Electrochemical Impedance Spectroscopy
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Lecture - 44
Two Step Reaction (Continued)

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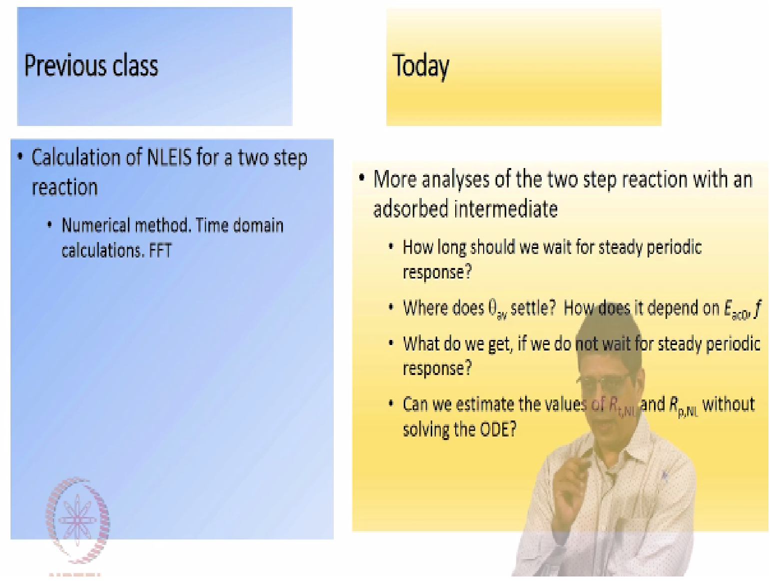

So last time we saw how we can calculate the nonlinear impedance for a reaction, two-step reaction with one adsorbed intermediate, at that time we saw that when you apply a sinusoidal potential it takes some time for the response to stabilize, that means when we apply the sinusoidal potential the current and the fractional surface coverage of the intermediate species, both of them they do not immediately give you a steady periodic result instead they will have a drift or change in the average value.

It will go for example like this, it may go like this, we have seen one example, it will change and then after sometime it will give steady periodic result, the average value of that fractional surface coverage or the average value of the current they will be different than the initial steady state value. So what I want to discuss today is how long should we wait, can we estimate it or do we have any idea on how it depends on the parameters such as the frequency or the amplitude.

Second, the average surface coverage it settles at value which is different from the steady state value. So when we apply only Edc, we get theta SS, when we apply Edc + Eac the theta has a sinusoidal oscillation after stabilization that average value of theta is not theta SS okay, we call it as theta average. Just to differentiate that from theta SS and where will it settle, how does it depend on the amplitude? how does it depend on the frequency?

Third, what if I do not wait long enough. In the simulations I have an idea okay. I can calculate and then say you wait for this much time; it will give you steady period result. In the experiment we usually take a system, run the experiment, we validate with KKT, if you do not wait for sufficient time before we take the data. Then the spectra we get is going to be different than the one we would get under steady periodic result.

So what happens when we get this, can we identify it? Can we identify and say we are taking data when it is not settled yet, when the current period oscillations have not settled yet. Nect without going through this entire simulation process can we estimate the value of at least few parameters, one is charge transfer resistance under nonlinear conditions, another is polarization resistance under nonlinear conditions without solving the ordinary differential equation.

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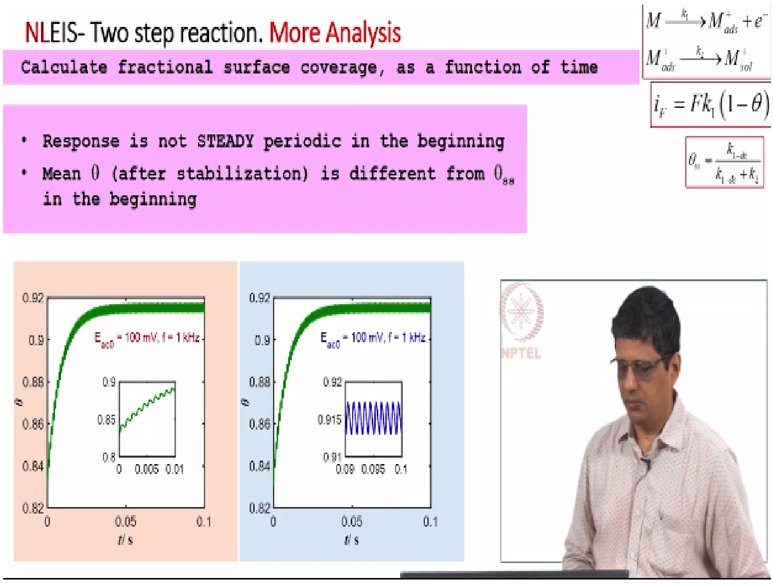

First just to refresh your memory for particular set of parameters and frequency and amplitude initially it oscillates, but the average value is not independent of time, it changes with time, after sometime when I go to in this case 0.09 to 0.1 second that is 90 to 100 milliseconds, it is more or less stable okay. So mean theta or theta average after stabilization and that is different from the initial value, initial value somewhere between 0.82 to 0.84 and the final value in this case this is closed to 0.91 or so.

