# Electrochemical Impedance Spectroscopy
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## Lecture – 49
## Detection on Nonlinearities Using KKT

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Okay, so in the last class, we saw how to handle the solution resistance effect, right whether we use a small amplitude perturbation or a large amplitude perturbation, we can modify the code that we normally used to simulate nonlinear EIS and account for solution resistance and then we can find the actual spectrum incorporating the solution resistance effects. Now, I want to show you what happens when you apply KKT on data that comes from large amplitude perturbation, okay.

When we apply KKT, will it always detect nonlinearity or will it detect sometimes and will it flag it as okay and other thing is we also seen that the code can be modified to account for instabilities and generate the spectrum, when we have instability, whether KKT does a good job in detecting the instabilities, okay.

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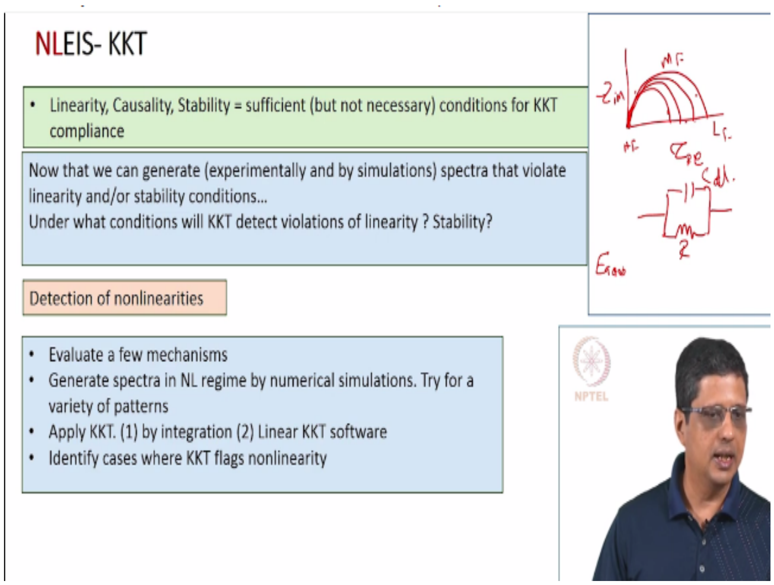


So, just refresh your memory, if the system is linear, causal and stable, then the resulting spectrum will be KKT compliance but it is a sufficient condition, it is not a necessary condition for KKT compliance. What it means is; it is possible that you may have a nonlinear system and that may be KKT compliance. If the system is linear stable, causal, it is guaranteed to be KKT compliance but just because some response says that its KKT compliance, does not mean it has come from a system which is linear, causal and stable, okay.

Now, we know how to generate EIS spectrum for cases with large amplitude perturbation, we know how to generate the EIS spectrum with instability and you can of course always add some noise and see how the spectrum will look, if the spectrum arises not just because of our perturbation but also because of the external noises, okay. Now, we want to do the following, we want to generate a variety of spectra for different mechanisms and then see whether in all cases, KKT can detect nonlinearities, in all cases can KKT detect instabilities, okay.

So, this is the methodology we used, evaluate a few mechanisms, generate spectrum in a nonlinear regime using numerical simulation and we aim to generate spectrum with different patterns, okay, then we apply KKT, there are many methods of evaluating for KKT compliance, direct integration is one method, okay, measurement model approach is another method and one variant of that is linear KKT software which makes it easy to implement this measurement model approach.

And then record whether this KKT program by integration or KKT validation by a measurement model approach, whether both of them are able to flag the nonlinearities, under what circumstances are they able to flag the nonlinearity, okay. To refresh your memory; under one condition, we know for sure that the data will be KKT compliance, even though it is coming from a nonlinear system, okay.

If we take a simple electron transfer reaction and if you generate a spectrum assuming there is no mass transfer limitation, assuming there is no solution resistance, in the complex plane plot, we know the spectrum will look like this, going from high frequency to low frequency, of course this is the mid frequency and if we apply a small amplitude perturbation, you might get a data like this for a particular scale.

If I apply large amplitude perturbation, we know that it is going to still be a semicircle with a smaller value of charge transfer systems and of course, polarisation resistance which means the system can be model by a circuit like this, so double layer capacitance here and this resistance when the perturbation amplitude, EIS is 0, is small, this resistance will be a constant depending on the kinetic parameter values and depending on the DC potential but that is going to be fixed.

When we increase perturbation amplitude, make it 50 millivolts, 100 millivolts, this will become a smaller resistance but still it is a constant resistance; constant impedance, independent of frequency and all this spectra will be KKT compliance, so this is one clean example where we know that the system response is not linear and yet KKT cannot detect or KKT cannot flag and say that there is something wrong with this spectrum.

So, it is possible that you have a nonlinear response and KKT will not be able to flagging but will it happen in all cases, will KKT say that all the spectra with nonlinear effects or KKT compliance.

