Electrochemical Impedance Spectroscopy
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Lecture - 42
Electron Transfer Reaction

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Previous class

- NLEIS introduction and mathematical background

Today

- Brief introduction to data acquisition
- Calculation of NLEIS for a simple electron transfer reaction

So in the previous class, we have seen the background for the nonlinear EIS okay. We have seen that if you apply large amplitude perturbation, you can get higher harmonics, when you measure the impedance that impedance will depend on the perturbation amplitude okay. If I give a small Eac0, the impedance will be independent of the amplitude. If you give a large Eac0, it can change okay.

And if I give large enough, it will definitely change. In order to understand or analyze this correctly, we need to have good mathematical background; specifically we have to have background in Taylor series expansion, in Fourier series expansion and in special functions. One type of special function called modified Bessel function okay. I want to give a very brief introduction to the data acquisition okay.

Later, we will see detailed information on what we should do to get good quality data for nonlinear EIS. In the beginning, I just want to give you a very quick or brief introduction and then we will move on to calculating nonlinear EIS for a simple electron transfer reaction. At a later stage, will go for reaction with adsorbed intermediate, we will go for more complex cases where solution resistance plays a role. So right now, we will start with this simple electron transfer reaction okay.

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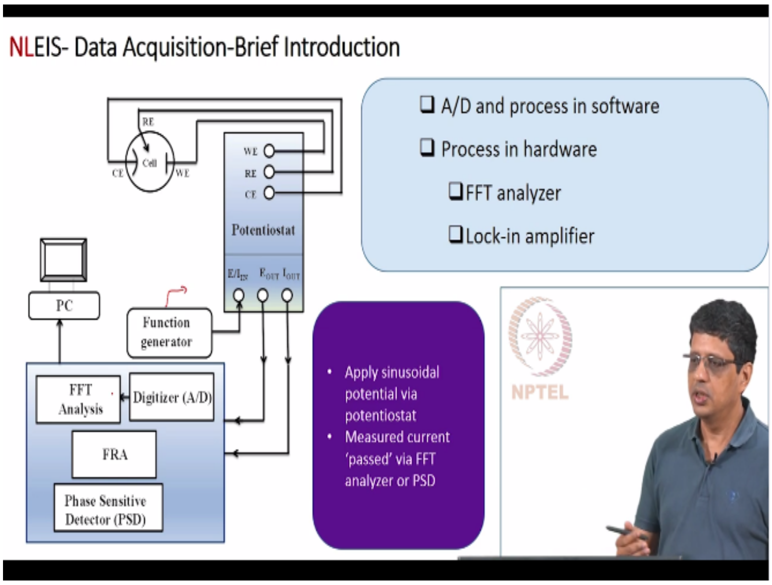

NLEIS- Data Acquisition-Brief Introduction

- ❑ A/D and process in software
- ❑ Process in hardware
  - ❑FFT analyzer
  - ❑Lock-in amplifier

- Apply sinusoidal potential via potentiostat
- Measured current 'passed' via FFT analyzer or PSD

So I have a potentiostat which is connected to the cell. You have to apply a sinusoidal wave, so we can apply a sinusoidal potential using what is called a function generator and that potential can be added to any dc bias that we want to give in the potentiostat and you can get the current. It is a good idea to measure both the potential that is applied onto the cell and the current that is measured from the cell okay.

We want to apply a dc bias and an ac potential, sinusoidal potential but we want to also make sure that the applied potential is actually correct okay. So the current that comes out, it can be subjected to Fourier series analysis. There are different ways of doing it, one method is to convert that current using an analog to digital board, it is called A to D and then use Fourier transform in the software.

Let us take the current values as a function of time and then subject that to Fourier transform. Another method is to use a hardware Fourier transform analysis. That is when it is measured, at that time itself subjected to Fourier transform within the hardware and then just get the Fourier coefficient. Another method is called phase sensitive detection in which case you multiply this by a sine wave, this can be done after digitization, it can be done in the analog domain itself.

And then find out the component at omega or at 2 omega whichever frequency we want to look at okay. So that is using what is called lock-in amplifier, it can be done within software, it can be done in the hardware either using FFT analyzer or using lock-in amplifier. Of course, if you want to do galvanostatically, it is possible to do provided we give a dc bias if necessary, we give a dc bias and a sinusoidal current and then measure the potential and then subject it to any one of these techniques.

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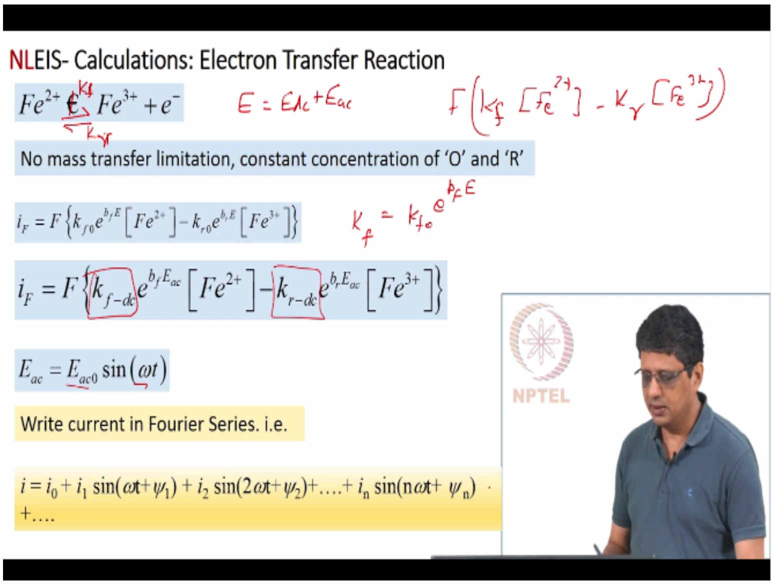