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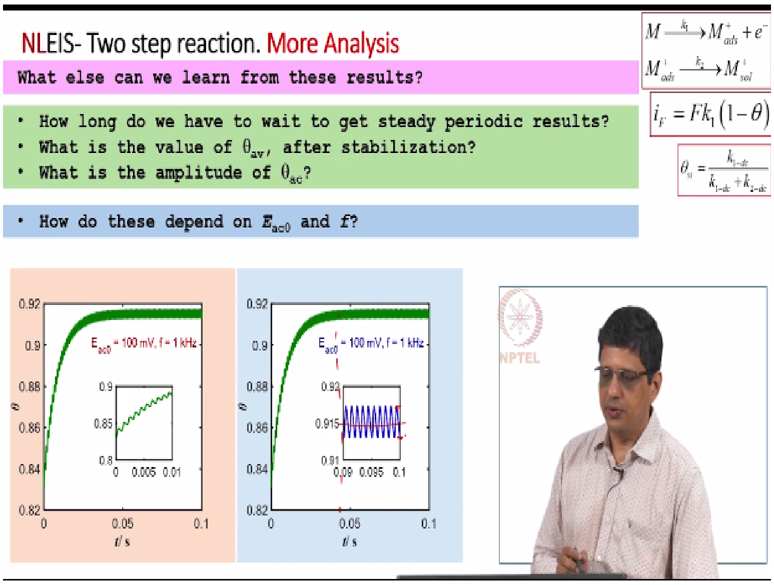

So what else can we learn from this? What I am going to describe to you is basically an empirical evidence that is we have done simulation for a variety of parameters, we have done simulations for variety of mechanisms. I am illustrating one set of parameters for one mechanism, but I would ask you to trust that it work similarly for other cases also okay. How long do we have to wait to get steady periodic results.

So in this case one can say 0.05 is good enough maybe 0.04, what is the value of theta average and how does the theta ac that is the amplitude here how does that vary and how do they depend on the 2 parameters that we control Eac 0 and f. Of course it also depends on the reaction, it depends on the DC potential, but at a given DC potential for a given reaction system they are going to vary frequency and the pertubation amplitude.

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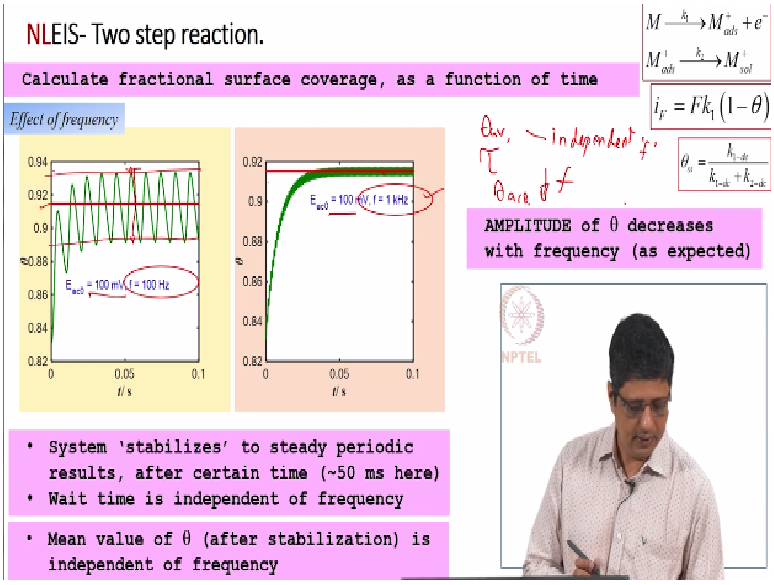

So here there are couple of examples, one, for the same system, same DC potential, same AC perturbation amplitude, I have shown one example with one kilohertz, another example with 100 hertz, both cases you can see 0.05 maybe 0.03, it would settle, that is the time it requires for giving a study periodic oscillation that is not strongly dependent on the frequency. So what it means is if I apply sinusoidal potential and as the instrument to wait for some time and then acquire data that will be correct.

If I ask it to give few cycles, 5 cycles and then take data that will not be correct at low frequencies it could wait unnecessarily long time, at high frequencies it will not wait long enough. So it should not be number of cycles that one needs to wait, it actually is the time duration that one needs to wait before it goes to study periodic result okay. So sometimes the equipment will give you or the software will give you an option.

Wait for certain time and then take data or wait for certain number of cycles and then take data. It is better to choose wait for some time and then of course assume that we are giving enough time okay, if we give too much time then you are wasting time, we do not have to wait for that long to take the data. If you give too little, then basically our results will not be in the steady periodic region.

But if you give for certain number of cycles that will be inappropriate. So in this case system stabilizers to study periodic results after certain time approximately 50 milliseconds and wait time is basically independent of frequency. The average value that we get is more or less same, if we just view it and then have to eyeball it you would say it is somewhere 0.915 is the theta average.

So for a given AC perturbation amplitude if we change the frequency it does not change the average value of theta, it does not change the time it takes for stabilization. However, notice that the amplitude here is half of the peak to peak value and the amplitude here is significantly smaller. Amplitude here it goes for example I can say it goes from 0.89 to 0.93 very roughly.

Here it says between 0.91 to 0.92, peak to peak value is much much smaller compared to this. So lower frequencies, the amplitude is more, that is to say the amplitude of theta that is theta ac0, it if write it as theta ac0 sin omega t, assuming it is a sinusoidal wave or assuming I can fit it to a sinusoidal wave, that decreases as expected. So basically what it means is if I give high frequency then the fraction of surface coverage cannot keep up with the changes in potential.

If I give low frequency potential change, low frequency sinusoidal wave then the rate constant changes slowly, the fractional surface coverage can keep up with that. So essentially theta average time required for settling these are independent of frequency. Theta ac0 decreases with frequency. So higher frequency it will be smaller amplitude. Of course this is on one case, but it basically works similarly for pretty much all the cases.