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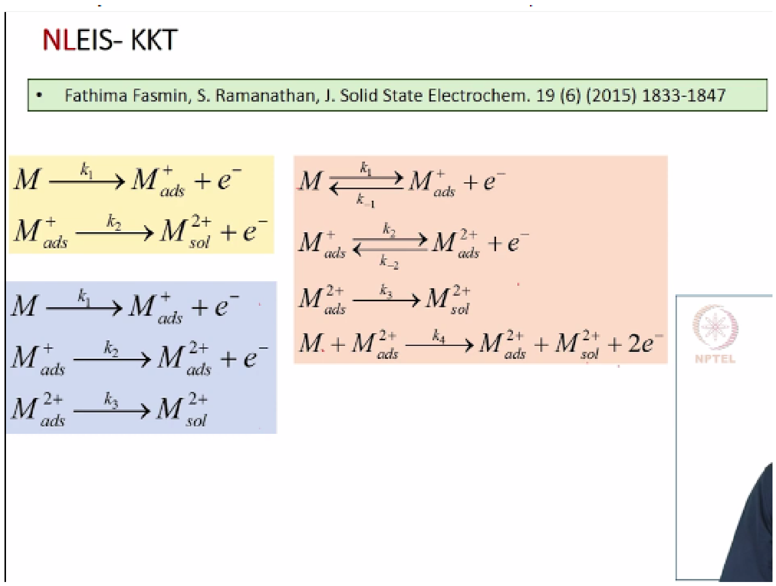


So, this work was published by a group in 2015, I will just summarise some of these results, we looked at 3 different mechanisms; first mechanism is metal going to metal 2+ into solution via one adsorbed intermediate, so the first step is the electrochemical step and the second step is also an electrochemical step, we have tried this for a variety of kinetic parameter values. The next example is with a different mechanism; it is still metal going to metal 2+ into solution but via 2 adsorbed intermediates.

The first and second steps are electrochemical steps, the third step is a chemical step, third example is little more complex, the first and second steps are reversible electrochemical steps, metal goes into metal+ adsorbed releasing an electron, metal+ becomes metal 2+ adsorbed species, again releasing an electron, third; a metal 2+ goes into metal solution, so until this, it is similar to the second mechanism we have tried, of course with reversible; in the first and second steps are reversible.

In addition, there is a fourth step, this is what we have referred to as catalytic step, so metal; bare metal right next to metal 2+ adsorbed species, bare metal becomes metal 2+ adsorbed, metal 2+ adsorbed becomes metal 2+ solution but in effect, metal 2+ adsorbed which is consumed here is produced here. We have seen how to generate the mass balance and charge balance equation for this before, so I will go through this code or details.

I just mention the certain kinetic parameter values, we used them and this is the spectrum that we get for small amplitude, for large amplitude and then we take those data and subject that to KKT validation and see what the results are, okay.

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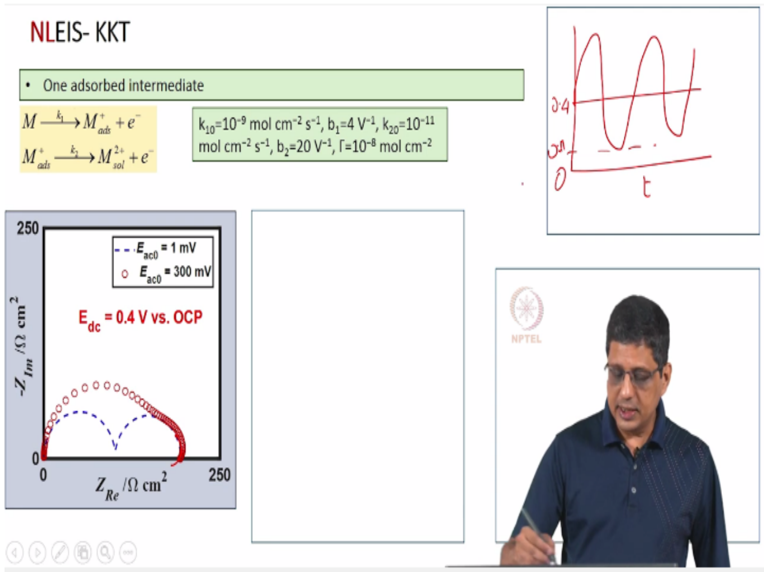


So, first example is with one adsorbed intermediate with certain kinetic parameter values, 10 power -9 moles per centimetre square for k1, the exponent for this is 4 volt inverse, k20 is of course 10 power -11, b2 is 20 and gamma is 10 power -8 moles per centimetre square and if you apply a DC bias of 0.4 volt versus OCP, right, this is in the anodic regime and in that case, if you use 1 millivolt, it is definitely in the linear regime, if you apply one millivolt perturbation, 2 millivolt perturbation and compare this spectra, they will overlap.

And if you apply very large perturbation, 300 millivolt, the spectra that you get are like this, 1 millivolt shows clean, well separated 2 semicircles, this 300 millivolts shows sort of 2 semicircles overlapping and in fact, this turns to the right somewhat like in an exaggerate fashion turns to the right somewhat like an inductive loop, normally one would not apply 300 millivolts of perturbation amplitude, right.

But here we want to exaggerate and see the features very clearly, see the difference between transformed and original data very clearly therefore, we have used very large perturbation amplitude. The code that is used to generate one millivolt can be used to generate 10 millivolts, 100 millivolts, any such amplitude, okay, since we are at 0.4 volt versus OCP, even when we apply 300 millivolt, the lowest point there, okay.

If you assume this is 0, this is 0.4, 300 millivolt perturbation amplitude will still be 0.1 volt above the open circuit potential, okay, so this is still in the anodic regime, so we do not have to worry about the cathodic reactions.

