Electrochemical Impedance Spectroscopy
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Lecture – 51
NLEIS Experimental Aspects. FFT, PSD, THD

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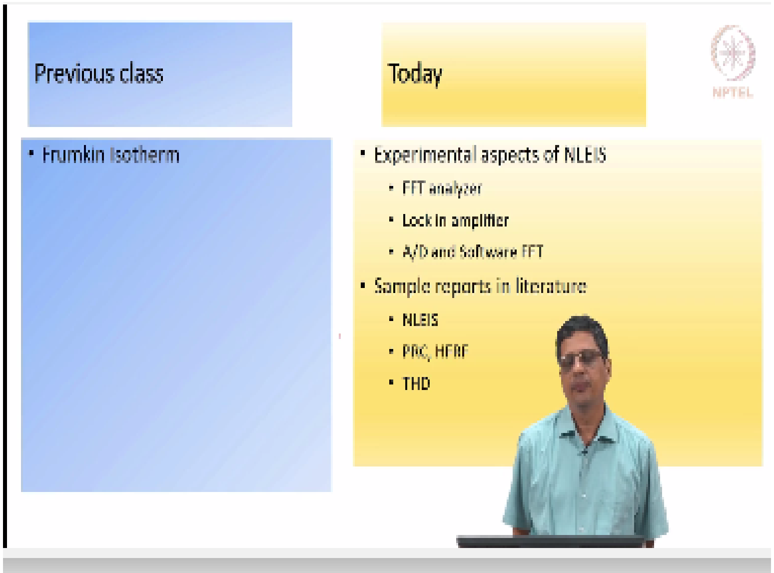

Previous class

- Frumkin isotherm

Today

- Experimental aspects of NLEIS
  - FFT analyzer
  - Lock in amplifier
  - A/D and Software FFT
- Sample reports in literature
  - NLEIS
  - PRC, HFRF
  - THD

So, in the previous class we saw how we can handle Frumkin isotherm, now what I want to show you is this experimentally, if you want to get NLEIS data, what are the choices we have, what are the precautions one need to take and I also want to give you a partial list of publications and describe what people have used that will give you an idea of what can be done to get NLEIS data.

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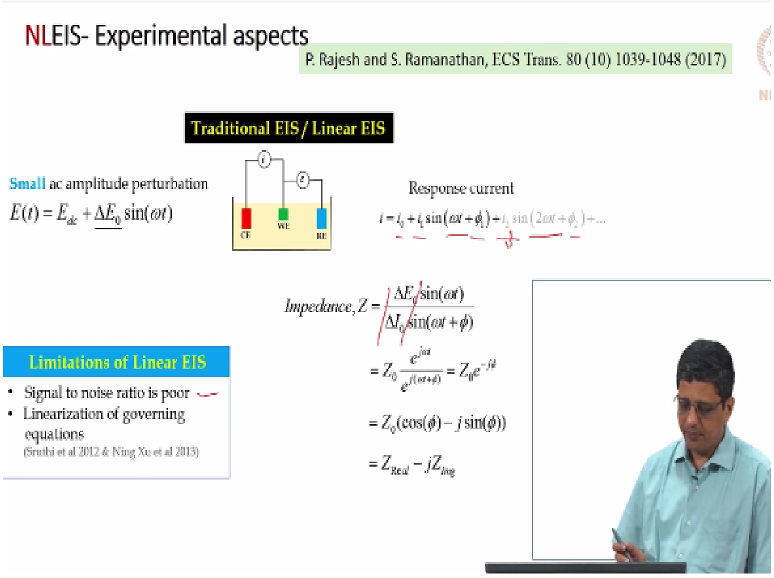

NLEIS- Experimental aspects

P. Rajesh and S. Ramanathan, ECS Trans. 80 (10) 1039-1048 (2017)

Traditional EIS / Linear EIS

Small ac amplitude perturbation

$E(t) = E_{dc} + \underline{\Delta E_0} \sin(\omega t)$

Response current

$i = i_0 + i_1 \sin(\omega t + \phi_1) + i_2 \sin(2\omega t + \phi_2) + \ldots$

$$Impedance, Z = \frac{\Delta E_0 \sin(\omega t)}{\Delta I_0 \sin(\omega t + \phi)}$$

$$= Z_0 \frac{e^{j\omega t}}{e^{j(\omega t + \phi)}} = Z_0 e^{-j\phi}$$

$$= Z_0(\cos(\phi) - j\sin(\phi))$$

$$= Z_{Real} - jZ_{Img}$$

Limitations of Linear EIS

- Signal to noise ratio is poor
- Linearization of governing equations

(Sruthi et al 2012 & Ning Xu et al 2013)

Just to refresh your memory, you have an electrochemical system with working electrode, counter electrode and reference electrode, traditional EIS; you can call it as linear EIS, okay, we have a AC potential, it can be superimposed on a DC, it may be with zero bias or some non-zero bias. As long as EIS is 0 is small, we can linearize this that is shown here, the actual current potential relationship may be described by a curve; may be described by a curve.

But if the changes in the potential are small, we can say that in this region the response is going to be linear, so the response; if I write it properly I should write it as i0, i1, sin omega t + phi1, i2 sin2 omega t + phi 2 but if EIS is 0 is small, the i2 is likely to be very, very small, I can neglect it that is the idea and once we have this we can always read the impedance as del E / del I.

In this case, we will write this as mod value here will tell us the magnitude, the phase difference will tell us the phase of the impedance and we can write it as real or imaginary, we can write in polar coordinate, Cartesian coordinate, etc. One problem in this is signal to noise ratio may be poor, if the noise level is high and we are restricted in the magnitude of EIS is 0, the value of EIS is 0, then signal to noise ratio is poor.

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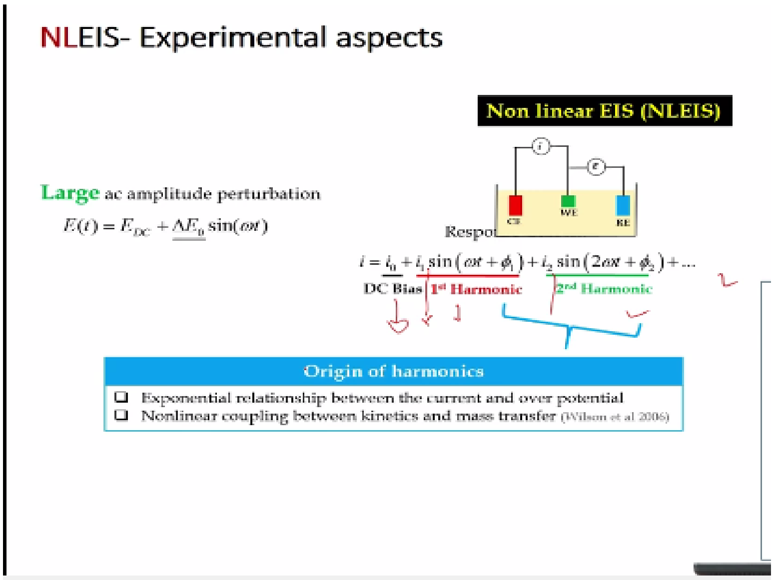

NLEIS- Experimental aspects

Non linear EIS (NLEIS)

Large ac amplitude perturbation

$E(t) = E_{DC} + \underline{\Delta E_0} \sin(\omega t)$

$i = \underline{i_0} + i_1 \sin(\omega t + \phi_1) + i_2 \sin(2\omega t + \phi_2) + \ldots$

DC Bias | 1st Harmonic | 2nd Harmonic

Origin of harmonics

- ☐ Exponential relationship between the current and over potential
- ☐ Nonlinear coupling between kinetics and mass transfer (Wilson et al 2006)

And we have to linearize the governing equations and solve for them, okay, if I give large EIS is 0, then I cannot neglect the second third harmonic, I will get a response at first or fundamental, I will get a DC response also, I will get second possibly third, fourth etc., this value will be large compared to the case of small amplitude perturbation, okay, now that means the signal to noise ratio here will be more, it is going to be better.

But the linearization will not be correct here, okay, we cannot linearize the equations so, the reason we get higher harmonics is because the relationship between current and the potential is not linear, it is exponential in a simple case, in other cases it is basically nonlinear, okay and another thing is so far we have taken; mostly, we have taken cases where mass transfer is not rate limiting step, mass transfer is very rapid.

But we have also seen cases where mass transfer can be slow, okay and when mass transfer is slow and coupling between the mass transfer and the kinetics can give rise to higher harmonics. In any case, once you have higher harmonics, we are basically in the nonlinear regime.

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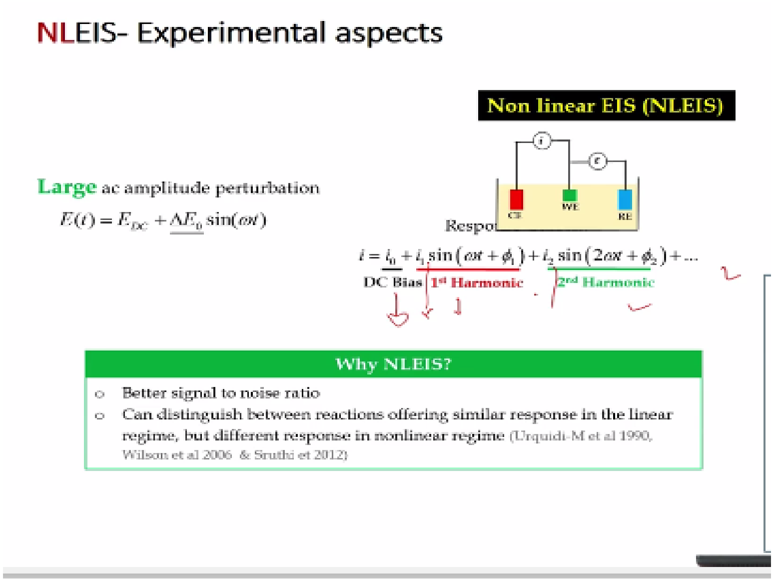

NLEIS- Experimental aspects

Non linear EIS (NLEIS)

Large ac amplitude perturbation

$E(t) = E_{DC} + \underline{\Delta E_0} \sin(\omega t)$

Respo

$i = \underbrace{\underline{i_0}}_{\text{DC Bias}} + \underbrace{i_1 \sin(\omega t + \phi_1)}_{\text{1st Harmonic}} + \underbrace{i_2 \sin(2\omega t + \phi_2)}_{\text{2nd Harmonic}} + \ldots$

Why NLEIS?

- Better signal to noise ratio
- Can distinguish between reactions offering similar response in the linear regime, but different response in nonlinear regime (Urquidi-M et al 1990, Wilson et al 2006 & Sruthi et 2012)

Now, why would we want to do NLEIS? One; at the fundamental, we will get better signal to noise ratio and there is a proposal or hypothesis that in some cases, two different mechanisms might give rise to the same spectrum but the higher harmonics may have a different signature experimentally, also some publications show that the fundamental response is more or less the same but the second or higher harmonic response can be different, okay we will come to that little later but there is a proposal.

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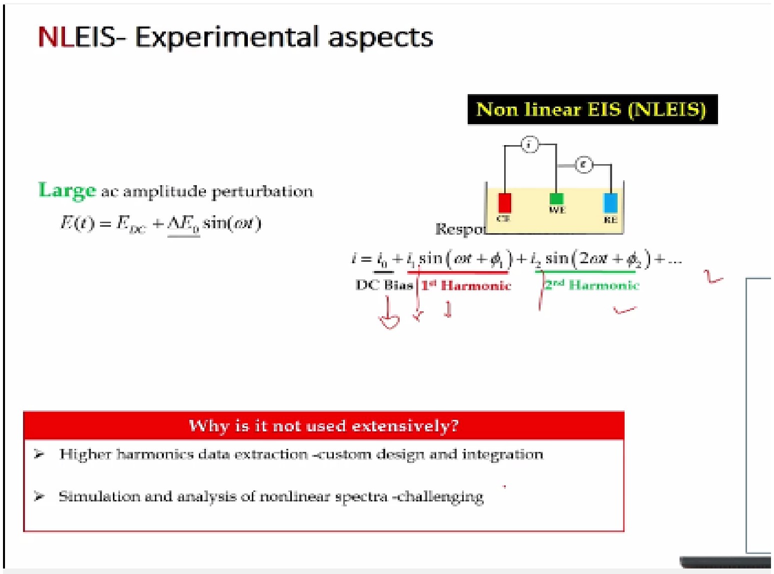

NLEIS- Experimental aspects

Non linear EIS (NLEIS)

Large ac amplitude perturbation

$E(t) = E_{DC} + \underline{\Delta E_0} \sin(\omega t)$

Respo

$i = \underline{i_0} + \underbrace{i_1 \sin(\omega t + \phi_1)}_{\text{1st Harmonic}} + \underbrace{i_2 \sin(2\omega t + \phi_2)}_{\text{2nd Harmonic}} + \dots$

DC Bias

Why is it not used extensively?

