Electrochemical Impedance Spectroscopy

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Chapter – 45
Rt and Rp Estimation

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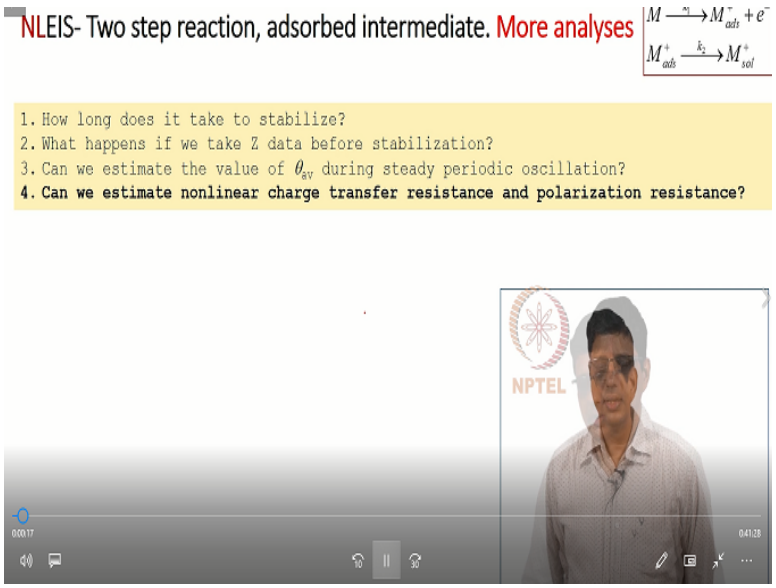

Next can we estimate them Nonlinear charge transfer resistance RtNL and the polarization resistance.

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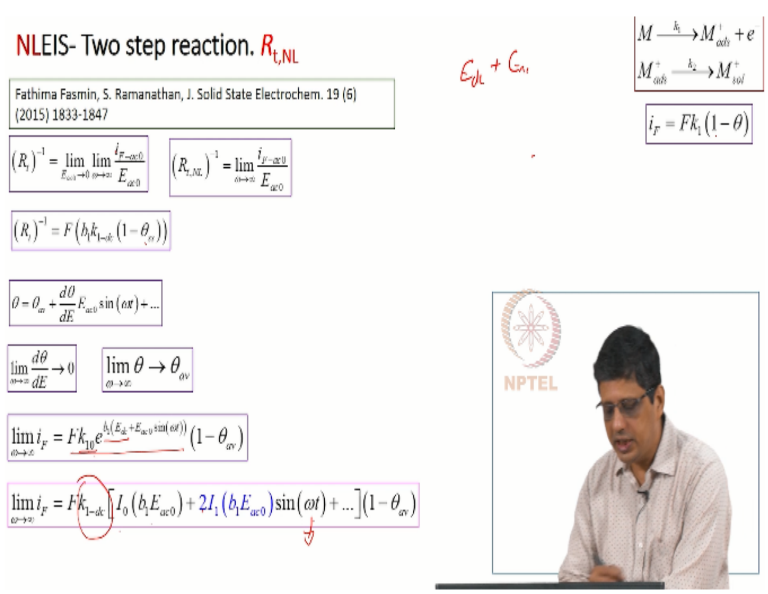

So this work is published by our group in 2015 just to refresh your memory charge transfer resistance is Rt and the definition is given here with the inverse of charge transfer resistance right here their limit of Eac tending to 0 and omega tending to infinity that is high frequency limit and small amplitude perturbation the faraday current that will not have any phase offset with respect to the potential.

And that impedance faraday impedance is inverse of the charge transfer resistance I am sorry faraday impedance is the charge transfer resistance under those conditions or faraday admittance is the inverse of charge transfer system. So we write it as Zf limit Eac tending Eac 0 tending to 0 omega tending to infinity that is charge transfer resistance I can write it as Zf I can write it sometime as del E/ del I I can write it del I for the faraday component.

I can write it as Eac 0/iFac 0 they all mean the same thing. Now same faraday impedance at the limit of omega tending to 0 under those conditions also it will be a real value it will not have any imaginary component and that limit the faraday impedance is called polarization resistance Now if I get rid of this constraint and say Eac 0 need not be small if I say Eac 0 can be an arbitrary value large or small it does not matter.

I would call that as a nonlinear charge transfer resistance. For example this mechanism we have an expression for faraday current only the first reaction contributes to the electrons and therefore we it as Fk1 1-theta that is the rate of the first reactions multiplied by faraday constant and at infinite frequency we know that d theta /de tends to 0 therefore its going to remain at theta SS or actually with theta AB.

But when it is small theta ss and theta we are more or less the same. The rate constant k1 if I take the derivative its going to be b1 k1 at that dc potential. So when I vary the potential close to the dc potential I will say Edc+Eac and when it is small amplitude perturbation we know that we can raise the charge transfer resistance as Rt inverse of Rt as f b1 k1 dc 1 -theta SS. This we have seen before.

The theta we will write it as average value steady state value+d theta /de Eac and so on and we know that when omega tends to infinity d theta/dE will tend to 0. Basically omega comes in the denominator of the expression for d theta/dE and theta tends to theta average when omega tends to infinity what happens to IF we can write f k1 1-theta and expand the k1 as k1 dc multiplied by E power b1 Eac yeah.

Now here I want you to try this instead of writing this in Taylor series and truncating after the first term. Let us write it in Fourier series so we keep the k1 0 e power b1 Edc and call that as k1 dc e power b1 Eac 0 sin omega t that I would like you to expand in Fourier series. So first term it is going to be i0 b1 Eac0 second term its going to be 2i1 b1 Eac 0 sin omega t + and so on. Right sin 2 omega t or cosine 2 omega t sin 3 omega etc +- all those things will come.

Multiplied by 1 – theta average now we want to look at the IFAC 0 the coefficient of the response at fundamental that is at omega. So we want to look at the coefficient of this and the coefficient of this is 2I1 b1 Eac 0.