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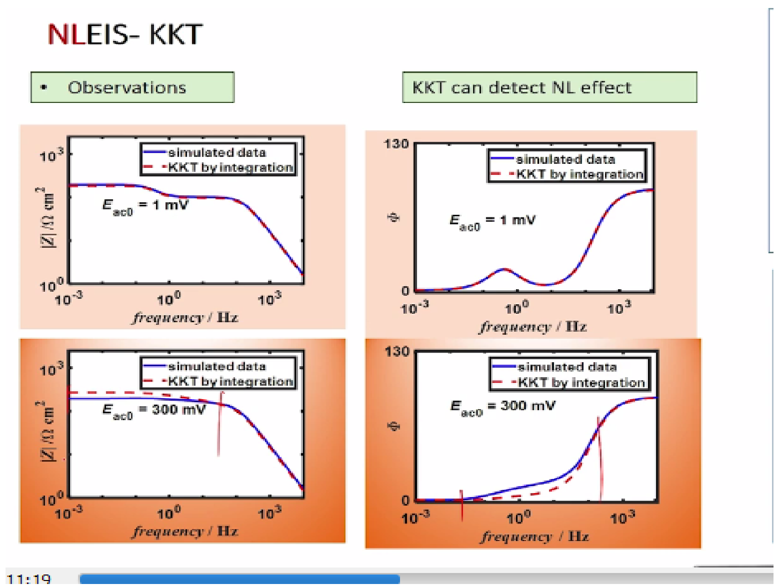


This is the spectra that we get and if we take 1 millivolt data and apply KKT, they simulate the data is what we have shown earlier as blue colour line and that transformed data, we use that software provided by a Professor (()) (10:15) and we get the KKT by integration, they pretty much overlap, so we can say yes, this is not violating KKT, therefore this is KKT compliance and of course we know it is coming from a small amplitude perturbation, so we are fine.

And if I take the data corresponding to 300 millivolt perturbation amplitude and plot the magnitude and phase as a function of frequency, it is board A plot, I can see that the original data; blue colour line is different from the KKT transformed data, so the transformed data is dashed red colour line and you can see that for mid frequencies and at low frequencies, is a clear difference, all right, so we can claim that KKT can detect the nonlinear effect.

See, once it is not compliance, KKT does not tell that the data is different from the original because of nonlinear effect or because of instability, it just says that it is not compliance, okay this case we know how the data was generated therefore, we can say that nonlinear effect is detected.

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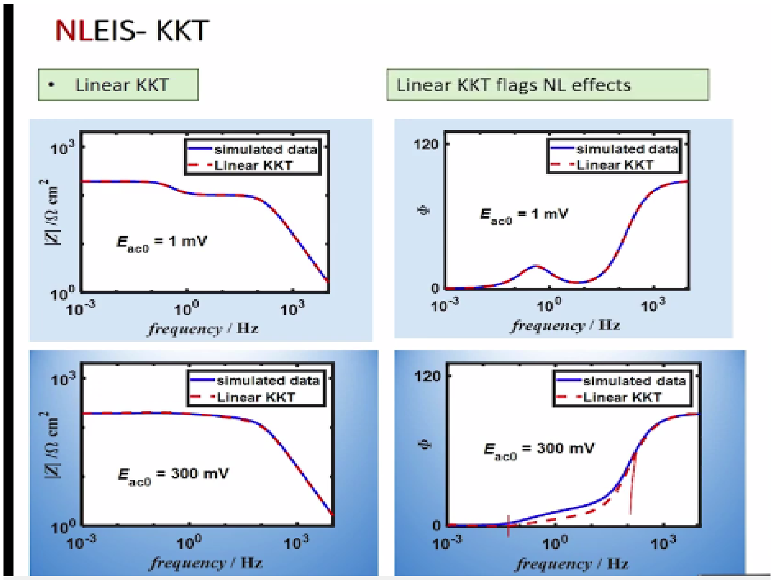


When you use a linear KKT software and compare the transformed data and the original data, they overlap very well for 1 millivolt data and at 300 millivolt, there is a difference especially at the mid frequencies, the magnitude appears to overlap very well, the phase is different which basically tells you that there is a difference between the original data and the transformed data, so it is not KKT compliance.

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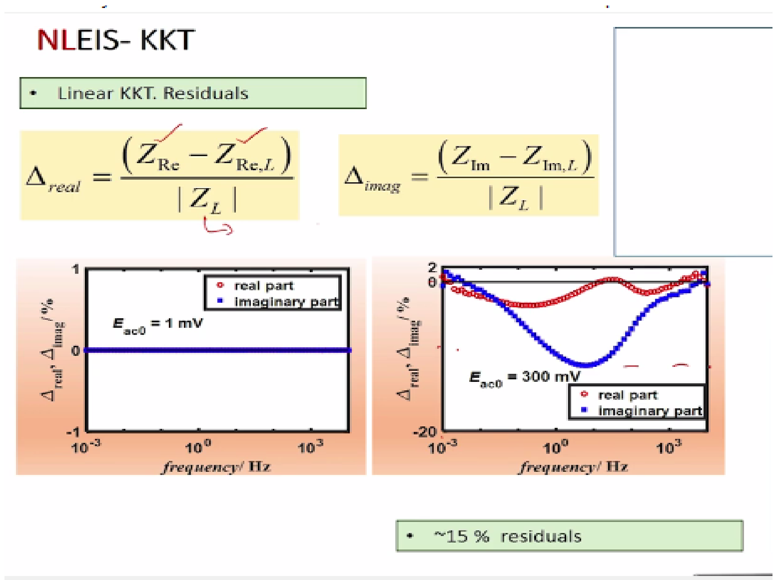


In case of linear KKT software, it is also good to look at the residuals, this also flags the nonlinear effect but one can calculate the residuals; the residual in the real values are basically, our simulation or original data minus the best fit, measurement model approach best fit data divide by the modulus of the Z, not Z real or Z imaginary but actual Z which is Z real + j Z imaginary.

And likewise for the imaginary part, the numerator consist of imaginary pat of the original data and the measurement model data or the linear KKT predicted data and the denominator consist of mod of Z, this is important because sometimes if you notice, Z imaginary may go to 0, may be close to 0, if you use Z imaginary here, you will get a very large value here and Z imaginary if it is exactly 0, it will in fact become infinity.

