Electrochemical Impedance Spectroscopy
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Lecture - 48
Solution Resistance Effects

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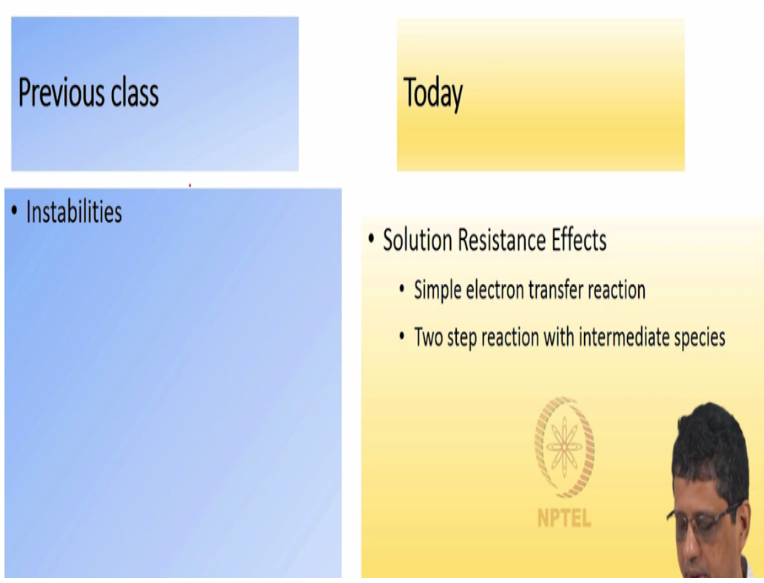

So in the previous class we have seen how to handle instabilities specifically when potential when the dc potential changes with time okay. Today I want to show you how we can handle solution resistance effect especially potentiostatic measurements okay. Earlier we have seen in galvanostatic measurements, solution resistance effects are easy to handle okay. Now we want to look how in case of potentiostatic measurements we can handle the situation okay.

So I want to show 2 examples. One is for a simple electron transfer reaction and second is for a two step reaction with intermediate adsorbed species okay and we will also go through an example code for this.

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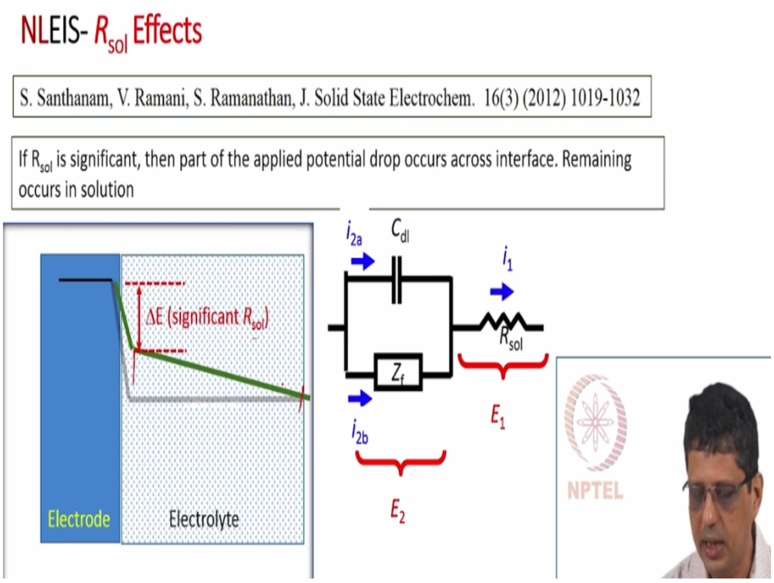

So some of this work we have published in 2012 this is a schematic, illustrating how the potential drops occurs this electrode, electrolyte interface if we have negligible solution resistance we can say that all the potential drop occurs across the interface and then we can model this with a circuit given here that is double layer capacitance being parallel with the faradaic impedance.

In case the solution resistance is significant then part of the applied potential occurs across the solution and part of the applied potential occurs across the interface. So you can say that the same potential drop as you measure or as you apply occurs but then only part of it occurs at the interface this del E in case of significant R solution the remaining potential drop occurs across the solution.

So we have to use a slightly different circuit which is to add this R solution to this schematic or to this equivalent circuit representation. So when we have this what are the governing equations.

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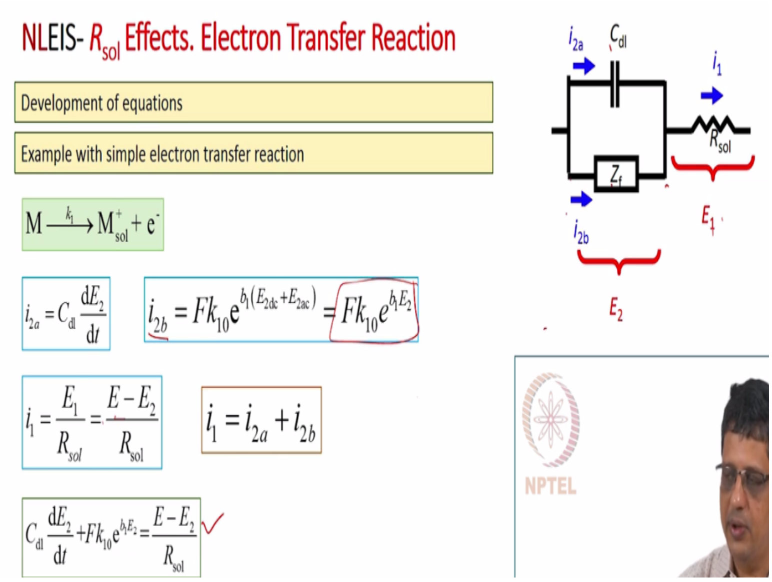

In case of a simple electron transfer reaction metal dissolving into a solution with a release of an electron. The current through this double layer capacitance is represented as i2a current through this faradaic impedance is represented by i2b. And of course the current through the solution resistance is given as i1 okay across the double layer capacitance the current is given by capacitance multiplied by dE/dt which is rate of change of potential with respect to time and for the faradaic impedance we know how to relate this current to the potential.