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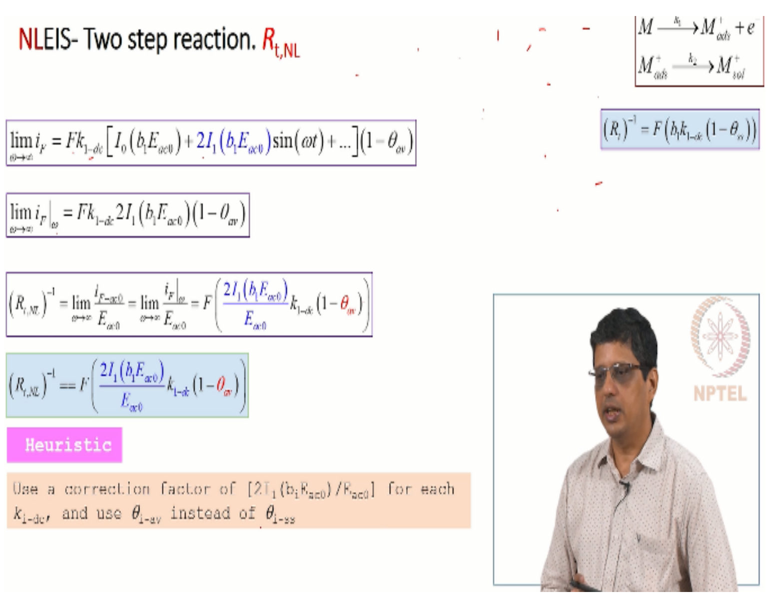

So if I write this I just copied from the previous page the iF value given by the Fourier series the iF coefficient corresponding to omega is given by Fk1dc multiplied by 2I1modified Bessel function of the first order b1 Eac 0 and then multiply by 1 -theta average this is going to be the iF

Eac 0 if I write iF as iFdc+iFac0 or iF1 sin omega t+iF2 sin 2 omega t sin or cosine it does not matter +phi 2 phi 1 etc.

Of course once they know the value of this coefficient I can take the ratio and call that as the charge transfer resistance or inverse of the charge transfer resistance because I do not make the assumption that Eac 0 is small I am just using the Fourier series of the full e power a sin theta I call this as the nonlinear charge transfer resistance and that is given by 2I1 b1 Eac 0/Eac0. So earlier we would have gotten an expression saying Rt inverse is f b1k1dc 1-theta ss.

Now when Eac is small theta average is going to be roughly theta ss and when Eac is small this value I1 of x under the limit extending to 0 is going to be x/2 this value when Eac is small it is going to be 2 multiplied by b1 Eac 0/2 and of course if you take the denominator this term given in the blue colour will tend to b1 at the limit of Eac0 being a small value and theta average will tend to theta ss when Eac 0 is small.

So you can see this expression will reduce to the familiar expression when Eac 0 is small. When Eac 0 is large this is what you should use to predict the charge transfer resistance. So what that means is you can write the expression for charge transfer resistance as you would do normally okay just replace theta ss with theta average and replace all the kinetic parameters b I with Eac0/Eac0.

So 2 times I1 of b1 Eac 0/Eac 0 I want you to remember this this is heuristic meaning its based on empirical evidence and based on some expansions for certain mechanisms and in our experience it seems to work but this is not proven analytically. Now basically what it means is use a correction factor of 2 I1 bi Eac 0/Eac0 this tells how it is going to depend on the Eac0 for each of these bi okay and use theta I average theta 1 average theta 2 average.

You may have multiple intermediate states for all of them you have to use the theta average in sort of theta statistics. Then so far we have been able to predict the RTNL correctly for practically all the mechanisms we have tried. For all the kinetic parameters we have tried.

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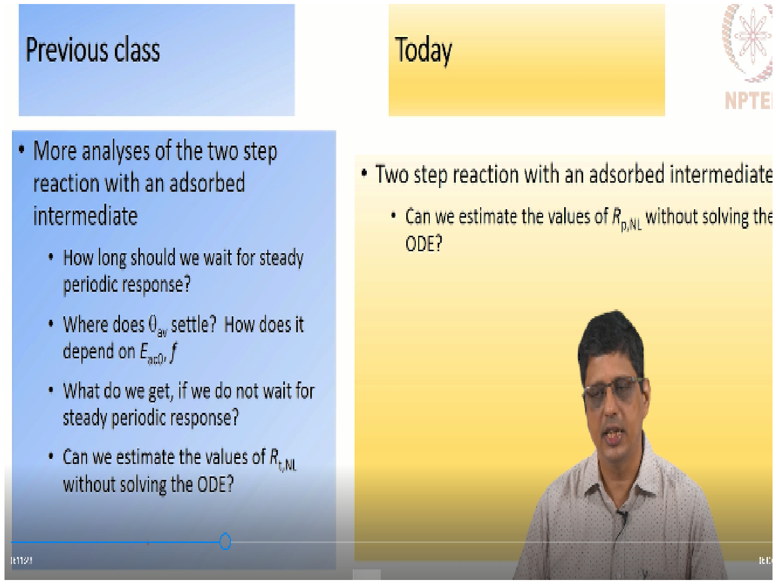

So earlier we saw that you can estimate the value of theta average when we apply sinusoidal potential it settles after some time we found that the wait time necessarily its independent of frequency it depends on the amplitude of perturbation it of course depends on the kinetic parameters also. We found that we can estimate the average value of the theta its independent of the frequency again.

But at least under high frequency limit we can show that it can be returned in terms of modified Bessel functions we also saw that if you do not wait for sufficient time and acquire data then the results are going to be different especially at larger amplitudes and we just mentioned that the results taken under those conditions will not be KKT complaint. We did not show that but we just mentioned that.

And we also saw that its possible to estimate the charge transfer resistance and that large amplitude perturbation using a heuristic method that is not proven to be valid under all conditions but it seems to be working correctly for at least the mechanism so you tried and the parameters we have tried. Now can we estimate the polarization resistance under large amplitude perturbation again without solving the ODE.

Of course if you can generate the spectrum then we can just look at what happens to the faraday impedance when we go to lower and lower frequencies and when it settles we say that is a polarization resistance. But if I have current if I have dc current as a function of dc potential it is possible to estimate the polarization resistance. If I have an expression for dc current it is possible to estimate the polarization resistance. And I want to describe that part.