And if there is a very slight variation between the transformed data and the original data, we do not want that to appear as a large error, okay, so it is important to use mod of Z rather than Z real or Z imaginary and when you use this for 1 millivolt data, it is exactly 0, so it means it is fitting perfectly. In case of the 300 millivolt data, be real and imaginary residuals are plotted as a function of frequency.

And you can say this is probably 0 to 20, 0 to 10, may be 10, 15 percentage residuals, so it is fairly large and that is what appeared as a difference in the phase value here and you can say, yes, this is a significant difference. So, even if you take data in real experiments with some noise, you should still be able to see a significant clear deviation, systematic deviation between the linear KKT predicted data and the original data.

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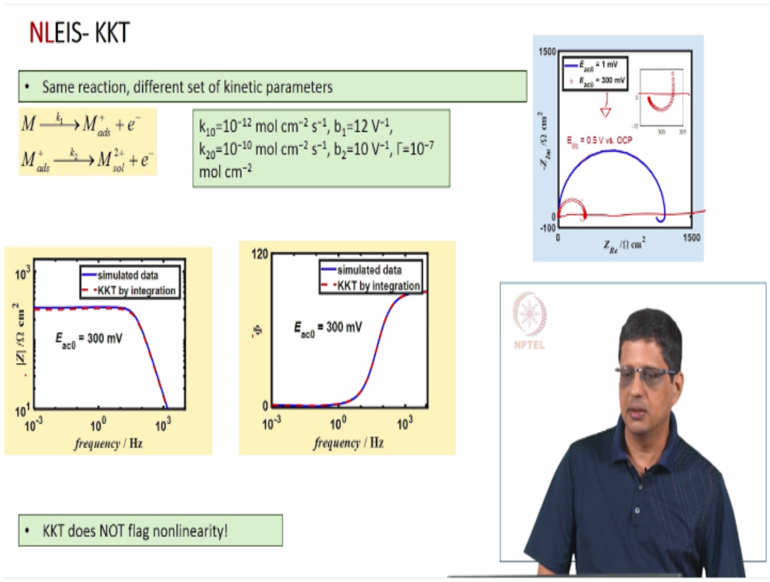


All right, now we have taken the same mechanism and tried different sets of kinetic parameters, different sets of DC potentials and in all cases, you would get spectra, we have tested many but we are showing a few here, okay, this is second example, same mechanism different set of kinetic parameters. Now, in this case we have taken the DC potential to be 0.5 volts versus OCP, we have tried 1 millivolt linear regime and 300 millivolt nonlinear regime.

So, 1 millivolt data shows a high and mid frequency capacity loop and a low frequency inductive loop, the large amplitude perturbation also gives you similar pattern except that in the same scale it is not so visible, not so clear but if you zooming here, you would see an inductive loop, it looks like it has shrunk, if I take the data at 1 millivolt and perform KKT by integration, the transform data and the original data will match very well.

I am not showing it here but when the system is linear, casual and stable, KKT by integration will give you a good much especially, when the frequency range is very wide because this is simulation we can choose the frequency range to be very wide, we have chosen from 10 power 5 to 10 power -3 that is 100 kilo hertz to 1 milli hertz and the data that we generate is KKT compliant.

In this case, even when the data is generated with 300 millivolt watts perturbation, we find that it is KKT compliant, so the real and imaginary part are phase and the magnitude, when I plot them in board A plot for the original data and compare with the transformed data, they overlap very well, KKT does not flag nonlinearity in this case although, by looking at this figure, we can clearly say, yes 1 millivolt data is different from the 300 millivolt data.

So, why is it that in the previous case same mechanism, different sets of parameters, KKT is able to flag the nonlinearity and this case, it does not seem to flag the nonlinearity.

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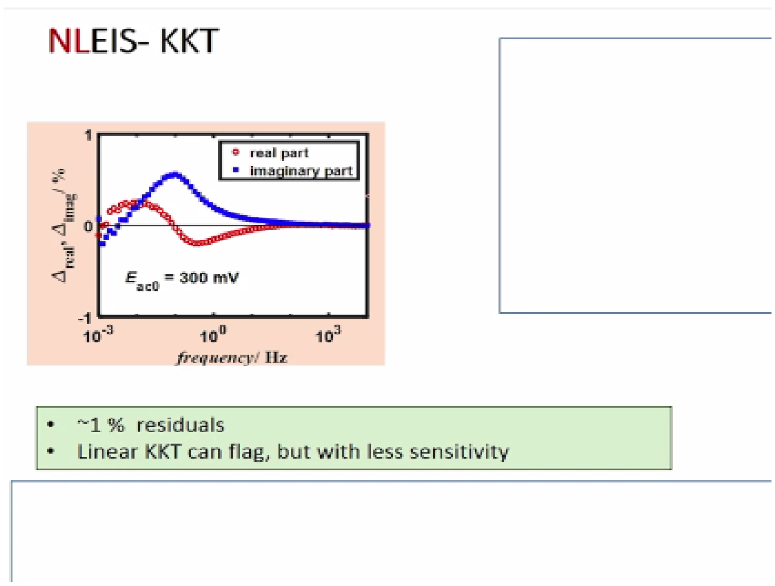


If you look at the linear KKT results; the same data, 300 millivolt data, if we subject a linear KKT, there is a systematic residual, okay, it is much smaller here though, its + or – 1%, previously it is 0% for 1 millivolt data and nearly 10, 15% for 300 millivolt data, here 1 millivolt data will give you 0% error, I am not showing it here but 300 millivolt data shows may be 1/2% or at the most 1% variation.

And if you have noise in the data, it is possible that the noise will subsume this, you may not see a clear systematic pattern, any case at least this is flagging it but sensitivity is not as high as it was in the previous case.

