Electrochemical Impedance Spectroscopy
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Lecture – 12
Introduction to KKT

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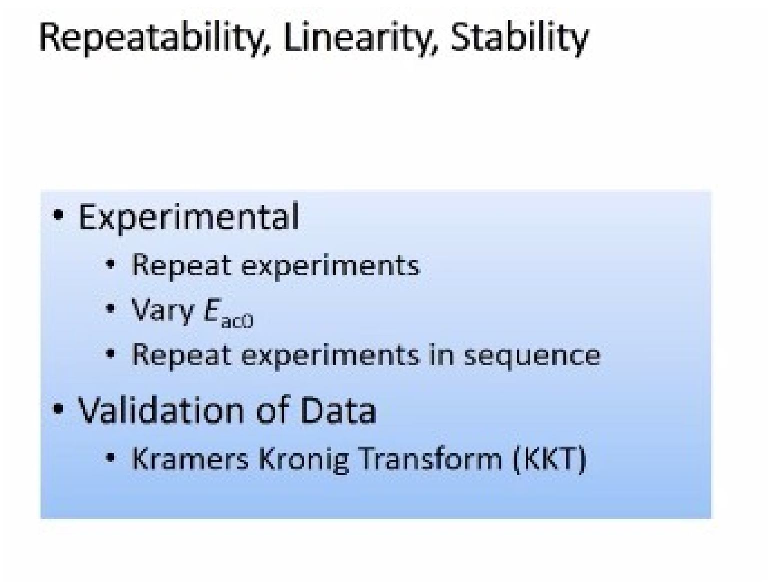

Now there are few things which we want to check, one *linearity* meaning the response can be represented by a linear system. Another term is *stability*; stability here means we apply a perturbation, sinusoidal wave, we stop that, wait for some time the system should come back to the original state, that is an assumption that, it will come back. So we get EIS data, we assume that, these assumptions are valid, and then we analyze the data.

One is called *causality*, causal, means we apply sinusoidal wave, we get a sinusoidal current, hopefully a sinusoidal current, we get a response, we analyze it thinking that the resulting current is due to the application of sinusoidal wave from our side, it is caused by what we do. It is not coming because of something else. In other words, it is not necessarily noise, noise level is low.

In technical term there is another way of thinking, they would say causality here means the response cannot come before the application of the perturbation, mean if I apply sinusoidal voltage, now I should not get the current before this, but in practical terms we are not going to measure before this. We are going to apply sinusoidal potential, get the response and hope that whatever response we get is because of the application of sinusoidal potential.

And one way to check is to do the experiment repeatedly and check whether you should get same data. Every time if it changes, something is not correct. Repeat experiments by dismantling the setup, arranging again and redo the experiment, and if you get the same data, it is repeatable. There will be some difference that gives you an idea of the noise level, in data acquisition.

I want to know check whether the data is linear. I can apply 10 mV, I can apply 20 mV , 5 mV, and see whether the response is same, within the noise level. If it is the same it is within the linear limit. If 5mV and 10mV perturbations are more or less matching, but 10 (mV) and 20 (mV) are different, try 20 (mV) and 30 (mV), they are different, you will say up to 10 mV it is linear, beyond this I cannot neglect the nonlinear effects.

All this means, you will need to spend substantial amount of time to get one set of data which you trust. It takes certain number of hours to prepare the setup, may be days depending on what you are testing. It will take at least few minutes maybe 10 minutes, maybe 20 minutes to run one EIS. So when I say repeat the experiments, nobody wants to do it, but if you want trust the data you have to do that.

If I say vary the perturbation, at least you should try 2 values, preferably many, if you want to study and say this is the linear regime you have to do it at multiple E_{ac0} and then see where this is more or less the same. So if I try, I will just make up this, for 10 mV perturbation and I get data like this. If I try 10 mV perturbation, I will get data more or less like this. I try one more time, I will get like this. Then I say it is repeatable and when it is repeatable I should worry about taking 5 mV data, impedance looks like this. I will say it is in the linear regime, 20 mV, it looks like this I will say it is in the nonlinear regime. If at 10 mV itself I get data like this, I have to figure out how to reduce the deviations here. Then I cannot say that a perturbation of 20 mV also look like this because the noise level is too much.

