Electrochemical Impedance Spectroscopy
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Lecture – 46
Galvanostatic Simulations

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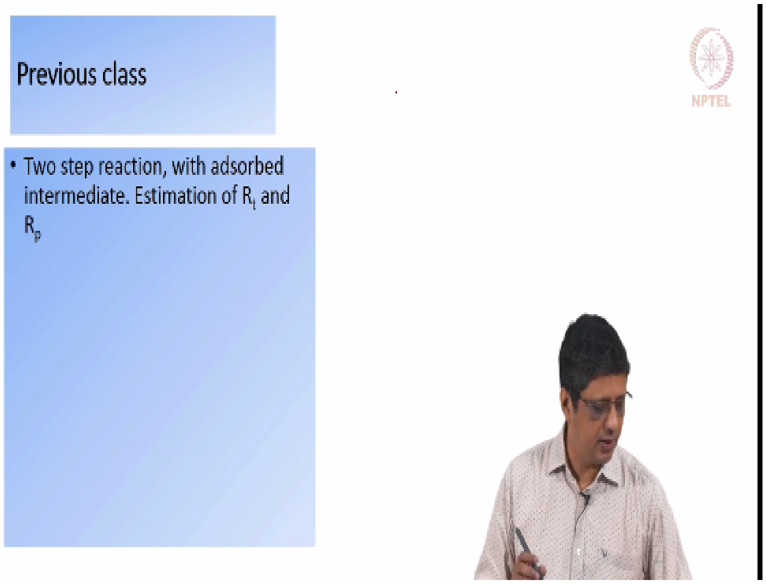

Previous class

- Two step reaction, with adsorbed intermediate. Estimation of R_t and R_p

So, far we have seen that you can write current expression mass balance expression for a given mechanism and then assuming pseudo potential static mode that is we have DC potential and super impose an AC on top of that. We have expanded that in Taylor series and in some cases we have expended in Fourier series and we have obtained expression for current and then we have taken the ratio of current to the potential or potential to the current call it as impedance.

Current to the potential call it as admittance and later we have also seen that when you apply large amplitude perturbations pseudo potential static mode. It is possible for us to use numerical method in some cases Taylor series some cases Fourier series. But in general numerical method to solve these equations unpredicted the current oscillation to the Fourier transform and predict the impedance.

And in corrosion experiments usually people use pseudo potential static mode in batteries and in fuel cells usually as experiments are done in galvanostatic mode. That means we have a constant current and on top of which we asked the instrument to apply a sinusoidal current and then monitor or record that potential. And then it performs the FFT on the potential measured our potential required to maintain that current.

And then we take the ratio of potential to the current and call it as impedance now when you apply a small amplitude perturbation. If it is a constant potential our constant current for the given DC potential that is DC current and if you apply a small amplitude perturbation whether we conduct the experiment potential statically or galvanostatically we will get the same impedance spectrum. When you apply relatively larger amplitude perturbation there is no one to one correspondence between these two spectrum.

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Previous class

- Two step reaction, with adsorbed intermediate. Estimation of R_L and R_p

Today

- Modeling Galvanostatic Measurements
  - Electron transfer reaction
  - Reaction with intermediates

Now using this numerical methods it is possible to simulate and model how a given reaction will respond if we perform the experiments in Galvanostatic. So, I want to show you two examples one is the simple electron transfer reaction next is a reaction with adsorbed intermediate. And as long as you know how to handle these two you should be able to handle any general mechanism.