In general, we would write it as E in this case we would write it as Edc+ Eac but that is only E occurring across this interface. So we call this part as E2 we call this potential we call this potential drop as E1 and the sum of E1 and E2 is what we apply. In this case this is more general representation and this is we represent this as dc+ ac, but we do not mean that all the time that ac is a sinusoidal. Dc is the average value ac is any value that is fluctuating.

So if we measure E2 it might be sinusoidal it might be another periodic pattern. We will say that this is E this is t. The average value is what we would take as dc and the value that is fluctuating we would call that as ac and then of course we have to employ Fourier transform to calculate what is the response of fundamental, what is the response of other harmonics etcetera.

Now the i1 can be related to the E1. We are seeing the simple expression E1/R solution is i1. E1 I can write it as E that is the applied potential- the potential drop across this interface. So whatever current that comes through the double layer and that comes through the faradaic process that sum of this algebraic sum of this should be= current that is passing through the solution.

So we can write i1 as i2a+ i2b. We have an expression for i1 written in terms of E2. We have an expression for i2a written in terms of E2 expression for i2b written in terms of E2. So we can put them together we have a ordinary differential equation incorporating the solution resistance effect we know E we control E we do not know E2 we have to find the E2 value, we have to find the E1 value so that we can estimate the i1 value i1 is the current that measure okay.

So we basically apply a dc bias and estimate the potential drop across the interface. We can only estimate we cannot measure it in the experiments. If we can minimize a solution resistance, we would just minimize it or eliminate it and then measure only the potential drop across the interface or control the potential drop across the interface. Since we cannot do that for whatever reason we have to estimate it.

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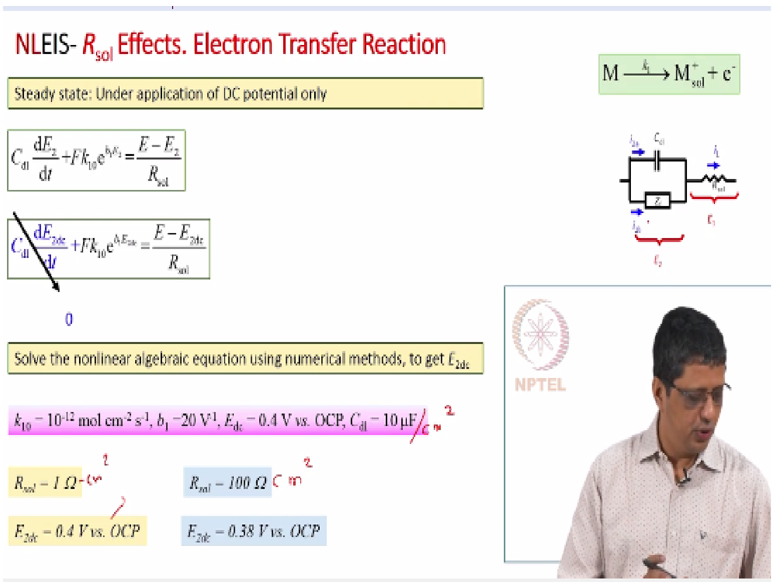

So if I apply dc potential and do not apply any ac potential that means E1 is going to be constant. Constant meaning it is going to be invariant with respect to time E2 is going to be constant. We can say that this goes to 0 dE1/dt goes to 0 and the remaining terms can be solved numerically it is an algebraic equation non linear algebraic equation, but you can solve this and get the value for E2 dc.

So it is a non linear algebraic equation you can use the numerical method to get E2 dc so it is an example. K10 is 10 power -12 moles per centimeter square per second b1 is 20 volts inverse dc potential that we apply is 0.4 volts with respect to OCP and we say that double layer capacitance is 10 microfarad per centimeter square all right and if the solution resistance 1 ohm's centimeter square.

You can solve this I am not showing the code for this but the value of E2 dc is going to be pretty much 0.4 it would not be exactly 0.4 but it will be close to 0.4 that means potential drop most of it occurs across the interface. If I change the solution resistance to 100 ohm's centimeter square about 20 millvolts across the solution resistance 380 millivolts still occurs across the interface.

So make the solution resistance even larger then you would see that more potential drop occurs the solution. Okay for a given case given solution resistance we apply a dc bias and on top of that we apply ac potential right.