Now we have to check the another criteria, *stability*; let us say you take the experimental setup; you do one experiment you get data like this. At the end of it, continue with one more experiment, same parameter set. If it gives you more or less like this, you are good. If it becomes (noisy) like this that means during this experiment system has changed to some level, so it has not been stable, at the end of this perturbation it has not come back to the original state. I have applied many sinusoidal sequences, but it has not come back to the original state, if it has come back to the original state within the noise level, I should get the same set of data. So this is one way to check whether the data, experimental data has come from a system which follows linearity stability and causal constrains.

It is also possible to validate the impedance data using a transform called Kramers Kronig Transform. This is somewhat special to impedance data among the electrochemical techniques, You take cyclic voltammetry data, you take chronoamperometry data and it looks good, you feel it is correct, it looks noisy you feel something is wrong. It looks weird you do not know whether it is good or bad, meaning, cyclic voltammetry data if you get something like this probably it is correct. If you get something like this, I think it is wrong, (or) I do not know. If I get something like this, I know it is noisy.

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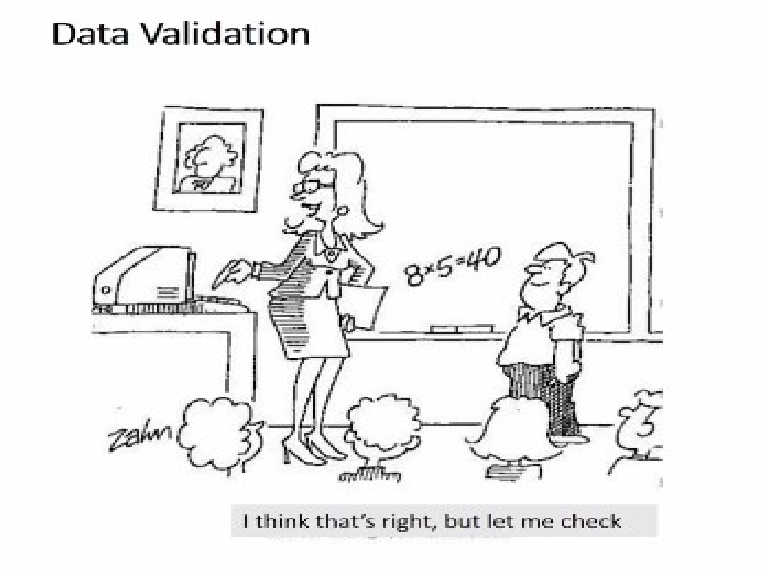

So as a cartoon of course this is shown to illustrate that people are relying more and more on computers and calculators, but here if somebody gives you a number if it is possible to check it, (and) you want to check it (before using the data).

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Kramers Kronig Transform (KKT)

- Linear, Causal, Stable
- Equivalent relationships in phase and magnitude are available
- **Pure mathematical relationships**

$$Z_{Re}(\omega) = Z_{Re}(\infty) + \frac{2}{\pi}\int_0^\infty \frac{xZ_{Im}(x) - \omega Z_{Im}(\omega)}{x^2 - \omega^2}dx$$

$$Z_{Im}(\omega) = -\frac{2\omega}{\pi}\int_0^\infty \frac{Z_{Re}(x) - Z_{Re}(\omega)}{x^2 - \omega^2}dx$$

