Electrochemical Impedance Spectroscopy
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Lecture - 31
Patterns Reported in Experiments

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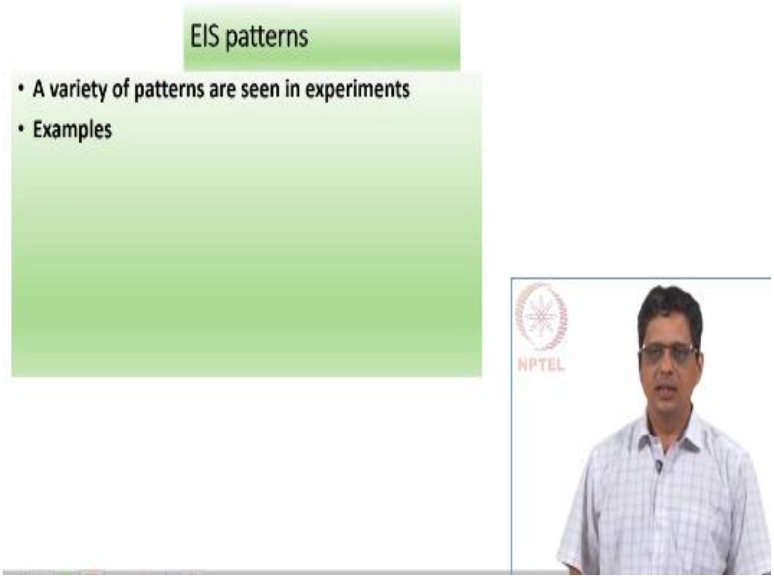

Earlier we have analyzed some mechanisms and we have seen that each reaction mechanism can give rise to a variety of patterns, patterns in the complex plane plot of the impedance spectrum. Now I want to show you some examples from literature, where people have seen certain patterns in experimental conditions and many a time they have analyzed it and using RMA, using reaction mechanism analysis, they have been able to model this spectra.

This is not an exhaustive list obviously there are there are many other publications with probably different patterns, but this gives you an idea of what are all possible.

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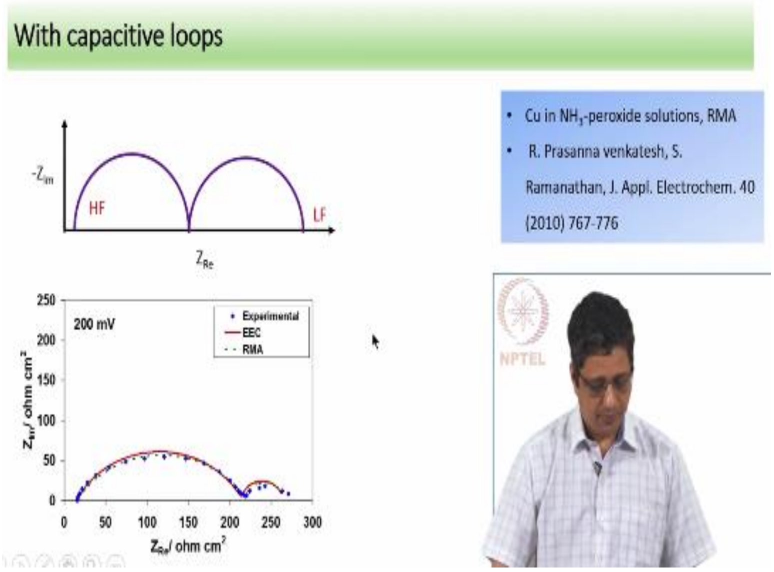

This is one of the simpler ones, of course people have seen data with just a semicircle or part of a semicircle. Here this is an example with two capacitive loops. In all these plots I am going to show you -imaginary on the y axis and real on the x axis.~~,~~ This is a starting point high frequency data and as you go to lower and lower frequencies it forms one capacitive loop followed by a second capacitive loop.

This can arise from many systems, but in this example, this has been seen for copper dissolving in a solution containing ammonium and hydrogen peroxide and this has been analyzed using mechanistic analysis. [Please refer to video 1:50] You can see that the loops that I have drawn here are more or less equal sized whereas the loop that are drawn here are obviously not of equal size. This is just to show that these patterns are possible okay. This is taken at one particular dc bias of 200 mV.

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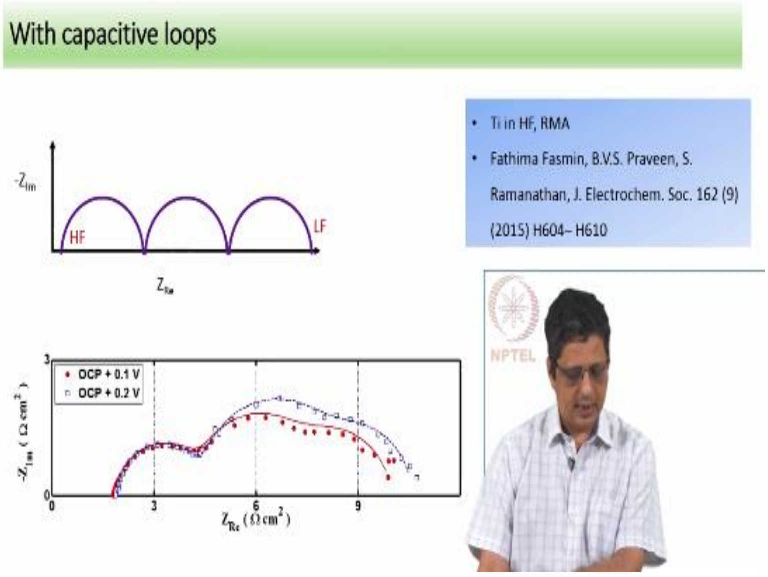

Now three capacitive loops again starting at high frequency data, high frequency data starting near R solution and then forming one capacitive loop, second capacitive loop and third capacitive loop. Here of course I have drawn them very nicely or neatly. It may not form very clearly distinguishable capacitive loops, some of them may overlap to some level, but if you do electrical circuit fitting or equivalent electrical circuit fitting you would note that two capacitive loop model will not be able to model this well. You will need a circuit with three time constant. One example of this is titanium dissolving in HF this shows the first loop coming out nicely. Second and third loops are not that well separated, but you can also see that it cannot be model with only one capacitive loop from the mid frequency to the low frequency data. These are taken at two biased conditions and at both conditions it shows three loops, for both conditions. And this is in the region called active dissolution region. This is in 2015 and this is also analyzed using mechanistic analysis.