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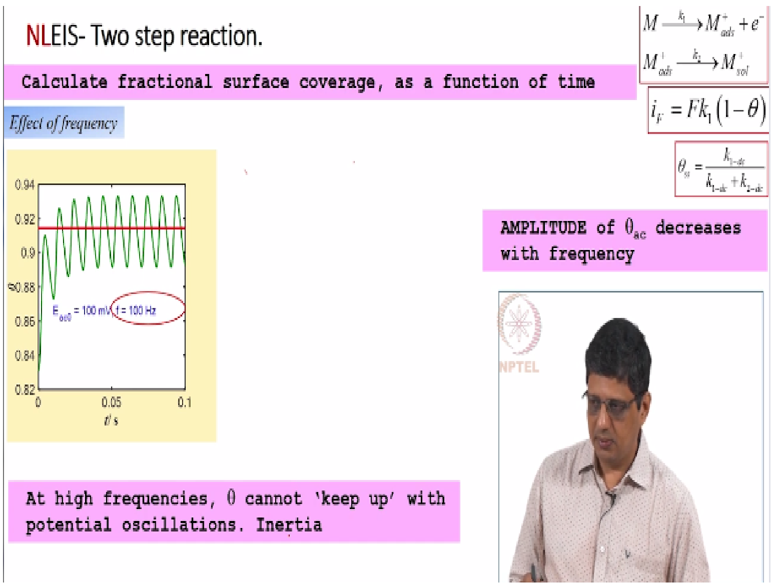

Now I would like you to look at this, we can write theta as theta average + theta ac where ac does not necessarily mean it is one sinusoidal wave it could be written in Fourier series with theta 1 sin omega T, theta 2 sin 2 omega T et cetera and approximately I can write it as d theta/dE Eac 0 sin omega T provided the higher harmonics are negligible. We have done this in linearization.

And when we have used this linearization we have derived that d theta/dE can be written as for this particular mechanism can be written as b1 K1dc 1 – theta ss/K1dc + K2 + j omega gamma. What this means is if I increase the omega d theta/dE the magnitude of that will decrease that is increase in frequency will decrease d theta/dE and that is actually going into the coefficient of this sin omega T.

This essentially is at least on the linear conditions you can see theta ac = theta 1 sin omega T and theta ac 0 is going to be = d theta/dE Eac 0 for a given perturbation amplitude if we change frequency d theta/dE will decrease. So essentially at high frequencies theta oscillations cannot keep up with the potential oscillations.

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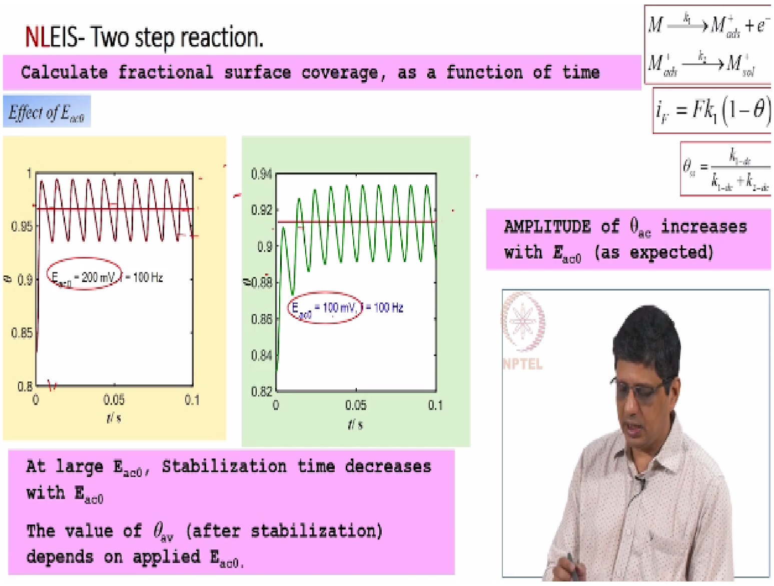

Now what happens if we change the Eac0, amplitude of pertubation. Going from 100 millivolts 200 millivolts, we maintain the same frequency of 100 Hertz. First thing to notice, this takes certain time to stabilize. This stabilizes much earlier okay. Second, in this example this settles at somewhere at around 0.91, this settles somewhere maybe 0.96, 0.97 in that region.

Third, the oscillations, it goes from maybe 0.94 to almost 1, let us say 0.99. This goes from 0.89, 0.93, so about 0.04 units here this is 0.05 units, maybe little more. So the amplitude increases with Eac 0. This works generally may not be always true. It may saturate at some level if average value of theta is close to 1, then theta cannot exceed 1 anyway. So by increasing the amplitude one may not expect that theta ac 0 would always increase.

It would increase it might saturate under certain conditions, but in general I expect that if I give a larger amplitude sinusoidal pertubation in potential, I would get a larger amplitude in theta oscillations. Stabilization time clearly decreases, when I go from 100 millivolts to 200 millivolts pertubation. If we go from 10 millivolts to 20 millivolts or 10 millivolts to 5 millivolts it may not change that much.

That means okay, coming back here, the average value depends on the applied Eac0, in this case it is average is around 0.91, this is about 0.96, it does not automatically mean that it will always increase. We have seen examples where it can decrease, some examples where it will increase, so it basically depends on Eac 0, but we cannot say it is monotonic change.