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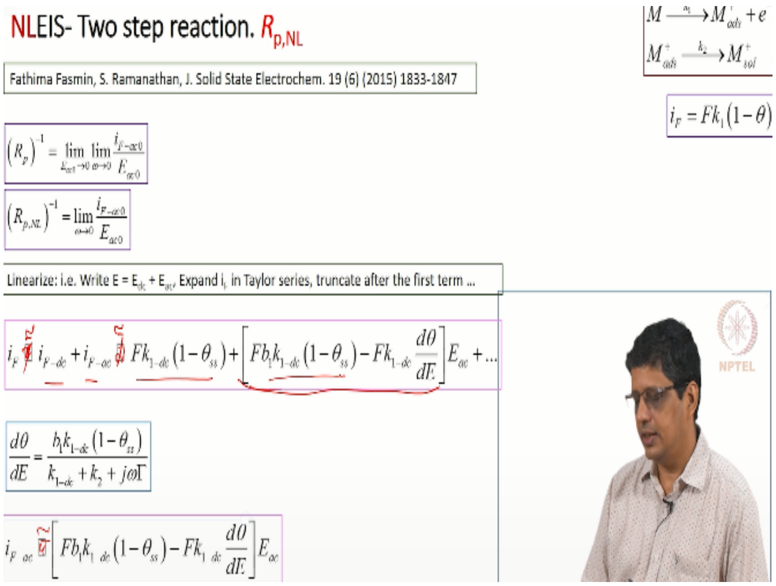

Now charge transfer resistance is faraday impedance at high frequencies and under small amplitude perturbation. Polarization resistance is faraday impedance at low frequencies at the limit of omega tending to 0 that impedance faraday impedance is called polarization resistance. Now if I get rid of the constraint saying Eac 0 has to be very small if I say Eac 0 can be large I still look at the faraday impedance at omega tending to 0.

That we can call us nonlinear polarization resistance when we want to calculate the polarization resistance we can write it as Edc+Eac 0 sin omega t that is the potential we have an expression for current expanding Taylor series truncate after the first term because it is a small amplitude perturbation and these are actually approximate signs. Faraday current is split into dc and ac component and that I can write as dc component here and ac component here.

We had done this before and we know the expression for d theta/dE comes as b1 k1 dc 1-theta ss for this particular mechanism and the denominator has k1 dc k2 and j omega gamma when omega tends to 0 d theta /de we can write it easily and iFac is the second term here so we take the second term this actually the charge transfer resistance or the inverse of charge transfer resistance this is the addition to estimate the value of polarization resistance.

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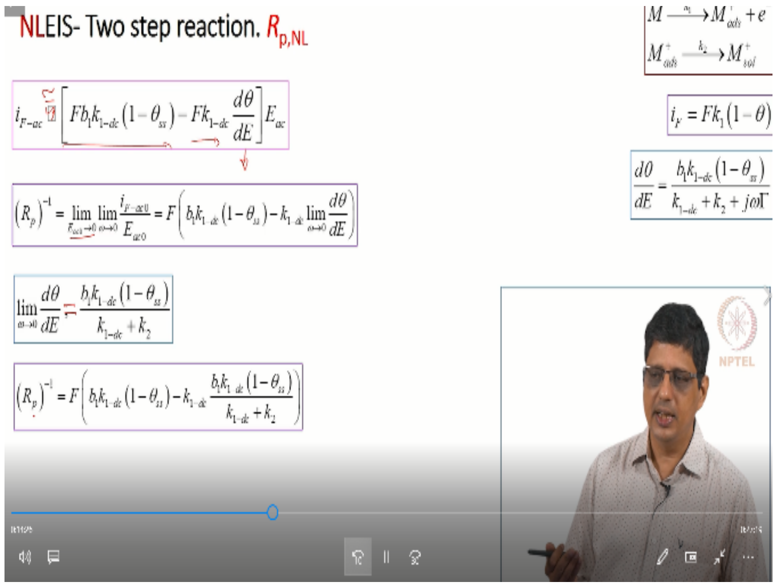

So we can find the inverse of polarization resistance as Rp inverse and under the assumption that this is small signal condition omega tending to 0 this is independent of omega this is independent of omega only this depends on omega and at omega tending to 0 this can be simplified easily the j omega gamma goes out therefore we can write an expression for polarization resistance for a given reaction with the assumption that mass transfer is.

And solution resistance is negligible. Now for small amplitude perturbation when polarization resistance is defined it is easy for us to calculate for any given mechanism. We can calculate the impedance at any frequency therefore we can calculate the importance at 0 frequency or infinite frequency no problem.

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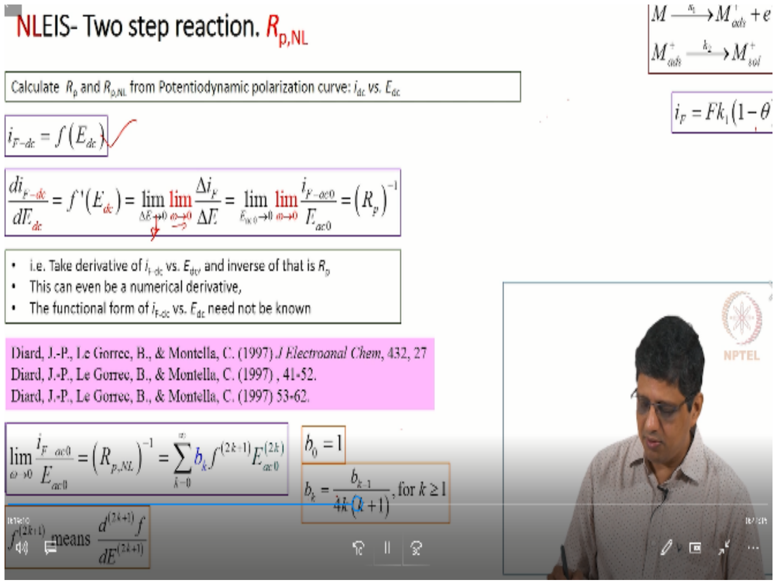

What happens when you have a large amplitude perturbation okay we can estimate the dc current for a given dc potential we can estimate the dc current value the faraday current. Okay so basically its this expression with the concern that potential e is Edc. So in general for any mechanism you would rate as a function of Edc in this case we know what the function is what the expression is.

When I make small changes I can say that result in change small changes del E the resulting changes del If and if you make the change slowly that is omega tending to 0 that is inverse of polarization resistance. I can write it in different notations I can write it as del If/del E I can write it as IFAC0 by Eac0 sometimes people also write it as prime indicating it is a derivative. If I have experimental data I If dc versus Edc let us see we do not even know the mechanism.