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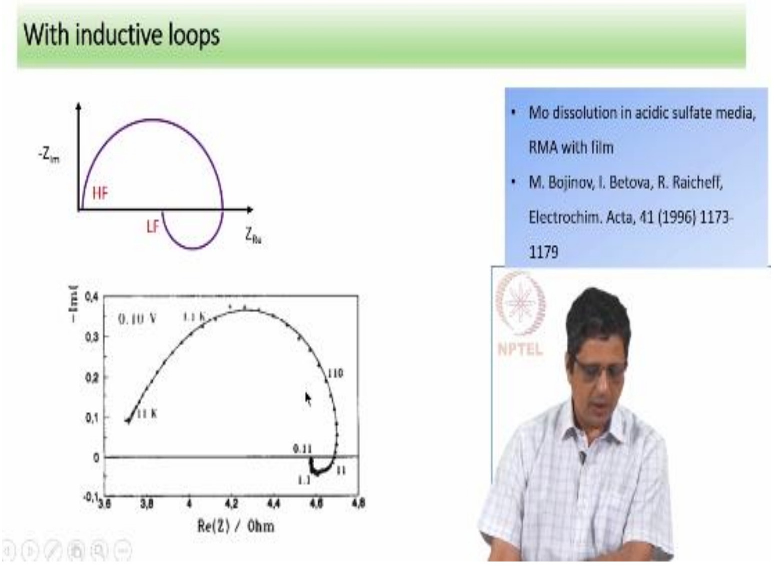

There are many publications which show that inductive loops at low frequency can form. Of course there are many more results with capacitive loops, but there are many publications or sufficient number of publications with inductive loops. [Please Refer to video 3.41] This example is given; publication by Professor Bojinov and this is molybdenum dissolution in acidic sulfate media. In this they have modeled it using a film with a reaction. So naturally here this is going from high frequency to mid frequency, low frequency. This is not a clean loop, but overall you can visualize and say this is a system where high frequency you have capacitive loop high and mid frequency you have capacitive loop and at low frequencies you have inductive loop.

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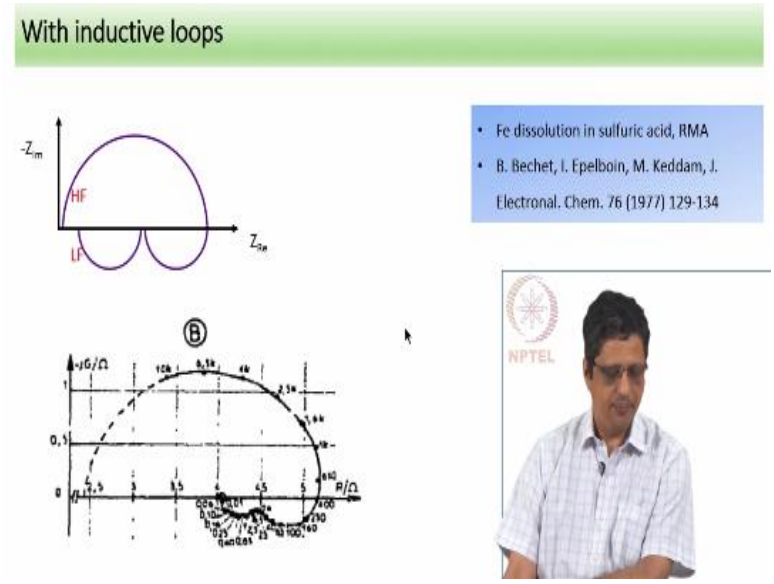

It is possible to have more than one inductive loop. So this starts at high frequency goes to middle frequency, forms one inductive loop and then subsequently it has another inductive loop and this is published in 1977 that means nearly four decades ago. This is ion dissolving in sulfuric acid and this has been analyzed using mechanistic analysis. I do not remember the biased used for this and I do not remember whether it is measured in pseudo galvanostatic mode or pseudo-potentiostatic mode.

In any case high frequency to mid frequency its capacitive loop and then middle to low and very low frequency it forms two inductive loops obviously of different sizes, but you can also clearly see there are two well separated inductive loops at the low frequencies. You can also understand that four decades ago the computation power available for someone to model this is lot less than what it is now.

There availability of software with optimization algorithm is also not going to be as good as it is now. So if somebody has done this 4 decades ago you can imagine how much challenge they have faced and overcome.

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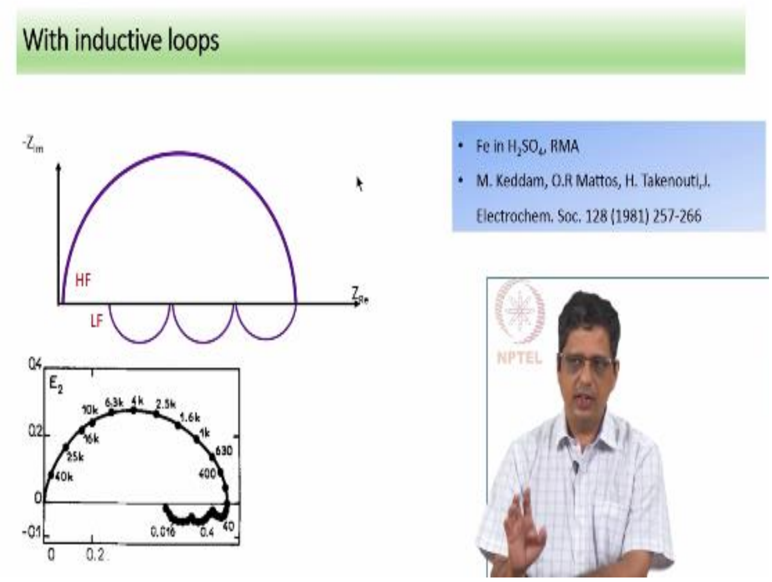

[Please refer to the video 5.45] Next example is a data with 3 inductive loops at the low frequencies. This is in case of ion dissolving in sulfuric acid this is published by Professor Keddam in 1981. This is the actual data I have taken this or adopted this from the publication showing 1, 2 and 3 inductive loops at the low frequencies and these are actually with biases.

And sometimes I will show you some examples with inductive loop, another examples with negative resistance, another example with capacitive loop it might be coming from one publication and this might be acquired in different conditions such as different dc biases, it might be acquired with different solutions. If it is in one solution, one electrode in one solution with different dc biases, all of them have been modeled using one set of kinetic parameters.

So I might show you one or two examples here, but they probably have modelled many of them simultaneously because the aim here is to show you some examples of different patterns. I am not collecting all of them and showing here. So in all this examples I do not mean to imply, that they have modeled this one spectrum with one set of kinetic parameters.

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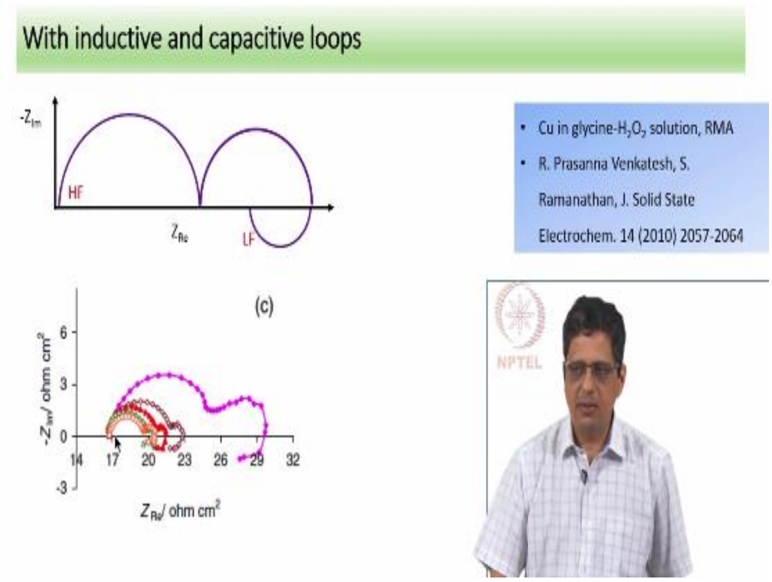

[Please refer to video 7.19] Now another example where you have high frequency capacitive loop, we have mid frequency capacitive loop and low frequency inductive loop. This is seen for copper dissolving in a solution containing glycine and hydrogen peroxide and we have published this in 2010. This is for different dc biases, you can see for all of them you have high frequency capacitive, mid frequency capacitive, low frequency inductive. It has not completed the loop probably because the low frequency data was noisy and it was taken out or not shown here and when we change the dc biases the size of these loops shrink, the pattern remains the same and this has also been analyzed using mechanistic analysis.