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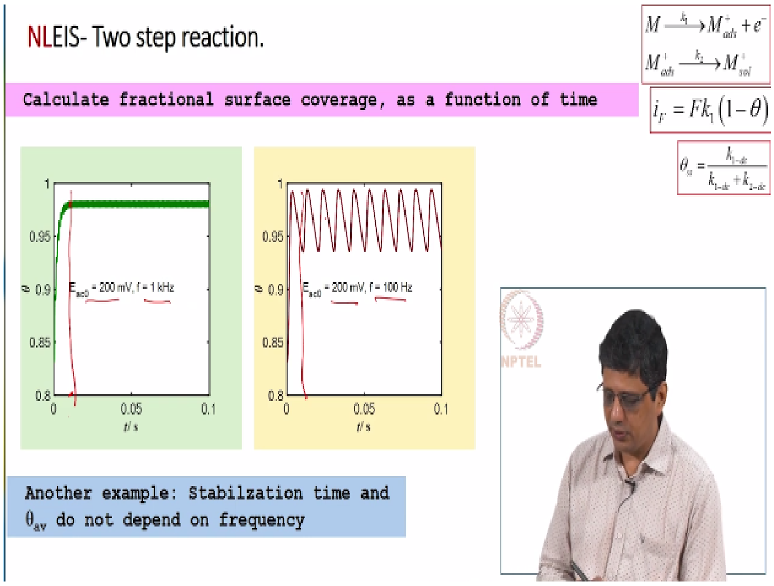

This is just another example where we maintain the same potential, same amplitude, but change the frequency. So when we apply 200 millivolts and 100 hertz it stabilizers very early, when we apply 200 millivolts on 1 kilohertz again it stabilizes very early, probably it is little easier to find the value here on what value it stabilizes at, but pretty much the time it takes to stabilize is independent of the frequency. It does depend on the pertubation amplitude.

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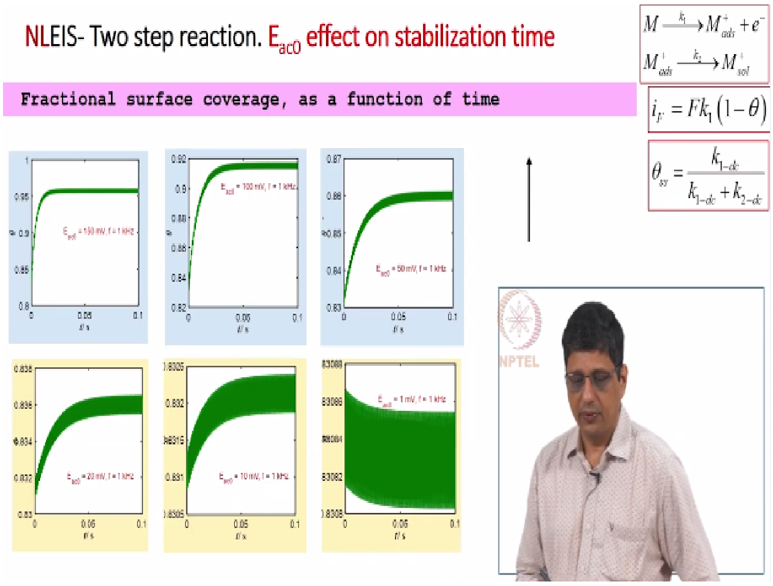

So this is at various values okay, 150 millivolts 1 kilohertz, 100 millivolts 1 kilohertz, 50 millivolts 1 kilohertz, 20 millivolts, so the same frequency, but decreasing values of pertubation amplitude. So if you notice it stabilizes at let us say 0.02 seconds, this may be little more than that. This is little more, close to 0.04, but then it is 0.04. Now look at this at 1 millivolt this theta average actually decreases that is it is lower than theta ss.

At 10 millivolts it is higher, that means at some intermediate value may be 5 millivolt, 2 millivolt, it would be more or less same, same as theta ss. That is one point, we will come to that, other thing is the time it requires for stabilization does not keep increasing when I decrease the amplitude. So when I go from 150 to 100 it increases a little, it stabilizes early, it stabilizes a little late here.

When you go from 100 to 50 millivolt it stabilizes a little later, 50 to 20 not much later, 20 to 10 more or less at the same 10, 10 to 1 more or less at the same time. So it does not keep increasing when you go to lower potential. When you go to higher and higher amplitude it does decrease, it become shorter, but when you go to lower potential, it does not keep increasing continuously, it increases and saturates at some level.

So summary is wait time, if I just draw it qualitatively, at large amplitude pertubation it is lower, at small amplitude pertubation it is more or less a constant. Of course this will depend on the kinetic parameters as well as the dc potential at which we are acquiring the data. For a given set of kinetic parameters and given Edc this is how would you expect to see.

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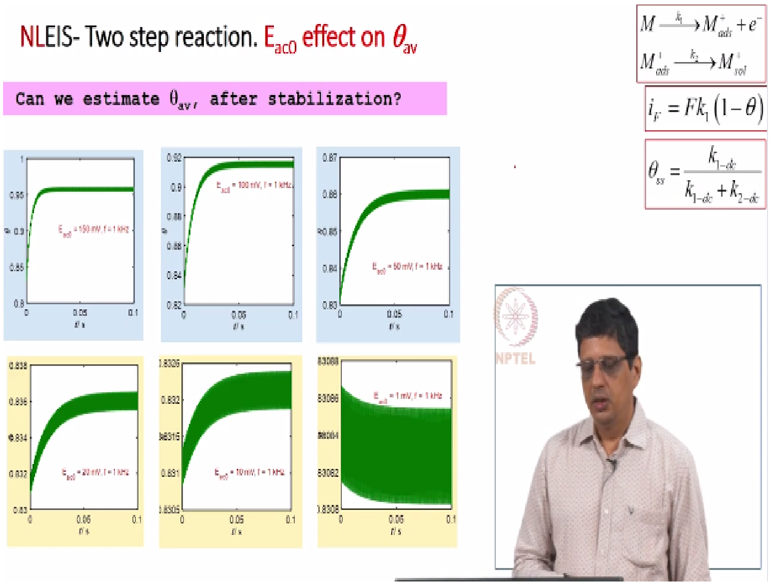

Next question, okay we know that theta average is different compared to theta steady state. Without doing the simulation, without solving it, can I estimate the value. We can estimate it provided this is kinetics limited that is solution resistance is negligible, mass transfer is rapid and our assumption that this reaction, this reaction here m going to m + adsorbed and m + adsorbed going to m solution is limited by kinetics. Under that condition we can estimated it, it is an empirical formula, but it seems to work.