We do not have an expression for this still if we take the derivative here using numerical method I can take 2 data points find the del If/del E that this find the value of the slope that slope is going to be di/de and that is going to be inverse of the polarization resistance. So this curve which we call as potential dynamic polarization the slope of the curve at any given point that has to be equal to the inverse of polarization resistance.

So if I acquire impedance data here that data may come like this it does not matter the low frequency limit there is Rp and that should be equal to the inverse of the slope of that curve. So you can take numerical derivative if you know the form of this faraday impedance if you know the dependence of faraday current on the potential you can take derivative and at the limit of omega tending to 0 you can get the expression anyway.

So it does not require us to solve ODE anyway for linearized cases we do not need to solve ODEs for this kind of expressions. In 1997 there were a series of publications by professor Diard Gorrec where they have shown even for large amplitude perturbation one can calculate the polarization resistance as long as we know the expression iF relating to Edc so when we get rid of the constraint that del E has to be is very small.

We can defend that as RpNL and the inverse of RpNL is given by this series this is the series that they have suggested and if i remember right they have used a notation like this. It does not matter we use a notation saying R subscript NL and they have given it by a series and out here f prime indicates the first derivative. f double prime will indicate this secondary derivative and f n indicates the nth derivative with respect to potential okay.

So f power 2k+1 means it is actually not f power nth derivative or 2k+1th derivative b0 is given as 1 and subsequent b values b1 b2 b3 etc can be obtained using this formula. So if I know b0 I can calculate b1 and once I know b1 I can calculate b2 and so on. So this is the expression they have derived so which means I need to know the functional form I need to have the ability to get n number of derivatives from this.

And when I take more and more numbers hopefully I will get more and more accurate estimate and beyond certain limit you may not need this anymore. Because this co efficient bk will become smaller and smaller when we go to larger and larger values of k.

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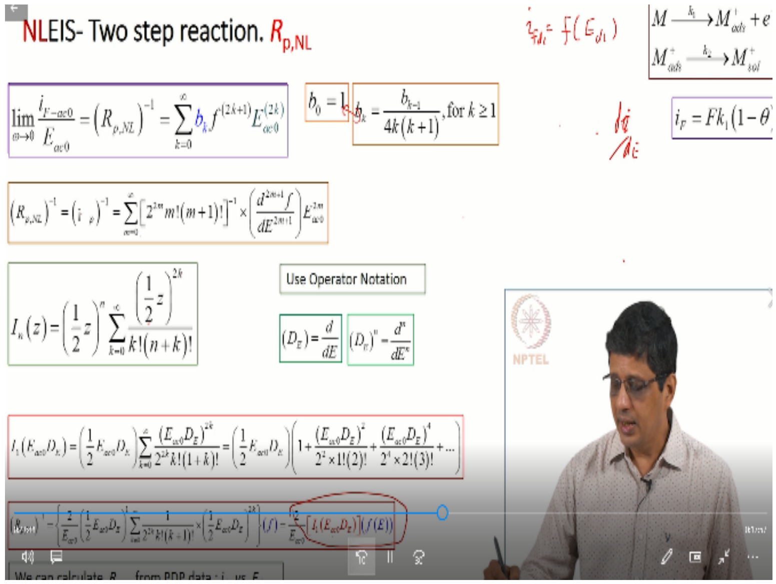

This has not come very nicely its alright this RpNL you can take this coefficient and you can rearrange it and you can show that this expression here is the same as the expression here instead of writing in these coefficients its pretty much the same you can give a slightly different format and get the expression for nonlinear politization resistance. Now I want you to look carefully here we want to use a slightly different notation operator notation.

We want to say upper case D with subscript e would represent d/dE and that is the derivative. If I write dE power n that is the nth derivative. So I want to use this expression operative notation here and substitute here second I want you to recognize or remember this the modified Bessel function of nth order is written like this 1/2 Z whole power n multiplied by this summation and this of course depends on k value and n value.

K going from 0 to infinity now if I take I1 and if I say I1 Eac 0 DE it is going to be named operator okay I can apply it on a function DE alone does not have any meaning unless its applied on a function. Now this if I substitute here I would find it is 1/2 Eac 0 DE and you can substitute in the expression here this 2 power 2k k factorial 1+ k factorial this 2 power 2 k comes from here and Z power 2k is Eac 0 DE power 2k this essentially is 1/2 Eac 0 DE.

You can expand this series and you can compare with the terms here they will basically mean that you write RpNL as 2/Eac 0 I1 of the operator DE Eac 0 is multiplying the DE applied on to the function f of E. So we have a function I faraday current =f of Edc iFdc =f of Edc if I use this notation its a compact notation this will tell me the nonlinear polarization resistance. So this part tells them low frequency limit current.

So this tells me iFac 0 when omega tends to infinity I am sorry when omega tends to be 0 and Eac 0 is arbitrary. When Eac 0 is small I1 of Eac 0 DE is approximately Eac0 DE/2 and of course when I multiply by 2/Eac0 I just get the derivative DE f polarization resistance inverse of that is di/dE this simplifies to the known expression when Eac 0 is small. So if you have Idc at various Edcs then you can calculate the polarization resistance.

Nonlinear polarization resistance either by taking n number of deliveries first derivative second derivative and so on around the DC potential where we want to estimate the polarization resistance. So in corrosion polarization resistance basically means at the open circuit potential but in general polarization resistance it can be acquired at any DC bias. So it means the low frequency limit of the impedance spectra with or without dc bias.