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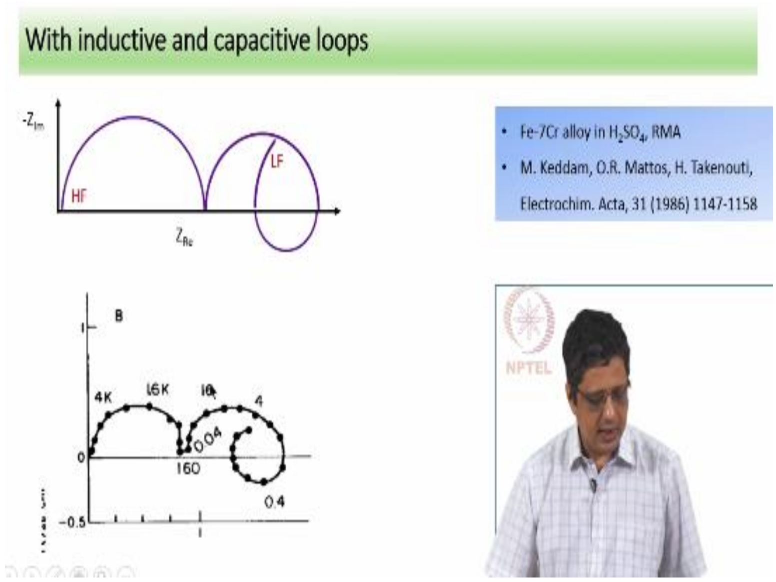

[Please refer to video 8.06] Now a little more sophisticated pattern. It is an extension of what we have seen before capacitive, capacitive, inductive followed by a capacitive loop. A capacitive loop in here, the data is little noisy here another clean capacitive loop, inductive loop and a capacitive loop. The numbers here represent the frequencies at which these data points have been taken and this is published in 1986 this is a iron chromium alloy dissolving in sulfuric acid again analyzed with mechanistic analysis.

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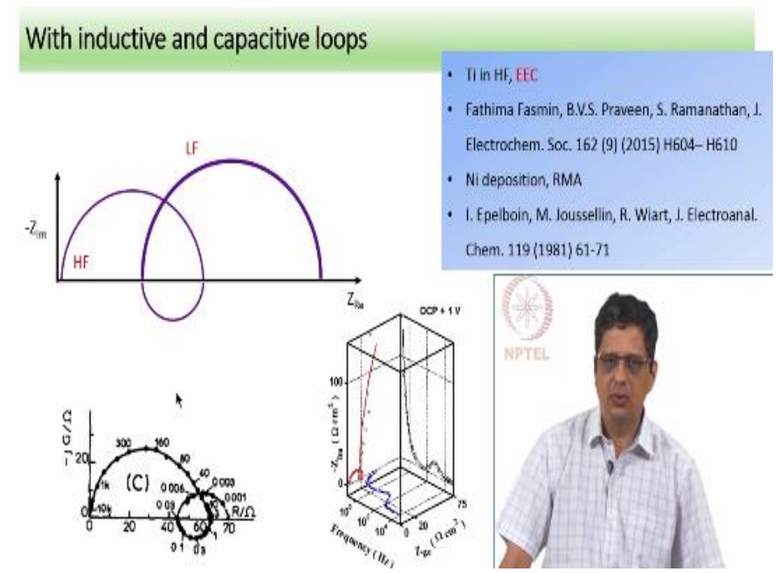

[Please refer to video 9.08] Now inductive loop at low frequencies is the example we have seen before. It is possible to see inductive loop at mid frequency. So capacitive loop followed by an inductive loop followed by a capacitive loop again. This is an example where you have a capacitive loop. It is drawn in 3D plot here so complex plane plot is shown on the red color and the blue color lines are actually form of bode plots where you plot imaginary value of impedance versus frequency. Real value of impedance versus frequency with the frequency in log scale. This is modeled using electrical circuit in this particular case. For Ti dissolving in HF at high dc potential, high dc potential meaning a large anodic potential where Transpassive dissolution occurs. So initially in this case active dissolution occur that means surface is not covered by protective oxide, then current decreases with potential with current decrease with an increase in potential. That happens in what is called passive region, but once the surface is completely covered with the passivating oxide if we give very large positive potential still dissolution can occur and that is called Transpassive dissolution, that was not analyzed in detail, but it was just modeled using electrical circuit. Another example is Nickel deposition this is published in 1981 by the group of Professor Epelboin. [Please refer to video 10.23]

and this shows clearly capacitive loop followed by an inductive loop at the mid frequencies and a low frequency capacitive loop and this was modeled using mechanistic analysis. You can see the notation is little different, some of us use Z imaginary, Z real, somebody else might use a slightly different notation to indicate R in Ohms, J in Ohms –jG to indicate it is R –JG.

R is the real part which normally we would write as Z_{real} real Z subscript real and G is what we would normally write as Z_{imag} subscript imaginary. They have written just –jG to indicate j is the imaginary number. So especially when you see some of the older publications you have to just look at it carefully and understand what they have given here.

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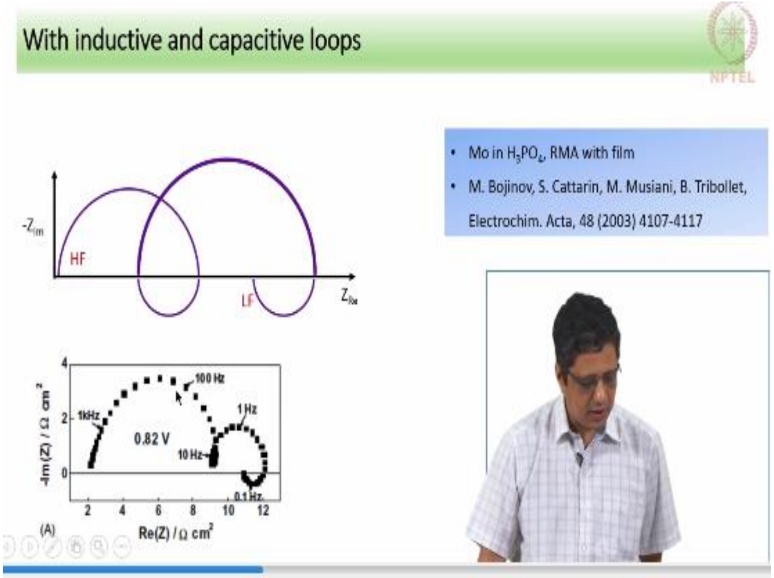

[Please refer to video 11.35] A further extension of this, you have high frequency capacitive, mid frequency inductive followed by a capacitive loop followed by an inductive loop and this has been shown or this has been observed for molybdenum dissolving in very high concentration of phosphoric acid. This was published by Professor Bojinov Acta in 2003 and this is modeled using a film dissolution occurring through a film.