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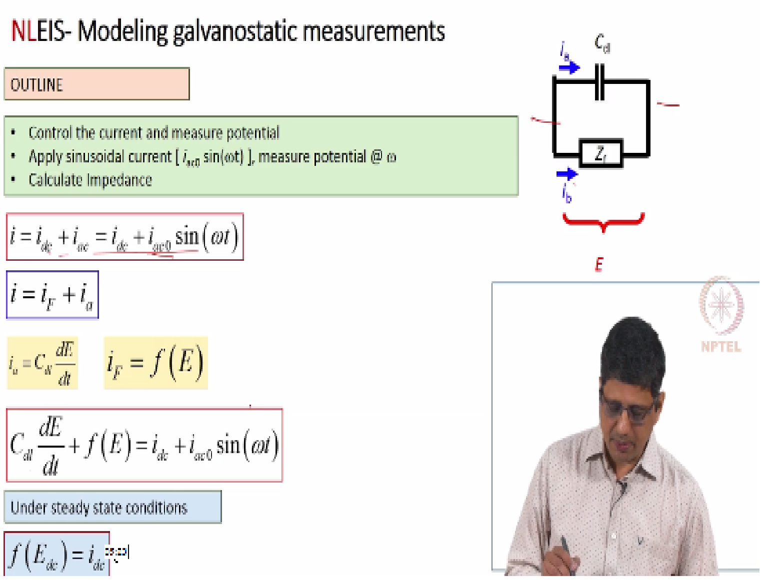

NLEIS- Modeling galvanostatic measurements

OUTLINE

- Control the current and measure potential
- Apply sinusoidal current [i_{ac0} sin(ωt)], measure potential @ ω
- Calculate Impedance

$$i = i_{dc} + i_{ac} = i_{dc} + i_{ac0}\sin(\omega t)$$

$$i = i_F + i_a$$

$$i_a = C_{dl}\frac{dE}{dt} \qquad i_F = f(E)$$

$$C_{dl}\frac{dE}{dt} + f(E) = i_{dc} + i_{ac0}\sin(\omega t)$$

Under steady state conditions

$$f(E_{dc}) = i_{dc}$$

So, the outline we want apply sinusoidal current and measure the potential at omega basically it means we will apply Fourier transform and then look at the magnitude and phase at the fundamental. Okay and then calculate the impedance first I want to look at the case where you have an AA capacitance with the faraday competence with parallel current that goes through the top. AA capacitance is denoted by IA.

Current that goes through the faraday competence we call it as IB. What we measure or what we control is the total current we cannot tell this much current has to go through AA capacitance and this much current has to go through a faraday competence. Because when we measure we do not even know what the AA capacitance is. And we do not know what the faraday competence is at any given frequency.

When we do the simulation we assume we know the CDL value we know that faraday competence or the expression for faraday competence. So, the current that we control is Idc+Iac here is Iac is 0 sin omega t so in the notation now this is something we control this one independent variable. We can also say the total current can be visualised as faraday current plus double layer current Ia here is that current through the double layer.

So, the current through the double layer can write the expression Cdl dE/ dt we can potential across this is the E and faraday current of course is a function of potential. When we add these to we should get the total current that we applied so in general we would write Cdl dE/dt + f of E is idc+iac0 sin omega t. Now potential is something we are going to measure as potential is something we have to calculate here.

Under steady state conditions that mean DC current and DC potential the capacitance will not allow any current passes through that. Okay because dE/ dt is 0 E is a constant dE/dt is 0. Therefore, we can take this expression and simplify it that is going to show f of Edc it is same as idc.

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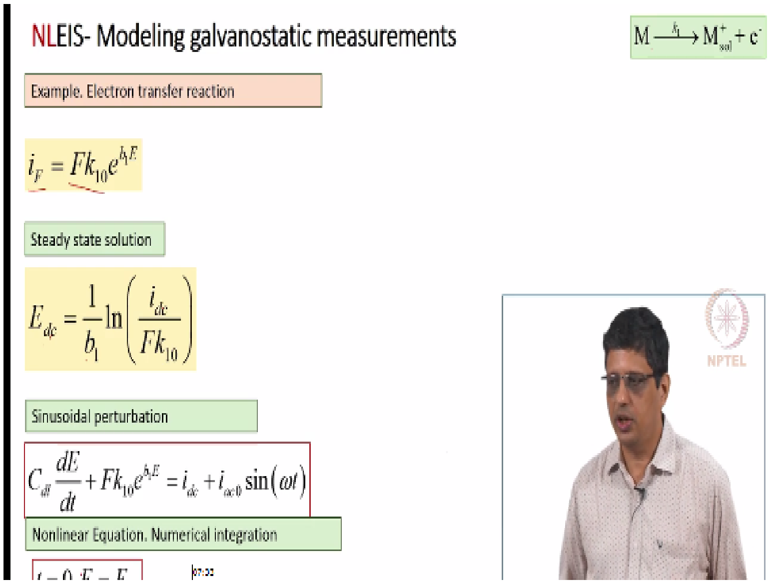