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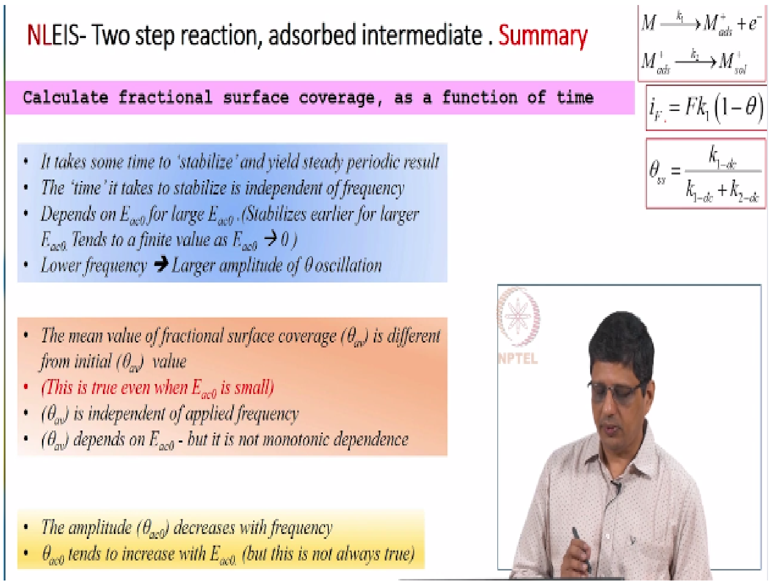

Now to summarize what we have seen so far. It takes some time to stabilize and give steady periodic results and the time it takes to stabilize or what we call as wait time in the simulation, we have to wait until that time and then only start taking data, that is independent of frequency and depends on Eac 0, when Eac 0 is large. When Eac 0 is small it is more of less constant.

And at lower frequencies the theta oscillations exhibit larger amplitude that is theta ac0 becomes larger at lower frequencies and we notice that the mean value of the surface coverage is different from the initial value that is theta steady state value and by the way although we are not showing it here even when ac pertubation amplitude is very small, even when you can approximate and say E power Eac is roughly 1 + Eac.

We can solve this case analytically and we can still show that theta average there will be different from theta ss. So it is not happening just because the ac perturbation amplitude is large. Even when it is small, it will be different and that is because the theta is given by the differential equation. It is not an algebraic equation. So when we write the theta under small amplitude pertubation can be written as theta steady state + d theta/dE * Eac.

That is actually only an approximation, for this as well as this. It is not exact for even for the average value, even when Eac 0 is small. Now the average value of theta is independent of the applied frequency and theta average depends on Eac 0, but it is not monotony. At least that is what we have seen in this example and in general that is true. The amplitude theta ac 0 will decrease with frequency and it tends to increase with Eac 0 but that is not always true.

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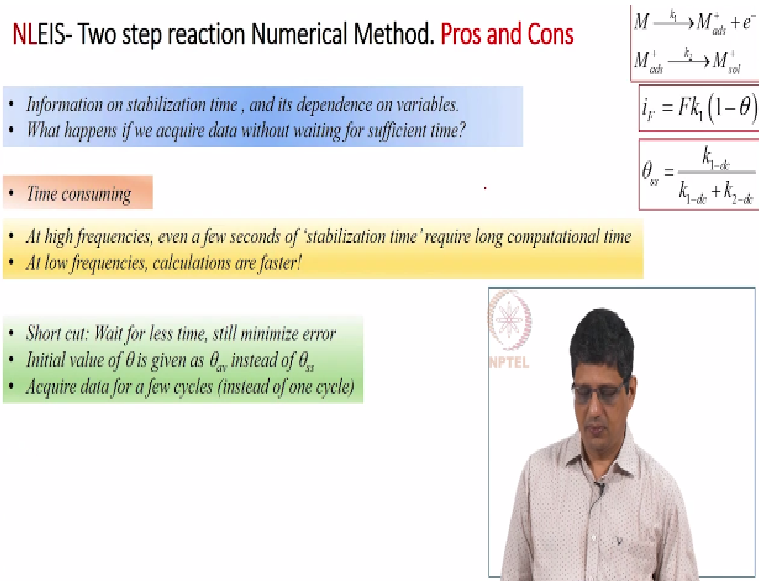

Now when we actually do the simulation versus when we do the experiments there are some differences. When you do the simulation it is actually very time consuming for the high frequency simulations. When you do experiments at high frequency they are fast meaning if I ask the instrument to take data at 10 kilohertz in 1 second it can complete 10,000 cycles that is good enough to take an average value and good enough to get a good signal to noise ratio.

So if I ask it to wait for 2 seconds it waits for 2 seconds and then takes data for maybe another 100 milliseconds and that is usually good quality data. When we do the simulations what happens is the following. In the simulations it oscillates very fast right, within 1 millisecond at 10 kilohertz it means 10 cycles are completed and we have to give certain accuracy, certain tolerance.

This takes actually quite some time in the computer to complete this. So basically what it means is in the numerical simulation, to complete a wait time of 1 second or 1 millisecond or few milliseconds especially at very high frequencies, it can take long time for the computer to complete this and then acquiring data under steady periodic conditions for few cycle maybe 100 cycles in the high frequency regimen.

When you actually look at the computation time, high frequency data it takes longer time in the computer to complete and if we say I want to perform simulations at 1 milli hertz, wait for 1 cycle that is waiting for 1000 seconds and then do simulation for one more cycle, it would actually take few seconds to do this and in the experiment of course if you say I want to complete 1 milli hertz cycle it will take 1000 seconds for that cycle even without any wait time.