So it involves mechanistic analysis, but it also involves film and this is the actual data or snapshot of the actual data adopted from that publication. So previously we showed a capacitive loop, inductive loop, another capacitive loop and inductive loop and if we remember the charge transfer resistance would be the point here whatever that value is and the polarization resistance will be somewhere here. So here the polarization resistance is more than the charge transfer resistance.

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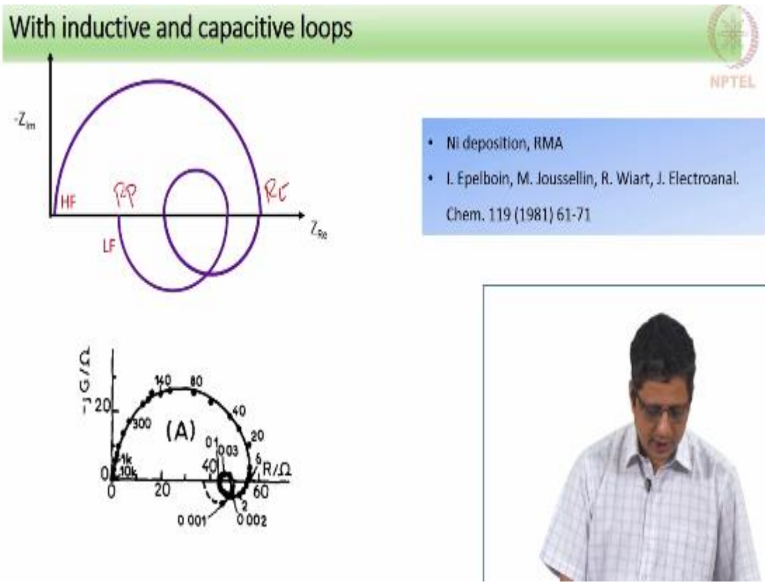

Same set of loops occurring in the same sequence, but with different magnitudes that is capacitive, inductive, capacitive and inductive, but with different magnitudes for these loops or for those inductor values and capacitor values, if we model this with electrical circuit that will give rise to a pattern like this here the polarization resistance is smaller compared to the charge transfer resistance that occur somewhere here, here where I trust the most.

[Please refer to video 13.23] This would be charge transfer resistance and this would be the polarization resistance, and this has been observed for Nickel deposition, electro deposition and this is published by Professor Epelboin in 1981. You can see that they have got data here first capacitive loop followed by inductive loop followed by capacitive loop followed by partial inductive loop. The dash lines here, show that they believe that if you extend and take data at lower frequency it would appear like this most likely they have taken data at lower frequency and it was noisy or not repeatable and therefore they have published only data that was clean and repeatable, but definitely beyond this capacitive loop at low frequency when you go to even further lower frequency you can see a partial inductive loop, and that is at 1 mHz.

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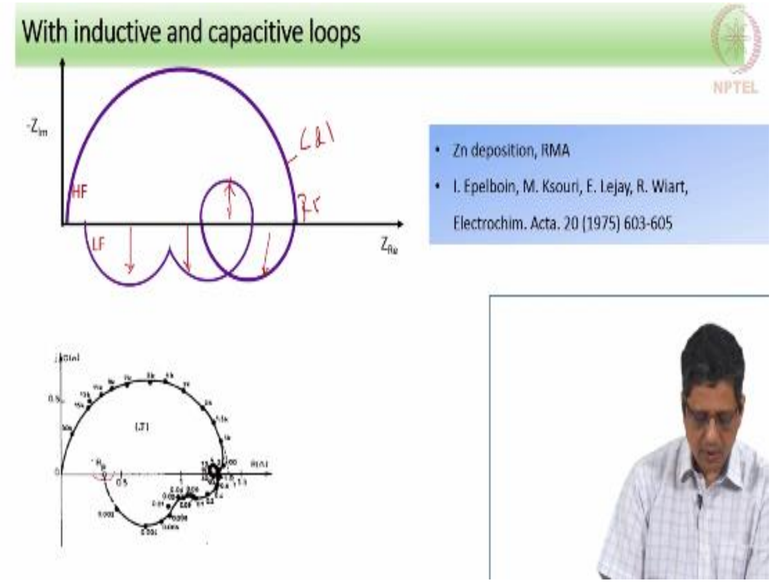

So now this element has three inductive loops and two capacitive loops, that means one high frequency capacitive loop can arise from charge transfer resistance and double layer capacitance. So this we can explain using charge transfer resistance and double layer capacitance and of course this offset is for solution resistance. This is one Maxwell element, this is one Maxwell element, this is one Maxwell element and this is one more Maxwell element.

So I have four Maxwell elements that means four intermediates if we are going to explain using mechanistic analysis without any film, without any mass transfer, without any porous electrode structure. So this was basically published, this was published by Professor Epelboin in 1975 and this is for zinc deposition and this was analyzed using mechanistic analysis. Although I have drawn them with certain magnitudes they are of different magnitudes you can see this first inductive loop is small, second capacitive loop is small next inductive loop is little larger and the last one is much larger and of course it was taken up to 2 mHz and extended to real axis to indicate where the R_P is likely to occur, and this of course turns in it is not so nice as I have drawn here. Of course what I have drawn is just artificially taken arcs and drawn them so it is not going to be clean in that sense. So they have marked R_T as most likely occurring here and R_P as most likely occurring here.

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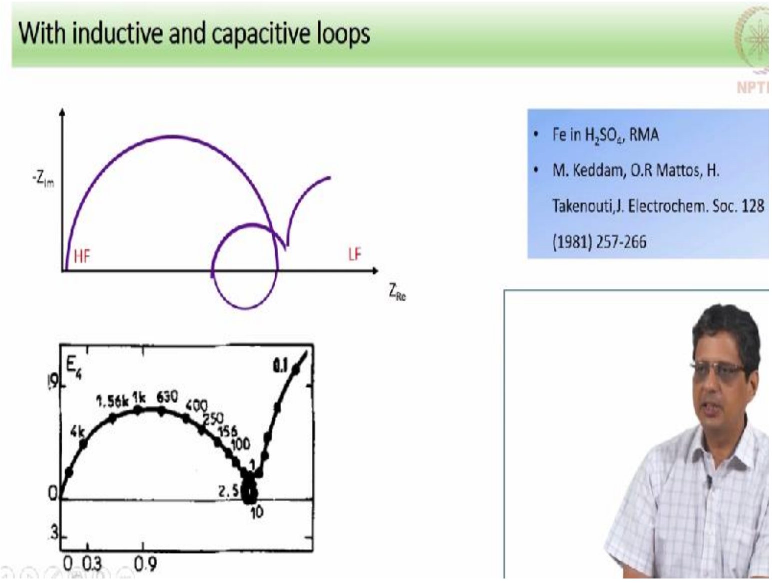

[Please refer to video 16.06] This is capacitive loop at high frequency, inductive loop at mid frequency two capacitive loops at low frequencies. Again seen in iron dissolving in sulfuric acid published in 1981 by Professor Keddam's group and this is analyzed using mechanistic analysis. If you see the actual data you can see the high frequency loop a small inductive loop followed by a small capacitive loop, but before it is completed next capacitive loop manifest here.