- Higher harmonics data extraction -custom design and integration
- Simulation and analysis of nonlinear spectra -challenging

So, if we can get data and if we can analyse the data, there is possibility that it is beneficial now, its not that common to find NLEIS data in the publications. There is a reason for that one; commercial instruments, there are many, many instruments or many, many manufacturers who would supply or who would sell traditional EIS equipment, so you can easily get a potentiostat, multiple vendors are there, they will offer potentiostat where you can control the DC bias, you can control the DC current you can run it in galvanostatic mode and run AS to get the response at fundamental.

You can apply a large amplitude perturbation but by and large most of them will give you the impedance that is ratio of potential to current at the fundamental, okay, higher harmonics should be there but you probably would not be able to record them so, it is not easy to get that instrumentation, when I say it is not easy to get, what I mean is; you will have to write your own code and it is possible only in certain instruments, not all the instruments have the architecture; open architecture.

So that means, in many cases you will have to get the commercial instrument along with the software and you cannot change that okay. In some cases, it is possible for you to get the instrument and along with the software that they provide, you might be able to write your own command and retrieve data in some cases, you will have to buy two or three instruments and put them together and write your own software to send the command, retrieve the data and synchronize this.

So, it needs a lot of work from your side, it is not off-the-shelf instrument okay that is one, second; after getting the data if you want to model it, simulation is also challenging; challenging meaning, if you linearize the equations, then to simulate the spectrum it takes very little time. For example, in Matlab at present in 2018, for any mechanism, once the equations are written, linearized, then given a set of kinetic parameter values, it just takes a second to calculate the impedance spectrum.

In case of NLEIS code, we will have to integrate, wait for some time and then take data and then do FFT, it should take anywhere between you know, few minutes to an hour or so, depending on the complexity of the mechanism, more importantly depending on how long we want to wait or how long we have to wait, okay, so this is definitely more challenging and not everybody is very familiar with this also.

In case of EIS; traditionally EIS, equal and circuit modelling is more popular and then commercial software's are available, in case of NLEIS, basically you are on your own, okay but we do believe that you get more information out of this, it is just little more challenging to get that data and little more challenging to analyse the data but there is more information here. When you do NLEIS, you can always go to the smaller amplitude perturbation and get the traditional EIS.

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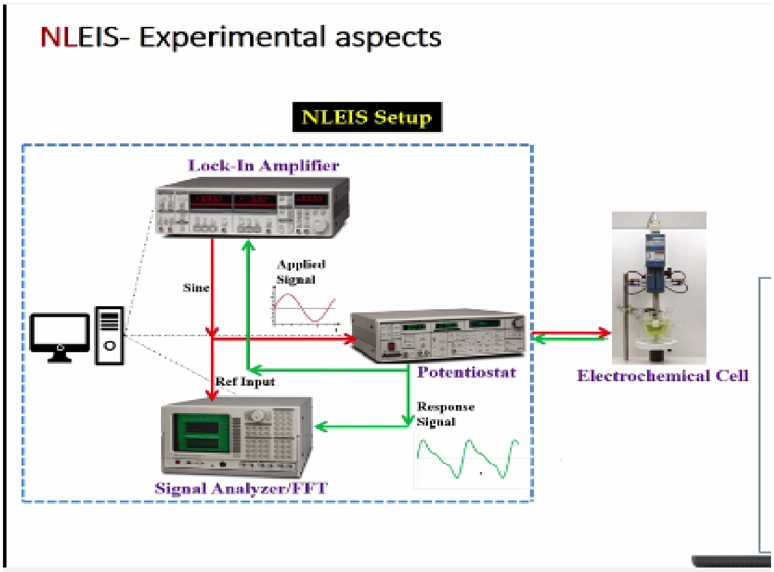

NLEIS- Experimental aspects

So, NLEIS is an extended version or more general version of EIS, now this is an example of experimental setup that we have constructed, okay, we have potentiostat, lock-in amplifier and an FFT analyser, okay, you can get NLEIS with potentiostat and lock-in amplifier alone or with potentiostat and FFT signal analyser alone. If we use this, we compared these systems, you can send sine wave from here, you can also send the sine wave from this particular instrument.

But way we have configured it is the sine wave we sent from the lock-in amplifier, this has a function generator and that is fed to the potentiostat, potentiostat adds the DC bias to this sine wave and then controls the electrochemical cell, the current response is converted to potential and given back to lock-in amplifier, it is also said to FFT analyser and to know the phase difference, a trigger way we send from lock-in amplifier to this, it is given as reference.

So, a sinusoidal potentially sent, a sinusoidal current comes, it might have a zero phase difference, it may have some other phase difference, trigger here says, when this; when the sinusoidal is starting that is when it crosses 0 in this location, crossing up is the one that triggers this, okay, so we apply a sinusoidal signal, response signal may or may not look sinusoidal, it should look periodic, wait for some time and then get steady periodic results and then analyse it.

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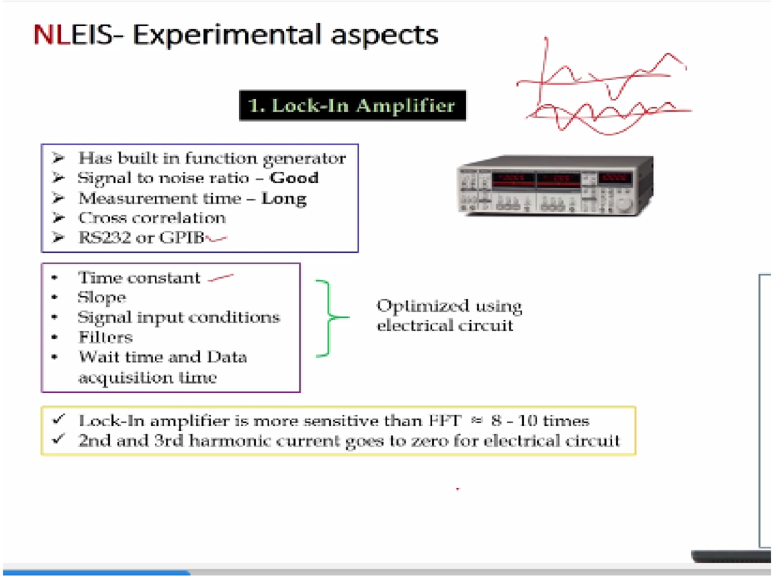

NLEIS- Experimental aspects

1. Lock-In Amplifier

- Has built in function generator
- Signal to noise ratio – **Good**
- Measurement time – **Long**
- Cross correlation
- RS232 or GPIB

- Time constant
- Slope
- Signal input conditions
- Filters
- Wait time and Data acquisition time

Optimized using electrical circuit

- ✓ Lock-In amplifier is more sensitive than FFT ≈ 8 - 10 times
- ✓ 2nd and 3rd harmonic current goes to zero for electrical circuit

Our experience; okay, lock-in amplifier gives you a good signal to noise ratio, sometimes up to an order of magnitude better, okay, compared to FFT analyser, it takes a little longer time for this to give you steady periodic results, so it is not just the cell, even the instruments do have a built-in time constant and for whatever reason, measurement time is longer here then we get good results, this uses method called cross correlation.

So, it basically takes the signal, whatever signal we get and multiplies that with the sine wave and also take the signal in parallel it multiplies with the cosine wave and from that it calculates the components fundamental, if you want the results at second harmonic, you have to multiply by sin2 omega t, if you want the results at third harmonic, it is possible to do that set it here and say that we send a wave of 1 Hertz, we want to look at the resulting component, we want to look at the component at 2 Hertz in the resulting current.

This particular case you can control it using RS232 connection or GPIB connection that is anywhere probably not very relevant, this you have to optimize certain parameters basically, we convey these instruments and we give the settings, we have to optimize time constant, we have to optimise the filter slope, signal input conditions basically, the scaling and you can apply filters, most of the time we do not want to apply filters unless it is very noisy.

And we have to set the wait time and data acquisition time, so we have to wait for some time and then acquire data for some more time, okay and that we can optimize using electrical circuit, get analytical circuit you know that electrical circuit with simple resistance, capacitance and inductance will not give rise to second harmonic, if you connect this instrument via potentiostat to the electrical circuit and then look for signal to second harmonic, you should get 0 or more or less 0.

So, we can optimize this and see at what condition we get the correct values, okay and of course when you take for a known system, electrochemical system you can connect it and measure the response at fundamental and calculate the impedance and that should match with what you get normally with commercial instruments. So, we find that it is more sensitive than FFT and second and third harmonic current goes to 0 for electrical circuit, it will go to 0 within the noise level available, it will pretty much go to 0, okay.

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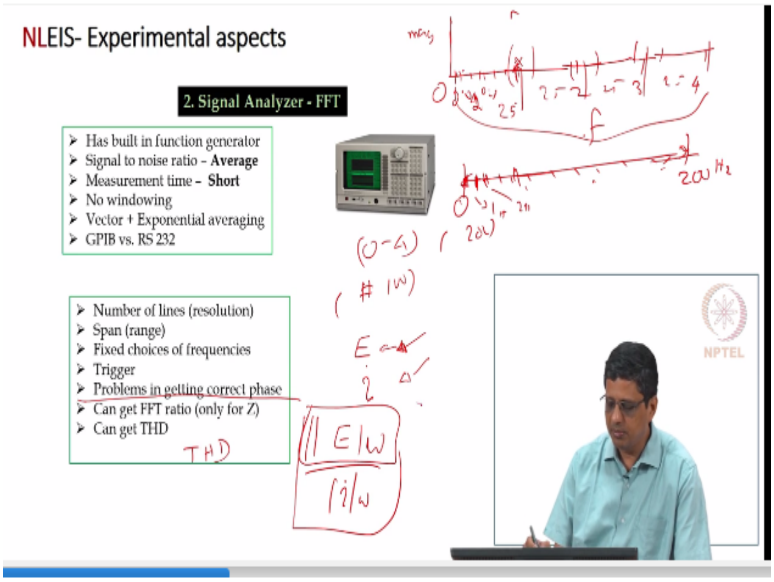

NLEIS- Experimental aspects

2. Signal Analyzer - FFT

- Has built in function generator
- Signal to noise ratio – **Average**
- Measurement time – **Short**
- No windowing
- Vector + Exponential averaging
- GPIB vs. RS 232

- Number of lines (resolution)
- Span (range)
- Fixed choices of frequencies
- Trigger
- Problems in getting correct phase
- Can get FFT ratio (only for Z)
- Can get THD

In case of FFT analyser, okay it does have little higher noise level, what it means is; if I take an electrical circuit and look at the second harmonic, even if I wait for long time, it will not go to 0, it will go to a low value, the signal to noise ratio is not as good as what we get from lock-in. This also has a function generator, signal to noise ratio is not as good as in lock-in, the measurement time is short here though, okay.

Even if we want to measure only the fundamental and not at higher harmonics, FFT analyser appears to have a shorter measurement time, okay, there are many choices available, windowing is something that we do not recommend, the moment you start windowing, a phase will go for a task, without windowing it is possible to set the parameters correctly, so that you can measure the phase correctly.

If you do not set the parameters or if you do not set the filters correctly, okay you can still measure the magnitude well but phase will go for a task, if you set the collection parameters correctly you can get the phase correctly, okay that is something that I want to emphasize. There are different options available, linear or exponential averaging, vector averaging is what we use, if you use vector averaging it will keep the phase and the magnitude.

If you use other choices like RMS, you will not be able to get the phase, it will apply multiple cycles and you can get exponential averaging which basically means, more weightage is given to the later or the most recent measurement and less weightage is given to the previous measurements. Again, you can connect by GPIB or RS232 but that is just an implementation issue.

In the FFT analyser either in this or in general, any analyser, you will have few choices, one is called number of lines, okay. In this case, I think we have number of lines is 200, 400 and 800. What it means is; in the frequencies, I can say 0, span tells from 0 to what? I can say 0 to 10 Hertz, within that if I say 200 lines, it is going to split this range into 200 segments, if I say, 800 lines, it is going to split it into 800 segments, okay.

So, the resolution will change now, one problem in the FFT analyser is because it is giving you certain spans and certain choices in the resolution, you cannot put arbitrary frequency, in case of lock-in amplifier, we can choose and say, apply sine wave at 0.1 Hertz; 0.11 Hertz, 0.235 Hertz, we can choose this within the resolution given by the instrument. In case of FFT analyser, the span values; there are limited numbers of choices.