NLEIS- Calculations: Electron Transfer Reaction

$Fe^{2+} \underset{k_r}{\overset{k_f}{\rightleftarrows}} Fe^{3+} + e^-$

$E = E_{dc} + E_{ac}$

$F\left(k_f [Fe^{2+}] - k_r [Fe^{3+}]\right)$

No mass transfer limitation, constant concentration of 'O' and 'R'

$i_F = F\left\{k_{f0}e^{b_f E}\left[Fe^{2+}\right] - k_{r0}e^{b_r E}\left[Fe^{3+}\right]\right\}$

$k_f = k_{f0} e^{b_f E}$

$i_F = F\left\{\boxed{k_{f-dc}}\, e^{b_f E_{ac}}\left[Fe^{2+}\right] - \boxed{k_{r-dc}}\, e^{b_r E_{ac}}\left[Fe^{3+}\right]\right\}$

$E_{ac} = \underline{E_{ac0}} \sin\left(\omega t\right)$

Write current in Fourier Series. i.e.

$i = i_0 + i_1 \sin(\omega t + \psi_1) + i_2 \sin(2\omega t + \psi_2) + \ldots + i_n \sin(n\omega t + \psi_n) + \ldots$

Now I want to start with a reaction which is Redox reaction. Fe 2+ is oxidized to Fe 3+ and with the release of electron, we are going to assume that there is no mass transfer limitation that is it is our rapid mass transfer, concentration of these two species are constant. Under that condition, we can write the faradaic current as Fk1 concentration of Fe 2+, of course k1 is the forward rate constant; k-1 is the reverse rate constant.

We can also write it as kf and kr, kf-k reverse Fe 3+ concentration and of course each of these rate constants are going to be written in terms of potential for forward reaction as well as the reverse reaction. Now total potential is dc+ac and rate constant value at the dc potential I can write it as kf dc and kr dc. So when I expand this, I would get an expression saying F*kf dc exponential of bf Edc with the concentration of Fe 2+ and correspondingly for the reverse reaction.

And ac is given by ac0 amplitude and the frequency omega and we want to write this faradaic current in Fourier series as I0 corresponding to the constant term i1 which is the magnitude of the response at fundamental with phase psi 1. I2 is the magnitude of the response at the second harmonic with the corresponding phase psi 2 and so on for any of this.

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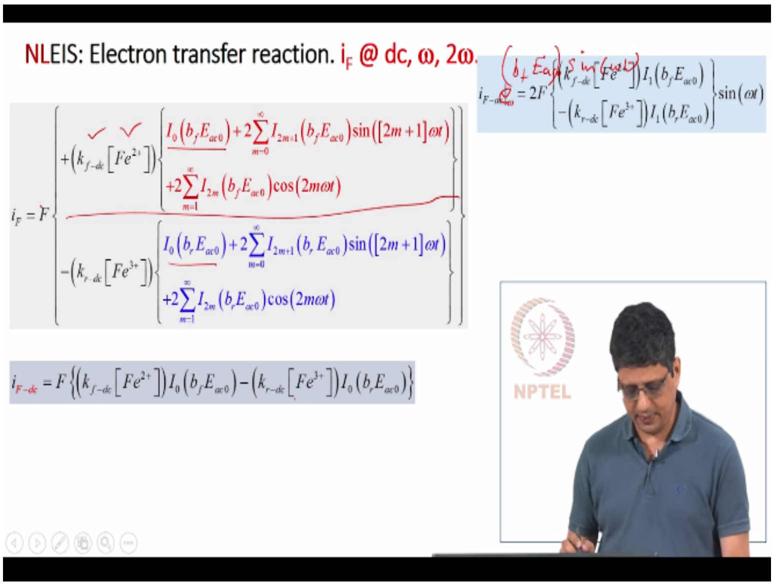

NLEIS: Electron transfer reaction. i_F @ dc, ω, 2ω.

$$i_F = F\left\{\begin{array}{l} +\left(k_{f-dc}\left[Fe^{2+}\right]\right)\left\{\begin{array}{l} \underline{I_0\left(b_f E_{ac0}\right)} + 2\sum_{m=0}^{\infty} I_{2m+1}\left(b_f E_{ac0}\right)\sin\left(\left[2m+1\right]\omega t\right) \\ +2\sum_{m=1}^{\infty} I_{2m}\left(b_f E_{ac0}\right)\cos\left(2m\omega t\right) \end{array}\right\} \\ -\left(k_{r-dc}\left[Fe^{3+}\right]\right)\left\{\begin{array}{l} \underline{I_0\left(b_r E_{ac0}\right)} + 2\sum_{m=0}^{\infty} I_{2m+1}\left(b_r E_{ac0}\right)\sin\left(\left[2m+1\right]\omega t\right) \\ +2\sum_{m=1}^{\infty} I_{2m}\left(b_r E_{ac0}\right)\cos\left(2m\omega t\right) \end{array}\right\} \end{array}\right\}$$

$$i_{F-dc} = F\left\{\left(k_{f-dc}\left[Fe^{2+}\right]\right)I_0\left(b_f E_{ac0}\right) - \left(k_{r-dc}\left[Fe^{3+}\right]\right)I_0\left(b_r E_{ac0}\right)\right\}$$

$$i_{F-ac\omega} = 2F\left\{\begin{array}{l} \left(k_{f-dc}\left[Fe^{2+}\right]\right)I_1\left(b_f E_{ac0}\right) \\ -\left(k_{r-dc}\left[Fe^{3+}\right]\right)I_1\left(b_r E_{ac0}\right) \end{array}\right\}\sin\left(\omega t\right)$$

$(b_f E_a) \sin(\omega t)$

Now exponential of a sin theta, we know it can be written as an infinite series in the modified Bessel function. It is actually a generating function. Likewise, for e power bf e Eac0 sin omega t. We can write in terms of the modified Bessel function at I0, I1, I2, I3, etc and similarly we can write it for the reverse reaction. So we have a fairly large number of terms but we will look at first few terms okay.