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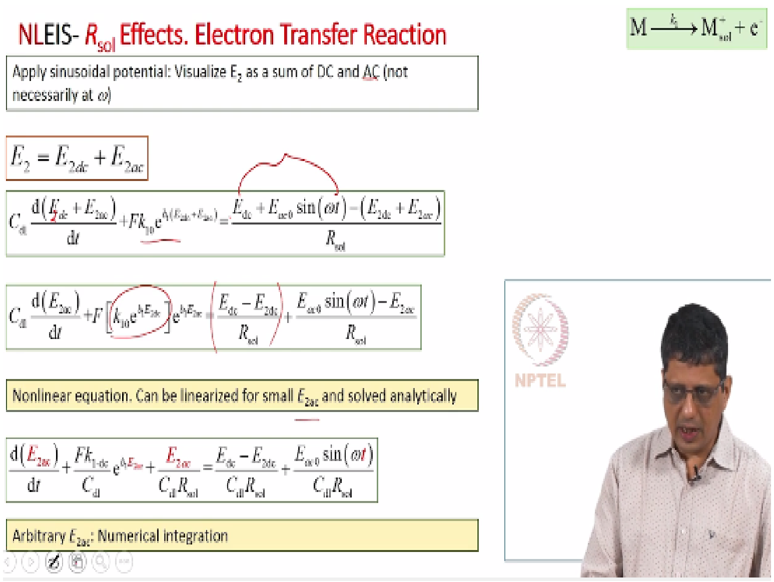

Now we have to visualize the E2 the potential drop across the interface as a sum of dc and ac but here I use the term ac in a loose fashion. It is not necessarily sinusoidal oscillation at frequency of omega. So you can write the equation instead of E2 you can write it as E2 dc+ E2 ac and this is what you would get. This is the potential that we apply a dc bias + an ac potential and that is at sinusoidal frequency omega we control that.

Of course by definition E2 dc does not vary with time therefore that goes away the remaining terms can be grouped k10 b1 E2dc can be written as k1 dc this Edc and E2dc can be grouped here sin omega t and E2ac can be grouped here. It is essentially a non linear differential equation. You can linearize this for a small e2ac and solve it analytically, but practically we want to solve it from the cases where we have large amplitude perturbation so you have to use numerical method.

So if you have an arbitrary value that is possibly a large value of E2ac you have to use numerical integration.

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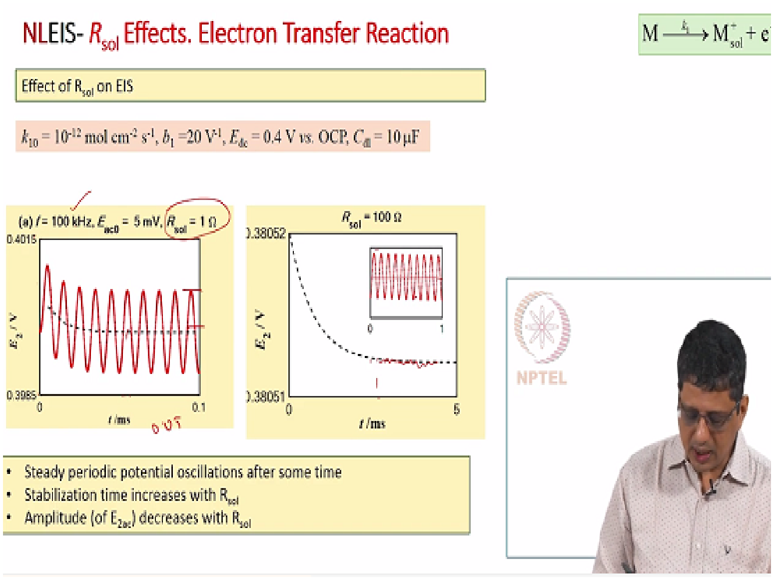

Now for a given set of kinetic parameter right if I apply a frequency of 100 kilohertz for a solution resistance of 1 ohm for a simple electron transfer reaction the potential oscillation stabilize after sometime. Earlier we have seen that when you have adsorbed intermediate the current oscillation will stabilize after sometime right.

Out here even for simple electron transfer reaction if we have a significant solution resistance when you apply a dc potential+ an ac potential you will not get as steady periodic current response right away. It will drift a little and then stabilize after sometime okay. In case of 1 ohm solution resistance it takes maybe 0.05 millisecond to stabilize. In case of 100 volt solution resistance it takes maybe 3 or 4 milliseconds to stabilize for this set of kinetic parameter at this dc potential.

What that means is how long does it take to stabilize depends on kinetic parameter, it depends on dc potential, it also depends on the solution resistance value. It typically increases with solution resistance value and if I have large solution resistance for same set of kinetic parameter that means for the same reaction this magnitude if I just see this 100 kilohertz here as well as 100 kilohertz here.

Although we can write it here it is the same 5 millivolt ac amplitude and 100 kilohertz frequency. This oscillation is going from 0.385 to4015 this goes on 38051 to 38052 it means in fact it much, much smaller than this scale. I just shown you the average and the oscillation are shown in the inset. So when you increase a solution resistance the current oscillations are smaller that is expected also.

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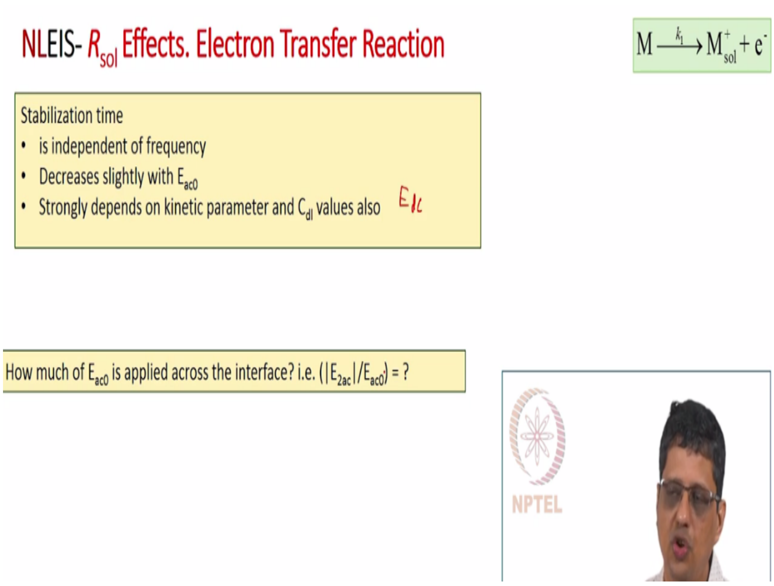