And of course, number of lines, limit number of choices, okay so, we have fixed choice of frequency, so you know you have few choices here compared to what you have in lock-in and of course, you have to start that trigger here, there are problems in getting the phase correctly, okay, I will give you an example, we do not know the reason but we know how to get the phase correctly, so I will describe that to you.

Let us just imagine, this is frequency axis and this is the magnitude of the signal similarly, you have something for the phase, okay. Let us say you are applying a signal at 1 Hertz, okay and you want to measure the current at 1, 2, 3, 4, this all you want now, we have a choice, you can say this span is 1 to 4, or 0 to 4 and number of lines is 100 that means, it is going to be 0.04, 0.08 etc, ets., so you will have 25 segments here, 25 segments here, 25 segments here, 25 segments here, 100 or 200, then it is going to be 0.02, okay 0.02 interval.

So, if you give very fine interval and 1 Hertz comes here, 2 Hertz appears here, 3 Hertz appears here, 4 Hertz appears at the end, then phase value is actually not good, when we look at the phase value at 1, 2, 3, 4 Hertz, it appears to be random, okay this actually very fine resolution, magnitude comes correctly, we do not have an issue but the phase value appears to be random here.

On the other hand, for the same input signal, I still want to look at 1, 2, 3, 4 Hertz, I can change the span and say go from 0 to 200 Hertz and use 200 number of lines that means, 0 is the DC, the first is 1 Hertz, the next is 2 Hertz etc., and of course, the signal is going to be very poor or very low in most of this, okay. These cases we get correct results for the phase, so initially we thought that if you have fine resolution, you would be able to get good value for the phase.

But we find that if you use fine resolution, the phase value goes for a toss, if you use coarse resolution just enough to get you the fundamental and high harmonics, then the phase values actually come out to be correct, okay, it also possible to get the FFT ratio that is we apply potential, we can collect signal from the potentiostat where the measured potential as well as the measured current these are taken.

And it is possible to say at E at omega divided by i at omega but it is not possible to get higher harmonics, okay. See, when we apply a sinusoidal potential, we hope that the potentiostat actually applies that potential without any distortion but what if the potentiostat applies that with some distortion, then it will be good to know what is the potential applied at the fundamental.

So, if I take the measured potential and do FFT ideally, I should get the magnitude as what applied but this just tells you it is possible to actually take the ratio of E/I, okay, this analyser we could also get what is called THD or total harmonic distortion, we do not use it in this example but it is something I want you to be aware of.

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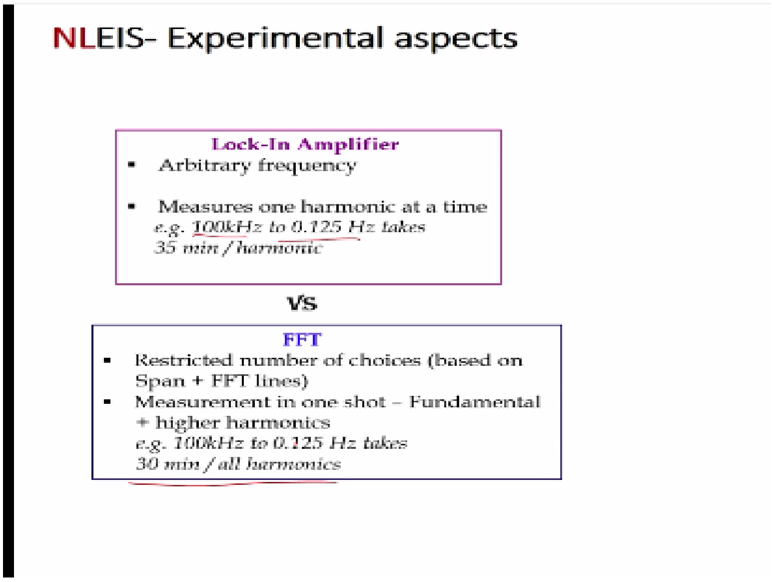

NLEIS- Experimental aspects

Lock-In Amplifier

- Arbitrary frequency
- Measures one harmonic at a time
  e.g. 100kHz to 0.125 Hz takes 35 min / harmonic

VS

FFT

- Restricted number of choices (based on Span + FFT lines)
- Measurement in one shot – Fundamental + higher harmonics
  e.g. 100kHz to 0.125 Hz takes 30 min / all harmonics

So, to summarise the comparison in the lock-in amplifier, it is possible for us to set the frequency to an arbitrary value within the limits and within the resolution specified by the instrument of course and one problem is; you can measure only one harmonic at a time either fundamental or higher harmonic, okay. Even, if I measure only one harmonic, if I go from 100 kilohertz to 125 milli Hertz, it takes about 35 minutes for one harmonic, okay to get good quality data.

In FFT, we have fewer number of choices but you can measure all the harmonics simultaneously and we can get this in 30 minutes from 100 kilohertz to 125 milli Hertz, 30 minutes we can get all the harmonics, okay and of course signal to noise ratio is better in lock-in amplifier to some extent.

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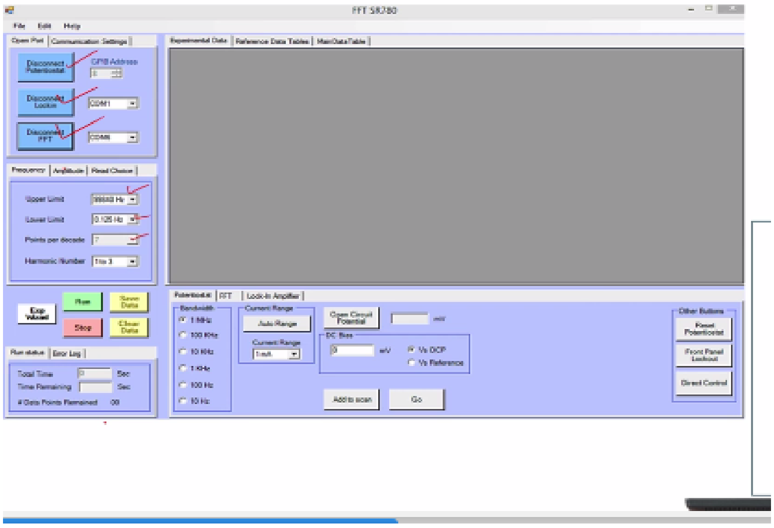
NLEIS- Experimental aspects



So, we have developed an interface where you can connect the potentiostat, lock-in amplifier and FFT analyser either using GPIB or with serial port, you can specify that upper and lower limit of the frequency, number of frequencies per decade whether you want to record harmonics from 1 to 3, we can also say 3 choices for amplitude. First run 10 millivolts then next run, 20 millivolts, next run 50 millivolts, you can have different choices, we have created different choices of recording the data.

Let us wait for short time, take data for few cycles or wait for long time, more number of cycles so, you can say higher quality data for the latter case, shorter measurement time for the former case and you can set for the choices, in the beginning when you apply, you can say wait for certain time and then start applying the sinusoidal potential, we can set the DC bias with respect to open circuit potential with respect to reference.

What it means is; in your lab also if you take some effort, you can do something similar now, as long as the equipment comes with an open architecture, you can write the software and control the equipment, acquire the data and analyse.

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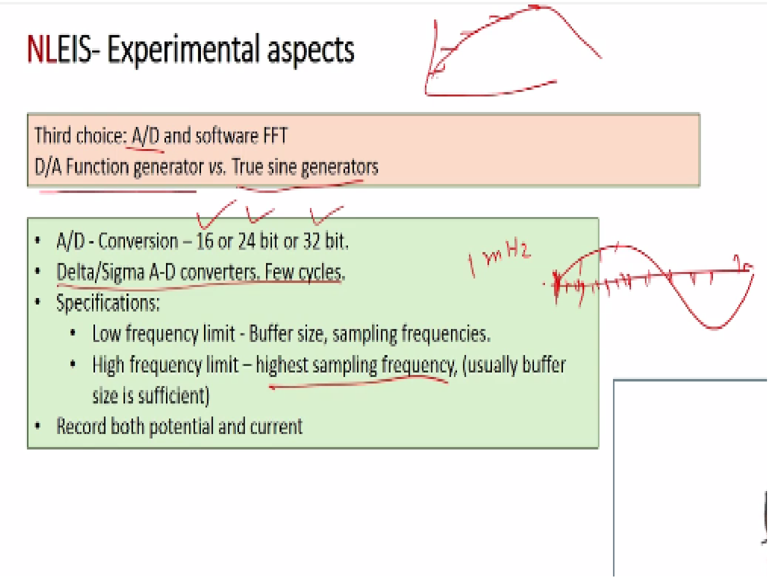

NLEIS- Experimental aspects

Third choice: A/D and software FFT
D/A Function generator vs. True sine generators

- A/D - Conversion – 16 or 24 bit or 32 bit.
- Delta/Sigma A-D converters. Few cycles.
- Specifications:
  - Low frequency limit - Buffer size, sampling frequencies.
  - High frequency limit – highest sampling frequency, (usually buffer size is sufficient)
- Record both potential and current

There is another choice, okay collect the data using analog to digital converter; A to D and then perform the FFT using software, you can also use DTA that is digital to analog to generate the sine waves and apply to the potentiostat but it is better to use what is called true sine wave generators. We specify the frequency, we specify the amplitude, instead of sending digital approximation to a sine wave, it is better than proper sine wave, okay.

Now, A to D converters; in the market if you buy the A to D converters, you can get it at 16, 24 bit and recently in 32 bit, okay these are called delta sigma converters, okay, they are not exactly 32 bit in one cycle, they will give you a 32 bit resolution, when the average over a few cycles till it is one of the better ones commercially, I think you can get 16 bit commonly you can probably get 24 bit in some instrument.

I am not very sure where you get it but it is possible that you can get 16 bit or possibly 24 bit, if you buy your own chip or the board and do this, you have to be aware of certain things. At the low frequencies, if you want to measure at low frequencies, the sampling frequency also has a limitation, so if I want to measure at very low frequency; 1 milli Hertz, 1 micro Hertz or 10 micro Hertz, I have to measure for a very long time.

And I want to take samples once in a while, right, I can take samples frequently but that is going to fill the buffer within the chip or within the board and overflow, so there is a limit on how many samples can be collected in one go, so if I want to space it far on farther away, so in one cycle, I will get 1000 samples, minimum sampling frequency there is period of sampling, there is a limitation, you cannot say measure every thousand seconds in all the chips.

Most of the chips would not give you that facility, maybe every half second, every 1 second, then it is okay, if the chip says you can measure at the minimum, every 100 milliseconds and not slower than that then, the frequency of measurement is limited, there is a buffer size, there is a minimum sampling frequency limitation that would tell you what is the low frequency you can measure and the high frequency of course what is the highest sampling frequency that decides what is the high frequency limit that you can measure.

Buffer size is usually not a problem in the high frequencies and ideally, you should record both potential and current, you cannot just say that I know I am applying a sinusoidal potential, so I will just take the current, it is better for you to acquire the current and record this potential and make sure that you are applying sinusoidal potential and current of course whatever comes you have to analyse, okay.

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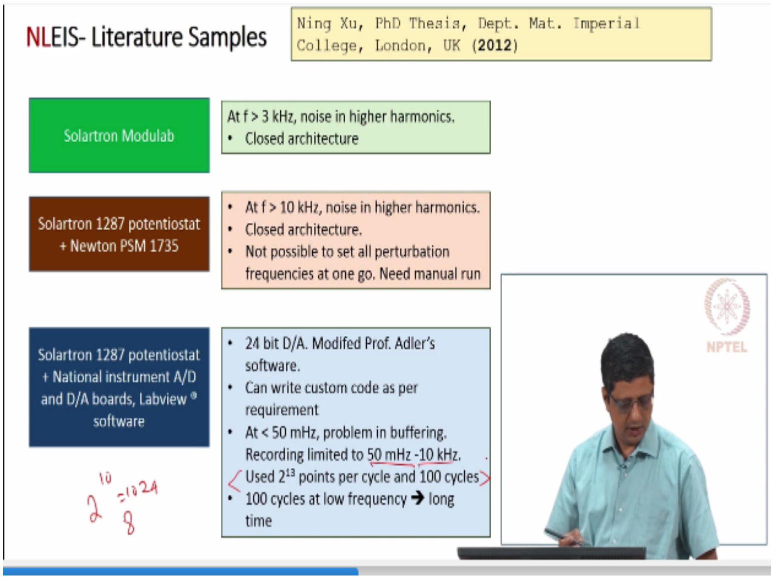

NLEIS- Literature Samples

Ning Xu, PhD Thesis, Dept. Mat. Imperial College, London, UK (2012)

Solartron Modulab	At f > 3 kHz, noise in higher harmonics. • Closed architecture
Solartron 1287 potentiostat + Newton PSM 1735	• At f > 10 kHz, noise in higher harmonics. • Closed architecture. • Not possible to set all perturbation frequencies at one go. Need manual run
Solartron 1287 potentiostat + National instrument A/D and D/A boards, Labview ® software	• 24 bit D/A. Modifed Prof. Adler's software. • Can write custom code as per requirement • At < 50 mHz, problem in buffering. Recording limited to 50 mHz -10 kHz. Used 2^{13} points per cycle and 100 cycles • 100 cycles at low frequency ➔ long time

$2^{10} = 1024$
8

Now, I want to show you some examples in the literature, this is from the PhD thesis of Dr. Ning Xu, published in 2012, what they had done is used different combinations, they have used solartron modulab that can give you fundamental and higher harmonics, they have used solartron potentiostat with an equipment called Newton PSM 1735, they have also used potentiostat with A to D that is data acquisition board, D to A board and control using a software called Labview software.