If you want to look at the dc component of this response, if you look at this, you can separate this as the one corresponding to the forward reaction, one corresponding to the reverse reaction. For the forward reaction, you have Faraday constant, rate constant at dc potential, concentration; these are all fixed numbers for a given dc potential. This is the only constant coming out of this expression.

And for the reverse reaction, the first term is the one that is a constant. So I can write it as Faraday constant kf dc Fe 2+*I0 evaluated at bf Eac0 and correspondingly for the reverse reaction.

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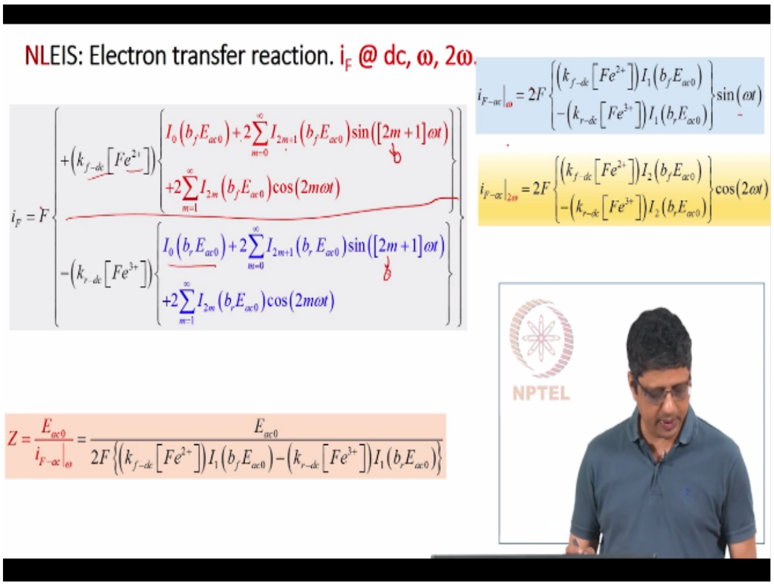

NLEIS: Electron transfer reaction. i_F @ dc, ω, 2ω.

$$i_F = F\left\{\begin{matrix} +\left(k_{f-dc}\left[Fe^{2+}\right]\right)\left\{\begin{matrix} I_0\left(b_f E_{ac0}\right) + 2\sum_{m=0}^{\infty} I_{2m+1}\left(b_f E_{ac0}\right)\sin\left(\left[2\underset{\downarrow 0}{m}+1\right]\omega t\right) \\ +2\sum_{m=1}^{\infty} I_{2m}\left(b_f E_{ac0}\right)\cos\left(2m\omega t\right) \end{matrix}\right\} \\ -\left(k_{r-dc}\left[Fe^{3+}\right]\right)\left\{\begin{matrix} I_0\left(b_r E_{ac0}\right) + 2\sum_{m=0}^{\infty} I_{2m+1}\left(b_r E_{ac0}\right)\sin\left(\left[2\underset{\downarrow 0}{m}+1\right]\omega t\right) \\ +2\sum_{m=1}^{\infty} I_{2m}\left(b_r E_{ac0}\right)\cos\left(2m\omega t\right) \end{matrix}\right\} \end{matrix}\right\}$$

$$i_{F-ac}\big|_{\omega} = 2F\left\{\begin{matrix} \left(k_{f-dc}\left[Fe^{2+}\right]\right)I_1\left(b_f E_{ac0}\right) \\ -\left(k_{r-dc}\left[Fe^{3+}\right]\right)I_1\left(b_r E_{ac0}\right) \end{matrix}\right\}\sin\left(\omega t\right)$$

$$i_{F-ac}\big|_{2\omega} = 2F\left\{\begin{matrix} \left(k_{f-dc}\left[Fe^{2+}\right]\right)I_2\left(b_f E_{ac0}\right) \\ -\left(k_{r-dc}\left[Fe^{3+}\right]\right)I_2\left(b_r E_{ac0}\right) \end{matrix}\right\}\cos\left(2\omega t\right)$$

$$Z = \frac{E_{ac0}}{i_{F-ac}\big|_{\omega}} = \frac{E_{ac0}}{2F\left\{\left(k_{f-dc}\left[Fe^{2+}\right]\right)I_1\left(b_f E_{ac0}\right) - \left(k_{r-dc}\left[Fe^{3+}\right]\right)I_1\left(b_r E_{ac0}\right)\right\}}$$

In case of the response at fundamental which we are denoting as iF ac at omega, in case of response at the fundamental, it is going to be at sin omega t which means m has to be 0, here also m has to be 0. When m is 0, we are going to get these terms and 2 I1. So I have taken the 2 out of this, 2 I1 bf Eac0-here also kr dc Fe 3+ 2 I1 br Eac0. At second harmonic, you can correspondingly find, it is going to be cosine.

Third harmonic, it is going to be sine but then it will come with a negative sign and so on you can do it for any harmonic. Now if I measure the impedance, if I give a large sinusoidal potential but I just use a traditional or normal equipment and measure the impedance, I am going to get Eac0/iF ac at omega. So it is going to subject that to Fourier transform, get the response at fundamental, take the magnitude and divide to get the magnitude of the impedance.

Here because it is sin omega t, the phase difference is 0. Therefore, we are going to look at it as a simple resistor. The expression we get is Eac0 by the entire iF ac at omega.

