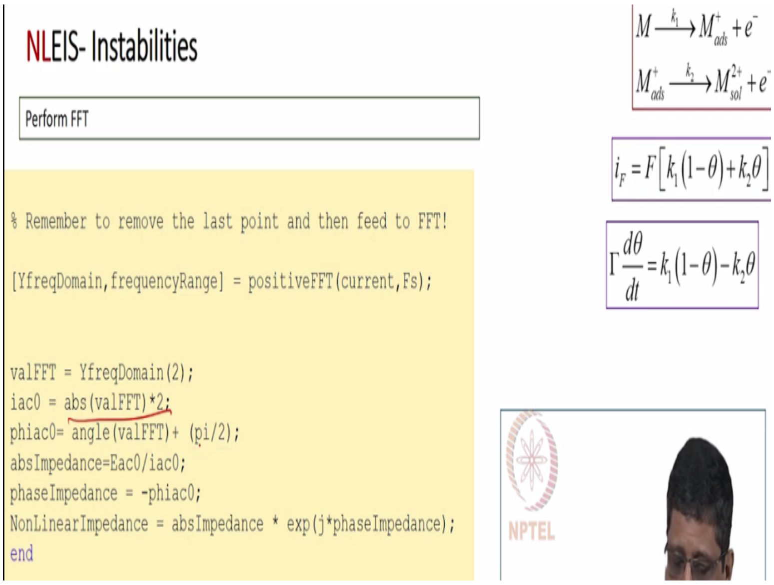

NLEIS- Instabilities

Perform FFT

```
% Remember to remove the last point and then feed to FFT!

[YfreqDomain,frequencyRange] = positiveFFT(current,Fs);


valFFT = YfreqDomain(2);
iac0 = abs(valFFT)*2;
phiac0= angle(valFFT)+ (pi/2);
absImpedance=Eac0/iac0;
phaseImpedance = -phiac0;
NonLinearImpedance = absImpedance * exp(j*phaseImpedance);
end
```

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

$$M^+_{ads} \xrightarrow{k_2} M^{2+}_{sol} + e^-$$

$$i_F = F\left[k_1(1-\theta)+k_2\theta\right]$$

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

And at the end of course we have seen this you can do the Fourier transform measure the value iac0, measure the value of iac0 you are multiplying by 2 as usual adding pi/2 for the phase you can calculate. So essentially what we are doing is mimicking what the instrument would do. In the equipment if you say that measure the open circuit potential and then apply a bias of certain voltage above or below the open circuit potential.

The instrument will still regulate that potential with respect to the reference electrode just before starting the experiment you can ask here to measure the open circuit potential so (()) (26:23) 0.2 volts with respect to reference and then if you say 0.5 volts with respect to open circuit potential it would apply 0.5 volts+ 0.2 volts so it will apply 0.7 volts with respect to reference electrode.

But it does not monitor how the open circuit potential changes with time or whether it is remaining constant or not. So you will get results which would be given by this if the potential was drifting. So if you take the system and monitor the open circuit potential and you find that it is changing with time and it does not settle quickly and you want to do impedance experiments before it settles.

Then the instrument would give you results which are given by this core provider this is the mechanism and these are the kinetic parameter.

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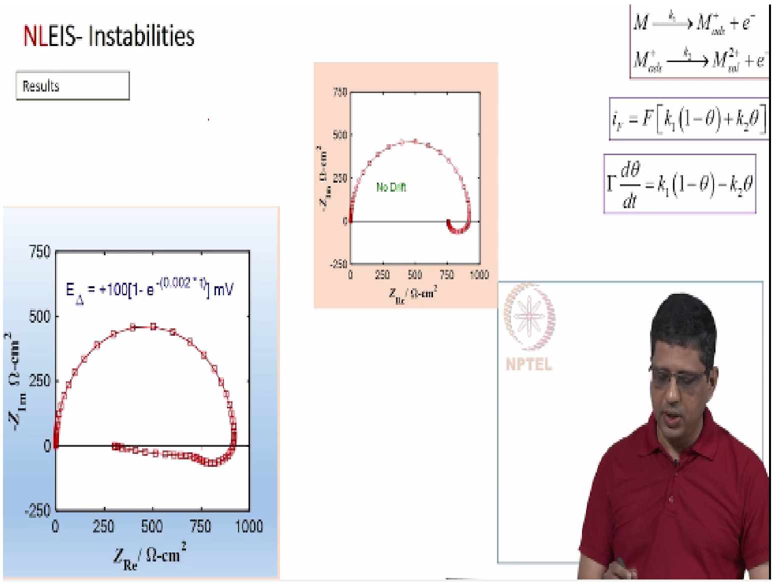

NLEIS- Instabilities

Results

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

$M^+_{ads} \xrightarrow{k_2} M^{2+}_{sol} + e^-$

$i_F = F\left[k_1(1-\theta)+k_2\theta\right]$

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

So in this case for a set of kinetic parameters which we saw before if there is no drift what you get will be a high frequency semi circle and a low frequency inductive loop, high frequency capacitive loop and a low frequency inductive loop. If I have exponential change in dc offset given by this number 0.002 second inverse and 100 millivolt+ 100 millivolt instead of settling here it will drift. So it will appear like a capacitive loop and inductive loop and sort of an inductive loop.