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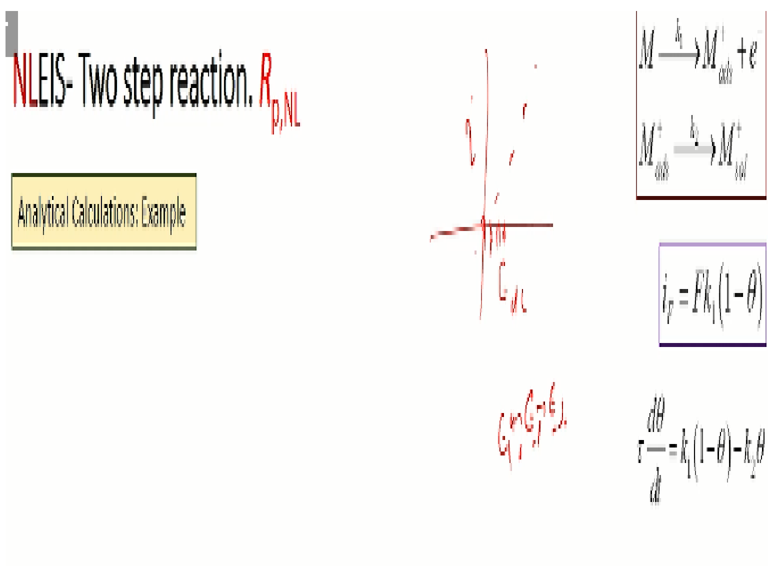

Now I have an expression iF is given as Fk1 1- theta at very low frequencies it is still valid just that I had to replace the k1 with k1 DC theta with theta ss and iF with iF DC. For this its possible to an analytical expression for the nonlinear polarization resistance we do not need to actually generate various iF values at various DC potentials and take the numerical derivative it is possible to do it you can take the numerical derivative.

But numerical derivative tends to be noisy and especially when you go for multiple order derivative 5th order 10th order 20th order when you go to a higher order derivatives you would have incorrect result. Roundoff error will play a role now if we take E1 E2 E3 and make them very small if we make the interval very small I get a little more accuracy. But again if you make it extremely small I will have round off errors.

So numerical derivative is something we should avoid if you can if it is possible to get an analytical expression it is better to use it. Now I also want you to notice the following.

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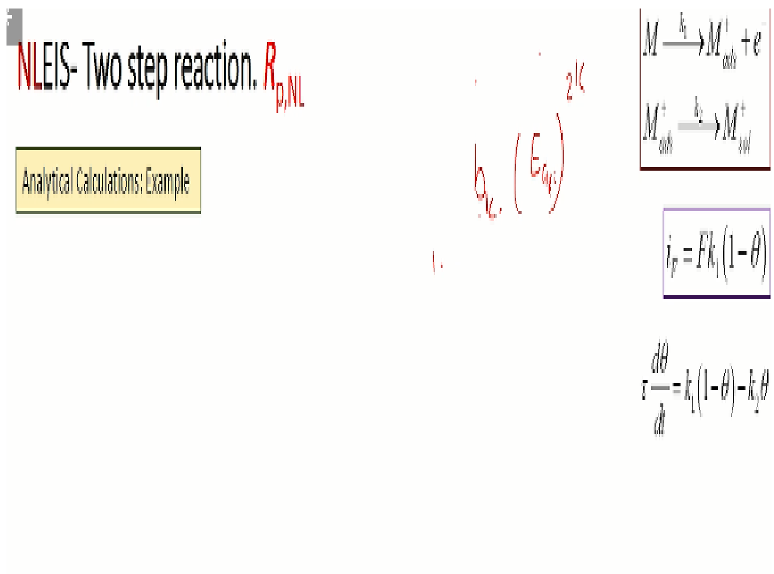

We have the expression which goes Eac 0 power 2k and then bk when you use large amplitude perturbation you need to use a summation k=0 to some value let us say 10 beyond that you can neglect the terms. If I use larger perturbation I should go to larger values here if you go to even larger Eac0 we can go to larger value here before I can neglect the remaining terms. So what level do we stop we cannot go to infinite summation.

Well actually there are some software which allow you to calculate those values or estimate those values. But in general if you are just writing your own program it is easy to calculate up to some level and then stop.

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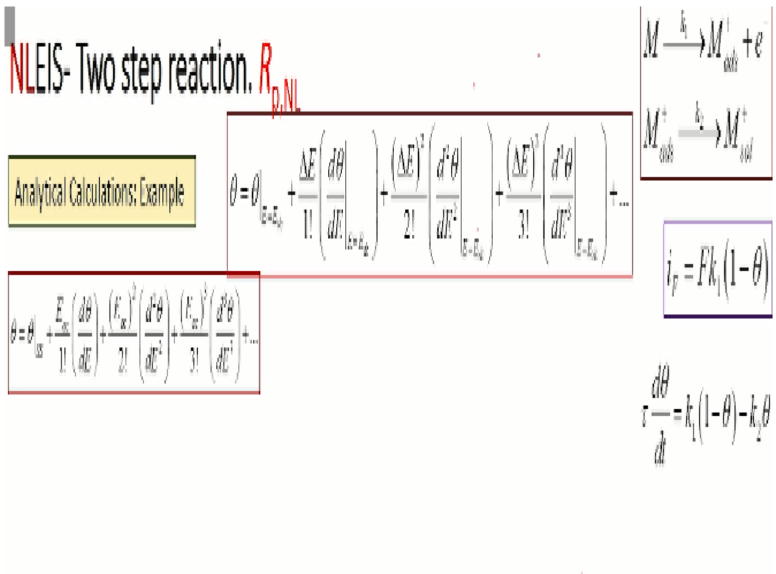

I want to expand the theta in Taylor series theta around Edc del E d theta/dE del E square/2 factorial d 2 theta/d E square del E cube this is how we would expand in Taylor series we would expand around x0+h this is similar to that. Now del E we can replace by Eac so I can rewrite that as Eac Eac square Eac cube and so on. Now I cannot say that Eac is small I cannot say that I can neglect these terms.

I actually want to use this to calculate the nth derivative of current with respect to potential in order to calculate this I need to be able to calculate the nth derivative of theta with respect to potential and we are doing some algebra here just so that we can get the expression for nth derivative it is lengthy but again its not particularly complex its not particularly difficult.

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I can write the k1 in this case k2 is a constant. In general I can write ki as ki at dc and then the derivative 1st derivative 2nd derivative nth derivative multiplied correspondingly by del E del E square and del E cube divided by 1 factorial 2 factorial 3 factorial and so on.