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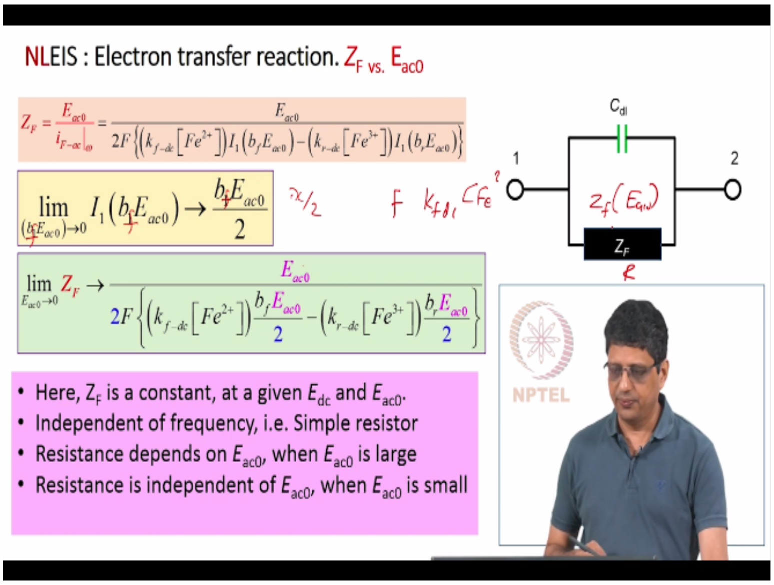

NLEIS : Electron transfer reaction. Z_{F} vs. E_{ac0}

$$Z_F = \frac{E_{ac0}}{i_{F-ac}\big|_{\omega}} = \frac{E_{ac0}}{2F\left\{\left(k_{f-dc}\left[Fe^{2+}\right]\right)I_1\left(b_f E_{ac0}\right)-\left(k_{r-dc}\left[Fe^{3+}\right]\right)I_1\left(b_r E_{ac0}\right)\right\}}$$

$$\lim_{(b_f E_{ac0})\to 0} I_1\left(b_f E_{ac0}\right) \to \frac{b_f E_{ac0}}{2} \quad x/2 \qquad f \; k_{fdc}, C_{Fe}$$

$$\lim_{E_{ac0}\to 0} Z_F \to \frac{E_{ac0}}{2F\left\{\left(k_{f-dc}\left[Fe^{2+}\right]\right)\frac{b_f E_{ac0}}{2}-\left(k_{r-dc}\left[Fe^{3+}\right]\right)\frac{b_r E_{ac0}}{2}\right\}}$$

- Here, Z_F is a constant, at a given E_{dc} and E_{ac0}.
- Independent of frequency, i.e. Simple resistor
- Resistance depends on E_{ac0}, when E_{ac0} is large
- Resistance is independent of E_{ac0}, when E_{ac0} is small

Now what happens when Eac0 goes to 0 that is when we use small amplitude perturbation, we should get the same expression as what we got before with linearization. So limit of x tending to 0, I1 x is going to be x/2, instead of x we use bf Eac0. We are going to get bf Eac0/2. This multiplied by 2 will give us f kf dc Fe 2+ concentration bf. Similarly, this side 2 I1 br Eac0 will come to just br Eac0.

So these 2’s will cancel out, Eac0 will cancel out and you will get an expression that is the same as what you got after linearization. So certain points I would like you to note. One is the faradaic impedance is a constant at a given dc and at a given Eac0. Constant here meaning, it is independent of the frequency that means it acts like a resistor. Now if it changes Eac0, the value of the resistance will change.

It is still independent of frequency but it will depend on Eac0 when Eac0 is large. When Eac0 is vanishingly small, very small, then that ZF that I calculate here will be independent of Eac0 which means these are cancelling out. It is just going to be a simple resistor, so this aligns with what we expect to see. When Eac0 is large, the impedance is going to depend on the Eac0 value.

When it is small, the impedance value is independent of the Eac0 value. So basically if I model it as a parallel combination of double-layer capacitance under faradaic impedance, I will get ZF, ZF here is a function of Eac0 when Eac0 is large. ZF here is just a simple resistance, constant resistance when Eac0 is small. When it is large, it is still the resistance but it depends on Eac0 okay.

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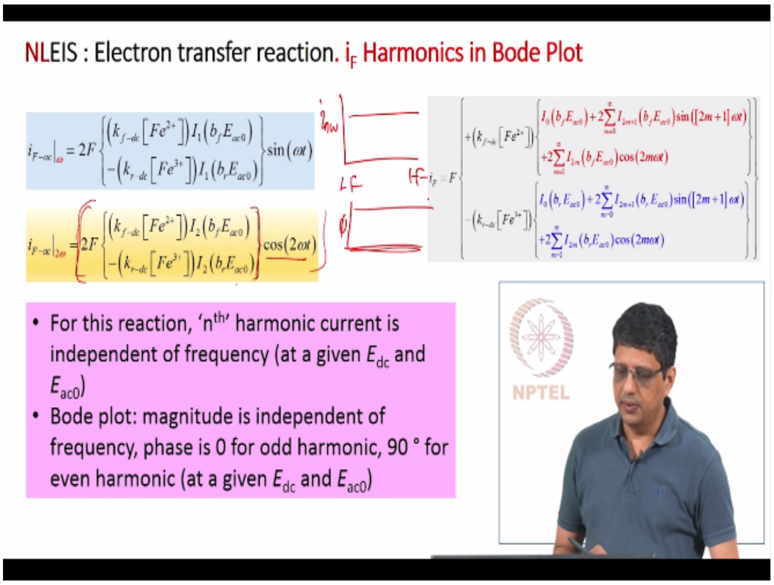