It is not really a clear inductive loop but it looks like it is another loop here. So this mean open circuit potential decreases with time and it can eventually settle at 100 millivolt less than what it started at. It is also possible with a open circuit potential will increase with time which means the dc potential versus OCP is going to decrease dc bias versus OCP is going to decrease and you can do the simulation with – 100 millivolt.

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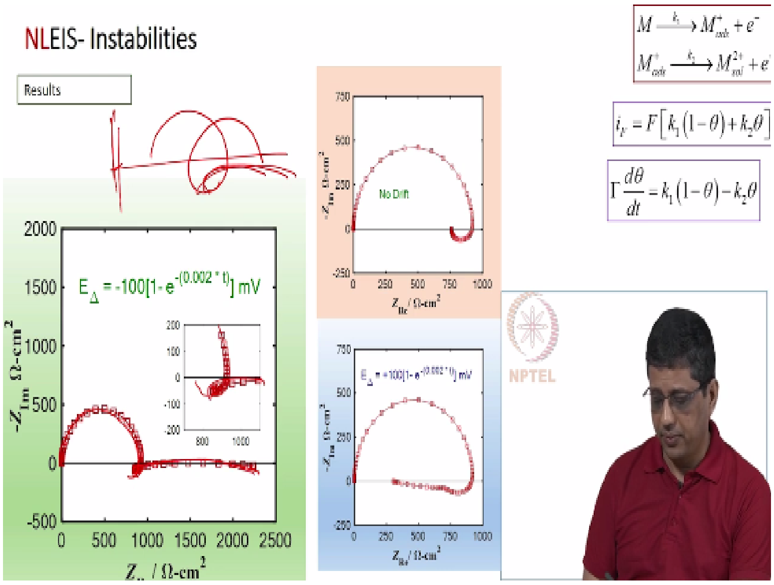

NLEIS- Instabilities

Results

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

$M^+_{ads} \xrightarrow{k_2} M^{2+}_{sol} + e^-$

$i_F = F\left[k_1(1-\theta) + k_2\theta\right]$

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

And what you get is a capacitive loop and inductive loop which does not complete instead it turns and goes like a very large or push down capacitive loop so it is not as clean as coming here and coming like this looks like this and from here it is still below that x axis, but it is a very gentle curve. Again if we see something like this of course you will have to do the other (()) (29:17).

If you see something like this you cannot always assume that it is because of drift, but you should not come to a conclusion that this means there is one more capacitive loop that this is specifying the charge transfer resistance in parallel with double layer capacitance. This inductive loop means there is a adsorbed intermediate. If this is the capacitive loop that would mean there is one more adsorbed intermediate.

Whereas we know the mechanism phase there is only one adsorbed intermediate. So you cannot come to that conclusion. You cannot also come to the conclusion that this is necessarily due to drift unless you do what unless you do KKT validation. Okay if you do KKT validation all the spectrum which arise with instability effects or which are coming from system which are not stable will be flagged correctly.

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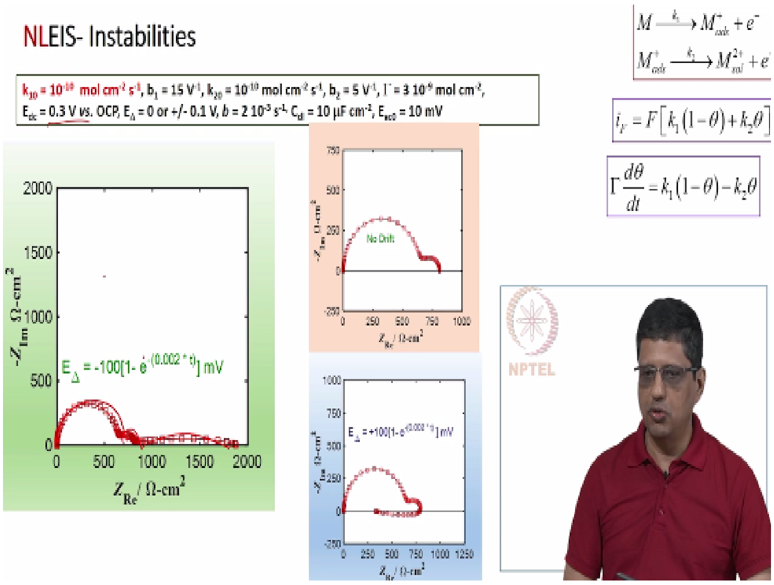