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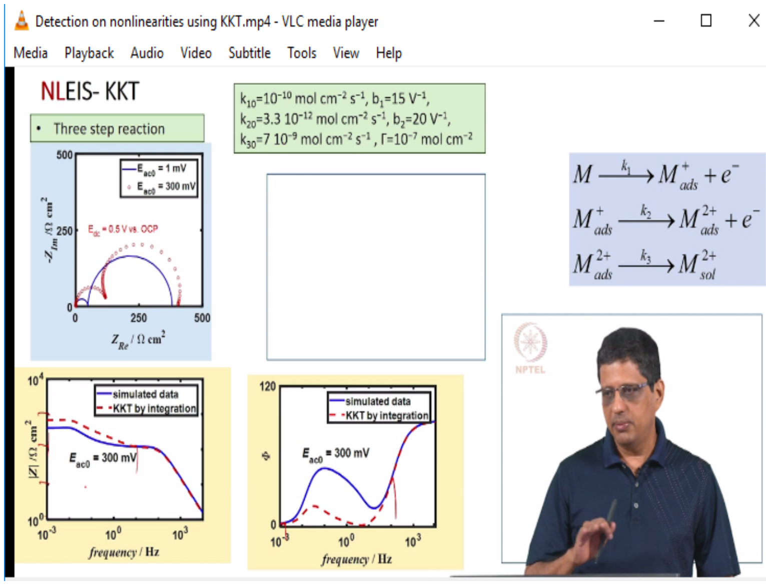


Next example is for a 3 step reaction to adsorb intermediates, so the mechanism we have seen this kinetic parameters we write it as 10 power -10, 15 for the first reaction, 3.3 10 power -12 and 20, 7 10 power -7 and of course third reaction is a chemical reaction, so there is no b corresponding to that and gamma is 10 power -7 moles per centimetre square. In this case, when we use 1 millivolt data, we get 2 semicircles.

In case of 2 adsorbed intermediate, you may be able get 3 semicircles, 3 capacitive loops but for these set of parameters, visually if you observe you can see 2 semi circles. When you go to large amplitude perturbation, this actually looks like a semicircle and this is like a distorted loop, I would not even call it a semicircle and when we try KKT by integration, it shows a clear deviation; very large deviation in fact for the phase.

And fairly, large deviation for the magnitude, you have to remember the magnitude is plotted as log of that mod Z, so it goes from 10 power 0, 10 power 1, 2, 3 and 4 and of course phase is in decrease, okay, so clearly this shows, yes this data is not a KKT compliant, 1 millivolt data is KKT compliant, you have to believe me in that.

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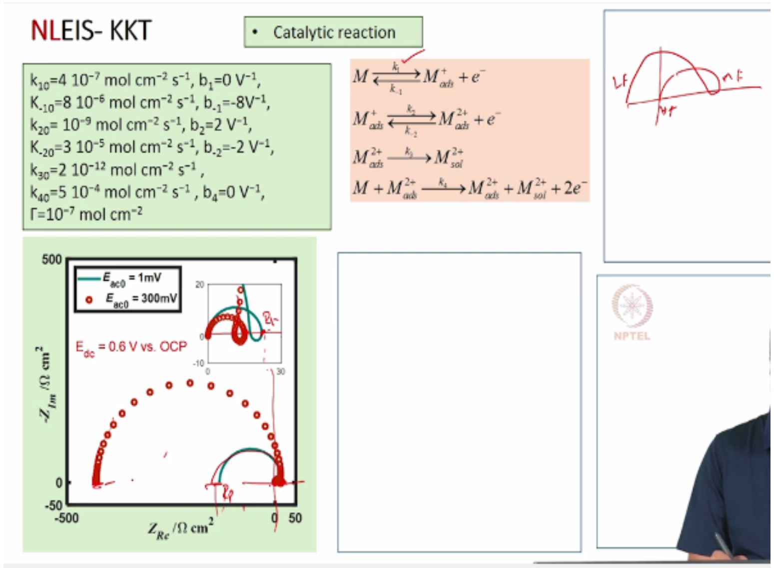


And linear KKT definitely detects, whenever the KKT by integration detects, linear KKT detects, even when KKT by integration does not detect the nonlinearity, linear KKT detects the nonlinearity, it is just that sensitivity is less now, the third party is the catalytic reaction. So, set of kinetic parameters here, b1, first reaction; forward reaction is with 0 volts that means, it is like a chemical reaction although, it is a electrochemical reaction, we say that the transfer coefficient is 0, reverse is -8, it is going to decrease.

The reverse reaction will decrease with an increase in potential, therefore it has a negative sign, b2 is +2, b -2 is -2, b3 of course is a chemical reaction and b4, even though it is a electrochemical reaction, we are setting the b4 to 0, this is one set of kinetic parameters of course, you can try for a wide variety of kinetic parameters and this is one of the examples where we see negative differential impedance, comes like this, this is the high frequency, mid frequency and low frequency data.

So, actually this is the origin, it is not very clear, so that zoomed in here, high frequency to mid frequency and then low frequency comes here, 1 millivolt data shows a charge transfer resistance here and polarisation resistance which is probably in the range of 50, 100, 150 something in that range and the charge transfer resistance is in the range of about 20, 25. When we go to large amplitude perturbation, the charge transfer resistance in this example decreases but the polarisation resistance, the magnitude increases; it is close to 400 Ohms with a negative sign, Ohm centimetre square.