NLEIS : Electron transfer reaction. i_F Harmonics in Bode Plot

$$i_{F-ac}\big|_{\omega} = 2F\left\{\begin{matrix}\left(k_{f-dc}\left[Fe^{2+}\right]\right)I_1\left(b_fE_{ac0}\right)\\ -\left(k_{r-dc}\left[Fe^{3+}\right]\right)I_1\left(b_rE_{ac0}\right)\end{matrix}\right\}\sin(\omega t)$$

$$i_{F-ac}\big|_{2\omega} = 2F\left\{\begin{matrix}\left(k_{f-dc}\left[Fe^{2+}\right]\right)I_2\left(b_fE_{ac0}\right)\\ -\left(k_{r-dc}\left[Fe^{3+}\right]\right)I_2\left(b_rE_{ac0}\right)\end{matrix}\right\}\cos(2\omega t)$$

$$i_F = F\left\{\begin{matrix}+\left(k_{f-dc}\left[Fe^{2+}\right]\right)\left\{\begin{matrix}I_0\left(b_fE_{ac0}\right)+2\sum_{m=0}^{\infty}I_{2m+1}\left(b_fE_{ac0}\right)\sin\left([2m+1]\omega t\right)\\ +2\sum_{m=1}^{\infty}I_{2m}\left(b_fE_{ac0}\right)\cos(2m\omega t)\end{matrix}\right\}\\ -\left(k_{r-dc}\left[Fe^{3+}\right]\right)\left\{\begin{matrix}I_0\left(b_rE_{ac0}\right)+2\sum_{m=0}^{\infty}I_{2m+1}\left(b_rE_{ac0}\right)\sin\left([2m+1]\omega t\right)\\ +2\sum_{m=1}^{\infty}I_{2m}\left(b_rE_{ac0}\right)\cos(2m\omega t)\end{matrix}\right\}\end{matrix}\right\}$$

- For this reaction, 'nth' harmonic current is independent of frequency (at a given E_{dc} and E_{ac0})
- Bode plot: magnitude is independent of frequency, phase is 0 for odd harmonic, 90 ° for even harmonic (at a given E_{dc} and E_{ac0})

Now if I look at higher harmonics, I can look at 2 omega, I can look at 3 omega. They are also fixed numbers, meaning if you look at the coefficient of 2 omega t, this is independent of omega. The coefficient of this is independent of omega, the phase difference here is 90 degree, cosine and sine are off by 90 degree. So nth harmonic current if you plot it in Bode plot if I say In omega from low frequency to high frequency, it is going to be a constant.

If you look at the phase value, it is going to be 0 for odd harmonic; it is going to be 90 degree for even harmonic okay.

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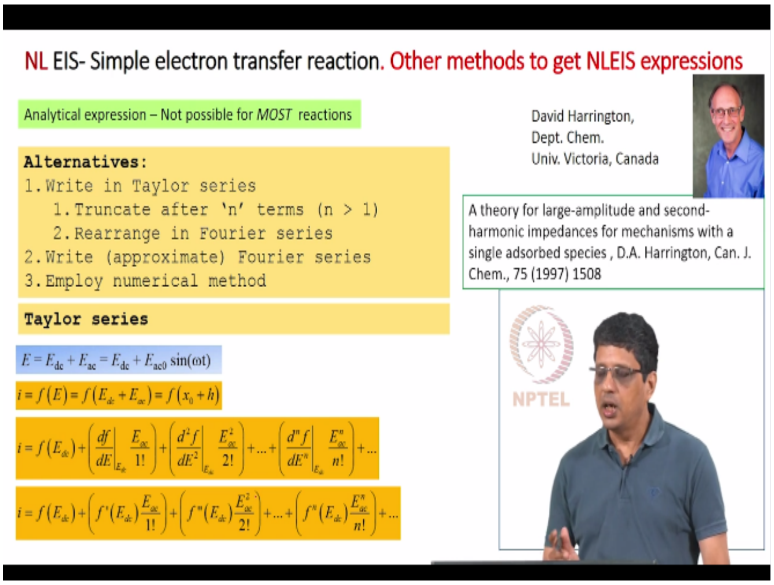

NL EIS- Simple electron transfer reaction. Other methods to get NLEIS expressions

Analytical expression – Not possible for *MOST* reactions

Alternatives:
1. Write in Taylor series
   1. Truncate after 'n' terms (n > 1)
   2. Rearrange in Fourier series
2. Write (approximate) Fourier series
3. Employ numerical method

Taylor series

$$E = E_{dc} + E_{ac} = E_{dc} + E_{ac0}\sin(\omega t)$$

$$i = f(E) = f(E_{dc} + E_{ac}) = f(x_0 + h)$$

$$i = f(E_{dc}) + \left(\frac{df}{dE}\bigg|_{E_{dc}}\frac{E_{ac}}{1!}\right) + \left(\frac{d^2f}{dE^2}\bigg|_{E_{dc}}\frac{E_{ac}^2}{2!}\right) + \ldots + \left(\frac{d^nf}{dE^n}\bigg|_{E_{dc}}\frac{E_{ac}^n}{n!}\right) + \ldots$$

$$i = f(E_{dc}) + \left(f'(E_{dc})\frac{E_{ac}}{1!}\right) + \left(f''(E_{dc})\frac{E_{ac}^2}{2!}\right) + \ldots + \left(f^n(E_{dc})\frac{E_{ac}^n}{n!}\right) + \ldots$$

David Harrington,
Dept. Chem.
Univ. Victoria, Canada

A theory for large-amplitude and second-harmonic impedances for mechanisms with a single adsorbed species , D.A. Harrington, Can. J. Chem., 75 (1997) 1508

So we got analytical expression here because we are able to expand exponential of a sin theta in Fourier series. Most of the cases, we will not be able to get analytical expression. So we have few choices; one write in Taylor series, expand up to some terms, instead of linearizing or instead of writing only up to the first frequency term, you can write for a few more terms and then truncate it and then rearrange, that is one possibility.

Second, in many cases you can also write an approximate Fourier series. This was published in 1997 by Professor David Harrington in Department of Chemistry University of Victoria in Canada. I had taken the image from the website. So for large amplitude perturbation, he has shown how to calculate it for a few reactions including reaction with adsorbed intermediates, for the response at fundamental, for the response at second harmonic, you can use numerical method.