NLEIS- Modeling galvanostatic measurements

$M \xrightarrow{k_1} M^{+}_{sol} + e^{-}$

Example. Electron transfer reaction

$$i_F = Fk_{10}e^{b_1E}$$

Steady state solution

$$E_{dc} = \frac{1}{b_1}\ln\left(\frac{i_{dc}}{Fk_{10}}\right)$$

Sinusoidal perturbation

$$C_{dl}\frac{dE}{dt} + Fk_{10}e^{b_1E} = i_{dc} + i_{ac0}\sin(\omega t)$$

Nonlinear Equation. Numerical integration

Now let say we consider a reaction very simple electron transfer reaction only forward reaction is considered here. For this particular case it is easy to rate the steady state solution I can rearrange it and say if by Faraday constant k 10 that will give me e power b1E if we take natural log on both sides and then rearrange. I can say Edc can be calculated for a given set of parameters and given idc value.

Of course this is valid only when we are in the very much positive direction when potentially is much above the open circuit potential. At open circuit potential current will be 0 and reverse reaction cannot be neglect. This is a dc potential corresponding to the idc if you apply in ac on top of the dc this e potential E will also have a dc component and a variable component. It may be sinusoidal and it may be higher harmonics depending on the value of iac 0.

If it is small, we can say this is also going to be sinusoidal we can neglect the higher harmonics if it is large we will not be able to neglect the harmonics but anything that is changing. We call it as Eac here and average call it as Edc so we need to take the total current and solve this equation. This is a first order nonlinear ordinary differential equation. Dependent variable is E and independent variable is t and starting point is at time t = 0 potentially Edc.

It is a nonlinear equation we will have to use numerical integration to solve this but it is fairly straightforward. You can use MATLAB solver such as Oda45 Oda15S or you can use any of the programming language or you can write your own solver.

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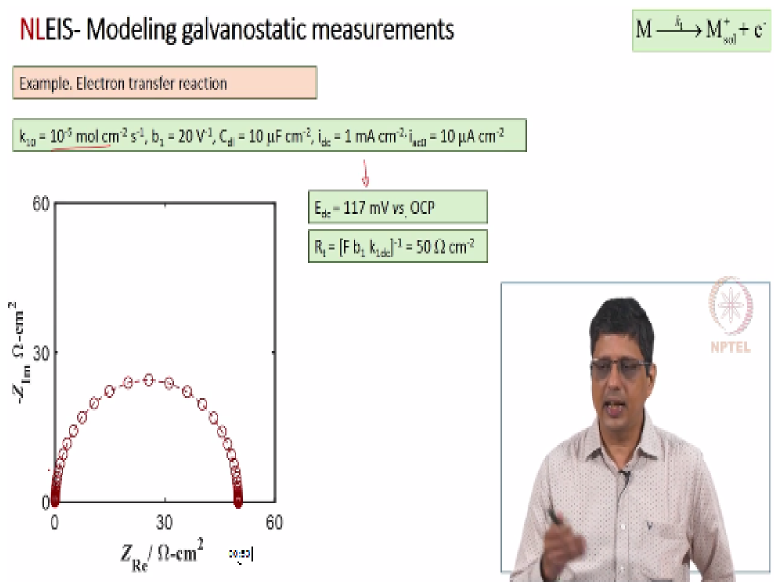

NLEIS- Modeling galvanostatic measurements

$M \xrightarrow{k_1} M^+_{sol} + e^-$

Example. Electron transfer reaction

$k_{10} = 10^{-5}$ mol cm^{-2} s^{-1}, $b_1 = 20$ V^{-1}, $C_{dl} = 10$ µF cm^{-2}, $i_{dc} = 1$ mA cm^{-2}, $i_{acll} = 10$ µA cm^{-2}