Frequency	Zre	-Zim	Z-abs	Phase
1.00E-03	1.20E+02	6.28E-04	1.20E+02	-5.24E-06
1.26E-03	1.20E+02	7.91E-04	1.20E+02	-6.59E-06
1.58E-03	1.20E+02	9.96E-04	1.20E+02	-8.30E-06
2.00E-03	1.20E+02	1.25E-03	1.20E+02	-1.04E-05
2.51E-03	1.20E+02	1.58E-03	1.20E+02	-1.32E-05
3.16E-03	1.20E+02	1.99E-03	1.20E+02	-1.66E-05
3.98E-03	1.20E+02	2.50E-03	1.20E+02	-2.08E-05
5.01E-03	1.20E+02	3.15E-03	1.20E+02	-2.62E-05
7.94E+03	2.00E+01	2.00E+00	2.01E+01	-9.96E-02
1.00E+04	2.00E+01	1.59E+00	2.01E+01	-7.93E-02
1.26E+04	2.00E+01	1.26E+00	2.01E+01	-6.31E-02
1.58E+04	2.00E+01	1.00E+00	2.00E+01	-5.01E-02
2.00E+04	2.00E+01	7.98E-01	2.00E+01	-3.98E-02
2.51E+04	2.00E+01	6.34E-01	2.00E+01	-3.17E-02
3.16E+04	2.00E+01	5.03E-01	2.00E+01	-2.52E-02
3.98E+04	2.00E+01	4.00E-01	2.00E+01	-2.00E-02
5.01E+04	2.00E+01	3.18E-01	2.00E+01	-1.59E-02
6.31E+04	2.00E+01	2.52E-01	2.00E+01	-1.26E-02
7.94E+04	2.00E+01	2.00E-01	2.00E+01	-1.00E-02
1.00E+05	2.00E+01	1.59E-01	2.00E+01	-7.96E-03

~~So~~ There is an equation it is written for impedance here. If a system is linear, causal and stable, and it gives a couple response for various frequencies. You can relate the real part and imaginary part using this set of equations. These are purely mathematical formulations, it is applicable for *impedance*, it is applicable for *admittance*, it is applicable for optical data, in optics you have what is called *refractive index*. Refractive index normally you would have seen water has a refractive index of one point something. It actually has two components, one is called real and another is called imaginary. Real component tells you the deviation, when you send the light at a particular angle it moves in another angle ~~etc~~. Imaginary component is related to how much is absorbed by the material and that depends on the wavelength, depending on the wavelength the refractive index which has a real and imaginary part will vary. Wavelength is another way of saying frequency. Now I can replace this with refractive index real part and imaginary part. This equations are valid, these are not derived specifically for impedance. These are just mathematical relationship for a function which has a coupled output, (that is) two outputs.

As long as it follows these constraints, I want you to note the following. ω here is the frequency, $2\pi f$. Real value of the impedance at infinite frequency. In complex plane plot this is the first starting point, this is the high frequency data, that cannot be obtained only from imaginary data, that has to be given in addition to giving me the imaginary data and frequency.

If you give that then the remaining all the real values, I can predict. If I want to predict the imaginary values, if you give me all the real values I can give, as an example, this relates real and imaginary there are equations which relate the phase and magnitude. You can go to reference books and you can get those and these are pure mathematical relationship. Pure mathematical relationship meaning when you derive these equations you do not have to say anything about impedance.

So this is an example, this is simulated data, I have taken it 1 mHz onwards, because of space I have just removed these data. Let us pretend that there is data from 5 mHz etc, few Hz, few hundreds of Hz, few kHz and then it goes up to 100 kHz, and we have saved the data real and imaginary part. So actually -imaginary so these values are positive. So this would actually look like a semicircle if I plot -imaginary versus real.

I can also plot this in Bode plot or any format. I can calculate the $|Z|$ and the phase value. Now let pretend that you have this data and somehow you lost these 2 columns. If you have deleted, before you saved it and then you realized you lost it, and in fact we will worry about the Z table later, we would not look at it now, we will just say we lost the imaginary part, I want to get the real part.

If this data set has come from a system which satisfies this relationship, then you can use this transformation and get the imaginary values. Now you cannot just tell me I know the frequency and I know the real value, tell me the imaginary value. You need to give the full array, and in theory you have to give from 0 to ∞. In practice you will get data from low value to high value of frequency.

Now here ω is the variable here, x is the dummy variable. If you do the integration with the lower and upper limit x will not come out of this equation. You will get this integration, you have an analytical expression, you may try doing this, numerically you can evaluate this. So to calculate Z real at one frequency, I have to know the Z real at infinite frequency, I need to know this value, in addition, I need to know all the imaginary values or skip this part now. To calculate the imaginary value at a frequency, any frequency, I need to know the real value of Z at all frequencies and the real value of Z at that particular frequency. Basically I need to know all this data and exist a dummy variable here which basically is a frequency here. If I do the integration, I will get all the imaginary value.