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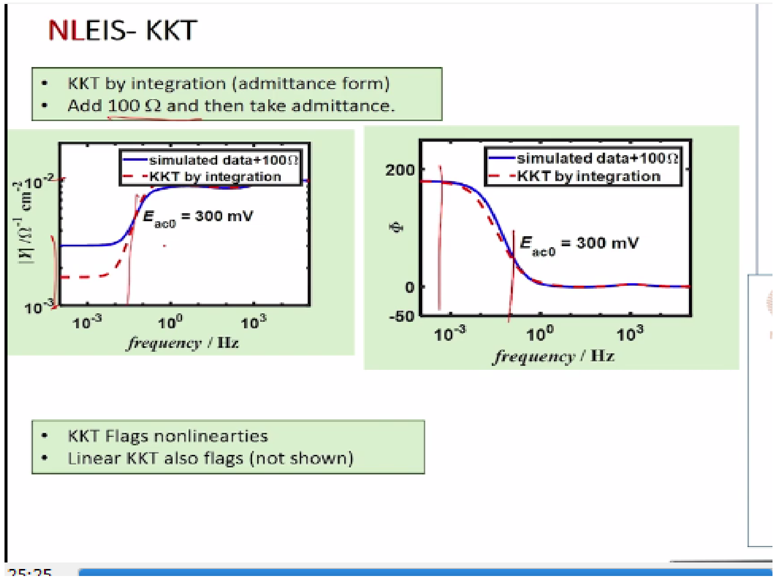


So, the actual value is lower but the magnitude is larger, this case since it goes to the left side on the complex plane plot, it goes to negative real values, we have to use the data in the admittance form and perform KKT by taking the data in the admittance form, okay, so we have to do KKT by integration using the admittance form, if you give it in the impedance from, even if it is KKT compliance, it is going to look like a mirror image that's transformed data will look like the mirror image of the original data, okay.

So, what we have done is the following, we have got data in frequency Z real, Z imaginary and of course, Z is given by Z real + j Z imaginary and Y is going to be inverse of Z but instead of directly taking the simulated data, we have done the following. So, we have data at 100 kilohertz and of course, many intermediate values, this is going to be very small number, close to 0 because we assume that the solution resistance is not there, right.

So, this is going to be very small value, this is going to be very small value and when we take the inverse to find the admittance, it is going to be extremely large and numerical round off error will come in and that means the admittance value, it is going to be very large number that is not easy to get accurate value in the Matlab program on any programming environment, so beyond a limit, when we use double or integer, whichever mode we use, it is going to be usually used in double but it has a certain limitation on the accuracy.

So, to avoid this problem what we have done is to take that impedance data and generate new impedance data by saying Z real is Z real of this + 100 volts, now if we take this and substitute here and find the inverse, that is going to be a finite number, it is not going to be extremely large, so essentially I take the data, add 100 Ohms to that and then take the admittance form and process it.

So, I can avoid some of this round off errors and after doing that notice the following, this is 10 power -3 and this is 10 power -2, so I take the inverse, it is going to be somewhere between 100 to 100 Ohms, here because this is admittance form, it is going to be in the range of 10 power -3 to 10 power -2, 1 millivolt data would come as KKT compliance, 300 millivolt data shows a clear difference here, interface as well as the magnitude.

Oftentimes, what people would do is; take the impedance, inverted to get the admittance, perform KKT in the admittance form, get the transform admittance and then invert it to get the impedance form and plot it that is also fine, you can plot it in the impedance form say that this is the simulated data and this is the transform data. In any case, you get a clear difference so, in this case KKT can flag the nonlinearity and linear KKT also flags the nonlinearity.

You have to remember to go to the software and choose the option to say that this has to be transformed in the admittance form and then it will detect the nonlinearity clearly, 1 millivolt data will be KKT compliant, when we transform in the admittance form, 300 millivolt data will not be KKT complaint and of course, you always have to transform in the admittance form whenever that data goes to the negative side in the complex plane plot or left side in the complex plane plot.

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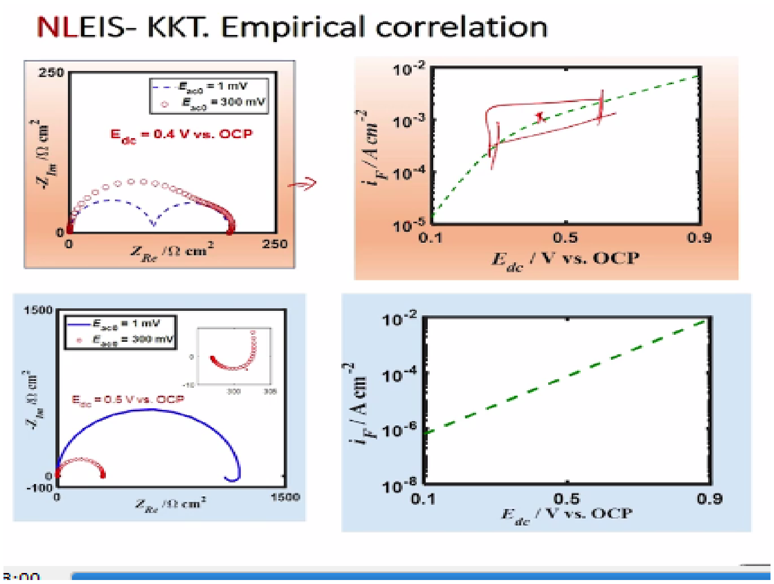


Now, after looking at this result, we know that sometimes KKT can detect, sometimes KKT cannot detect the nonlinearity. They looked at various possibilities and this is the conclusions we have come to, first set of spectra, right, 1 millivolt and 300 millivolt, this KKT was able to detect the nonlinearity, if I plot the potential dynamic polarisation plot, log current versus potential, current is in the log scale.

And If I take 0.4volt and I use 300 millivolt range, this range log Idc versus Edc is not linear now, here is the thought process, if I take I versus E, for a simple electron transfer reaction meaning, reversible reaction, this is going to be exponential and this is going to be exponential, if I draw it as log, of course I cannot draw, I cannot find the log of 0, if I go to a large enough potential and draw it as log i versus potential, this is linear and I can even neglect the reverse reaction.