Now how long does it take to stabilize it is independent of frequency. It does vary with Eac 0 and it is strongly depends on the kinetic parameter values, double layer capacitance values and the dc potential at which we acquire the data. Now if I apply an ac potential not all of that falls across the interface a part of it falls across the solution. Now how much of the Eac 0 applied actually falls across the interface.

So if I take the magnitude of E2ac and take the ratio of that magnitude to Eac0 ideally I should get 1 all the potential that we apply should fall across the interface and that will happen only when solution resistance is 0.

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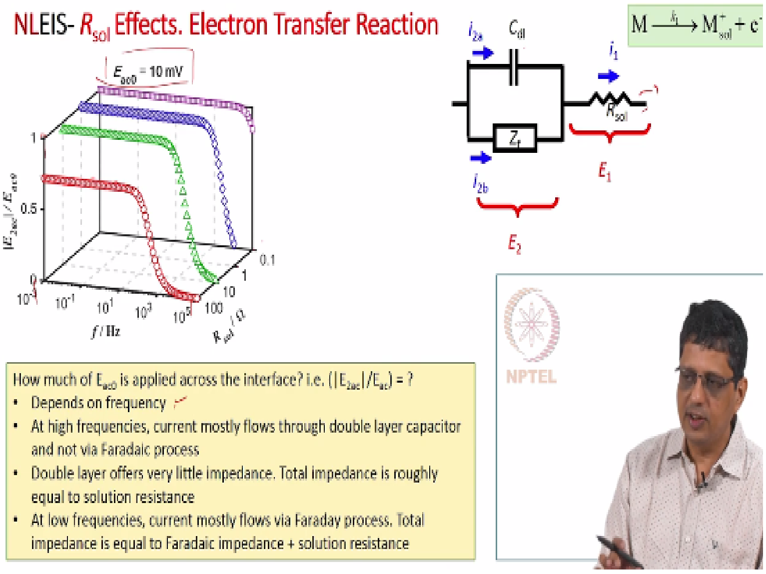

Now we can do the calculation for a variety of solution resistance values and for various frequencies okay for one perturbation amplitude 10 millivolt this is what we see. At low frequencies it is more independent after frequency at high frequency it is very small and at intermediate frequency of course it falls from high value to a low value and ideal value is of course 1. When solution resistance is small pretty across this frequency region it is more or less 1.

When solution resistance increase less and less applied potentials falls across the interface and more of it falls across the solutions. So what fractions of it occurs across the interface that depends on the frequency. At high frequencies what happens is this pretty much all the current goes through the double layer capacitance because if offers negligible impedance. When this impedance is negligible.

And this is anyway a finite number you can say total impedance is more or less solution resistance that means more or less all the applied potential will fall across the solution resistance. When you go to low frequencies this double layer capacitance offers very large impedance. So most of the current will flow through this faradaic process. Faradaic process of course the impedance value depends on the kinetic parameter, depends on the mechanism, depends on the dc potential dc bias.

And this is comparable or larger than this you would see most of the potential drop across the interface. So that is why at low frequencies more of this applied potential falls across the interface at high frequencies it mostly falls across the solution.

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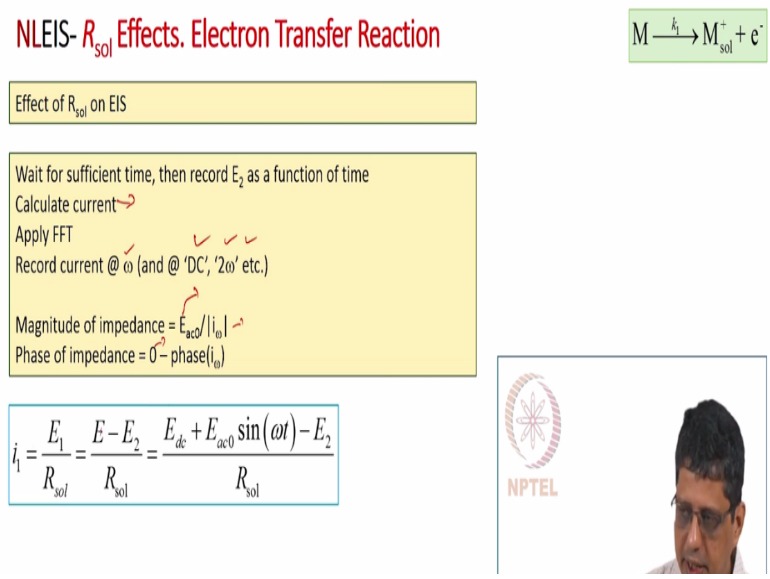

So the way we do this is apply a ac potential wait for some time to get steady periodic response and then in simulations we can record E2 as a function of time. Once you record E2 you can calculate E1 and then calculate the i1 that is basically calculate the current and then apply Fourier Transform mark the current at omega fundamental as well as at 2 omega, 3 omega dc any other frequency you want you can calculate that and record that.