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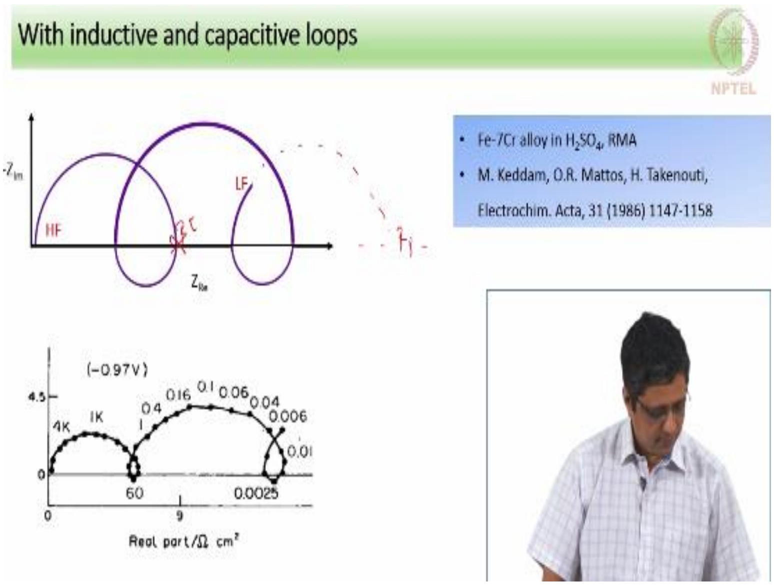

This is a staggering of capacitive loop followed by inductive loop followed by capacitive loop followed by inductive loop followed by capacitive loop again. So this is R_t, this point here is Rt one absorbed intermediate, two absorbed intermediate, three absorbed intermediate, four absorbed intermediate this presumably will extend here, and settle here at R_P. Of course if you actually model this and project this you will not have that much confidence in the value of R_P, but most likely the data at the lower frequency were noisy or not reproducible.

This was seen for iron chromium alloy dissolving in sulfuric acid and again published by Professor Keddam group in 1986. So this is the actual data taken up to 6 mHz.

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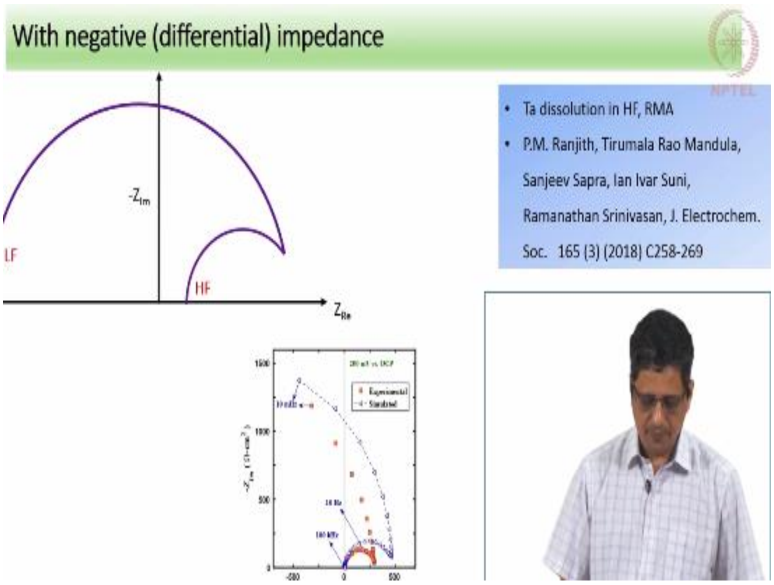

Now I want to show you some examples which give negative impedance, negative impedance meaning, at low frequencies the data settles at the real axis and the value is negative that means R_P polarization resistance is negative, and we know that it is possible because it is a negative differential impedance it is not negative impedance per se and often we call it as negative resistance.

We have seen this for Tantalum dissolving in HF and this is one of our recent publications. At 200 mV versus OCP in the passive region, that is 200 mV anodic of open circuit potential the experimental data shown in red color squares clearly shows that high frequency it is a capacitive loop, low frequency is a capacitive loop, but with negative polarization resistance.

We analyzed it using electric circuit, if we use electrical circuit you can fit it well, but then getting physical meaning out of that is difficult. We have also analyzed it using mechanistic analysis where we fitted data not just with this data, but polarization data as well as impedance data at multiple dc potentials, and if I remember right at two different HF concentrations and model this the fit is not as good as what one would get from EEC.

But the information we get out of this fit even if it is moderate quality fit, information we get out of that is lot more.

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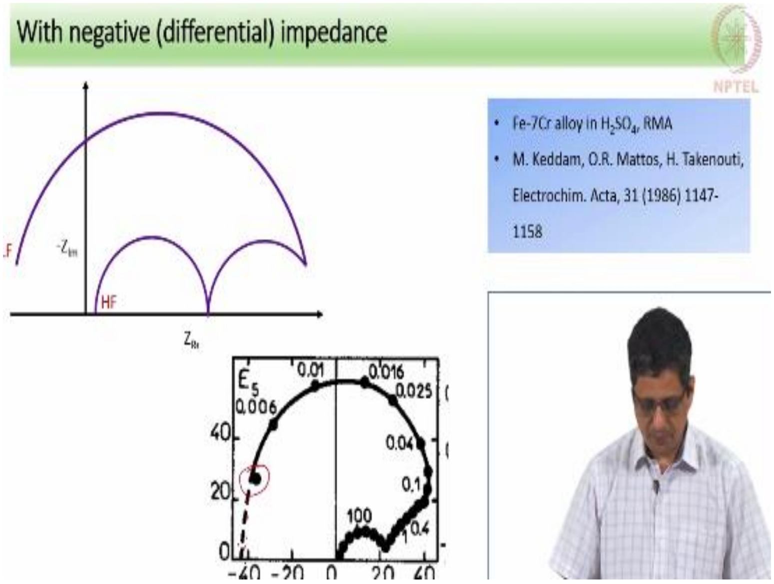

[Please refer to video 19. 20] Another example to show negative differential resistance occurring with a different pattern high frequency capacitive loop, mid frequency capacitive loop and low frequency capacitive loop with negative resistance, seen in iron chromium alloy. So if you see some publications in 1980s with iron dissolving in sulfuric acid, iron chromium alloys dissolving in sulfuric acid, Nickel deposition, zinc electro deposition published by Professor Epelboin's group and Professor Keddam's group, they have analyzed quite a variety of patterns and we are able to model this. So a lot of this example that I show you here we would take from those publications. So this is the data with first capacitive arc second arc not going to completion, but rather half way the third arc manifest and at low frequency it has come up to this presumably if we extent it, it will settle at the real axis at close to -40 Ω or Ωcm^2.