In the Modulab, what they have mentioned is that more than 3 kilohertz, noise is high, they cannot change the way, it is control a way data is acquired because of closed architecture, okay. Second; in the second combination at more than 10 kilohertz, its noise is high and again it is not possible to write our own code to control this or acquire data and the way it was done, it is not possible to say run experiment starting at 100 kilohertz or 10 kilohertz at few frequencies per decade and go till 1 milli Hertz or go till 1 Hertz.

You will have to go and change it every time this frequency, record all the harmonics then manually go and change it and record all the harmonics which means it is cumbersome. The third combination actually uses 24 bit digital to analog and this is actually taking Professor Adier's software, I will come to that little later and modified that and because its code written by them, they can modify it as they want.

At < 50 milli Hertz, there was a problem in buffering so, the recording was limited to 50 milli Hertz on the lower end, 10 kilohertz on the higher end and they have used 2 power 13 points per cycle, so we can see the 2 power 10 points is 1024, 2 power 13 is going to be around 8000 points per cycle and they used 100 cycles. If you can imagine at low frequencies, for example, 100 milli Hertz, 0.1 Hertz that would take you 10 seconds, 0.01 Hertz will take you 100 seconds, okay.

So, the acquisition time will keep increasing if we take many, many number of cycles and I would guess that one would take many number of cycles because that fewer cycles the quality of the data or signal to noise ratio was not that good, it is a possible explanation.

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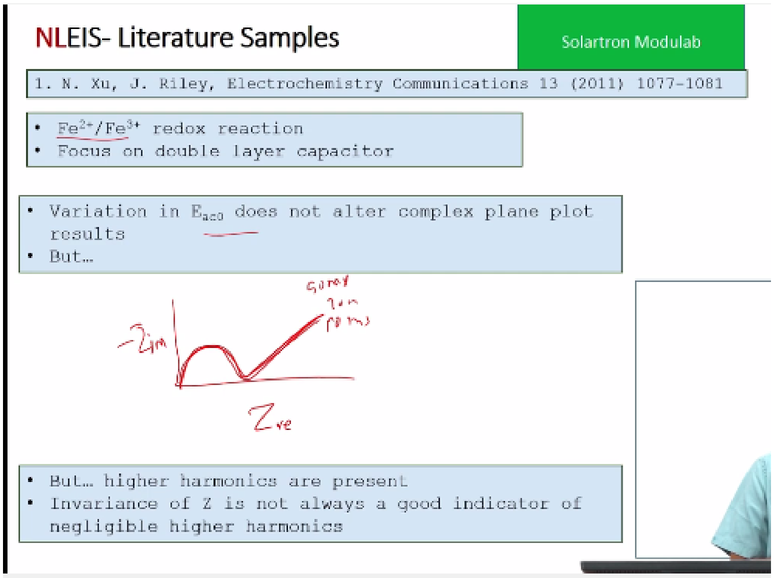

NLEIS- Literature Samples

Solartron Modulab

1. N. Xu, J. Riley, Electrochemistry Communications 13 (2011) 1077-1081

- Fe^{2+}/Fe^{3+} redox reaction
- Focus on double layer capacitor

- Variation in E_{ac0} does not alter complex plane plot results
- But…

- But… higher harmonics are present
- Invariance of Z is not always a good indicator of negligible higher harmonics

So, in one of the publication's, electrochemistry communications in 2011, they taken the simple reaction, Fe2+ to Fe3+ and in this publication, they have focused on the double layer capacitor, okay, so they performed experiments using modular and varied EIS is 0 and this is with no stirring, no rotation therefore, it is semi-infinite boundary layer thickness, mass transfers limited at low frequencies.

So, what they say is; if I change EIS is 0 and plot Z imaginary versus Z real; -Z imaginary versus Z real, at different EIS 0's, they see more or less the same result up to a limit of course, so if I take 10 millivolts, 20 millivolts and possibly even 50 millivolts, I am recalling from memory, okay, they see more or less same spectrum but if they measure the higher harmonics, they do say, there is a difference between 10 and 20 and 50 millivolts perturbation results, okay.

What it means is; if you take A as spectrum, apply a sinusoidal potential, take the spectrum increase the sinusoidal potential, take the spectrum again, if they overlap, we hope that it is in the linear regime, if they are quite different we know that it is a nonlinear regime. If they overlap, it does not guarantee that it is in the linear region, it is possible that higher harmonics are present they are not negligible which means, basically we are in the nonlinear regime.

But the response at fundamental may not change okay, so basically if the response at fundamental changes, you are definitely in the nonlinear regime, if response at fundamental does not change, we hope that we are in the linear regime.

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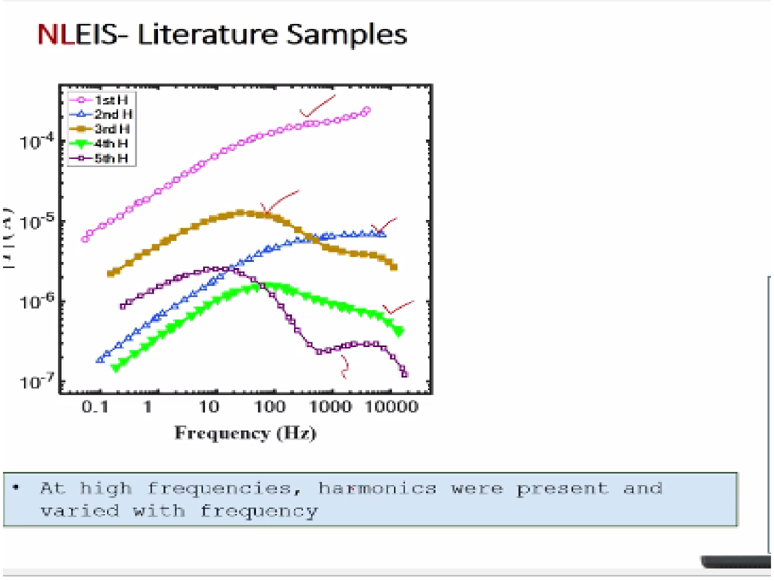

NLEIS- Literature Samples

- At high frequencies, harmonics were present and varied with frequency

So, they measured response at fundamental, this is actually current; magnitude of current, first is given by the pink colour line here, second is given by the blue triangle, third is by this yellowish colour, fourth of course is the green colour and the fifth is the violet colour. Now, the thing is this, at high frequencies harmonics are present and they also depend on the frequency, okay, so they come up with explanation.

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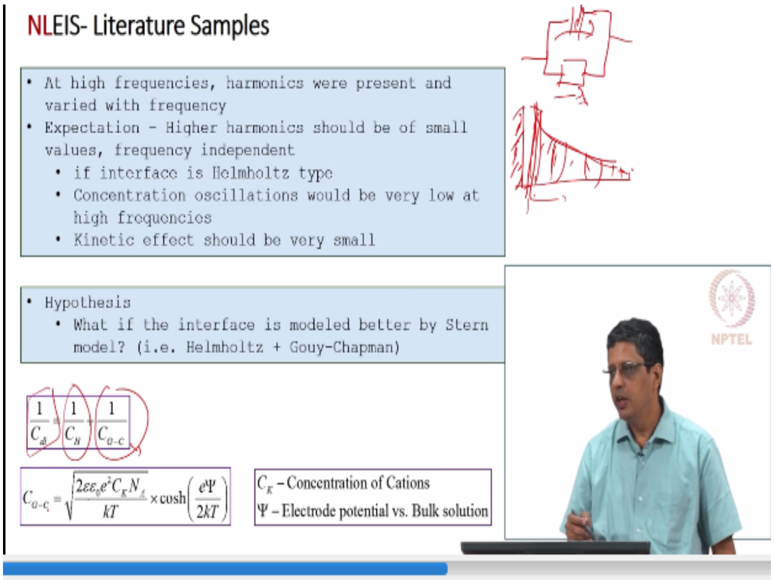

NLEIS- Literature Samples

- At high frequencies, harmonics were present and varied with frequency
- Expectation - Higher harmonics should be of small values, frequency independent
  - if interface is Helmholtz type
  - Concentration oscillations would be very low at high frequencies
  - Kinetic effect should be very small

- Hypothesis
  - What if the interface is modeled better by Stern model? (i.e. Helmholtz + Gouy-Chapman)

$$\frac{1}{C_{dl}} = \frac{1}{C_H} + \frac{1}{C_{G-C}}$$

$$C_{G-C} = \sqrt{\frac{2\varepsilon\varepsilon_0 e^2 C_K N_A}{kT}} \times \cosh\left(\frac{e\Psi}{2kT}\right)$$

C_K – Concentration of Cations
Ψ – Electrode potential vs. Bulk solution

Expectation is higher harmonics will not be significant at the high frequencies basically, double layer, if we assume that the system can be modelled by capacitance with a faraday process at high frequencies, double layer capacitance will offer very little impedance that means, most of the current will go through this and very little current will go through this; very little current goes through this, the response at fundamental itself is going to be small, response at higher harmonics will be much smaller, okay.

Provided, we assume that this is a simple straightforward capacitor Helmholtz type because it is semi-infinite boundary layer thickness, you will have a boundary layer which is very large in this case, it is going to be till the wall of this beaker; beaker or whatever cell that is used, going from the electrode till the boundary, concentration oscillations will be very, very small at high frequencies.

Concentration will not be able to keep up with their frequencies so, there will be very small and kinetic effect basically should be small that is the view, okay and that should be frequency independent, at least in the high frequency region it has to be small and negligible and pretty much independent of frequency but practically, they see that it is not negligible and that does vary systematically with frequency.

So, the proposal is; maybe it is not correct model the double layer capacitor using a simple Helmholtz model, there is another model called Gouy-Chapman model where it says that the charge distribution is not like an electrode on one side and ions lined up right next to that it is distributed like this that means, there are more number of ions here but there are fewer ions here, fewer ions here but it is distributed over a distance maybe few nanometers, in which case if you use a stern model which is there is a significant number of ions distributed here.

So that is like a plate but there is also some distribution along this distance perpendicular to the electrode, then you can combine Gouy-Chapman capacitance and Helmholtz capacitance by adding the inverse of them to get the effective capacitance and the Gouy-Chapman model describes the capacitance as a function of potential because the ions alignment will vary with the potential.

So, psi here is electrode potential with respect to the bulk solution, okay and CK is the concentration of cation here, Na is the Avogadro number, K is the Boltzmann constant, T is the temperature, this is the directed constant and E is the charge of an electron, so this expression describes how the capacitance here will vary with potential. So, if you apply DC potential, if you apply sinusoidal potential, the capacitance is not a constant, it is going to vary and this is the equation that describes the variation of capacitance with potential.