You can calculate the magnitude of impedance as Eac0/I omega here meaning that current at the fundamental omega and the phase of course 0-0 is for the potential. This is the phase of I omega you can calculate the impedance. This essentially source the equation relating E2 to the i1.

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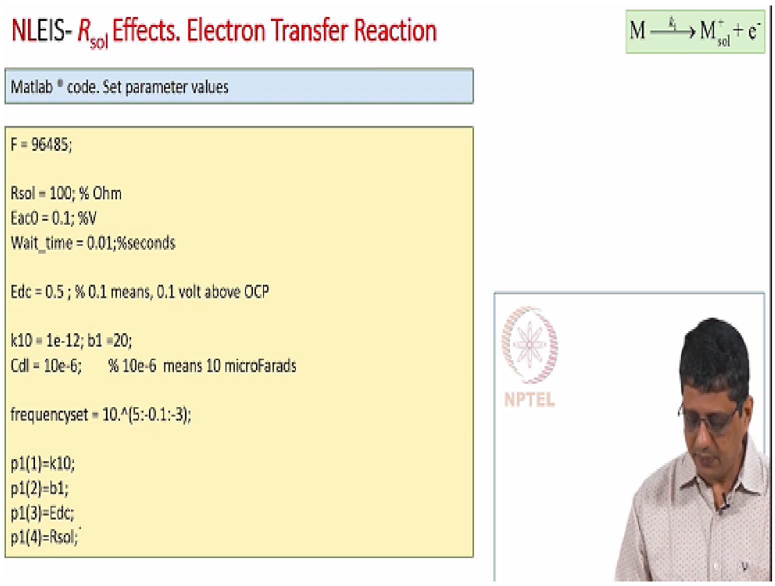

So as an example 100 ohm solution resistance Eac0 is 100 millivolt you can say (()) (15:51) is 10 milliseconds we apply a dc potential we set the kinetic parameters values and set the frequency range. We want to pass the kinetic parameter values as vector.

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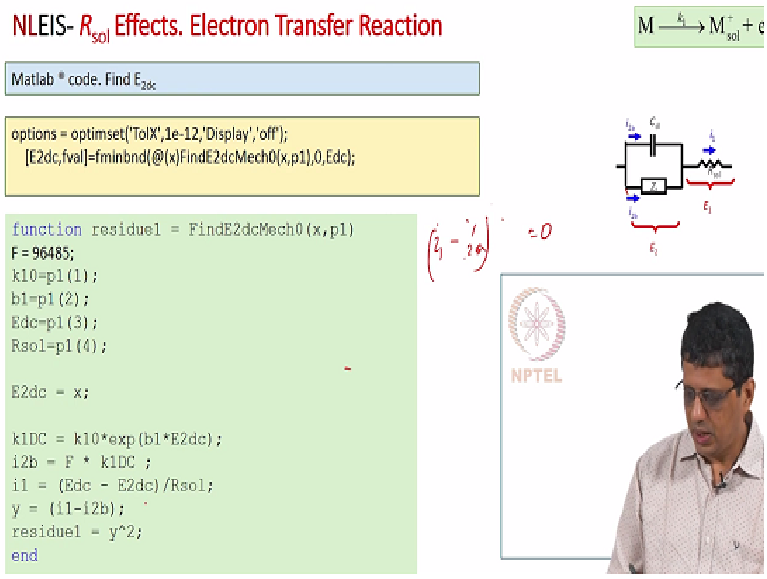

And then first find the dc potential occurring across this interface and we need to give that as the initial value for the integration okay. So in this case I have used the function called fminbnd. So essentially what we do is to take the dc equation which is i1-i2a-i2b=0. I1 is Edc-E2dc/R solution i1b faradaic current is F k1DC and i2a is 0 because when you apply dc potential no current passes through the double layer capacitance.

Ideally this should be 0 i2b so numerically we want to calculate the residual and then take the square of that, that should become 0 or minimum here.

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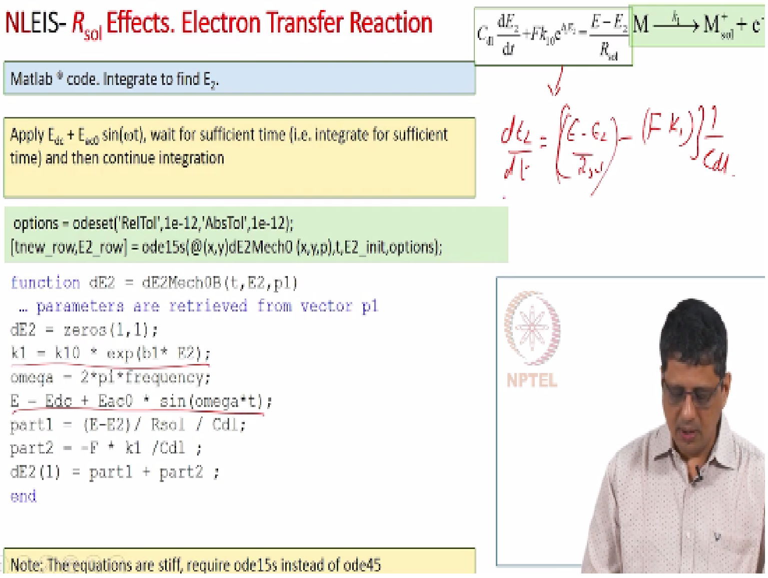

And once you find the E2dc use that as initial value and you have integrate this equation which is basically take this equation rearrange as d E2/dt as E- E2/R solution- F k1 the entire thing/Cdl. So we take the parameter we need to use ode15s because it is a stiff equation we find the value of k1, we write the value of E the first part we write it as E-E2/R solution/Cdl second part we write it as F k1/Cdl and this is the derivative.