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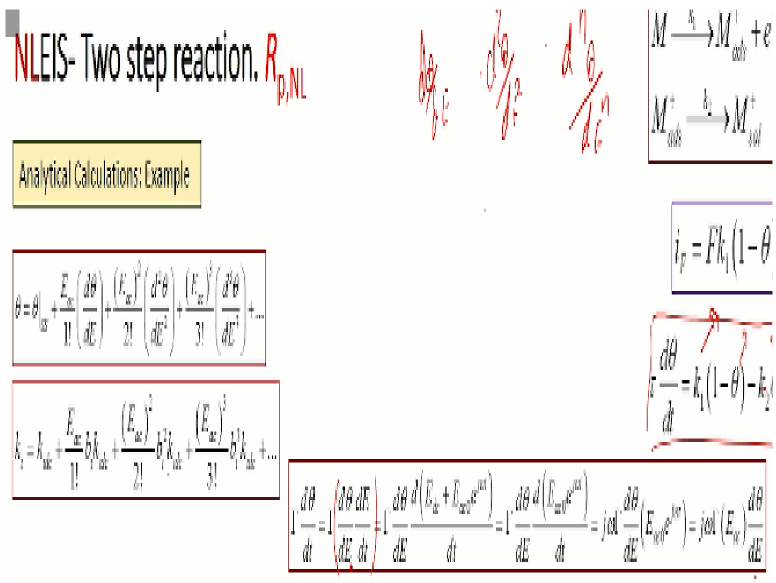

Again I can be replace that by k idc Eac and the 1st derivative is going to give me bi 2nd derivative is going to give me bi square this is actually simple. So basically I want to take this expression I find the value of d theta/dE I want to find the value of D square theta/dE square I want to find the value of d n theta /d E power n. So I can write this easily expanded I can explain this in this Taylor series.

I can expand this in the Taylor series this is the constant on the left side we have seen this before very early when we look at the linear decision. We would have written gamma d theta/dt as d theta/dE multiplied by dE/dt and we would get j omega gamma Eac d theta/dE. We have done this n number of times so we will just continue with this.

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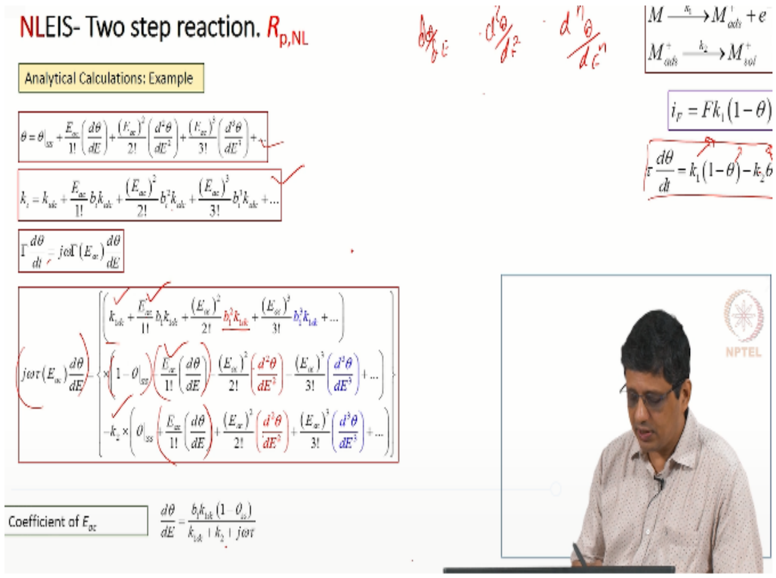

Now if I take this equation and substitute without linearization. So I substitute for k1 from the expression here I substitute for theta from the expression here k2 is left as it is multiplied by theta. Now this expression is valid under all Eac that means I should be able to isolate the coefficients of Eac and equate them. Coefficients of Eac square and equate them Eac cube and equate them.

So I had to find what terms here will give me Eac square what terms will give me Eac cube right now I am just focusing on Eac square now look at this this coefficient its a coefficient of Eac square this is a co efficient of Eac square this is a coefficient of Eac square. All the cubic terms are given in blue colour but not only that if I multiply term here with term here I will get Eac square.

If you multiply this term with this term I will get cube if you multiply this term with the term here I will get a cube so I had to look at it carefully coefficient of Eac alone it is pretty straight forward it can be taken from this multiplied by 1 -theta this multiplied by factor here this multiplied by the factor here and of course the factor here.

And it would give us what we got earlier d theta/ dE is going to be given by the expression we are familiar with j omega gamma.

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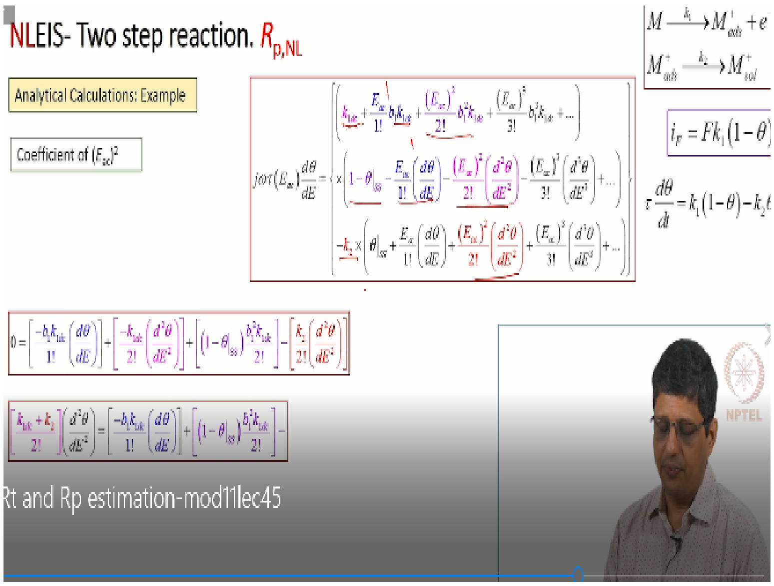

Now if you take the coefficient of Eac square we saw that we had to look at it carefully now I have arranged them or coloured them so that the same coloured numbers if you multiply it you would get Eac square the pink colour, blue colour factors and violet colour factors they would give you Eac square here the red colour factor would give you the Eac square so I can group them here other times it will give you higher order terms.

So we are not going to worry about them on the left side there is no Eac square so it is going to be a 0 on the right side I would get b1 k1 dc multiplied by d theta/d E we are taking the Eac square term out and then grouping the remaining terms k1 dc multiplied by 1/2 factorial d square theta/d E square with of course the negative side and the violet colour b1 square k1 dc and 1-theta SS and of course k2 multiplied by d square theta/d E square.