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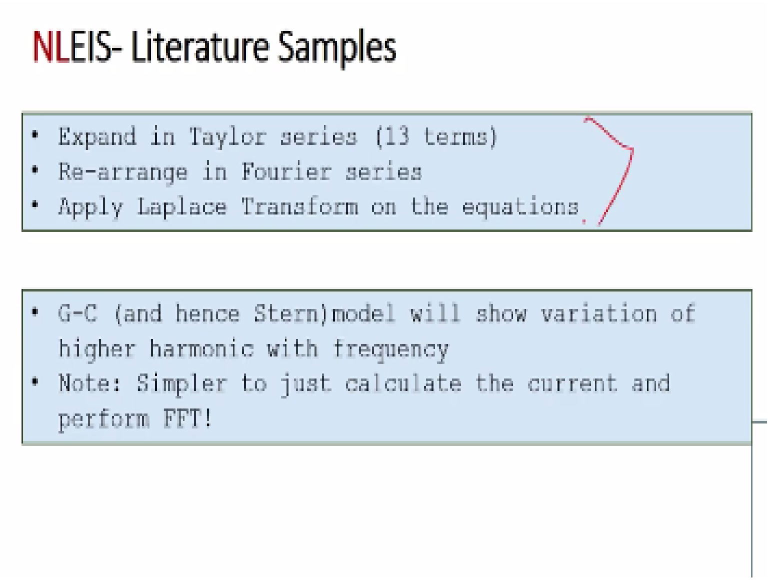

NLEIS- Literature Samples

- Expand in Taylor series (13 terms)
- Re-arrange in Fourier series
- Apply Laplace Transform on the equations

- G-C (and hence Stern)model will show variation of higher harmonic with frequency
- Note: Simpler to just calculate the current and perform FFT!

Now, what they have done is; taken the expression expanded that in Taylor series, taken up to 13 terms and rearranged that in Fourier series and then apply Laplace transform to the equations, okay. The GC; the Gouy- Chapman and the stern model right, that will show variation of higher harmonics with frequency of course, another method to do that is to use numerical method, you do not have to expand in Taylor series and truncate after something, just write the expression, calculate the current and do FFT, okay that is another method.

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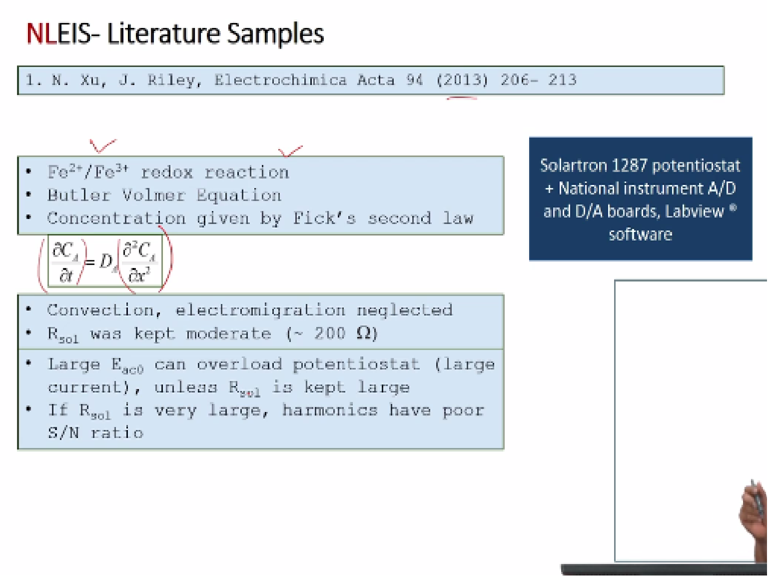

NLEIS- Literature Samples

1. N. Xu, J. Riley, Electrochimica Acta 94 (2013) 206- 213

- Fe^{2+}/Fe^{3+} redox reaction
- Butler Volmer Equation
- Concentration given by Fick's second law

$$\left(\frac{\partial C_A}{\partial t}\right) = D_A\left(\frac{\partial^2 C_A}{\partial x^2}\right)$$

- Convection, electromigration neglected
- R_{sol} was kept moderate (~ 200 Ω)
- Large E_{ac0} can overload potentiostat (large current), unless R_{sol} is kept large
- If R_{sol} is very large, harmonics have poor S/N ratio

Solartron 1287 potentiostat + National instrument A/D and D/A boards, Labview ® software

But what they have done is given here and qualitatively would predict that the response at higher harmonics would be present and they will vary with frequency. Same system, this is published in 2013 in Electrochimica Acta and this uses potentiostat along with the A to D chord and custom software. What they have taken is Butler Volmer equation to describe the kinetics here and the concentration is described by the Fick's second law.

If this is assuming that the boundary layer does not have significant amount of convection, a more general equation will account for convection and also for electro migration because these are charged species but this has been used to generate the expression for Warburg impedance and as an approximation, this can be used. So, neglected the convection and neglected the electro migration effect.

Solution resistance here; it was not kept very small, it was kept at a moderate value of 200 Ohms and it was discussed, why its kept at a moderate value, okay. If you keep very low solution resistance, then at high frequencies, the current becomes very large and the potentiostat may not be able to handle it okay, so all solution has to be kept to some moderate value, a large value.

If you keep it very large, what happens is the current value is small at all the frequencies and higher harmonics become very, very small that means, you will get poor signal to noise ratio, so as a compromise they are kept it at 200 Ohms.

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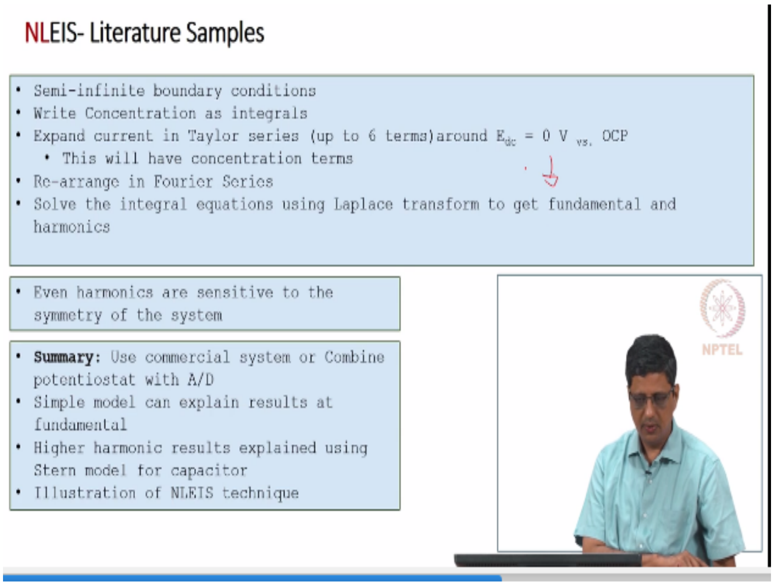

NLEIS- Literature Samples

- Semi-infinite boundary conditions
- Write Concentration as integrals
- Expand current in Taylor series (up to 6 terms)around E_{dc} = 0 V $_{vs.}$ OCP
  - This will have concentration terms
- Re-arrange in Fourier Series
- Solve the integral equations using Laplace transform to get fundamental and harmonics

- Even harmonics are sensitive to the symmetry of the system

- **Summary:** Use commercial system or Combine potentiostat with A/D
- Simple model can explain results at fundamental
- Higher harmonic results explained using Stern model for capacitor
- Illustration of NLEIS technique

So, the concentrations are written as integrals here, concentration of species A and B, ferro and ferri species, okay and then in this case, they expanded the Taylor series up to 6 terms around DC potential of zero voltage and current will have concentration terms, rearranged this in Fourier series and solve the integral equations using Laplace transform, not sure how easy it is to extend this to nonzero DC with respect to open circuit potential.

And in any case, you are truncating after certain number of terms, so accuracy will become less and less as you increase the amplitude. Now, the conclusion of this study is the even harmonics are sensitive to the symmetry of the system, if the mass transfer effects are not symmetric, you will have even harmonics, if the charge transfer coefficient is not 0.5, you will have even harmonics, if the DC bias is not 0, you will have even harmonics.

In general, summary is this; you can get commercial instrument or you can combine instruments, commercial instruments or you can combine commercial instruments and A to D board that is also of course obtained commercially but you have to write your own software and a simple model can explain the results at fundamental, so the results at fundamental could be modelled using Helmholtz capacitance.

But when you look at the higher harmonics you realize that is not sufficient, so you will have to go for a more complex system or more complex explanation, so higher harmonics can be explained using Stern model and this is basically an illustration of NLEIS technique, so this is a pair of publications.

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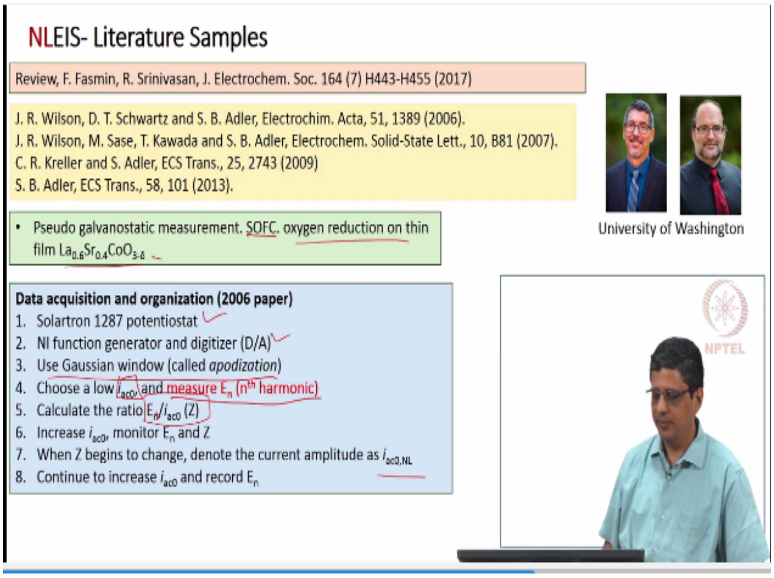

NLEIS- Literature Samples

Review, F. Fasmin, R. Srinivasan, J. Electrochem. Soc. 164 (7) H443-H455 (2017)

J. R. Wilson, D. T. Schwartz and S. B. Adler, Electrochim. Acta, 51, 1389 (2006).
J. R. Wilson, M. Sase, T. Kawada and S. B. Adler, Electrochem. Solid-State Lett., 10, B81 (2007).
C. R. Kreller and S. Adler, ECS Trans., 25, 2743 (2009)
S. B. Adler, ECS Trans., 58, 101 (2013).

- Pseudo galvanostatic measurement. SOFC. oxygen reduction on thin film $La_{0.6}Sr_{0.4}CoO_{3-\delta}$

Data acquisition and organization (2006 paper)

1. Solartron 1287 potentiostat
2. NI function generator and digitizer (D/A)
3. Use Gaussian window (called *apodization*)
4. Choose a low i_{ac0}, and measure E_n (n^{th} harmonic)
5. Calculate the ratio E_n/i_{ac0} (Z)
6. Increase i_{ac0}, monitor E_n and Z
7. When Z begins to change, denote the current amplitude as $i_{ac0,NL}$
8. Continue to increase i_{ac0} and record E_n

Then there is a review, so I am going to give a couple of examples from the review, review is written by our group in 2017 and a series of papers are published by group from University of Washington, Professor Schwartz and Professor Adler, so I will describe 1 or 2 examples here, so this is done on solid oxide fuel cell, okay and it is done in a galvanostatic mode, if you remember well, the experiments typically are done in galvanostatic mode for fuel cells and batteries, okay.

This experiment focuses on oxygen reduction on a particular film, lanthanum strontium cobalt oxide with some vacancies, so delta if it is 0, it is a proper oxide, if it is non-zero, it indicates oxygen vacancies. So, the way it is done, data acquisition as well as analysis, okay, chooses a potentiostat, national instrument function generator and digitizer, this uses Gaussian window, they call it as time apodization.

And initially, they choose a small amplitude perturbation for the current iac is 0, it is a galvanostatic mode, you should remember that and then measure the potential fundamental second third fourth harmonic, right and then the calculate the value of En/ac0 at the fundamental that is E1, now keep increasing the iac 0 and see when this ratio starts to change, okay, so until then you are in linear regime, at a particular iac is 0 and beyond that we are in the nonlinear regime.

So, we record this is iac is 0, where you start seeing nonlinear effect, okay and that is denoted by iac0 NL, then continuity increase and record E1, E2, E3 for a variety of iac0’s.