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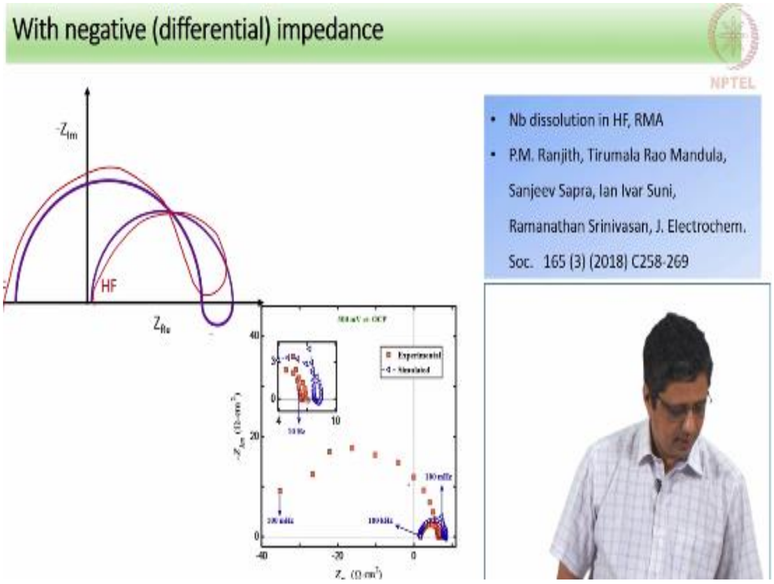

[Please refer to video 20.30] Next example which shows a capacitive loop followed by an inductive loop followed by capacitive loop with negative differential resistance at low frequencies. Although I have drawn here with inductive loop going below, it is also possible that inductive loop may appear above this. And if we use electrical circuit you will need an inductor to model this or you will need to use a Maxwell element with resistance and capacitance, but allow negative value which is basically saying you need to use inductor in the circuit to model this.

This was seen for Niobium dissolving in HF, this is again the same publications where we analyze data of Niobium dissolving in HF and Tantalum dissolving in HF. So here at high frequency, the red square show that experimental data you have a loop at mid frequency you have a inductive loop, high frequency you have a capacitive loop and low frequency you have a capacitive loop with negative resistance.

The mid frequency inductive loop is not very clear in the main picture therefore it was zoomed in or expanded and shown in the inset here. Model of course captures the main feature although it does not really match exactly for the data especially at the low frequency the quantitative match is very poor.

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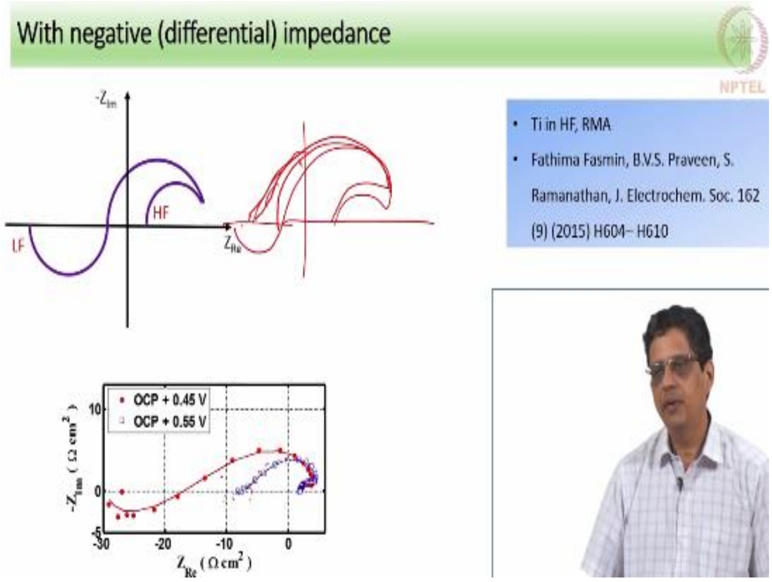

So another way to get the differential resistance, so it is not just going to go to the right side and come back and settle not all the time. [Please refer to video 22.08] You can have a capacitive loop followed by a capacitive loop with negative resistance followed by an inductive loop. So finally it still settles at the negative value. This is seen for Ti dissolving in HF, in the passive region it is published in 2015.

This dimensions are not the same right the capacitive loop is small the negative capacitive loop is much larger and at two different potentials the data were taken. If I remember right the lines represent the electrical circuit modeling. In one of them the negative capacitive loop followed by the inductive loop is clear in the other one, it is not very visible. On the other hand, when you use electrical circuit, if I model with only one Maxwell element even allowing for negative values it will not model this well it will actually come and settle like this. To capture this trend better, we need to use an inductive loop all that it means is in some cases you might see a data which goes like this and comes down and settle here. Another case if you do not have good quality data at low frequencies it is possible, it goes like this comes here inductors effect appears as a change in this behavior. If I have a pure capacitor, it will look like this because there is an inductive effect at the lower frequencies it is getting extended. Perhaps if you are able to take data with low noise at lower frequencies we might get a better data, but if it is noisy then you will have to settle at some point. But the main idea is it is possible to get these type of patterns also.

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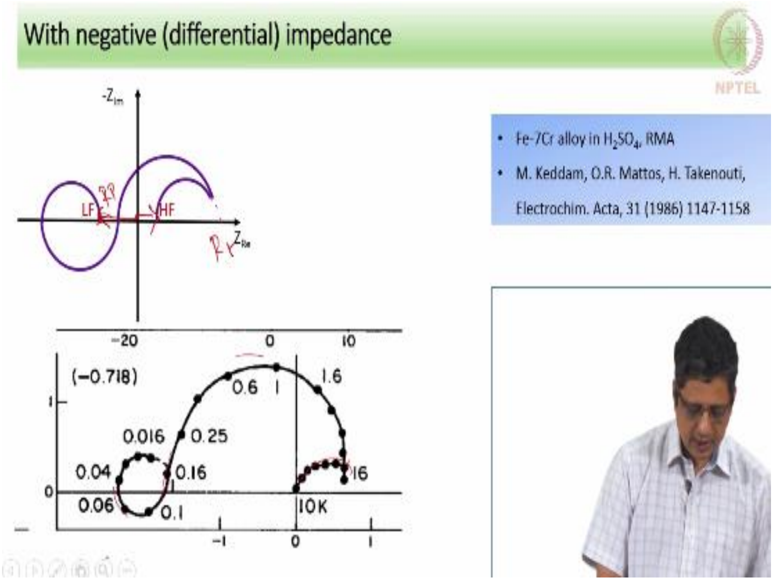

[Please refer to video 22.50] Not just that, extend further with another capacitive loop still settling at negative values at the low frequency. So for this R_T is going to be somewhere here. R_P is the low frequency impedance of course accounting for solution resistance. So it is going to be value somewhere from this location to this location. This was seen in iron chromium alloy dissolving in sulfuric acid, as I have mentioned before that this publication has shown quite a variety of patterns published by Professor Keddam Group in 1986.