Now I can rearrange you can rearrange and write basically d square theta/d E square in terms of other parameters known parameters.

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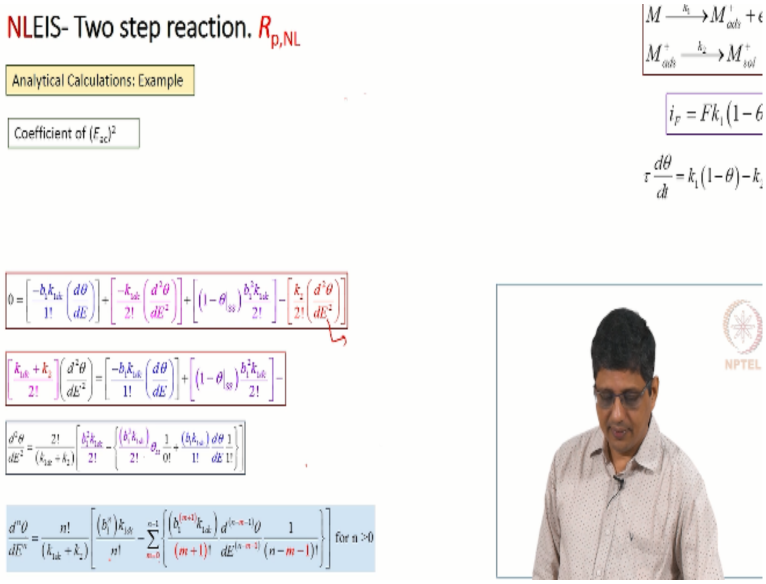

I can write it as d square theta/ d E square is 2 factorial/k1+k2 it is going to depend on d theta/d E. Now if you look at it is independent of omega well it is not really independent of omega. Omega does not appear explicitly here d theta/dE depends on omega and of course. We are writing all this under the limit of omega tending to 0. Now this depends on theta it depends on the d theta/dE and the remaining terms are arranged.

Here I am going to regroup them slightly differently but it is possible to show that in general you can do this for the 3rd order once you do it for 1st 2nd 3rd you can look at that and tell that for any nth order I can write it as n factorial/k1 dc+k2. B1 raised to the power n k1 dc/2 factorial for this particular mechanism and this entire term on the bracket can be written as a summation with m going from 0to n-1 etc b1 power n+1k1 dc this derivative basically goes from a constant.

So if I say dn /dEn of theta n=0 it means there is no derivative just functioning theta n=1 it is 1st derivative n=2 it is 2nd derivative and so on. So this expression for the mechanism given here for any kinetic parameter as omega tends to 0. This expression is valid and its not that difficult to calculate once you write a program for this it is easy to calculate only problem is when you want to go to many terms then n factorial will become a problem each operating system.

And each software for example if I want to get 100 factorial in 64 bit it is possible if you want to get 1000 factorial it would give me a number in scientific notation it would not be accurate. Okay so it will have to truncate after certain number of decimals and it will write in scientific notation it cannot give me the entire number as an integer unless we have some special program for that.

There are some programs which will allow you to change the accuracy but if I use for example Matlab typically there is a limit on what factorial can I get without loss of accuracy. So basically what it means is. I cannot just blindly write a program in C or Fortran or any of such languages and then say go to 1000 factorial or 1000 terms I will have to be aware of the limitation. I have to know under what condition I can get accurate answers and under what conditions we are going to face truncation errors.

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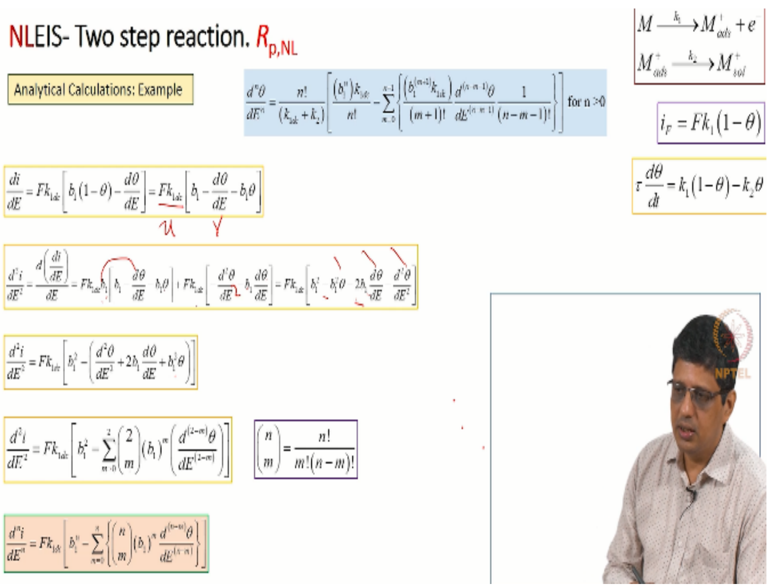

So in this we can write the expression for the nth derivative of theta now look at the current value di/dE 1st derivative I can easily write we had done this before Fk1dc b1-1- theta d theta/dE. Now I just arranged it slightly differently so that its easy to generalize later instead of rating b1 1-theta I will write it as b1 -d theta/dE-b1 theta. I can take the 2nd derivative if I take the 2nd derivative.

This gives rise to I can say this is u v so I take the u dash v +u v dash right k1 dc if I take the derivative again I will write b1 k1 dc and this of course remains the same here u it remains the same this if I take the derivative b1 becomes 0 this becomes d square theta/dE square term is missing and of course this becomes this -b1 d theta/dE. I can rearrange it I can multiply and then rearrange f k1 dc I can keep it outside retain it.

B1 square then b1 square theta then I have 1 b1 d theta/dE with a negative sign I have another d b1 d theta/dE with a negative thing so it becomes -2 b1 d theta/dE and of course I have – d square theta /d E square and likewise I can write for 3rd derivative 4th derivative etc. But I have rearranged it such that b1 square is here with a negative sign d square theta d theta b1 square theta so if you look here this is b1 square this is 2 b1 no co efficient before that it is just 1.

And this can be written as a binomial series m=0 0 to 2 2 to m b1 power m and 2-mth derivative of theta of course here n m we call it as ncm is n factorial /m factorial n-m factorial and I can write the nth derivative as fk1 dc b1 power n. So essentially I can write the nth derivative of the current in terms of the nth and lower derivatives of theta with respect to potential and for each of them we have got an expression before.