So we have done some research on that and I will describe how you can use numerical method to handle situations where we do not know how to get analytical expression. So if you want to look at the example of Taylor series analysis here, potential of course is Edc+Eac where Eac can be considered as a small number, it can be a large number also. When you write this in Taylor series, we want to write current as a function of potential.

Potential at x0+h where x0 you can replace by Edc, h you can replace by Eac. Now we would write in Taylor series as f of x0+derivative first order derivative*h second order derivative*h square/2 factorial and so on and in this case, we are going to write it as f at Edc, f prime at Edc, f double prime second derivative at Edc correspondingly Eac, Eac square and so on.

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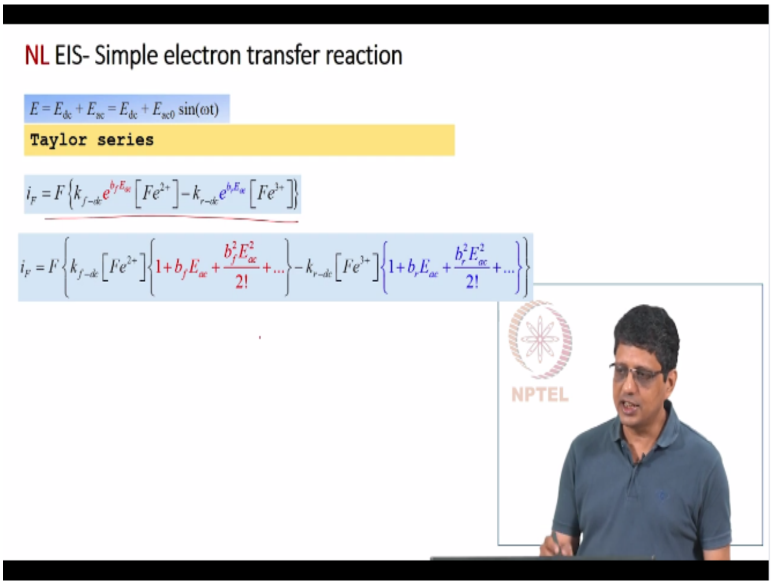

NL EIS- Simple electron transfer reaction

$E = E_{dc} + E_{ac} = E_{dc} + E_{ac0}\sin(\omega t)$

`Taylor series`

$i_F = F\left\{k_{f-dc}e^{b_f E_{ac}}\left[Fe^{2+}\right] - k_{r-dc}e^{b_r E_{ac}}\left[Fe^{3+}\right]\right\}$

$$i_F = F\left\{k_{f-dc}\left[Fe^{2+}\right]\left\{1 + b_f E_{ac} + \frac{b_f^2 E_{ac}^2}{2!} + \dots\right\} - k_{r-dc}\left[Fe^{3+}\right]\left\{1 + b_r E_{ac} + \frac{b_r^2 E_{ac}^2}{2!} + \dots\right\}\right\}$$

And then we are going to truncate after certain terms. So when you write this in case we did not know how to write this exponential of sin theta, we know of course that we can write the exponential of sin theta as Fourier series with modified Bessel functions as coefficients but in case we did not know, we can still write it as sin theta, sin square theta, sin cube theta and so on and truncate it after certain number of terms.

In this case, truncate it after 3 terms and then rearrange it, use power law, write it in Fourier series for sin square, sin cube, etc and then rearrange it.

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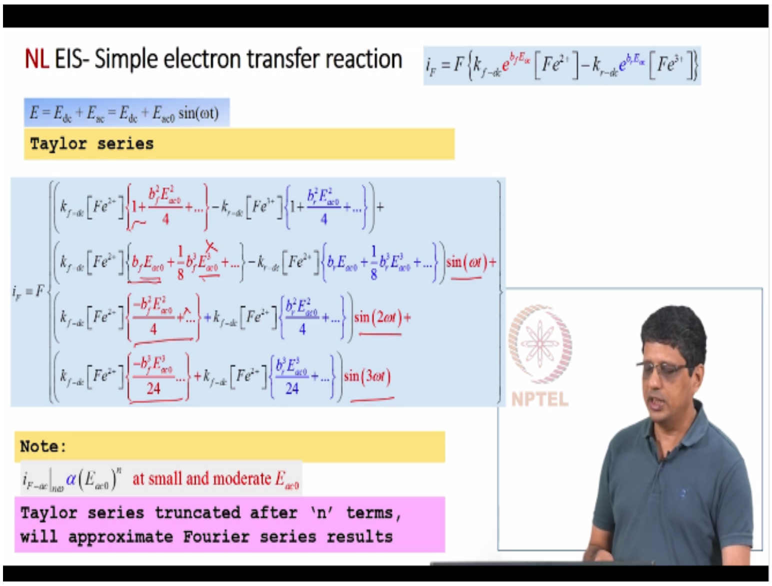

NL EIS- Simple electron transfer reaction

$i_F = F\left\{k_{f-dc}e^{b_f E_{ac}}\left[Fe^{2+}\right] - k_{r-dc}e^{b_r E_{ac}}\left[Fe^{3+}\right]\right\}$

$E = E_{dc} + E_{ac} = E_{dc} + E_{ac0}\sin(\omega t)$

`Taylor series`

$$i_F = F\left\{\begin{array}{l}\left(k_{f-dc}\left[Fe^{2+}\right]\left\{1+\frac{b_f^2E_{ac0}^2}{4}+...\right\}-k_{r-dc}\left[Fe^{3+}\right]\left\{1+\frac{b_r^2E_{ac0}^2}{4}+...\right\}\right)+\\ \left(k_{f-dc}\left[Fe^{2+}\right]\left\{b_fE_{ac0}+\frac{1}{8}b_f^3E_{ac0}^3+...\right\}-k_{r-dc}\left[Fe^{2+}\right]\left\{b_rE_{ac0}+\frac{1}{8}b_r^3E_{ac0}^3+...\right\}\right)\sin(\omega t)+\\ \left(k_{f-dc}\left[Fe^{2+}\right]\left\{\frac{-b_f^2E_{ac0}^2}{4}+...\right\}+k_{f-dc}\left[Fe^{2+}\right]\left\{\frac{b_r^2E_{ac0}^2}{4}+...\right\}\right)\sin(2\omega t)+\\ \left(k_{f-dc}\left[Fe^{2+}\right]\left\{\frac{-b_f^3E_{ac0}^3}{24}...\right\}+k_{f-dc}\left[Fe^{2+}\right]\left\{\frac{b_r^3E_{ac0}^3}{24}+...\right\}\right)\sin(3\omega t)\end{array}\right\}$$