So there is some difference between simulating low frequency data and actually doing experiments at low frequencies and likewise stimulating high frequency data and doing experiments at high frequencies. We take certain shortcuts in the simulations, so I want to just describe that to you. We do not want to wait for a long time especially at high frequencies and still get good quality data.

So we take a shortcut, we want to wait for less time and still minimize the error okay. So if you remember theta values would start here under steady state condition. When we apply AC perturbation it is going to drift like this and then settle or like this and settle. Now if I know the value where it is going to settle and if I give that as initial value then if you give it very accurately then I do not need to wait at all.

It would give you steady periodic result from the beginning itself. If I give it close enough then after few cycles it will settle or even if it is drifting when I take data for a few cycles and do Fourier transform the results will be accurate. So there is an advantage in knowing especially in simulations in knowing what is the value of theta average without actually solving the ODE with application of sinusoidal potential.

And after waiting for some time even if it take only one cycle the study period results that is sufficient to get impedance value, but if I take it for few cycles then if there is a slight drift that can be taken care of. That means I will get reasonably accurate results even if there is a slight drift. So how do we predict the value of theta average.

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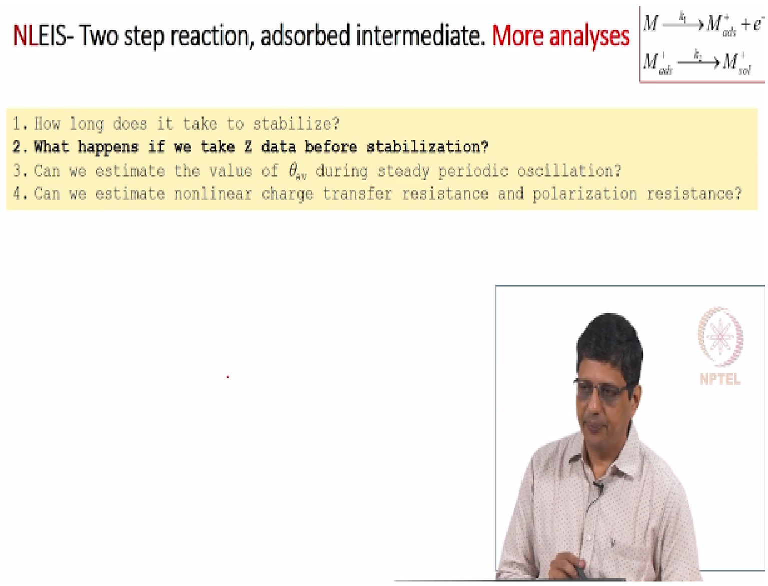

I will come to that a little later okay. What happens if we take impedance data before the current oscillations have stabilized, before we get steady periodic results.

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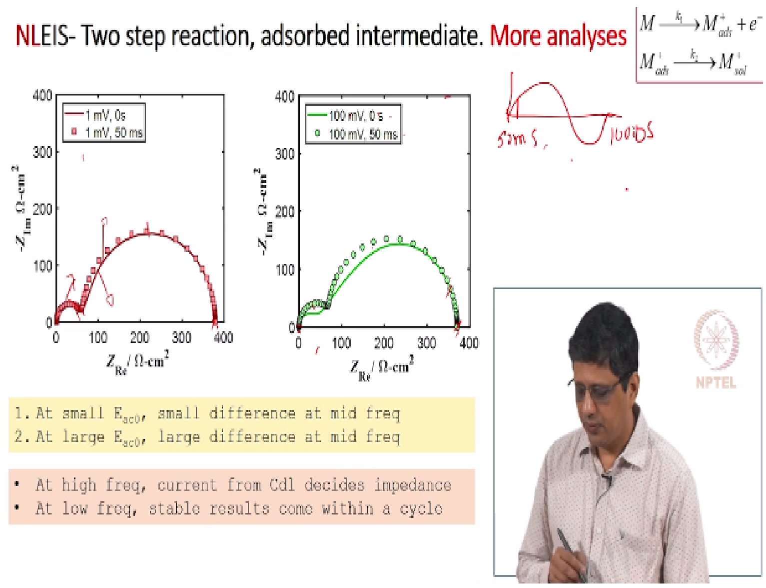

So I have done the following, I have taken 2 amplitudes 1 millivolt and 100 millivolt. In both cases I have waited for 50 milliseconds and then taken further data, taken the current, done the FFT and then calculated the impedance. Other case what I have done is apply sinusoidal potential, the response maybe still not stabilized, it may be going like this or going like this does not matter.

I take the first cycle, basically I do not wait at all. I just apply 1 sinusoidal pertubation, look at the resulting current and then take the FFT and then take the ratio of potential to current. So I would call 0 second as unstable, unstable does not mean the system is unstable, it just has not settled yet. We can call it unstable, we can call it sometimes drifting, meaning, the current is, average current is changing.

But that is changing because we are applying sinusoidal potential and if we wait for long enough time it will give steady periodic result. If we stop applying the sinusoidal potential, it will again drift and come back to the original theta ss. I would leave that as exercise for you. If you look at 1 millivolt data, I millivolt here is the pertubation amplitude, high frequencies, that is pretty much no difference. The line here represents the drifting condition and the points here represent the stable steady periodic result.

If we look at low frequencies, again it is pretty much the same. If you look at intermediate frequencies there is a difference, not very different, but there is slight difference and of course these are simulated data so there is no noise. If you take real life data with some noise you may not be able to see clear difference between the 2 in this particular case. Look at 100 millivolt, very high frequencies they are the same, low frequencies they are the same at mid frequencies there is a huge difference.

Now I also want you to compare 1 millivolt data and the stable condition and 100 millivolt data and the stable conditions that is the green colour circles and the red colour squares. Although you have to compare 2 different plots, you can see that they are more or less the same. There is some difference, slight difference, but not very much. There is some difference in this region.