NLEIS- Instabilities

$k_{10} = 10^{-10}$ mol cm^{-2} s^{-1}, $b_1 = 15$ V^{-1}, $k_{20} = 10^{-10}$ mol cm^{-2} s^{-1}, $b_2 = 5$ V^{-1}, $\Gamma = 3\ 10^{-9}$ mol cm^{-2},
$E_{dc} = 0.3$ V vs. OCP, $E_{\Delta} = 0$ or +/- 0.1 V, $b = 2\ 10^{-3}$ s^{-1}, $C_{dl} = 10$ μF cm^{-2}, $E_{ac0} = 10$ mV

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

$$M^{+}_{ads} \xrightarrow{k_2} M^{2+}_{sol} + e^{-}$$

$$i_F = F\left[k_1(1-\theta) + k_2\theta\right]$$

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

So if we change the kinetic parameter values for example same mechanism just a slight change in the kinetic parameter value maybe a different reaction, different concentration of chemical, different dc potential potentially. No drift iac 2 capacitive loops. So same mechanism just change in kinetic parameter values of course you know you can get inductive loop or a capacitive loop because you have an adsorbed intermediate.

No drift I have 2 capacitive loop this of course comes from charge transfer resistance and double layer capacitance. This comes from the adsorbed intermediate species. Of course here I have simulated with 10 millivolts but you can also simulate with 100 millivolt the methodology, numerical methodology does not require that this perturbation potential has to be small it can be large.

And similarly you can get the second and third harmonics and other harmonics it is not at all a problem right now we are mimicking experimental measurement of impedance spectrum using normal equipment which may or may not be able to give you higher harmonics data but this method methodology it is pretty straight forward to get the higher harmonics data okay and I am showing this in the non linear EIS section because the code that we use is meant for non linear EIS.

You can use it with small amplitude perturbation and get the response at linear regime okay it is more general compared to what we had done in the earlier classes. The first 10 weeks we have focused on linear traditional EIS. So you cannot take the results there and directly get the results of the large amplitude. Now if there is a drift you can guess how it is going to appear.

It is not going to look like this right. So if there is a drift where the open circuit potential decreases with time that is dc bias versus OCP increases with time we see something similar to an inductive loop not a clean capacitive and inductive loop instead it looks like a distorted inductive loop if you will and if the potential changes negative you can guess it is going to be one loop. second loop and a poor distorted capacitive loop that is one way to look at it.

It is not the correct way but one might interpret it like this if you are not careful okay.

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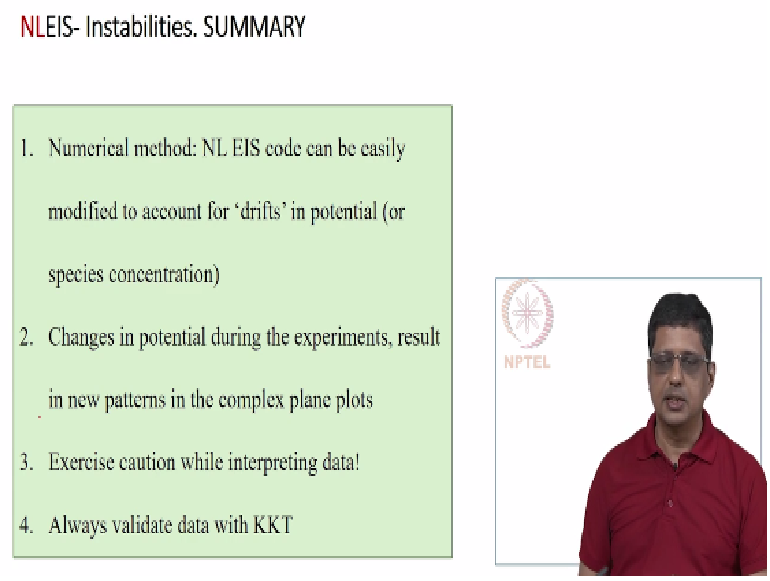

NLEIS- Instabilities. SUMMARY

1. Numerical method: NL EIS code can be easily modified to account for 'drifts' in potential (or species concentration)
2. Changes in potential during the experiments, result in new patterns in the complex plane plots
3. Exercise caution while interpreting data!
4. Always validate data with KKT

So in summary you can use the numerical method and modify and account for changes in potential what you have seen is changes in potential, but I also claim that you can do this for changes in surface areas, you can do it for changes in solution concentration or rate constant by some effect. This change in potential during the experiments results in what appears to be a distortion.

We are not just going to get the same pattern with a slightly larger or smaller value you are going to get at different pattern which can lead to misinterpretation if you are not careful and the right way to handle this is to first validate all the data with KKT and then analyze the data which passes this KKT test if it does not pass KKT test it is better to repeat the experiment and see if you can get stable system.

Wait for sufficient time and do the experiment and if you cannot wait then you might have to do simulation numerical simulation like what we have shown here and then see if it matches with the experimental results and if it does then you will say yeah probably there is a drift. We will stop here today.