The capacitive loop, followed by a capacitive loop with negative resistance polarization resistance, inductive loop followed by a capacitive loop. They have taken data up to 16 mHz presumably if we extend it, it will settle somewhere here. So it actually extends like this and settles somewhere here.

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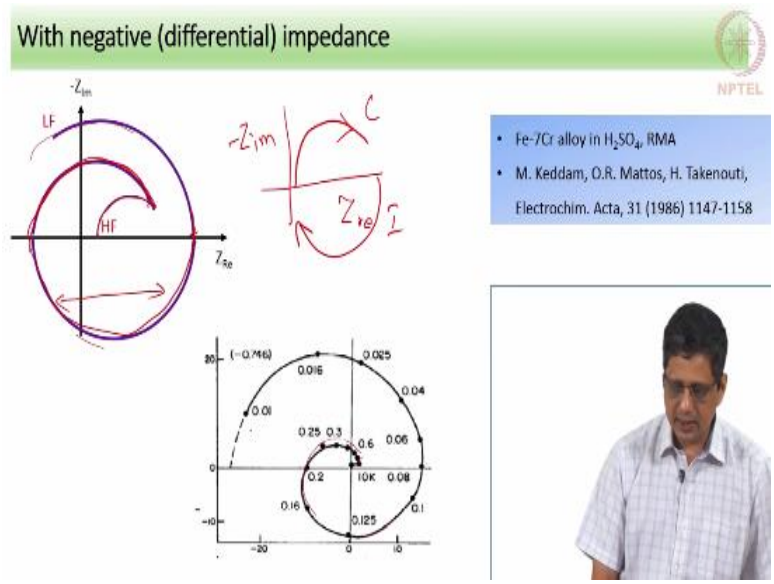

[Please refer to 24.41] This is a data where you have a capacitive loop followed by another capacitive loop followed by another loop which goes like this, it is followed by another loop which goes like this. So this is an inductive loop, but is flipped. This is for example a capacitive loop, but it is flipped basically it means it is a capacitive loop but associated with negative resistance. This is inductive loop associated with negative resistance this is a capacitive loop associated with a negative resistance.

Normally when we plot –Z imaginary versus Z real we expect when we go from high frequency to low frequency a capacitive loop, capacitive loop here means capacitance in parallel with a resistance will go like this and inductive loop will go like this. A capacitive loop with a negative resistance will go in the opposite direction and inductive loop with a negative resistance will go in the opposite direction, these are inductive loop with a negative resistance capacitive loop with a negative resistance.

So this basically has one capacitive loop one inductive loop, one capacitive loop so three intermediate species. So the high frequency capacitive loop is not very clear, but it is somewhere here, and then at little lower frequency you can call mid frequency so it is a capacitive with negative resistance, low frequency inductance with negative resistance even lower frequency it is a capacitive with negative resistance.

And this is settling at 10 mHz the data is taken at 10 mHz at lower frequencies probably it will settle somewhere here.

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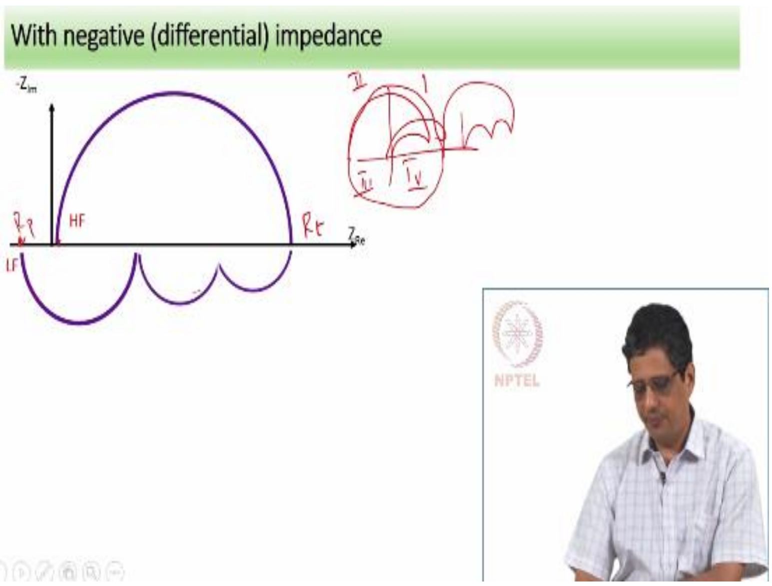

Now negative differential resistance, does not always mean that it has to go on the second quadrant, first, second, third quadrant and fourth quadrant. Many times when we see negative differential resistance actually we do not see negative differential resistance that often compared to a normal data, but the positive regime positive regime, meaning to the right side of this axis.

We see it less frequently, but when we look at it, mostly we will see it is going to go like this or it is going to go like this. Perhaps with one more loop here, but it is also possible that is starts here it does not go to the second quadrant at all, i t just goes by a fourth quadrant and the third quadrant and settles at negative value here. That means this is the solution resistance at high frequency, this is the charge transfer resistance. We have one inductive loop, second inductive loop, third inductive loop which is large such that it actually settles at a negative value here.

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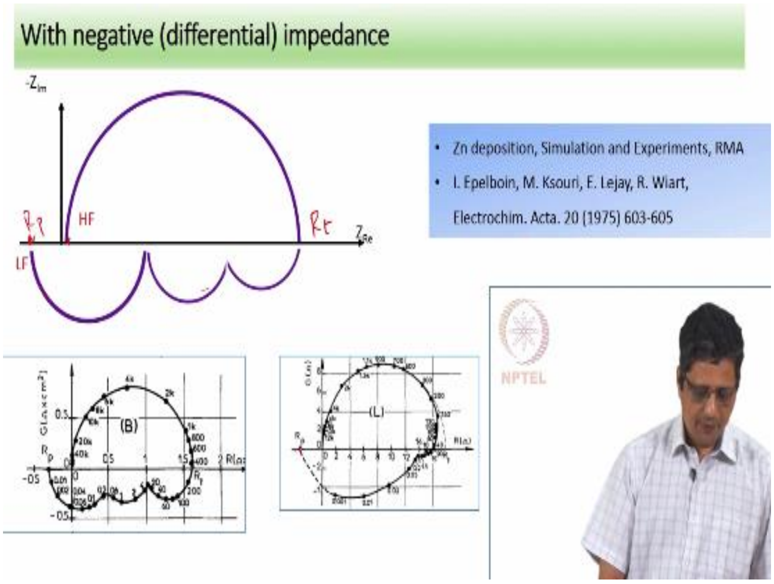

This has been done in simulation when the data of zinc deposition, if I remember right under galvanostatic conditions was analyzed by Professor Epelboin and others published in 1975. In simulations they have seen a high frequency loop here, low frequency inductive loop, second inductive loop and third inductive loop, which still settle at the negative value. In experiments they have taken a data, it has come here one inductive loop is seen here.

It is not very clear and another inductive loop might be present or the time constant may overlap in which case we cannot see it that clearly. At lower frequencies they had taken data to 1 mHz and it looks like it will go and settle at the R_P value here. So you can say experimentally they have seen data up to this, they do not have a conclusive proof that it will settle here, but most likely if you model this you can see that it could settle here.