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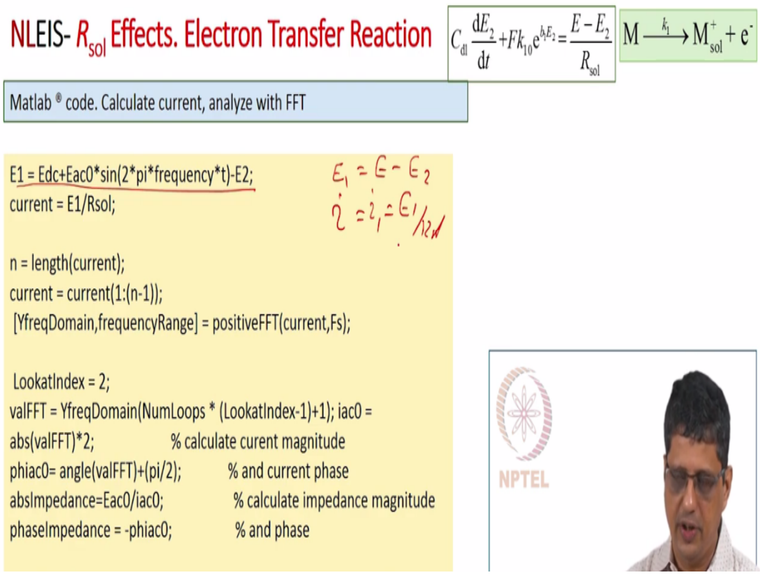

And after you integrate this you can estimate the value of E1 saying E1 is E- E2 current of course is I that is-i1 E1/R solution and then the standard procedure of applying Fourier Transform. So we calculate the impedance at 1 frequency if we repeat it for n number of frequencies we can get the spectral.

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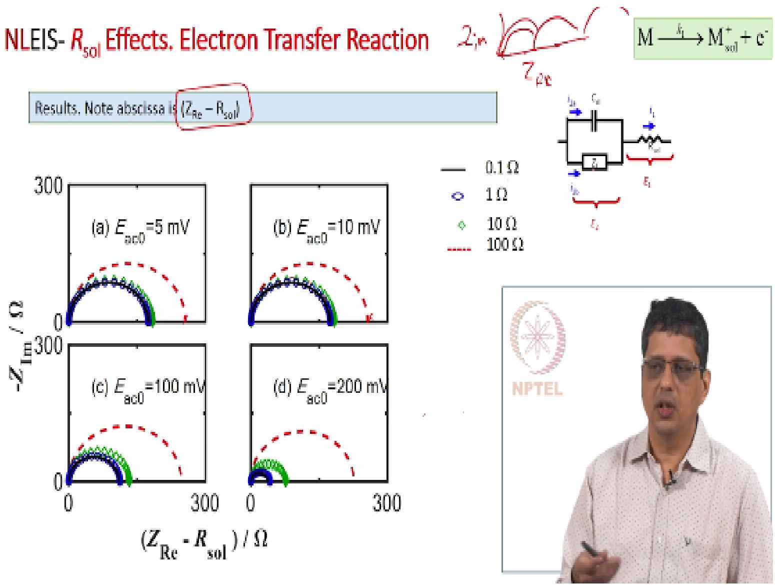

So when you plot it I can vary the R solution I have tried 0.1 ohm centimeter square after that 1 ohm, 10 ohm, 100 ohm actually this should be ohm centimeter square all right. When we plot normally we will plot –z imaginary/z real that means 0.1 ohm would probably would start here 1 ohm would start somewhere here 10 ohm would be much later. 100 ohm is going to be much, much later. In order to compare that what I have done is after calculating all the impedance values I have subtracted the R solution and then plot it that in the abscissa.

Ordinate of course I keep –z imaginary. So what you see is the following you can calculate this for small or large amplitude perturbation using this methodology and you can calculate it for small solution resistance or a large solution resistance value. Now when I increase the solution resistance value obviously the measured impedance increases. What that means is if I have a low solution resistance I have a spectrum like this if I have a large solution resistance.

In the beginning we said it is just going to shift to the right that is correct when you have an electrical circuit. When you have a reacting system it is not just going to shift to the right it is also going to change in magnitude. It is showing an increase here it may not always be an increase. So what it means if solution resistance is not just going to shift the impedance spectrum it is also going to make changes to the values other than just adding R solution.

But then it takes quite some time to do the integration and get the results and it has to be done pretty much by numerical methods for most of the reactions. There may be 1 or 2 exceptions but by and large you will have to use numerical methods which means give a set of kinetic parameters, given a solution resistance value to generate the spectrum if we have an analytical expression in a computer.

We can generate that in a second may be much less than that. If we use the numerical method, it will take probably half an hour or so. So if you want to change the parameter and optimize it is not practical to do in this method. This is the right method but it is very time consuming. So what we end up doing is we generate the spectrum assuming that the solution resistance is negligible and then add the solution resistance.

Although we know that is not the best way practically that is probably the only way we can do right now. If you are able to get an analytical expression, then we can use the correct expression or if we get faster code or faster computer maybe we can try that.