So I will have to take this value substitute, $\omega = 2\pi f$, here also $\omega = 2\pi f$ and f = 1e-3, f = 2e-3 and so on. Each time I had to do integration, so if I want for 1,000 points, I need to do thousand times this integration. If I do that I will get set of values for Z_{imag}. Now we are not going to lose data, hopefully not. We get data with frequency real and imaginary. What we do is to get the set of values, predicted values, we call transformed values. So I will use all the imaginary data and get the real values. I will use all the real data and get the imaginary value, and then compare with the data that is available. If they match then I can claim most likely this data set has come from a system which does not violate linear, causal and stable criteria most likely, because this Kramers Kronig Transform is not a necessary and sufficient condition.

In mathematics you will say if and only if, so in the Kramers Kronig Transform if the system is linear, causal and stable, it will definitely satisfy this, but if the relationship is satisfied I hope this is true, but it may or may not be true. It can come from a system which is not linear. In other words, if it does not satisfy Kramers Kronig Transform I know there is a problem. If it satisfies KKT most likely there is no problem. But I cannot guarantee it, so the best we can do is to check whether it satisfies this relationship or not. If it does not satisfy we recognize there is a problem, if it satisfies we hope everything is okay, but this self-consistency check is available only when you have the real and imaginary part or the phase and magnitude as a function of frequency. Now how do we implement it, how do you actually go about it. Because I do not have data from 0 to ∞ and I can nicely show many frequencies here, but in real life it will take very long time to get lot of data.

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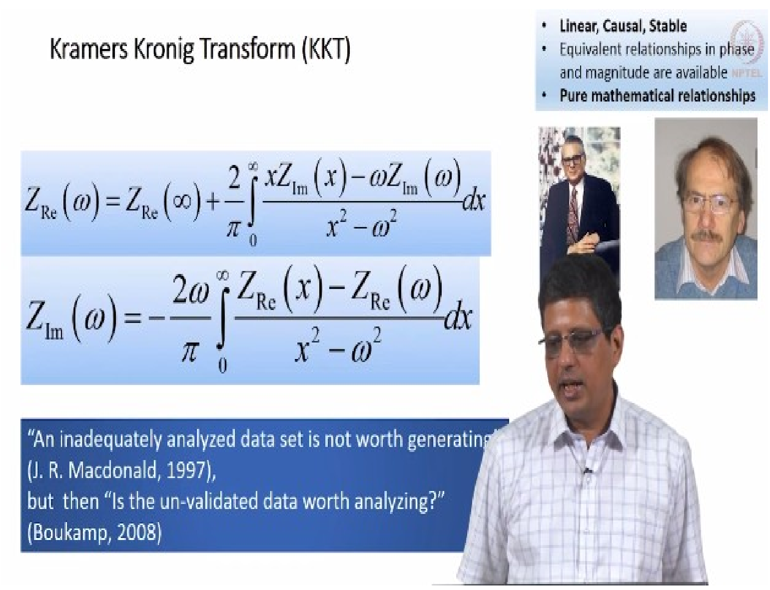

Now, this is Ross MacDonald senior professor of North Carolina, I think. So if you do not really analyze the data properly what is the point of taking the data and as a corollary, Prof. Boukamp, if you do not have a validated data what is the point of analyzing it? ~~So~~ In impedance there is a possibility for us to validate it. First thing you should do when you acquire data is to subject it to KKT.

When it is the data is KKT compliant, then you analyze the data subsequently. So Boukamp is in University of Twente, I think Netherland and is given a program which you can use to verify whether the data is compatible, (that is) KKT compatible.