And we know when log I versus E was linear, this reaction, the resulting spectra where KKT compliant for a simple electron transfer reaction, so perhaps even in other reactions, if log I versus Edc is linear, may be the spectra that we get would be KKT compliant and if it is non-linear perhaps it is not KKT compliant, so with that hypothesis, we have check. This case, log I versus E with DC log I versus Edc, it is not linear and this is not KKT compliant.

If I look at the second set of data, if I look at log I versus Edc, it is linear and KKT by integration is not able to detect this violation of linearity and linear KKT can detect it but it is less sensitive.

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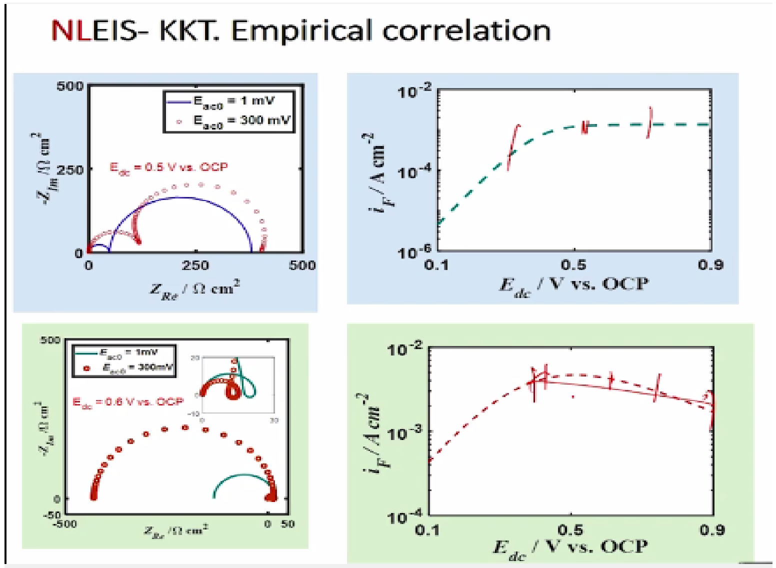


Three step reaction with 2 adsorbed intermediate, again at 0.5 volts, if I go to 300 millivolts range, it is not linear, log I versus Edc is not linear, here at 0.6 volts, of course it has a negative slope that is why the low frequency impedance settles at negative real value and this also if I go to + or - 300 millivolts, 0.6 + or - 300 (()) (28:30) fairly large, it is non-linear, so the hypothesis is that whenever log I versus E is non-linear KKT by integration can detect the nonlinearities, linear KKT software can detect the violation of linearity.

If log i or natural log i versus Edc is linear, then KKT by integration does not seem to detect it and even linear KKT detects it but with less sensitivity, okay. We have tried it for few more kinetic parameter values, few more sets of kinetic parameter values and in all cases, it seems to work, so based on this empirical study, we think this is true.

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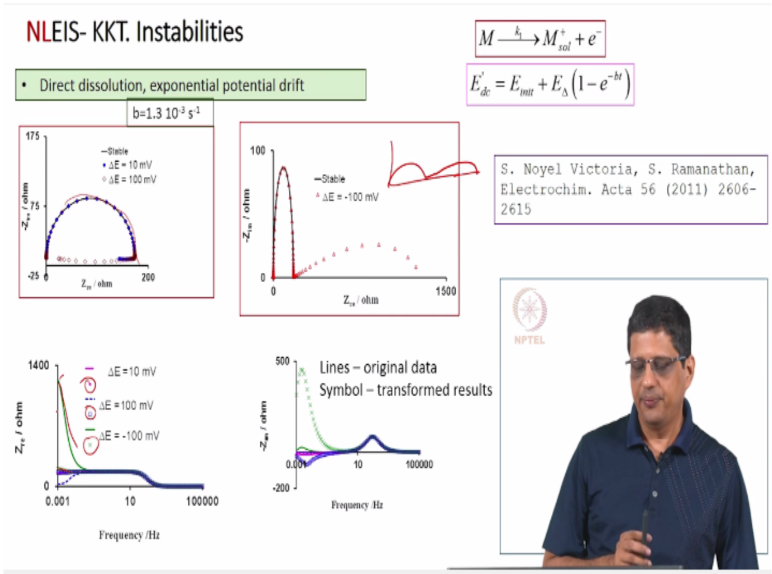


Next, okay we know how to generate the spectrum incorporating the instability effects or drifts, we seen this in the previous class, so I want to show you an example where we have taken the simple electron transfer reaction and we apply an exponential drift, okay, this is published in 2011 by our group and we have seen before that if you have 10 millivolts or 100 millivolts drift, maximum possible drift with a particular b value, this is the data that you would get.

And if it is -100 millivolts, it is going to look like a; in a proper scale, it is going to look like this, in a distorted scale, it is going to look like this. If I take this data and apply KK transform, I will always find that KKT will show that the data is not KKT compliance, here the lines are the original or simulated data and the symbols here are the transform data, these are the transform data.

Here, I have plotted Z real versus frequency and Z imaginary versus frequency, it is not that common but it is also done sometimes, the main point is the original data and the transform data do not match especially, at the low frequencies, okay, you can also see the high frequency region, this stable which is shown by a continuous line, and the points which correspond to the unstable system, they are more or less the same.

So, at the high and mid frequencies, there is not much of a difference between the stable and unstable system, at the low frequencies is a clear change and that is shown in the transform data also at the low frequencies it deviates and whatever cases we have tried, whenever there is instability, KKT is able to flag this, whether we use KKT by integration or KKT by linear KKT software.