Now what that means is if I take data without waiting at 1 millivolt and if I take data without waiting at 100 millivolt, I will get clearly 2 different sets of data, one of them will be KKT compliant, more or less, it is not going to be exactly compliant, but more or less compliant, this is definitely not going to be compliant, but it is not because this is taken at 100 millivolts, it is because we are taking at a condition where it is still drifting.

So the data is not KKT compliant, but we would just look at this data and look at this data and if we did not know that if we did not realize that we have not waited and that can cause an problem, we would just say that this data is at 100 millivolt and it is not KKT compliant. Whereas if I take the data which is acquired after stabilization in 1 and 10 millivolt or 1 and 100 millivolt case both of them might turn out to be KKT compliant.

So this may be one example where KKT is not able to identify the nonlinearity. So in summary at small amplitude there is some difference at mid frequencies with large value of Eac 0 there is significantly larger difference especially at the mid frequencies. So the reason is this. At high frequencies most of the current goes through the double layer capacitor. So if you remember this is a pictorial representation.

This is the double layer capacitor and this is the Faraday process, but high frequencies you get an impedance which basically is negligible for capacitance so most of the current will go through this. This would offer certain resistance; this offer no resistance so everything goes through that. So in that case it does not matter. The current going through the faradaic impedance is very small.

So total current is pretty much dominated by double layer capacitance. At low frequencies what happens is all the current pretty much goes through the Faradaic impedance, but if you go to 1 milli Hertz the response is unstable only for the first 50 millisecond and this is going to seek 1000 seconds. So pretty much the entire response is in this stable regimen, only a small fraction of it is in the drifting region.

So again the response is not going to be very different whether it wait long enough or you do not wait. So essentially at high frequencies going via Cdl decides impedance and at low frequencies, stable results come in initial part of the cycle itself. So I am not showing it here, but spectra acquired without stabilization will not be KKT compliant. So if you take data and if it not KKT compliant one thing you should try is see if the amplitude is small enough.

Another thing you should try is see if the data can be acquired after waiting for some time, sometime meaning 1 second, 2 second. Next, can we estimate the value of theta average.

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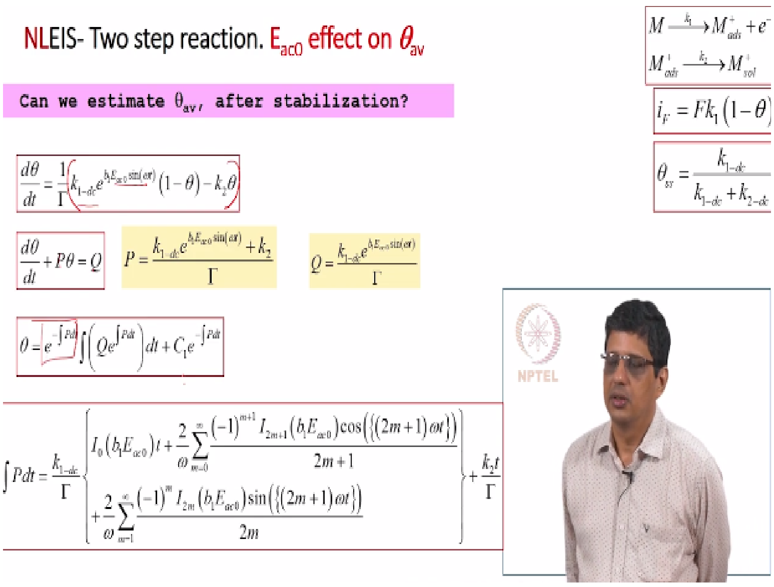

So this will require some mathematics, follow me with patience. If you look at the mass balance equation, we would write it as gamma d theta/ dt as k1 1- theta – k2 theta so it comes with the parenthesis and the k1 I can write it as k1dc E power b1 Eac and expand it as Eac 0 sin omega t, 1- theta of course remains as it is and k2 is a constant so we do not expand it. This equation I can rearrange and write as d theta/dt + P theta = Q.

Where P is the function of time, Q is the function of time and after rearranging I would get P as the expression given here. So I get k1dc, b1 Eac0 sin omega t + k2 all divided by gamma and for the terms that are without theta remaining on the right side it is just going to be k1dc, b1Eac0 sin omega t/gamma and for this type of differential equation we can calculate what is known as integrating factor and we would write that as e power Pdt * theta.

And we can show that d/dt of this can be rearranged in this form and the solution for this differential equation we can write as theta = the expression given on the right side, this is basically inverse of the integrating factor. We have to take the cube multiply by the integrating factor and then integrate with dt. This C1 is the integration constant. So we would actually get result saying theta e power integral Pdt = something on the right side and then we can take this to the other side and it becomes expression given here.

Now if I take integral Pdt, integral Pdt can be expanded like this where I take e power a sin theta or b1 Eac 0 sin omega T, we can write it as series in modified basal function, we have seen this before, it is lengthy, but just stay with me because the point we want to make is modified basal functions will come in the estimation of theta average and I want you to know how they come.

So we can expand this e power sin theta or a sin theta as I0 of a + this entire series, all of this multiplied by k1dc/gamma. This is for the first part. The second part of course remains as k2/gamma and integral Pdt gives us k2t/gamma. So if I integrate this this gives me k2t, so the I0 gives you I0 t this sin omega t gives you 1/omega, cos omega t and cos omega T gives you 1/omega, sin omega t.