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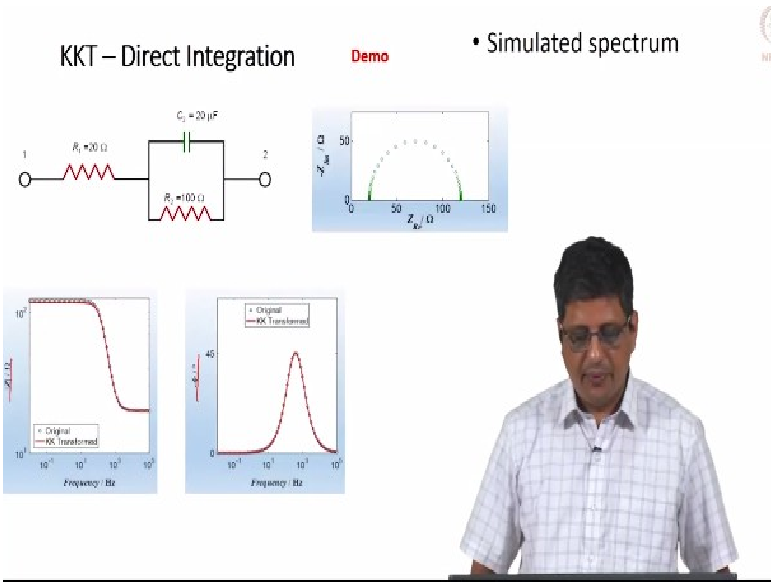

~~So~~ Here I take an example circuit this is consisting of passive elements, meaning it does not have any triode or diode or transistor, it has simple resistor and capacitor. A spectrum that comes from this will definitely be compliant, KKT compliant that means it is coming from a linear, causal, stable system there is no noise introduced here, I am simulating the data and if I simulate the data, in the complex plane plot it will look like a semicircle starting at 20 Ω ending at 120 Ω.

We have seen this before, now if I do the transform and plot it in the body format, so I plot magnitude and phase as a function of frequency. The original data is shown as points here, and the transform data is shown as line here and as expected, they are matching. So I want to show you; if there is a software, you can contact the faculty and get this from professor MacDonald in University of Berkeley. Double-click the software you will get something like this, this is the interface.

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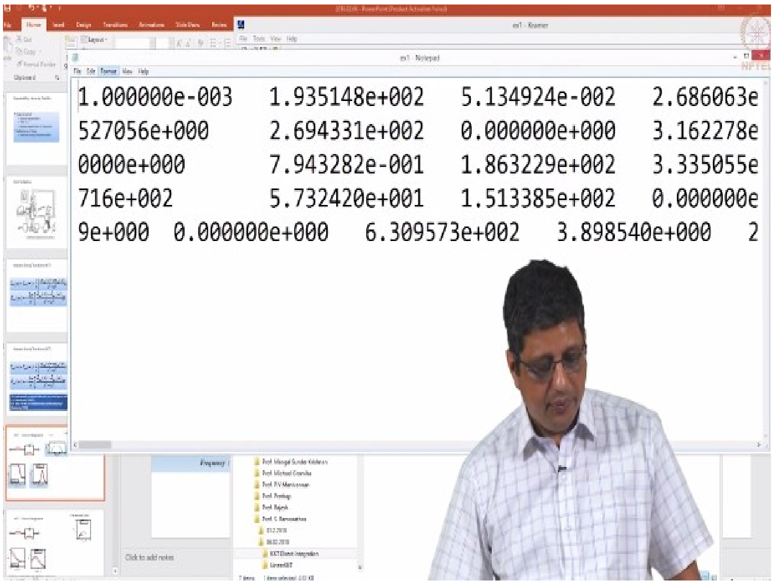

Data (file has to be inserted), without any header you can have the data showing frequency, real and imaginary. In addition, you can also calculate, the CAL is the calculated value since I have already done this, it fills with this, otherwise you will have only frequency, real and imaginary parts of impedance. The EX stands for experimental data and these two will be zeros. The way it is implemented after loading the data, you have to say interpolate. And you can say calculate real which means calculate the real value from the imaginary values and do you want to integrate only within the limits, integrate from 0 to ∞ what is required, but we have data from mHz to maybe multiple kHz. So I can do two things; one I can say integrate only within this and hope everything is ok or use some extrapolation, whenever you extrapolate there is a possibility that it will not work correctly. But the at the high and low frequency is a possibility. We do not need to do, this is the simulated data with good coverage of the frequencies, so can press yes.