Simulation definitely they have seen that means in mechanistic analysis, it is possible for one to propose a mechanism and come up with the set of kinetic parameters such that a negative polarization resistance can come with the impedance data in the complex plane plot occurring in the first, fourth and the third quadrant only.

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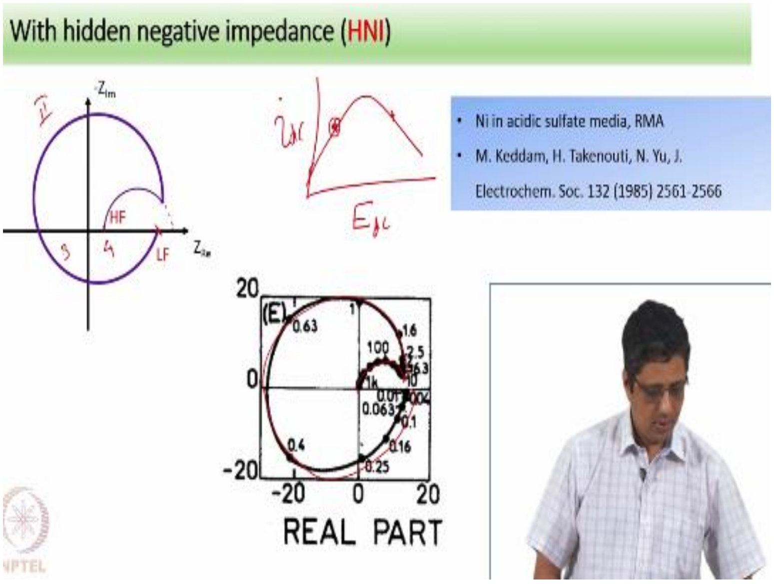

Now I want to describe what is called hidden negative impedance. We know what negative impedance is if I look at a polarization curve that is i_{dc} versus E_{dc} if that has a negative slope. We know that the low frequency data in the impedance spectrum will come to negative values and will settle at negative real axis if I take data at that dc bias. Now if I look at data here, if I take data here data here meaning if I take impedance data here I would expect that the data will settle in the positive region.

I do not have any recent thing that it may have a negative real value that is if I look at the Z_{Re} and Z_{Imag}, frequency Z_{Re} and Z_{Imag} I do not have any reason to think that impedance data acquired at this dc potential will show a negative value for Z_{Re}. That means from the polarization data I cannot guess that this spectrum can have negative values here for Z_{Re}.

However, when you actually take the data you see that R solution is here charge transfer resistance is there it is anyway going to be positive. A negative capacitance loop going through the second quadrant followed by inductive loop going through the third and fourth quadrant and settling at the positive value. So it will settle at the positive value as indicated by the slope in the polarization curve.

But it is hidden meaning by looking at the polarization curve you cannot guess or estimate that it will have a negative value for this for Z real. So that is why it is called hidden negative impedance. It is usually seen in cases where stability problem arise. This is not one of those cases at least not that I remember it was published in 1985 for Nickel dissolving in acidic sulfate media. I am not very sure whether it is dissolution or deposition, I will have to check.

It has been analyzed using mechanistic analysis and you can see capacitive loop going through the second, third quadrant and settling at the positive real axis.

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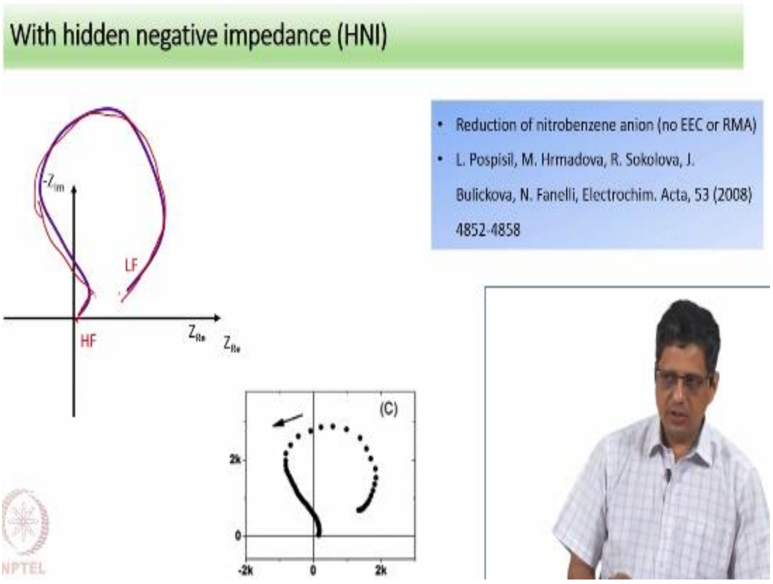
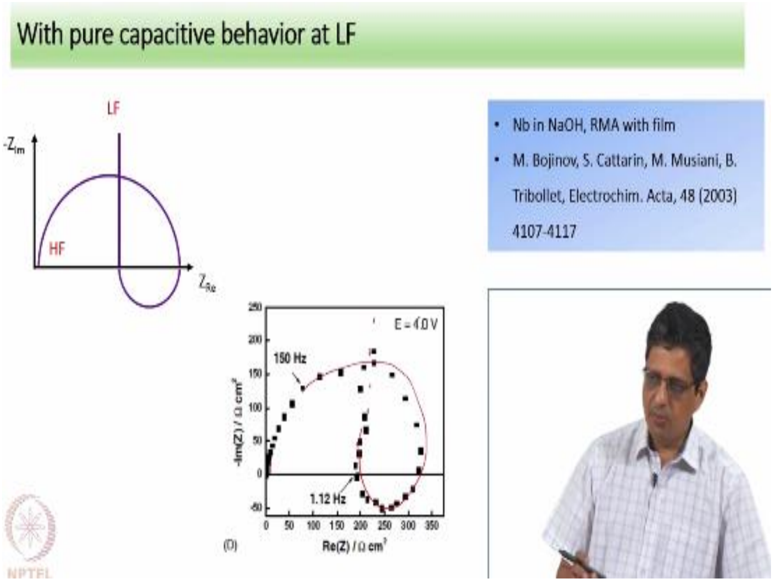


[Please refer to 32.01] There are few other cases, this is also quite unusual data starts here goes at the capacitive loop and then goes to the left goes to the second quadrant comes back to the first quadrant and settle somewhere here. This was published as data by Professor Pospisil and other in 2008. This data has been shown and I think arguments were given on why it appears like this I do not remember to the best of my knowledge, I do not think EEC are RMA analysis was done for this.

But basically this shows this kind of data is possible one can observe this in actual experimental cases.

(Refer Slide Time: 32:35)



[Please refer to 33.30] And finally I want to show an example where you have high frequency data after normal capacitive data, mid frequency inductive data and at low frequency it behaves pretty much like an ideal capacitor. So it just goes as a vertical line as straight line. This was seen in Niobium dissolving in concentrated NaOH, possibly at elevated temperatures and published by Professor Bojinov and others in 2003.

You can see the data coming like this settling here and going more or less like a vertical line, at very positive potential that means it is thick film must be formed on the top and it is acting like a capacitor. We will stop with this.