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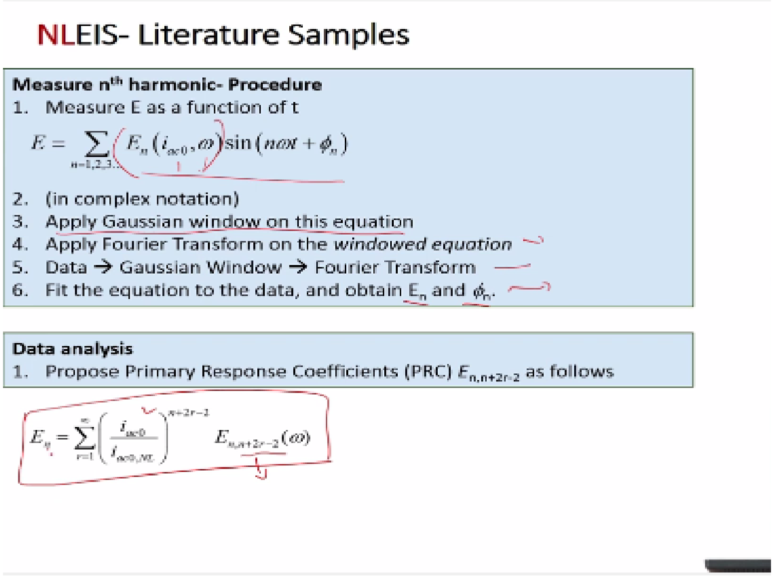

NLEIS- Literature Samples

Measure nth harmonic- Procedure

1. Measure E as a function of t

$$E = \sum_{n=1,2,3..} \left(E_n \left(i_{ac0}, \omega \right) \sin \left(n\omega t + \phi_n \right) \right)$$

2. (in complex notation)
3. Apply Gaussian window on this equation
4. Apply Fourier Transform on the *windowed equation*
5. Data → Gaussian Window → Fourier Transform
6. Fit the equation to the data, and obtain E_n and ϕ_n.

Data analysis

1. Propose Primary Response Coefficients (PRC) $E_{n,n+2r-2}$ as follows

$$\boxed{E_n = \sum_{r=1}^{\infty} \left(\frac{i_{ac0}}{i_{ac0,NL}} \right)^{n+2r-1} E_{n,n+2r-2}(\omega)}$$

To measure the nth harmonic, this is the procedure they have adopted, you can write the E in Fourier series, it is a function of iac0 and omega, this is the amplitude, E1, E2, E3 etc., sine n omega t + phi n, the complex notation. Instead of taking the potential and applying FFT on it, what they are done is take this equation, apply Gaussian window on this equation because in the experiment also, they are applying the Gaussian window.

They are not performing FFT in the very beginning, they apply Gaussian window and then do Fourier transform, so in the expression also, they apply a Gaussian window, do Fourier transform and then get an expression for the Fourier transform expression that is you take this equation multiplied by the Gaussian window and then do a Fourier transform, you get an expression, results from the experiment you would fit it to this expression which is not the original Fourier series.

Fourier series experimentally transform or experimentally apply a Gaussian window in the equations apply Gaussian window, apply FFT, equations apply FFT, you get an expression here, then the results that are obtained here are fitted to this equation and from that they have taken En and phi n, at least that is my understanding and they call this En is again fitted to another expression because they are taken data at multiple iac0, they have written it as a series, this is called primary response coefficient, this is E1.

They are defining E1, 1, E1, 3 etc., E2 can be written like this, E3 can be written like this, okay, these primary response coefficients would be independent of iac0 value. E1, E2 etc., will be dependent on iac0 value.

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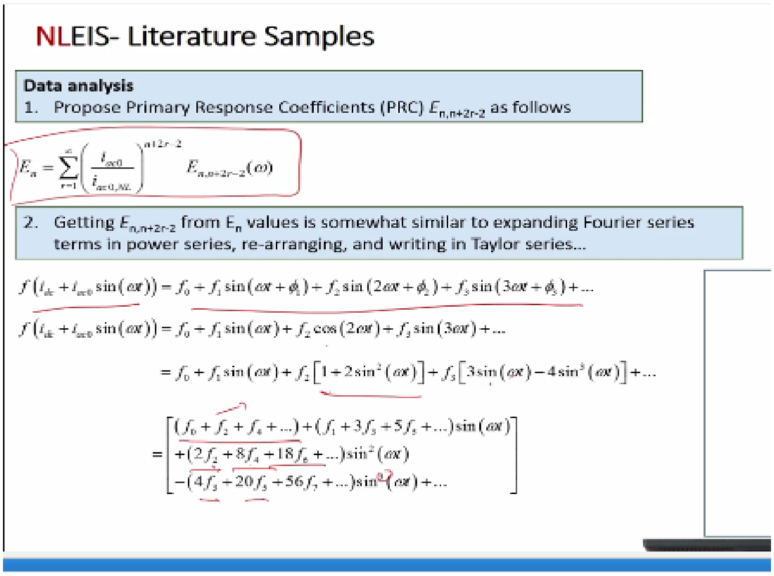

NLEIS- Literature Samples

Data analysis

1. Propose Primary Response Coefficients (PRC) $E_{n,n+2r-2}$ as follows

$$E_n = \sum_{r=1}^{\infty} \left(\frac{i_{ac0}}{i_{ac0,NL}} \right)^{n+2r-2} E_{n,n+2r-2}(\omega)$$

2. Getting $E_{n,n+2r-2}$ from E_n values is somewhat similar to expanding Fourier series terms in power series, re-arranging, and writing in Taylor series...

$$f\left(i_{dc} + i_{ac0}\sin(\omega t)\right) = f_0 + f_1 \sin(\omega t + \phi_1) + f_2 \sin(2\omega t + \phi_2) + f_3 \sin(3\omega t + \phi_3) + \ldots$$

$$f\left(i_{dc} + i_{ac0}\sin(\omega t)\right) = f_0 + f_1 \sin(\omega t) + f_2 \cos(2\omega t) + f_3 \sin(3\omega t) + \ldots$$

$$= f_0 + f_1 \sin(\omega t) + f_2\left[1 + 2\sin^2(\omega t)\right] + f_3\left[3\sin(\omega t) - 4\sin^3(\omega t)\right] + \ldots$$

$$= \begin{bmatrix} (f_0 + f_2 + f_4 + \ldots) + (f_1 + 3f_3 + 5f_5 + \ldots)\sin(\omega t) \\ +(2f_2 + 8f_4 + 18f_6 + \ldots)\sin^2(\omega t) \\ -(4f_3 + 20f_5 + 56f_7 + \ldots)\sin^3(\omega t) + \ldots \end{bmatrix}$$

To get this En, n + 2r – 2, from this n values, if we look at the expression, this is similar to expanding in Fourier series and then rearrange it, rearrange it here meaning, you first write it as sin omega t + phi 1 of course and then sin2 omega t, sin3 omega t etc., now, write this as sin square and sin, I am sorry, sin square and a constant, this has sin cube and sin, phi as sin power 5 sin power 3 sin power 1.

So, convert the Fourier series to Taylor series earlier, we seen examples where you have converted Taylor series to Fourier series, this is the reverse or inverse of that so, this fitting this is somewhat similar to taking a Fourier series and converting it to Taylor series for example, idc + iac0 sin omega t, you can write this in theory as a Fourier series.

Of course, this with the phase, I would write it as cosine 2 omega t, if this phase is pi/2 and this can be written as 1 + 2 sin square 3 - 4 sin cube and all the sin omega t terms can be grouped together, all the sin square can be grouped together, all the sin cube can be grouped together and you would get an expression which goes like this, all the even numbers; f0, f2, f4 from the Fourier series will come to the constant, f1, 3f3, 5f5 will come for sin omega, 2f2, 8f4, 18f6 etc., for sin square.

If it is sin cube, it has to start at f3, if it is sin power n, it has to start at fn with some coefficient and then it is going to go with an increment of 2, so it is going to be 3, it is going to be 3, 5, 7, etc., 2, 4, 6, etc.

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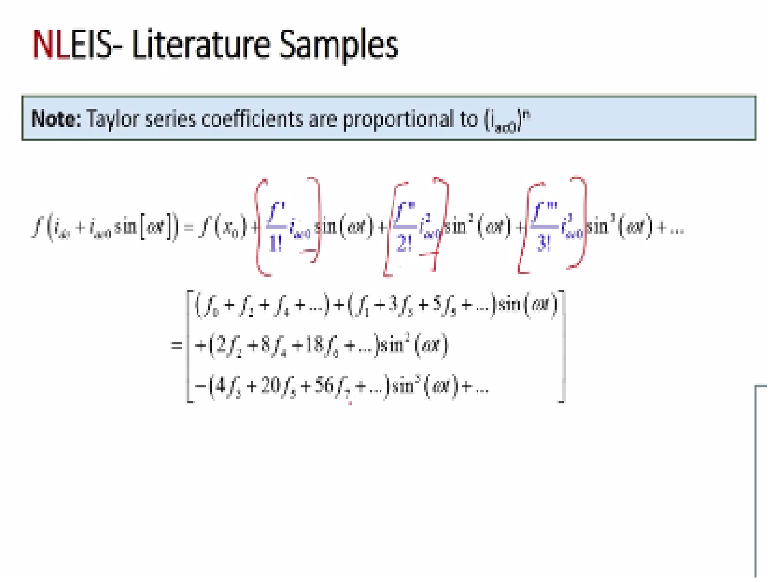

NLEIS- Literature Samples

Note: Taylor series coefficients are proportional to $(i_{ac0})^n$

$$f\left(i_{dc}+i_{ac0}\sin[\omega t]\right)=f(x_0)+\frac{f'}{1!}i_{ac0}\sin(\omega t)+\frac{f''}{2!}i_{ac0}^2\sin^2(\omega t)+\frac{f'''}{3!}i_{ac0}^3\sin^3(\omega t)+\ldots$$

$$=\begin{bmatrix}(f_0+f_2+f_4+\ldots)+(f_1+3f_3+5f_5+\ldots)\sin(\omega t)\\ +(2f_2+8f_4+18f_6+\ldots)\sin^2(\omega t)\\ -(4f_3+20f_5+56f_7+\ldots)\sin^3(\omega t)+\ldots\end{bmatrix}$$

If you write this in Taylor series, you would write it as first derivative divided by 1 factorial iac0, second derivative divided by 2 factorial iac0 square etc., now this is proportional to iac0, this is proportional to iac0 square, this is proportional to iac0 cube, in general the nth term will be proportional to iac0 power n and that is the same as what you would get from the Fourier series.

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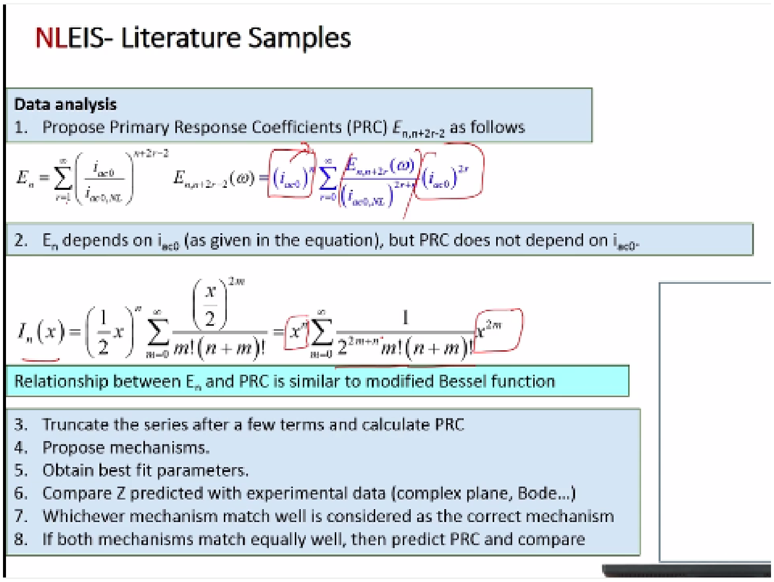

NLEIS- Literature Samples

Data analysis

1. Propose Primary Response Coefficients (PRC) $E_{n,n+2r-2}$ as follows

$$E_n = \sum_{r=1}^{\infty}\left(\frac{i_{ac0}}{i_{ac0,NL}}\right)^{n+2r-2} E_{n,n+2r-2}(\omega) = \boxed{(i_{ac0})^n}\sum_{r=0}^{\infty}\frac{E_{n,n+2r}(\omega)}{(i_{ac0,NL})^{2r+n}}\boxed{(i_{ac0})^{2r}}$$

2. E_n depends on i_{ac0} (as given in the equation), but PRC does not depend on i_{ac0}.

$$I_n(x) = \left(\frac{1}{2}x\right)^n \sum_{m=0}^{\infty}\frac{\left(\frac{x}{2}\right)^{2m}}{m!(n+m)!} = \boxed{x^n}\sum_{m=0}^{\infty}\frac{1}{2^{2m+n}m!(n+m)!}\boxed{x^{2m}}$$

Relationship between E_n and PRC is similar to modified Bessel function

3. Truncate the series after a few terms and calculate PRC
4. Propose mechanisms.
5. Obtain best fit parameters.
6. Compare Z predicted with experimental data (complex plane, Bode...)
7. Whichever mechanism match well is considered as the correct mechanism
8. If both mechanisms match equally well, then predict PRC and compare

If you look at this, it is very similar to the expansion for modified Bessel function, I want you to look at this, modified Bessel function of the first kind In, it is expanded like this, we have seen this before and you can rearrange it a little and write it as x power n, x power to 2m divided by 2 power 2m + n m factorial n + m factorial, what they have given can be rewritten, you can take iac0 power n outside, all the terms with or should be inside.