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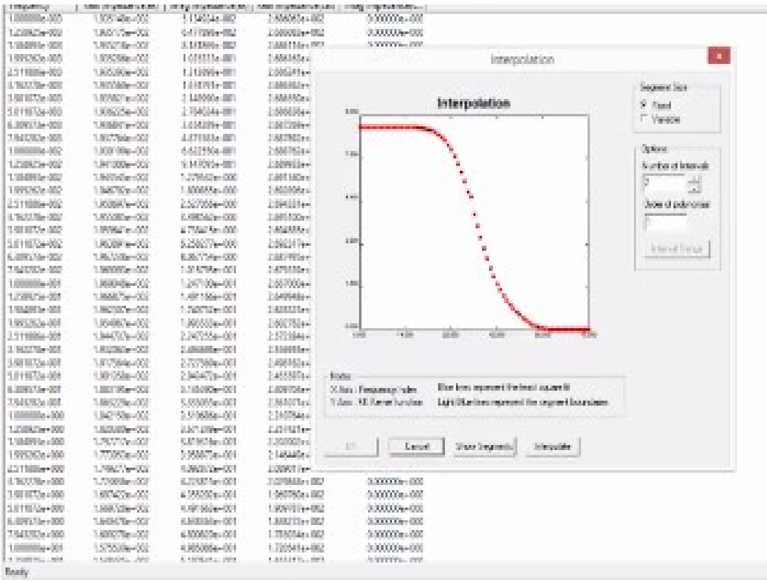

So this plot the values, the segment here, basically what it does is, you want to do integration, it is a numerical integration. You can do numerical integration and in real life you will have data points with some noise. So you can say divide this into multiple segments, within each segment fit it to a quadratic equation or fit it to a straight line, fit it to a cubic equation and then integrate that function, that is going to be better than trying to integrate through the numerical method with the points. If the points are very finely spaced then you can use trapezoidal integration, Simpson rule and get good data. If the points have noisy, fitting it to a function locally, piecewise fitting it to a function and then integrating those is a better choice. So in this case I am going to say 20 intervals with the polynomial order, if it is 1 it means it is a straight line segment, if it is 2 it is going to be a quadratic equation. And this works for fixed segment, it does not work for variable segments. In practice, ideally if I have many data points in some frequency range and fewer data points in some frequency range maybe I got data, they are noisy, I threw them away, remaining data I want to analyse, then I might want to use different segment lengths, but it does not work here for whatever reasons, so you stick to fixed segment size and instead of saying perform KKT, the command here is interpolate.

The blue line is the line, it is fitting and that is what it is going to use for integration which looks fair enough. If you are satisfied at this time, it will be populated with all this data. This is the transform data and I can also look at that, saying I can plot experimental versus calculated, (which is clearly) no(t) good. I had taken a data which does not actually satisfy KKT. I have not taken the semicircle here, I taken a slightly different, now I can save this.

If I save it, it is going to slightly alter the format, but it will save it in 5 columns, you can copy it and paste it into for example Excel and you will get four columns with nonzero values, fifth column will be zero. I can say I want to calculate the imaginary and go through the same process, fixed segment size, give values 20 (and) 2 (in respective columns), interpolate and claim. Now you see the first, second, third columns remain as they are.

Fourth column has become zeros, the previously calculated values have gone. Fifth column is populated now. You should save this in a different file, and then use Excel or some other software to get all the columns. That is how it is implemented, it is a free software, so we better take, whatever is available, but you should use KKT to verify and this is one free software, free meaning I had requested by email I think if you request for academic purpose you would get it for free and you can use it.

So using this software I have generated these plots. In this example I have simulated data therefore I have got good data from very low to very high frequency.

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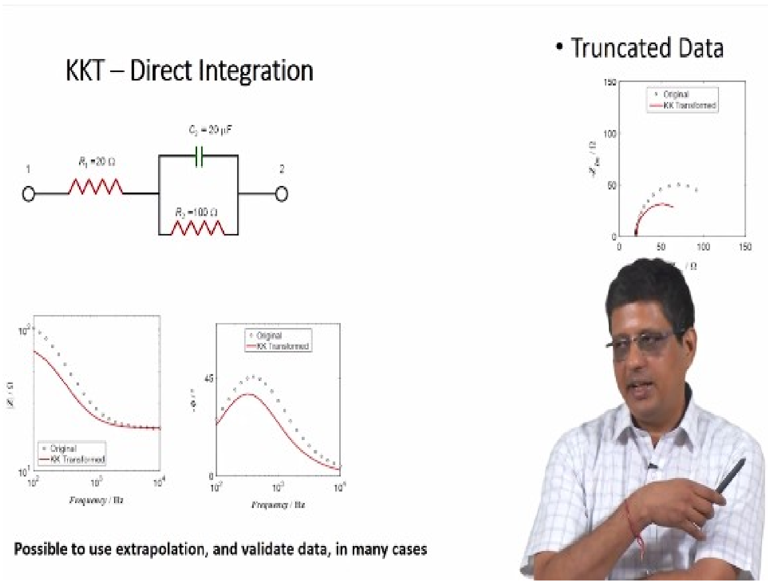