`Note:`

$i_{F-ac}|_{n\omega}\ \alpha\left(E_{ac0}\right)^n$ at small and moderate E_{ac0}

`Taylor series truncated after 'n' terms,`
`will approximate Fourier series results`

Since you have done this example before, I will go through it little fast okay. So we know that the coefficient, constant coefficient will get terms from sin square, sin cube will give sin theta and sin 3 theta. Sin power 4 will give constant coefficient and sin 2 theta actually cosine but it is alright, sin 2 theta with phase sin 4 theta okay. So if we look here, constant term can be written as 1+Eac0 square+Eac0 power 4 etc and similarly for the reverse reaction.

Response at fundamental, response at sin omega t can be written as Eac power 1 Eac power 3 Eac power 5 and so on. Response at 2 omega t can be written as Eac square Eac power 4 Eac power 6 and so on and 3 omega t of course as cube+Eac power 5+Eac power 7 and so on. Now if you look at it, if Eac0 is small or moderate, I can say this is roughly 1. This is roughly proportional to Eac0, this is roughly proportional to Eac square, this is roughly proportional to Eac cube.

That is why if I take the Fourier component at n omega, at sin omega, sin 2 omega, sin 3 omega, sin n omega at small and moderate values, it is going to be Eac0 power n. When you go to larger amplitude, I cannot neglect this, I cannot neglect the further terms. So it will not be always proportional to Eac power n, only at small and moderate values it is going to be proportional to that.

At higher values, it is going to be dependent. In this example for this reaction, it is going to dependent as described by the modified Bessel function. For other reactions, the dependence is hard to get because we do not have an analytical expression. So this is just a reemphasize of the Taylor series expansion truncating after n terms and then rearranging will approximate the Fourier series results.

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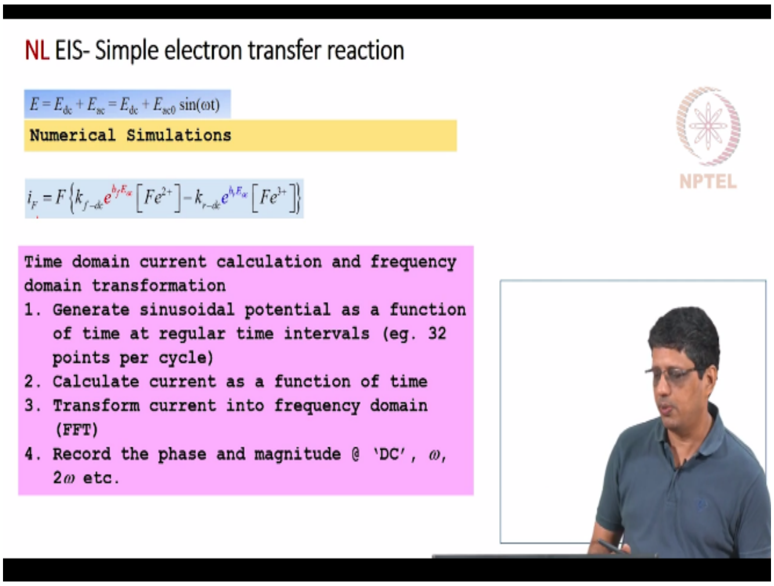

NL EIS- Simple electron transfer reaction

$E = E_{dc} + E_{ac} = E_{dc} + E_{ac0}\sin(\omega t)$

Numerical Simulations

$i_F = F\left\{k_{f-dc}e^{b_f E_{ac}}\left[Fe^{2+}\right] - k_{r-dc}e^{b_r E_{ac}}\left[Fe^{3+}\right]\right\}$

Time domain current calculation and frequency domain transformation

1. Generate sinusoidal potential as a function of time at regular time intervals (eg. 32 points per cycle)
2. Calculate current as a function of time
3. Transform current into frequency domain (FFT)
4. Record the phase and magnitude @ 'DC', ω, 2ω etc.

I will also describe how we can do numerical simulation for this. It is not necessary to do numerical simulation for this but if we learn how to do the numerical simulation for this, later when we go to other examples where numerical simulation is the only way or probably the easiest way, then it will be easy to follow how to do this okay. So we know the expression for faradaic current here.

So numerical simulations what we do is the following. We first write the time domain expression for the current and apply a sinusoidal potential so we say generate the sinusoidal potential as a function of time, meaning we have a series of time and correspondingly we have series of potential values. So we have a time going from 0, 1 millisecond, 2 millisecond, 3 millisecond and so on.

Correspondingly, we have potential starting at some value and then changing as given by this sinusoidal equation and then calculate the current as a function of time and then subject this to Fourier transform and get the Fourier series coefficients okay. We can record the values at dc; we can record the values at fundamental, second harmonic and so on. Once you know the response at fundamental, you can calculate the impedance.

Once you know the response at any other harmonic, you can plot that in Bode plot, the current response in Bode plot.