And if you look this and this, look very similar to x power n and x power to 2m, so the remaining terms are related to the other factors here, so it is similar to, it is not identical, it is similar to the expanded version of the modified Bessel function. Now, what they done is truncate the series after few terms and calculated, then you can propose the mechanism for different mechanisms, you can get different predictions and you can compare with the experimental results and see where the mechanism predictions match with the experimental results and you try evaluating few mechanisms only one of the matches we hope that is the correct mechanism.

Initially, you try with the impedance, if multiple mechanisms show good match with the impedance, then you can compare the higher harmonics coefficient, in this case the primary response coefficient at 2 or 3.

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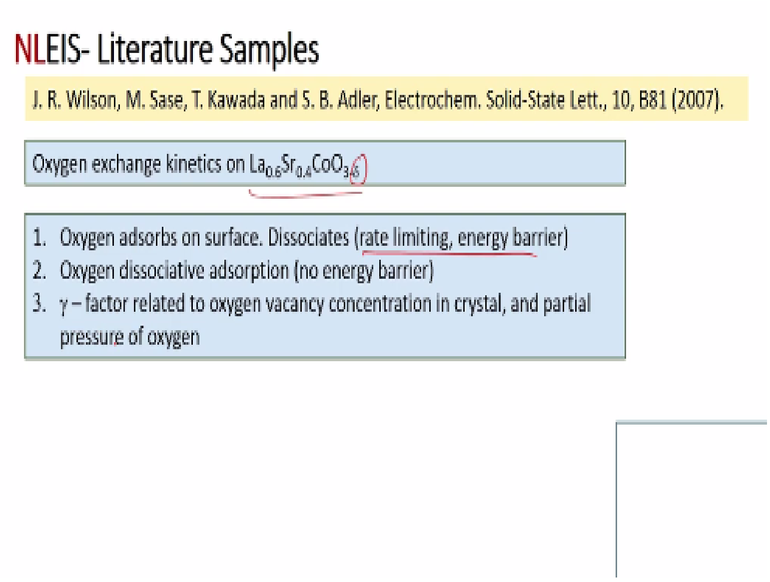

NLEIS- Literature Samples

J. R. Wilson, M. Sase, T. Kawada and S. B. Adler, Electrochem. Solid-State Lett., 10, B81 (2007).

Oxygen exchange kinetics on $La_{0.6}Sr_{0.4}CoO_{3-\delta}$

1. Oxygen adsorbs on surface. Dissociates (rate limiting, energy barrier)
2. Oxygen dissociative adsorption (no energy barrier)
3. γ – factor related to oxygen vacancy concentration in crystal, and partial pressure of oxygen

So, they have published this in 2007, it is for oxygen exchange kinetics on this particular membrane or thin film, they looked at two different mechanisms. In one; oxygen adsorbs on the surface and then dissociates; dissociation is the rate limiting step and it goes over an energy barrier. Another choice for the same overall reaction is for oxygen to dissociatively adsorbed that means, when it adsorbs, that time itself it dissociates and adsorbs.

And that step without energy barrier, those are the two mechanisms they are compared and they use the factor called gamma factor that is related to the oxygen vacancy concentration, the delta as well as the partial pressure of oxygen used in the experiments. We do not need to worry about it, we just want you to get an overall idea of what is done.

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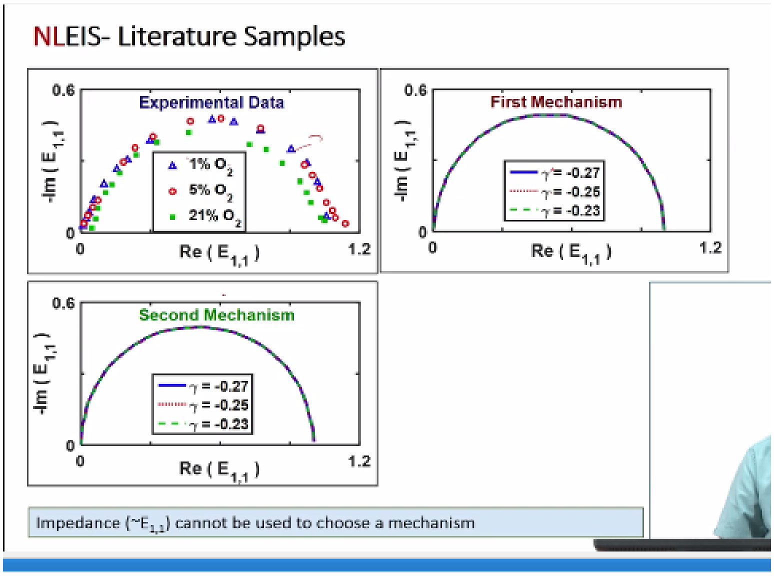

NLEIS- Literature Samples

Impedance (~$E_{1,1}$) cannot be used to choose a mechanism

So, E1, 1 is basically response at fundamental, instead of plotting the ratio of potential to current, they have plotted the potential value itself. So, for 3 different values of partial pressure, it looks like a semicircle, not exactly a semicircle somewhat distorted semicircle. First mechanism for 3 different gamma values corresponding to these partial pressures predicts and these 3 you can say a more or less you know, more or less overlapping.

First mechanism best fit parameters predict that all 3 values would give you same result, second mechanism also predicts this well that means, for optimised set of parameters, we cannot distinguish between these two mechanisms, we cannot say this mechanism describes the results correctly and the other one does not, both of them describe the result correctly. So, the response at fundamental or the impedance alone is not sufficient to identify which mechanism is the right one.

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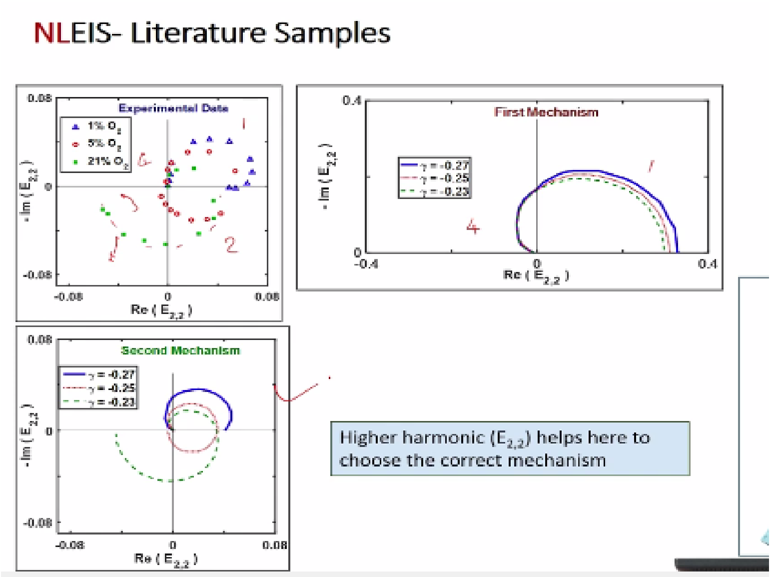

NLEIS- Literature Samples

Higher harmonic ($E_{2,2}$) helps here to choose the correct mechanism

Now, if you look at the response at higher harmonics which is written you know, converted and written as E2, 2, you have a difference at 3 different partial pressures, 21% is given by the green colour square, 5% is given by the red colour circle and 1% where results are given by the blue triangles. First mechanism, show some difference but all these things are present only in the fourth and the first quadrant, whereas here results are present in first, second and third a little bit of that is present in the fourth quadrant.

Second mechanism for the optimized parameter, they get results which are similar to what they see in the experiments, blue colour line corresponding to the 1 percent, red colour corresponding to the 5 percent and green colour dashed line corresponding to the 21 percent, you can definitely say that these predictions give you a better match compared to the prediction from the first mechanism.

So, the summary here is higher harmonics here help you choose the correct mechanism, so this is one example.

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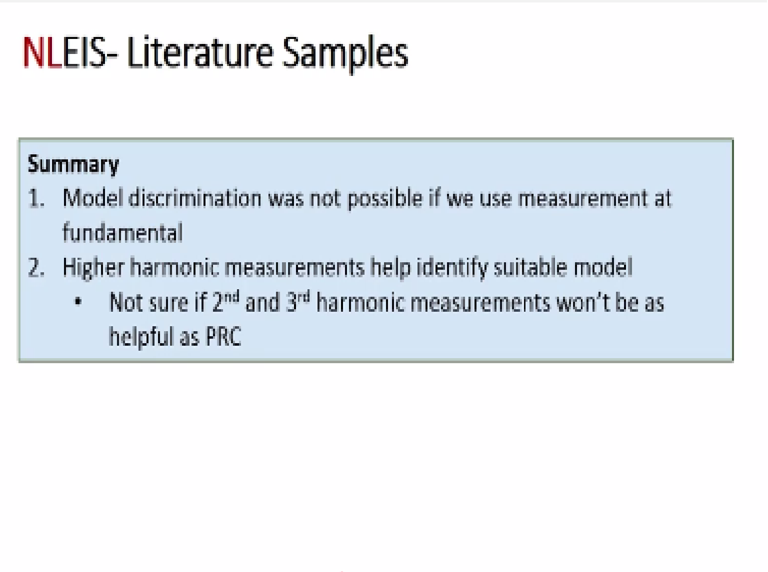

NLEIS- Literature Samples

Summary

1. Model discrimination was not possible if we use measurement at fundamental
2. Higher harmonic measurements help identify suitable model
    - Not sure if 2nd and 3rd harmonic measurements won't be as helpful as PRC

So, model discrimination was not possible using only the results at fundamental now, if we use second harmonic instead of primary response coefficient, I am not very sure that the conclusions will be very different, okay you can use second harmonic and third harmonic as long as you can measure them and as long as you can predict them, you should be able to compare.

If the primary response coefficient at the second or third order give you good match; my guess is second and third harmonic would also give you a good match but we have not tried it, okay.

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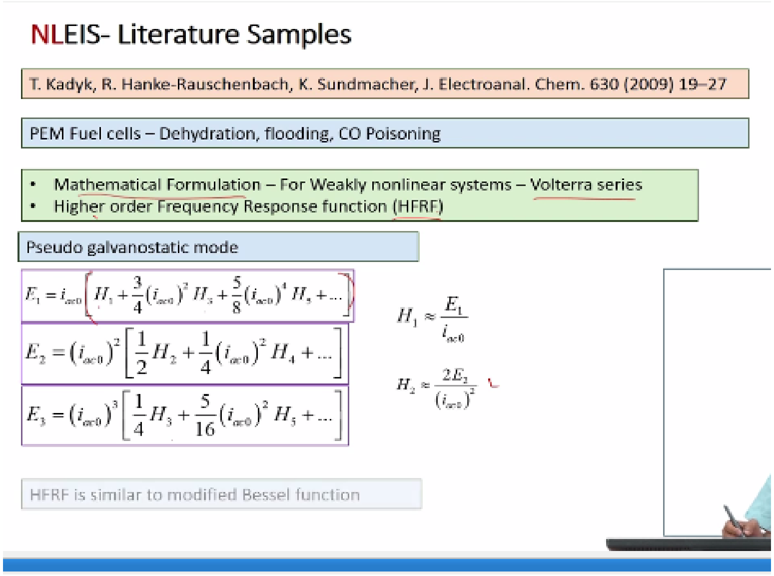

NLEIS- Literature Samples

T. Kadyk, R. Hanke-Rauschenbach, K. Sundmacher, J. Electroanal. Chem. 630 (2009) 19–27

PEM Fuel cells – Dehydration, flooding, CO Poisoning

- Mathematical Formulation – For Weakly nonlinear systems – Volterra series
- Higher order Frequency Response function (HFRF)

Pseudo galvanostatic mode

$$E_1 = i_{ac0}\left[H_1 + \frac{3}{4}(i_{ac0})^2 H_3 + \frac{5}{8}(i_{ac0})^4 H_5 + \ldots\right]$$

$$E_2 = (i_{ac0})^2\left[\frac{1}{2}H_2 + \frac{1}{4}(i_{ac0})^2 H_4 + \ldots\right]$$

$$E_3 = (i_{ac0})^3\left[\frac{1}{4}H_3 + \frac{5}{16}(i_{ac0})^2 H_5 + \ldots\right]$$

$$H_1 \approx \frac{E_1}{i_{ac0}}$$

$$H_2 \approx \frac{2E_2}{(i_{ac0})^2}$$

HFRF is similar to modified Bessel function

Results from another group, this is published in 2009 and they instead of higher harmonics, they use similar to primary response coefficient, they use what is called frequency response function, they have analysed PEM fuel cells and in the fuel cell, during normal operation you would get a spectrum, you can deliberately dehydrate the membrane and get a spectrum, you can deliberately cause what is called flooding and get a spectrum.