So let us pretend that we did experiment and due to some reason below certain frequency, I could not take data, it is very noisy or I had to finish the experiment and this is all I have. Now I want to use this KKT and verify. So instead of saying 0 to ∞ Hz, I am saying 1 mHz to 100 kHz. Now I will say I have data only from 10 Hz to 100 kHz, that is not going to transform correctly.

Even if I use extrapolation sometimes it will work sometimes it will not work and this is not transforming correctly not because the system is having any problem not because system is not linear or causal or stable, because I am approximating 0 to ∞ with a much lower or shorter truncated value, and that is not a good approximation. So if we transform the data and it does not match, first thing you need to ask is, am I giving it in a wide enough range, am I approximating the integral correctly. If I am approximating the integral correctly and then it does not match I have a problem. If I am not approximating the integral correctly I need to find some other way of handling this, that is one aspect. It is possible to use extrapolation in some cases, it will work and tell you it is compliant, some cases it will still say it is no compliant and you do not know whether it is problem with extrapolation or problem with the data.

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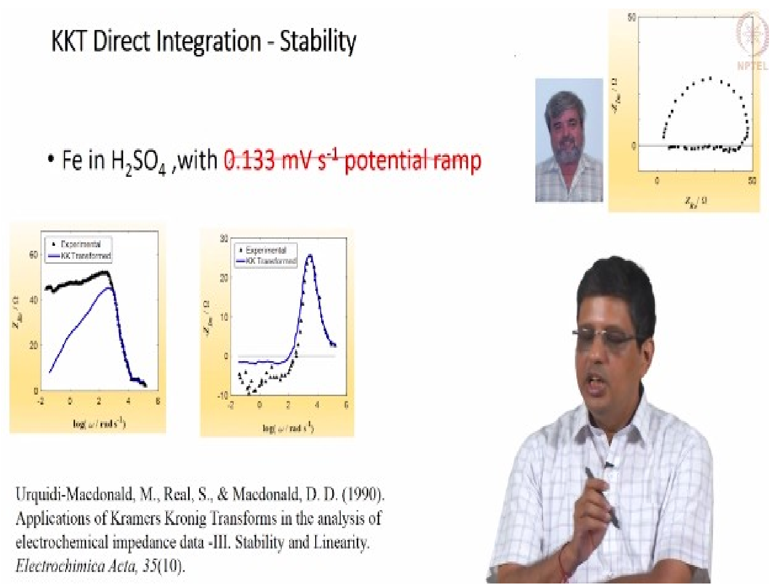

This is actually a photograph of Prof. MacDonald who has been doing this for like many years or you can say few decades. So he has taken a data, iron dissolving sulfuric acid and while taking the data they have superimposed a potential ramp meaning the DC potential is supposed to be here and they are supposed to apply a AC potential here. Deliberately they have applied potential, I do not remember whether it is going up or down. But the sinusoidally superimposed along with the ramp that means at the end of this when you stop this data acquisition potential is not here, it is at some other value and it has been changing throughout this experiment. So artificially he has changed this to create a response from a system that is not stable, and if you take this data and do the transformation you will find there is a clear variation. And if you take the data without the ramp, stable system, you will see that, it matches well. I have not shown you the data here, but if we take a data for the same system without this potential ramp it will match well, with the potential ramp it does not match well. So you get a data like this you do KK transform, you know there is a problem, it would not tell you the problem is in stability. It will tell you there is a problem, do not analyze the data thinking it is coming from a linear causal stable system.