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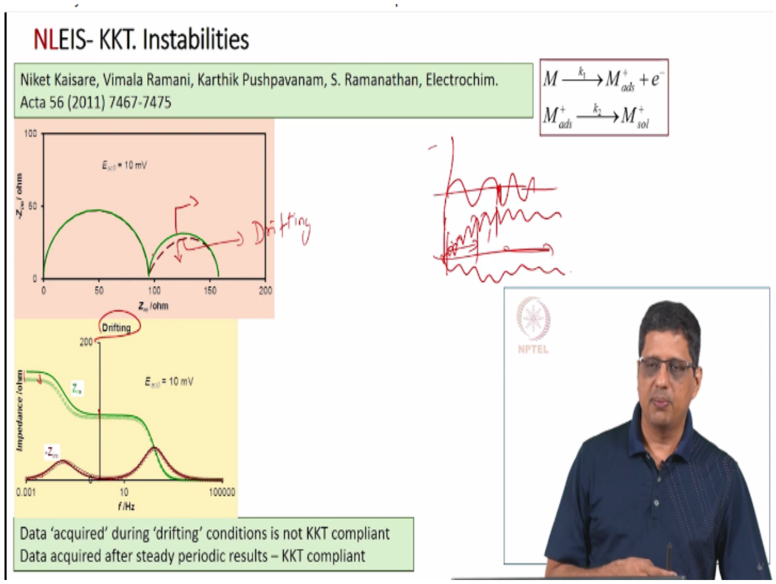


Next, normally when we say that system is stable, what we mean is the following; we have a DC potential, they apply a AC potential, if we stop the perturbation and wait for some time, the system should come back to the original condition, then we would call that as a stable system, okay. Now, there is a subtle thing when we apply AC potential, we have seen that it does not give you steady periodic results immediately.

It can take some time for us to get the steady periodic results, now I apply AC potential on top of DC, the current would do this and then settle or do this and settle. Now, if I stop applying the AC potential here and wait, it should come to the original condition, the system would revert back to the original condition however, if you record the data here and call that as impedance, then normally one would not say that the system is unstable, system is stable.

Because when apply a perturbation, it responds, when I stop the perturbation, it goes back to the original condition that is all right but there is one more point that is when you record the data that should come from steady periodic result, if you take the data before the system achieve steady periodic condition, then what happens is this. We have looked at the data like this, if you get results after steady periodic conditions, the green colour line is what you would record.

If we take the data before coming to steady periodic condition, if we take the data in the first few loops, may be first loop or first few loops, at high frequencies and at low frequencies you will not see much of a difference for different reasons. At high frequency because, majority of the current goes through the double layer capacitance, at low frequencies because, system would come to stable condition even before half loop is completed.

At mid frequencies, a significant current goes through the faraday process and system would not have come to stable condition or steady periodic result, so there is a difference. If I take the data that is under what I call as drifting condition, you can also say before coming to steady periodic results, initial conditions and perform the KKT by integration, what we see is the following. Z real; there is a significant difference, imaginary; there is slight difference is not very clear in this scale.

But KKT will show a difference even though, this is 10 millivolt data and if we take the stable data, it will be KKT complaint, if we take the data in the initial condition where it is not giving you steady periodic result, this data will not be a KKT compliance, so if you look at this, if you just look at the overall definition of is the system stable or unstable normally, people would say that this is stable.

But the data should also be acquired under steady periodic response, if it is acquired during the initial condition where it is not reached steady periodic results that data will not be KKT complaint, okay.

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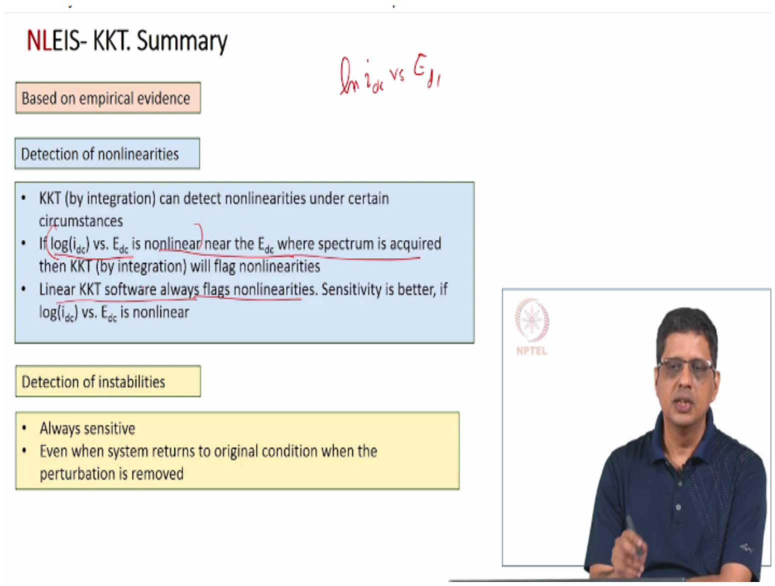


So, in summary, based on empirical evidence that means we are not shown theoretically that when log I versus E is a straight line, when it is linear, the violations of linearity will not be captured by KKT, KKT will not flag the spectrum acquired at large amplitude perturbations but with a number of simulations what we conclude is that if log I versus Edc is non-linear near the Edc where the spectrum is acquired.

Then, KKT by integration will flag the non-linearities, okay, linear KKT software always flag the nonlinearities, however if this comes from a system where log i versus Edc is linear, then the sensitivity is less and when you look at the instability, when a system is unstable, KKT will always flag it, whether it is linear KKT or by integration and even when the system returns to the original conditions, if we acquire data during the time where the system has not settled and it has not begun to give steady periodic response, then also KKT will flag the spectrum.

So, KKT is actually very sensitive to stability criteria, okay, we will stop here today.