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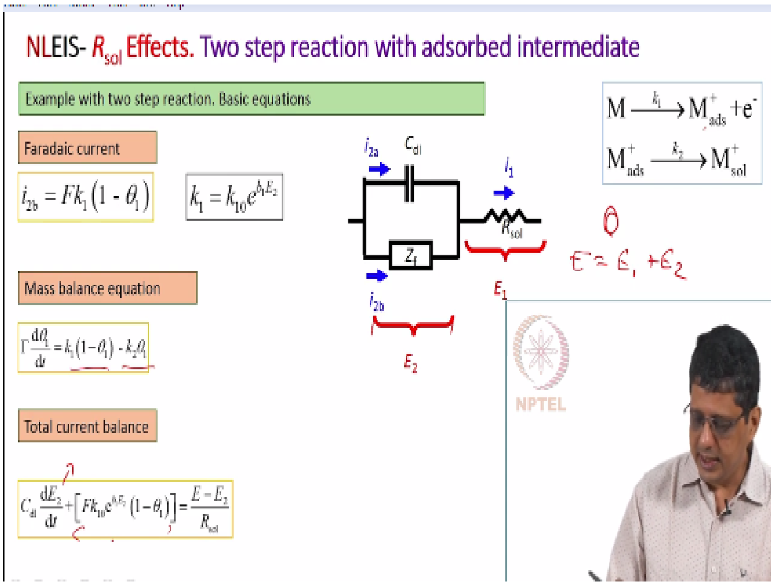

Now what happens when you have an intermediate species it is an example two step reaction with an adsorbed intermediate. So the same electrical circuit equivalent circuit the faradaic current I would write it as F k1 1-theta for this theta is the fractional surface coverage of the adsorbed intermediate and k1 is related to the potential as k10 b1 E2 it is not k10 b1E. Mass balance equation of course we are seeing this before it is gamma d theta 1/dt.

The first step forms theta second step removes theta so we have k1 and – k2 and the total current i2a+ i2b is i1. So earlier we have written this i2a as Cdl de2/dt we have written that. The second expression because the reaction is different here it is going to F k11-theta and on the right hand side of course i1 is related to the E1 as E-E2/R solution. Now you can understand you can write the dc expression for this solve it get the steady state value.

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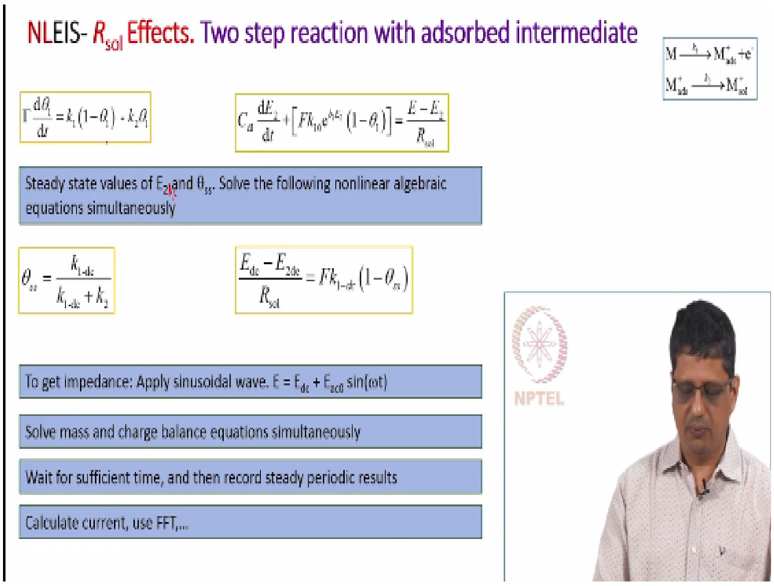

In order to get the steady state value, we say this goes to 0, this goes to 0. We have 2 equations here k1 depends on e2dc. So we have 2 equations to our notes we do not know E2dc and we do not know steady state value of theta. You can solve this. These are 2 algebraic equation non linear equation, but you can solve them and then get the values of E2dc and theta ss use that as the starting point or initial value and integrate these 2 equation simultaneously.

So we have independent value as time we have E2 and theta 1 as the dependent variable. We have theta ss and E2dc as the initial points. So we have to charge mass and charge balance equation simultaneously. Again you have to see how long it takes for it to stabilize wait for sufficient time and then takes steady periodic results and record you get a value of E2 as a function of time theta as a function of time.

We need only E2 to calculate E1 and we need only E1 to calculate current we do not need to use the theta, but we will have to integrate them together to get the value of E2 and then we go through the same procedure right get the current value apply FFT get the ratio of potential to current with the impedance.

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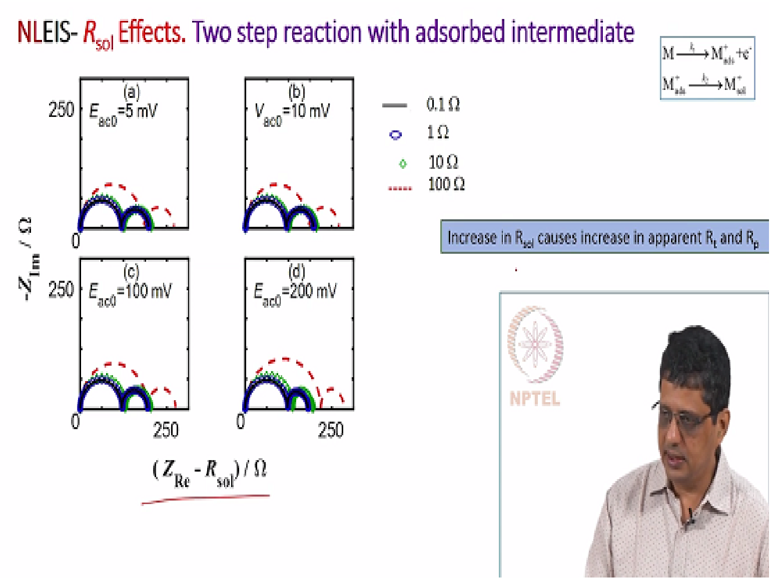