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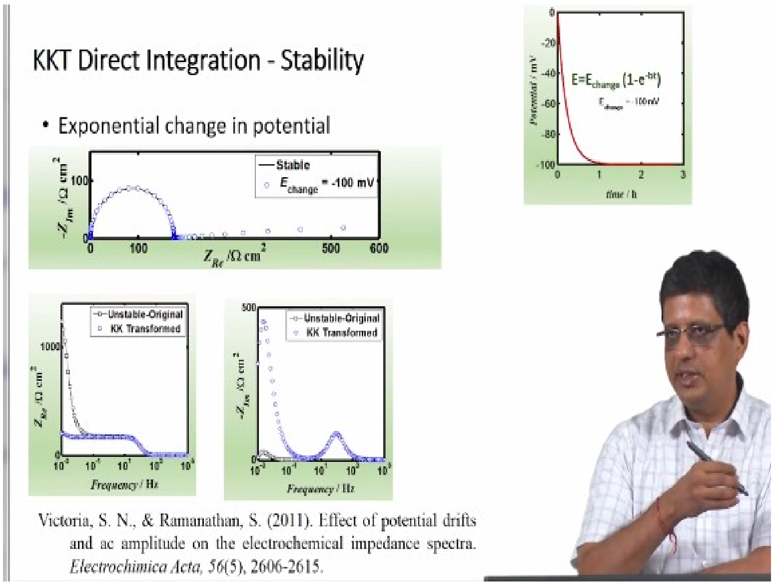

We had done some simulations where initially the potential is at some location. After some time, it is gone up quickly and then stabilized here or gone down quickly and stabilized here, that also is likely to happen in real life, open circuit potential may drift over time, unstabilize and we have modeled this using an exponential function. Normally we will expect a semicircle if there is no stability issue. Because there is a stability issue, the stable one will give you a semicircle, the unstable one will give you a semicircle with a tail. Also notice that this scales are equal, they have to be equal, only then you can clearly see, otherwise if I truncate this, or push this it may even appear like this which is caused by diffusion. We will come to that later, but this is just to illustrate that you have to look at the scales and you have to draw the scales correctly. And if I do transformation, original here is the data that I simulated, this is the transformed data and you can tell there is a problem. This is just again to illustrate that you should use KKT and of course in these examples we are simulating the data so we can take at any frequency, we can say take, meaning we can simulate that at any frequency. We can say go to very low frequency, very high frequency without any problem.

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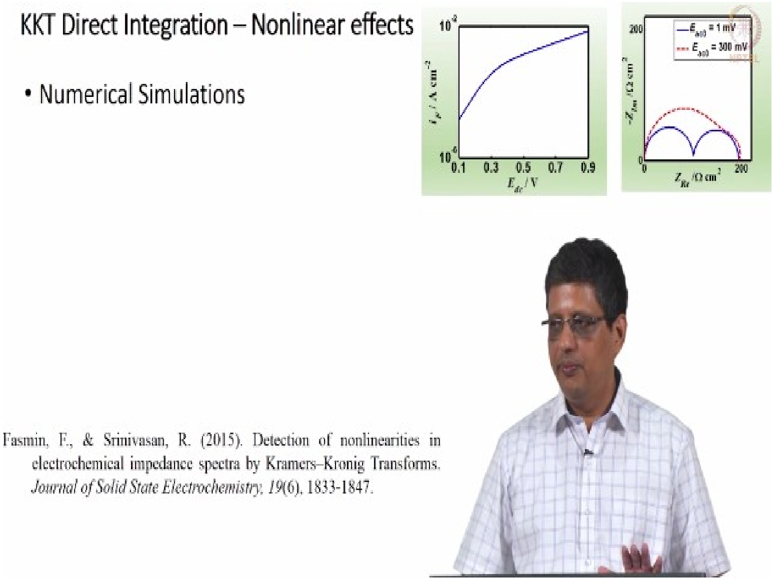

(We) will continue tomorrow. Basically we can do this and show that in many cases you will find or you will capture the problem in the beginning and whenever you analyze impedance data first thing you need to show is I have performed KKT or equivalent test, it is satisfactory and therefore analyzing the data, we will stop here today.