These are undesirable processes, it is possible to have carbon monoxide poisoning, this also not desirable but we can deliberately introduce this, and see the result, okay. So, in the mathematical formulation for weakly nonlinear systems, okay, they have taken what is called Volterra series and written expressions for what they describe as higher-order frequency response function FRF; HFRF.

And again, this is a fuel cell, it is run into the galvanostatic mode, E1, E2, E3 corresponds to the potential response at fundamental second and third harmonic, right and when it is written in terms of the FRF, they have written a series, H1, H3, H5; H2, H4 for the second harmonic, 3, 5 etc., for the third harmonic, so qualitatively if we look at it, it looks similar to the primary response coefficient expansion.

And naturally, it looks similar to the expansion for modified Bessel function now, if you go to moderate amplitude, you would get response at second harmonic, you will not get any response at third harmonic or you will not get significant response at third harmonic, so they have done the experiments at moderate amplitudes.

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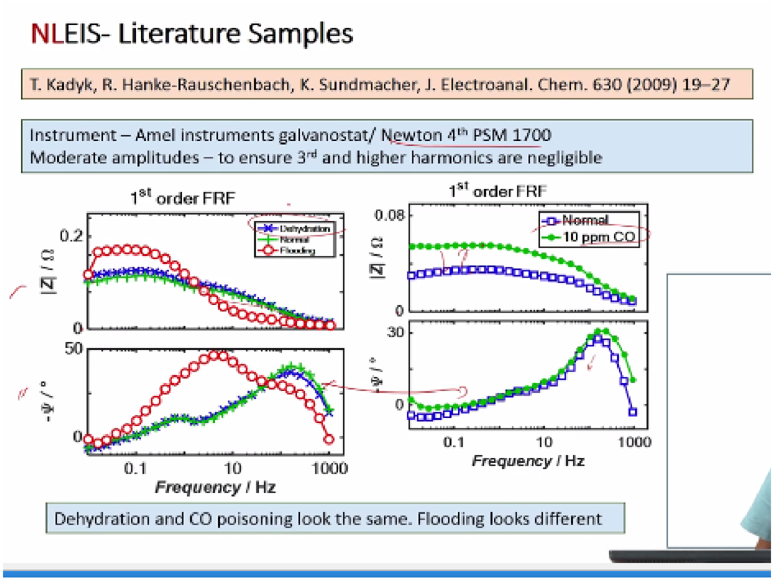

NLEIS- Literature Samples

T. Kadyk, R. Hanke-Rauschenbach, K. Sundmacher, J. Electroanal. Chem. 630 (2009) 19–27

Instrument – Amel instruments galvanostat/ Newton 4th PSM 1700
Moderate amplitudes – to ensure 3rd and higher harmonics are negligible

Dehydration and CO poisoning look the same. Flooding looks different

Instrumentation; okay, they used a galvanostat along with phase sensitive detector and they used moderate amplitude to ensure that third and higher harmonics are small and this results are published in 2009, so the response at the fundamental is shown here, they call it as first-order FRF basically, it is a response at fundamental. Magnitude and phase in board A plot as a function of frequency in the log scale, normal operation results are given by the green colour line here.

If they cause dehydration, there is a slight increase in the magnitude and there is a slight change in the phase, if you cause flooding, there is a significant change in the magnitude and phase, so flooding can be easily identified. In another experiment, they have operated it normally, they have also operated by introducing 10 ppm concentration of carbon monoxide and that causes an increase in magnitude under slight change in phase.

Now, if you compare these two, you can say that the red colour circles are completely different; significant difference is there between the red colour circle and the other two but these two are slight differences and look at the scale, this is going from 0 to 2 and this is going from 0 to 0.08 so, this difference if I put it in the same scale here, I cannot really tell whether the increase is because of carbon monoxide poisoning or increase is because of dehydration.

Both dehydration and carbon monoxide poisoning have the same signature and quantitatively, it is not very clear difference whereas, flooding causes a significant difference, so response at fundamental is not sufficient to distinguish between dehydration and CO poisoning at 10 ppm level.

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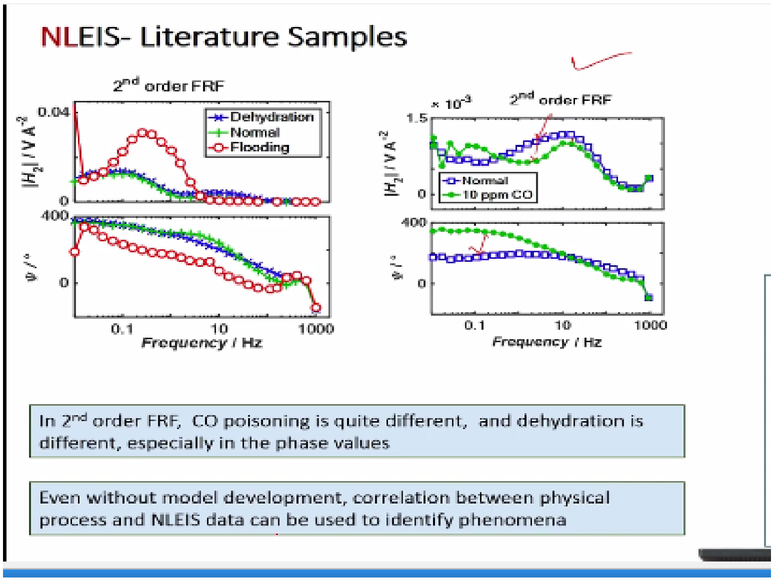

NLEIS- Literature Samples

In 2nd order FRF, CO poisoning is quite different, and dehydration is different, especially in the phase values

Even without model development, correlation between physical process and NLEIS data can be used to identify phenomena

Whereas, if we look at the second-order frequency response function, CO poisoning gives a significant difference in the phase and in the magnitude whereas, dehydration shows a slight difference. So, if you look at the frequency range and look at the signal in actual operation when you do not know what the problem is, in these cases they have controlled this environment and cost dehydration they have control the environment, introduce CO poisoning.

During operation, if you measure the FRF and measure the response at fundamental and second then, if there is a problem you would be able to identify whether there is a dehydration or whether there is CO poisoning or whether there is flooding, okay that is the idea behind this experiment. So, if you measure the first and second FRF, then you can distinguish between normal operation and dehydration and CO poisoning and flooding, okay.

Now, this even without model development just by measuring this and analysing the data, it is possible to do of course, if you can develop a model, it is better but correlation between physical process and NLEIS data is still useful.

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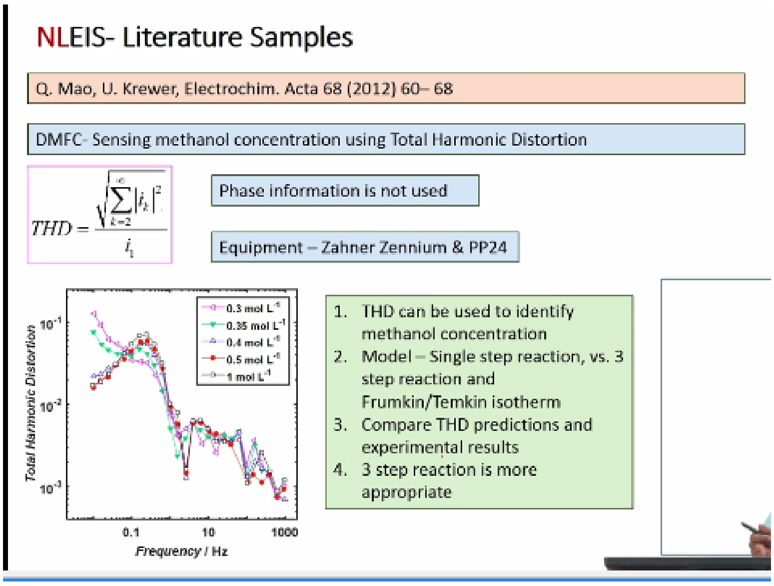

NLEIS- Literature Samples

Q. Mao, U. Krewer, Electrochim. Acta 68 (2012) 60– 68

DMFC- Sensing methanol concentration using Total Harmonic Distortion

$$THD = \frac{\sqrt{\sum_{k=2}^{\infty} |i_k|^2}}{i_1}$$

Phase information is not used

Equipment – Zahner Zennium & PP24

1. THD can be used to identify methanol concentration
2. Model – Single step reaction, vs. 3 step reaction and Frumkin/Temkin isotherm
3. Compare THD predictions and experimental results
4. 3 step reaction is more appropriate

There is another way to use the NLEIS data instead of measuring second harmonic, third harmonic etc, etc., you can measure what is called total harmonic distortion, okay imagine you are applying a pseudo potential static mode, you are playing a sinusoidal potential on top of a DC potential, you have response at i0 dc, i1 as fundamental, i2, i3, i4 for higher harmonics, take the absolute value of all those magnitudes, square them and add, okay square them and add them.

Take square root of that and take the ratio of that value to the response at fundamental, this is called total harmonic distortion, THD. Phase information is not collected here only the magnitude information is collected and used and this particular experiment is done for sensing methanol concentration in DMFC, okay, direct methanol fuel cell, this is published by another group in 2012 by Professor Krewer.

This equipment used is Zahner Zennium and PP24, other equipment also can give you a total harmonic distortion and what they are done is look at THD as a function of frequency for various methanol concentrations and the summary is that you can use THD to calculate the concentration, they propose two different models; one is a single step reaction now, there is a three step reaction with adsorption isotherm given by Temkin or Frumkin isotherm them.

And compared the predictions with the experimental results, I am not showing you all the details but by comparing these results, they claim that three step reaction is more appropriate to describe this DMFC operation, okay.

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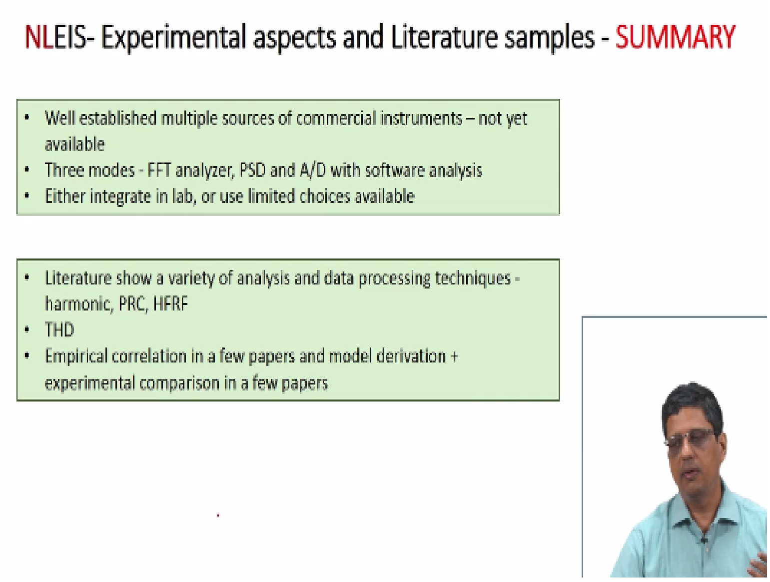

NLEIS- Experimental aspects and Literature samples - SUMMARY

- Well established multiple sources of commercial instruments – not yet available
- Three modes - FFT analyzer, PSD and A/D with software analysis
- Either integrate in lab, or use limited choices available

- Literature show a variety of analysis and data processing techniques - harmonic, PRC, HFRF
- THD
- Empirical correlation in a few papers and model derivation + experimental comparison in a few papers

So, to summarize; NLEIS measurements are fewer, you do not find them as common as what you see for traditional EIS, main reason being there is no well-established commercial instrumentation available from multiple manufacturers. In case of EIS, you can get instruments from many manufactures and tests, in case of nonlinear EIS, there is no well-established standard, okay.

There are different methods of analysing; one is FFT analyser, another is phase sensitive detector, lock-in amplifier, the other is to take the data and use software to analyse this, use software to perform the FFT and there are few choices available either you have to use the few choices or you have to do the work of integrating and writing the code, okay but I think in the future more and more of this analysis features will become standard in the equipment in the few years perhaps.

And the literature shows a variety of analysis and the data processing techniques, people use harmonic, people extract information from the harmonics and call it as primary response coefficient or higher order frequency response function, sometimes people use a total harmonic distortion and mostly right now, what you see is empirical correlation between physical processes and the results but in the future hopefully, there will be more physical model-based interpretation of the data, okay, we will stop with this.