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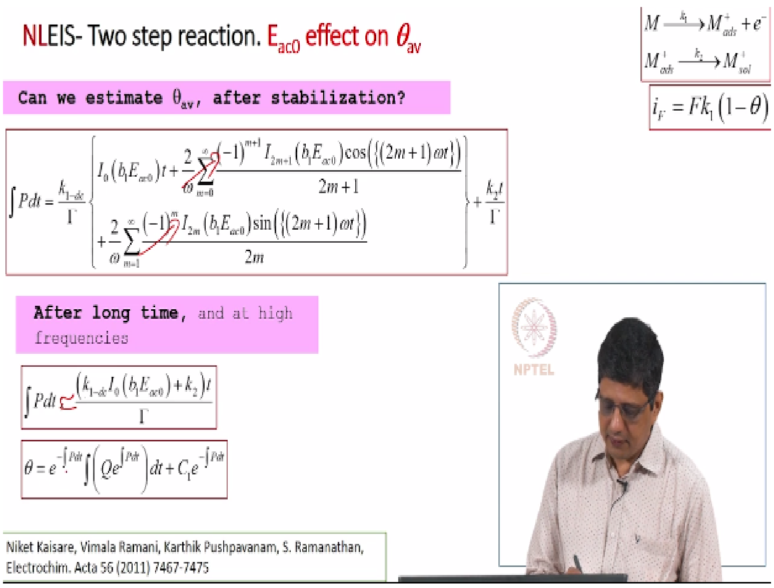

$$M \xrightarrow{k_1} M^+_{ads} + e^-$$
$$M^+_{ads} \xrightarrow{k_2} M^+_{sol}$$
$$i_F = Fk_1(1-\theta)$$

$$\int P dt = \frac{k_{1-dc}}{\Gamma}\left\{ I_0(b_1E_{ac0})t + \frac{2}{\omega}\sum_{m=0}^{\infty}\frac{(-1)^{m+1} I_{2m+1}(b_1E_{ac0})\cos(\{(2m+1)\omega t\})}{2m+1} + \frac{2}{\omega}\sum_{m=1}^{\infty}\frac{(-1)^m I_{2m}(b_1E_{ac0})\sin(\{(2m+1)\omega t\})}{2m}\right\} + \frac{k_2 t}{\Gamma}$$

$$\int P dt \cong \frac{(k_{1-dc}I_0(b_1E_{ac0}) + k_2)t}{\Gamma}$$

$$\theta = e^{-\int P dt}\int\left(Qe^{\int P dt}\right)dt + C_1 e^{-\int P dt}$$

So I just brought this here and this is published in 2011 by our group. So if you wait for long time and at high frequencies omega tending to infinity it is possible to show if you wait for long time integral Pdt will come like this k1 dc I0 b1 Eac0/gamma + k2 all of this multiplied by t and when omega tends to infinity we can say this goes away, this goes away and at that condition integral Pdt can be approximated by this expression and therefore I can write theta with the approximation.

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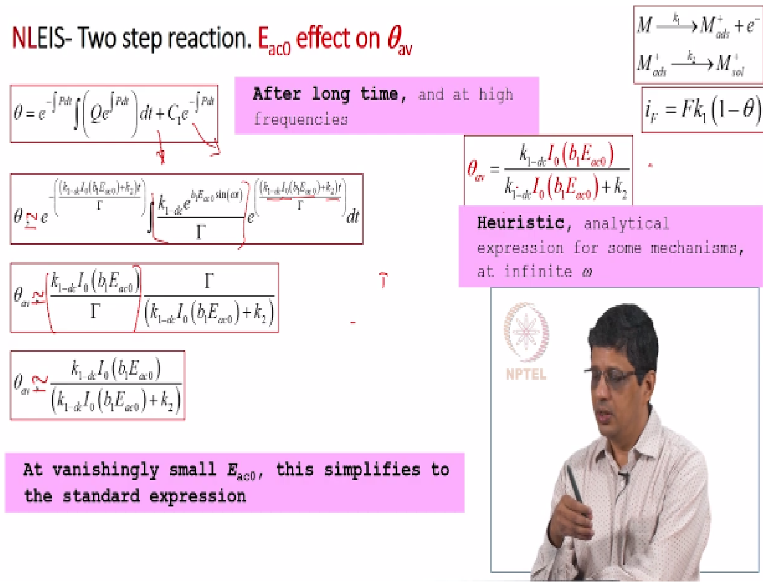

I can take this equation, this is precise and I can approximate that by theta is approximately = e power so much. Here of course Q is left as it is, this integral Pdt is substituted with the approximation and this goes away when time is very long. It is going to exponentially decrease and this we do not need to worry. So we are looking only at the average value, if you can show that it is going to be k1dc I0 b1 Eac 0/gamma, this term after multiplying this and taking the integration you are going to get gamma/k1 Idc I0 b1ac0 + k2.

So the gamma will go away and you would get an expression saying theta average is k1dc/k1dc + k2 but each one of this k1dc is multiplied by a what we can think of as a correction factor. So normally I would write k1dc/k1dc + k2 as theta ss. When we apply sinusoidal potential it drifts and oscillates around a new value which is theta average that case we have to multiply this by I0 b1Eac 0 and this also by I0 b1 Eac 0.

When Eac 0 is small as X tends to 0 I0 of x tends to 1, so this will come back towards theta ss, but it will never be equal to theta ss unless Eac 0 is exactly 0. Now this is one example, one mechanism; however, we have tried few mechanisms and we have tried few sets of kinetic parameters. In all these cases we have found that whenever we replace the kIdc, any rate constant that depends on potential, we correct it with modified basal function of 0 order with the corresponding bIEac 0 it seems to work.

So we call it heuristic because we cannot prove it analytically for all cases, but it seems to work and this analytical expression at least for the mechanisms we have tried we have tried for maybe 4 or 5 mechanisms and at high frequencies this seems to be valid. So you can use this to estimate what would be the average value after applying steady periodic condition for a given reaction mechanism and given kinetic parameters.