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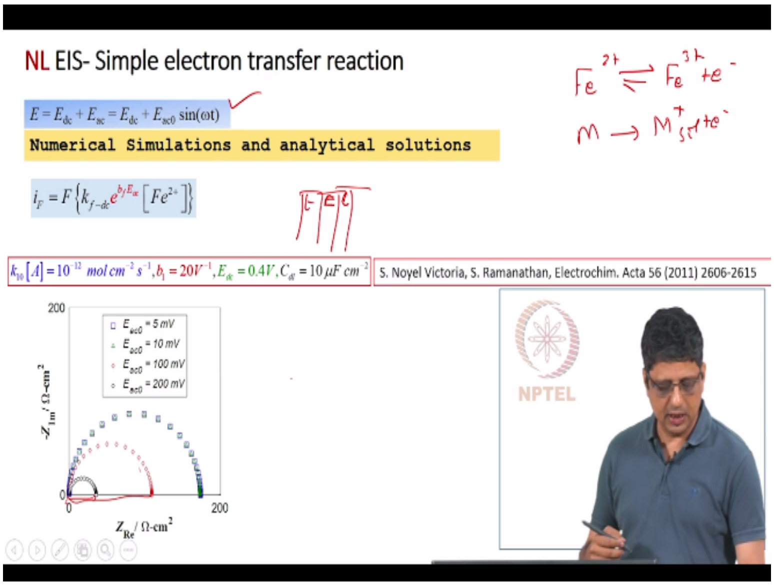

NL EIS- Simple electron transfer reaction

$E = E_{dc} + E_{ac} = E_{dc} + E_{ac0}\sin(\omega t)$

Numerical Simulations and analytical solutions

$i_F = F\left\{k_{f-dc} e^{b_f E_{ac}} \left[Fe^{2+}\right]\right\}$

$k_{10}[A] = 10^{-12}\ mol\,cm^{-2}\,s^{-1}, b_1 = 20V^{-1}, E_{dc} = 0.4V, C_{dl} = 10\,\mu F\,cm^{-2}$

S. Noyel Victoria, S. Ramanathan, Electrochim. Acta 56 (2011) 2606-2615

$Fe^{2+} \rightleftharpoons Fe^{3+} + e^-$

$M \rightarrow M^{+}_{sol} + e^-$

This was published in 2011 by our group. This is an example with a simplified version of the reaction instead of taking Fe 2+ going to Fe 3+ with an electron release. We have taken a simpler equation where metal dissolves into the solution, reverse reaction is neglected. So for certain value of the rate constant and certain value of the exponent, bf are given by b1 here at dc bias of 0.4 voltage with an assumed capacitance double-layer capacitance of 10 microfarad per square centimeter.

For different ac perturbations right, 5 millivolt and 10 millivolt give you more or less the same spectrum. So 5 millivolt results are given as blue squares, 10 millivolt results are given as green triangle and you cannot really distinguish between them because they pretty much overlap. If we increase the amplitude to 100 millivolt, the spectrum will still be a semi-circle but the charge transfer resistance is going to be less.

If we increase this to 200 millivolt, it is given by the black color circles here; charge transfer resistance decreases a lot. So it is still modeled by a double-layer capacitance with the charge transfer resistance but this is a much smaller value compared to what we got in 5 millivolts or 10 millivolt perturbation. So essentially what is done is we got a time, we calculate the potential using the first expression, we calculate the current using the second expression, current and then we subject this to Fourier transform.

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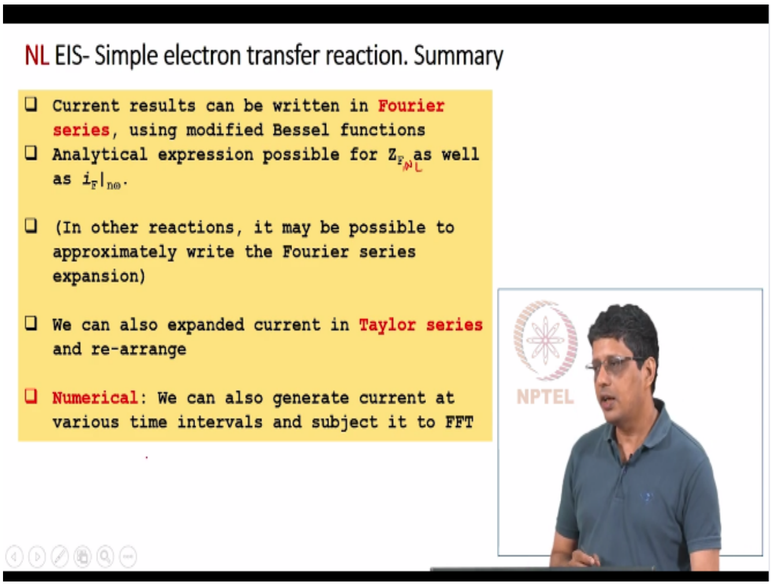

NL EIS- Simple electron transfer reaction. Summary

- ❑ Current results can be written in Fourier series, using modified Bessel functions
- ❑ Analytical expression possible for $Z_{F_{NL}}$ as well as $i_F|_{n\omega}$.
- ❑ (In other reactions, it may be possible to approximately write the Fourier series expansion)
- ❑ We can also expanded current in Taylor series and re-arrange
- ❑ Numerical: We can also generate current at various time intervals and subject it to FFT

So in summary, we can write the current results in Fourier transform because here we know how to get the analytical expression, we can use modified Bessel functions. So it is possible to get an analytical expression for impedance, nonlinear impedance. It is also possible to get analytical expressions for the current response at any frequency, second harmonic, third harmonic and so on.

In other reactions, it may be possible to use approximate Fourier series; you can refer to the publication by Professor David Harrington. In some cases, you can also expand in Taylor series and rearrange but when you do that you have to be very careful because when you expand too many number of terms, the chances of mistake become more okay. You can also use numerical method.

Numerical method has some advantages and disadvantages but after describing it for few examples I will discuss with you on what are the advantages and disadvantages. You can apply it for a variety of reactions. It is possible to analyze variety of reactions using numerical method. It is not that easy to generate Fourier series or Taylor series expansion and get accurate values for all reactions.