I am not showing you the code I am just showing you the final results this case for this given set of kinetic parameter you get 2 capacitive loops. When you change the solution resistance here it increases, but I also want you to note the following. I have plot a different perturbation amplitude here you can replot it for a given solution resistance different amplitudes and in all cases we have plotted real part of impedance after subtracting the solution resistance.

Now increase in R solution causes an increase in the apparent value of Rt and Rp at any potential amplitude.

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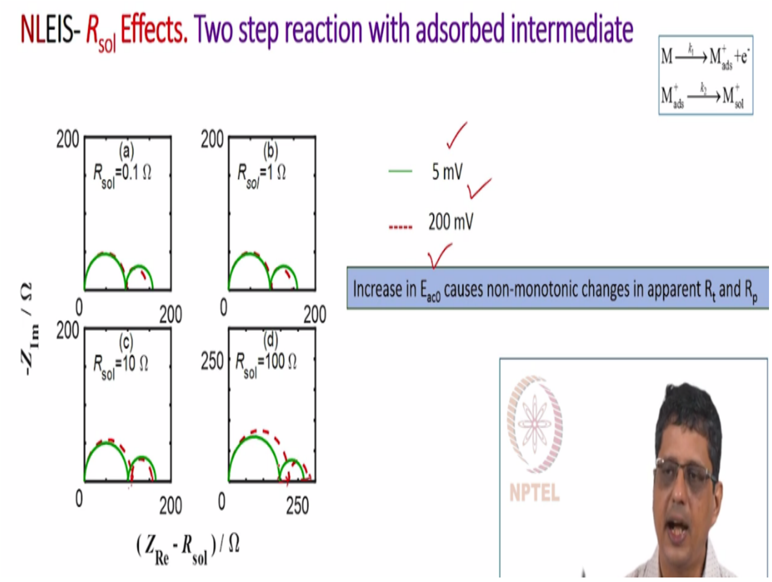

Now if I fix the solution resistance and replot that so that I plot only 5 millivolt and 200 millivolt ac you can also plot the intermediate ones, but this is sufficient to illustrate. When you look here when I increase the ac potential perturbation charge transfer resistance seems to increase for this. Polarization resistance seem to decrease. At 100 ohm charge transfer resistance increases polarization resistance increases.

So what that means is when you change the solution resistance, when you go to large amplitude perturbation you do not always have a monotonic trend okay. Increase in Eac0 causes non monotonic changes in apparent Rt and Rp values. Some cases it looks like it is more or less same some cases it looks like increases some cases it may show a decrease, but it will cause a change.

All that it means is you cannot just take a solution resistance and add it at the end.

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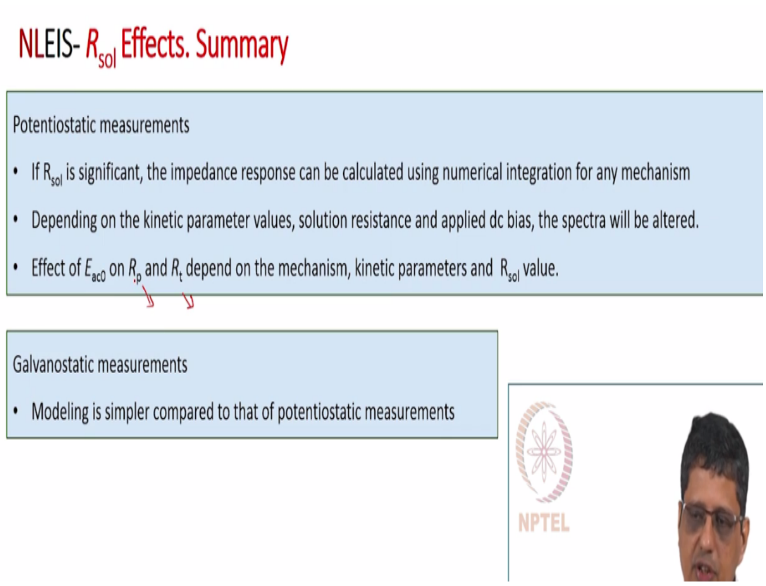

So all this is done for n potentiostatic measurements right. When solution resistance is significant you can calculate the impedance response using numerical method. You have to use integration for pretty much any mechanism and depending on the dc bias, depending on the kinetic parameter values, depending on the mechanism, depending on the solution resistance the measured spectrum or simulated spectrum will change.

And it is not always monotonic change even for the limiting values of polarization resistance and charge transfer resistance. Whether it is linear or non linear regime (()) (27:34) it does not matter you cannot say that it is going to be monotonic okay. We have seen earlier that in case of galvanostatic measurement it is actually lot easier or simpler to model this you have to just model the interface and add the solution resistance a bit late.

So it is lot easier than doing it in the n potentiostatic measurement when we talk about simulations. In terms of experimental measurements there is no extra difficultly incorporating solution resistance effect. In fact, is harder to reduce a solution resistance in some cases okay. We will stop here today.