So we should be able to calculate and actually if you calculate it for any given Eac 0 you would be able to get the polarization resistance value.

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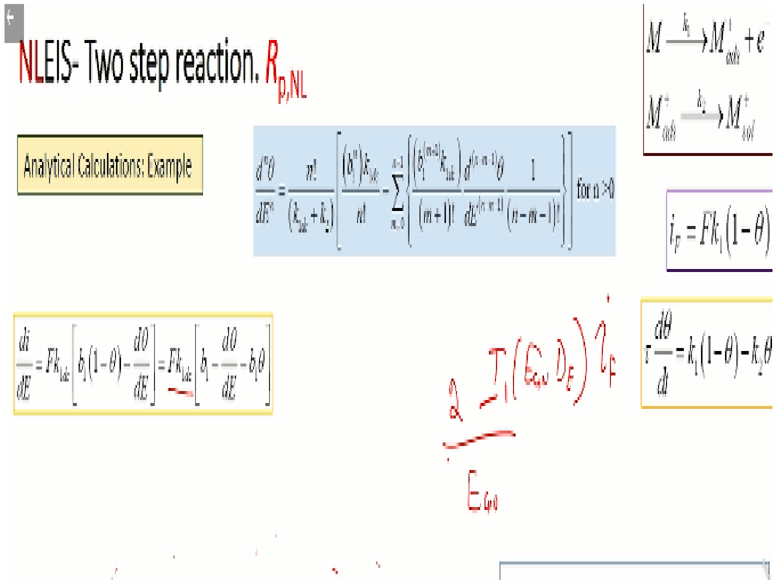

So essentially we saw that the polarization resistance can be written in terms of the I1 Eac0 de of the I faraday or we can call it as f of Edc. So in order to calculate this we need to be able to take the derivative 1st order 2nd order 3rd order and so on. And in order to calculate those derivatives we need to be able to take the derivative of theta with respect to potential once you have analytical expression for this for any given Eac 0.

We can substitute in that formula and it does match with the polarization resistance that you would get by solving the ODE and calculating the impedance what we had done before for the nonlinear impedance.

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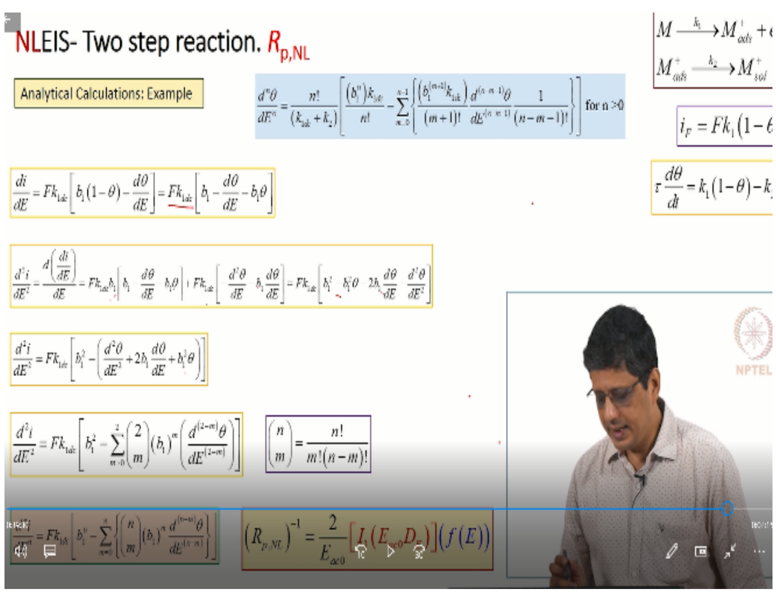

So the point is it lengthy but its doable and once you write a program for it its actually pretty fast so we do not need to solve the ODE. You do not need to write a program for calculating these values.

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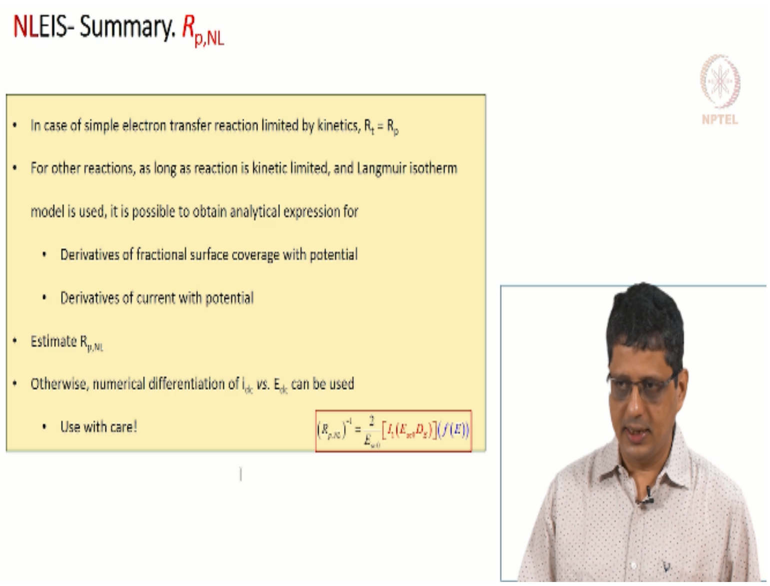

So in summary in case of simple electron transfer reaction charge transfer resistance and polarization resistance are the same as long as its limited the kinetics assuming that mass transfer is rapid and solution resistance is not high. For other reactions as long as we can say that the kinetics is limited and Langmuir isotherm model is applicable we can estimate the polarization resistance.

Using analytical expression basically we can calculate the change in fractional surface coverage with respect to potential the derivatives and we can calculate the nth derivative of current with respect to potential and then using this expression or the equivalent of this expression we can calculate the polarization resistance and in case solution resistance is important we have to write this as RpNL+R solution inverse of this okay.

Now what happens if mass transfer is not rapid even in that case as long as we can get the nth derivative of current with respect to potential perhaps using numerical method we can still calculate the polarization resistance we can still calculate the nonlinear polarization resistance it is just that when you take numerical derivatives you have to be very careful. We will stop here today.