$E_{dc} = 117$ mV vs. OCP

$R_t = [F\, b_1\, k_{1dc}]^{-1} = 50\ \Omega$ cm^{-2}

So, just as an example for simple electron transfer reaction for a given set of kinetic parameters here k1 is written as 10 power – 5 moles per square centimetre per second exponent b1 is 20 inverses of volts double layer capacitance is assume to be microfarad per centimetre square. And if we use a DC current of 1 milli amp per centimetre square and apply AC of 10 micron per centimetre square.

First we calculate the dc potential and that is 117 milli volts versus OCP that is nearly a 100 milli volts above OCP. It is not probably not a good idea to neglect the reverse reaction but we will go ahead with the story anyway. Once you know the DC potential one can calculate the charge resistance in this case charge transfer resistance on polarization resistance are the same they happen to have the same value.

Faraday competence is the independent of the frequency therefore charge transfer resistance and polarization resistance are the same and that comes to about 50 ohms centimetre square. We can solve the ordinary differential equation numerically for various frequencies and then calculate the impedance. What we calculate here is the total impedance including the double layer capacitance.

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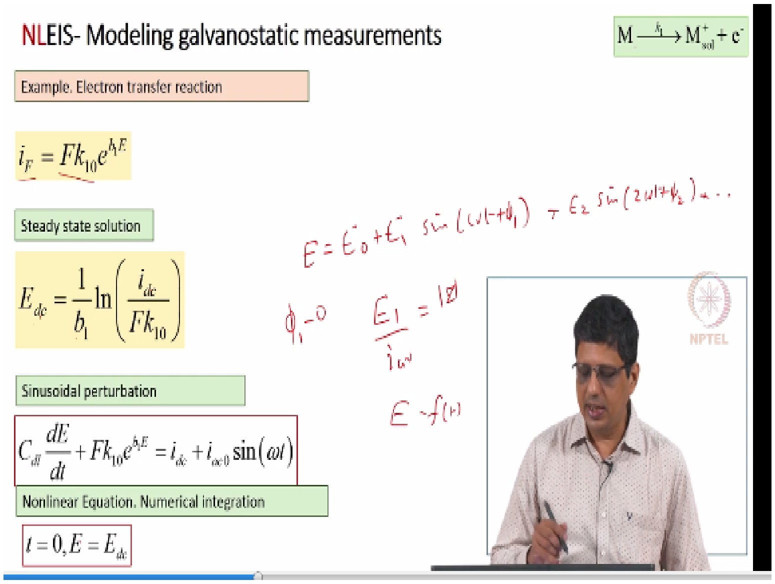

NLEIS- Modeling galvanostatic measurements

$M \xrightarrow{k_1} M^+_{sol} + e^-$

Example. Electron transfer reaction

$i_F = Fk_{10}e^{b_1E}$

Steady state solution

$E_{dc} = \frac{1}{b_1}\ln\left(\frac{i_{dc}}{Fk_{10}}\right)$

Sinusoidal perturbation

$C_{dl}\frac{dE}{dt} + Fk_{10}e^{b_1E} = i_{dc} + i_{ac0}\sin(\omega t)$

Nonlinear Equation. Numerical integration

$t = 0, E = E_{dc}$

$E = E_0 + E_1 \sin(\omega t + \phi_1) + E_2 \sin(2\omega t + \phi_2) + \dots$

$\phi_1 - 0$

$\frac{E_1}{i_{ac}} = |Z|$

$E - f(t)$

So, whatever we calculate out of this equation will give us E as a function of t we subject to Fourier transform and write the E as E =E0+E1 sin omega t + Phi 1+ E2sin 2 omega t +Phi2 and so on. And we take E1/ iac 0 as the magnitude of impermanence. We take Phi 1 - 0 because we give the current the time or t=0 we say Edc and after that this is the expression which describes the current so Phi 1 - 0 gives us the face of this impedance.

So, if you plot the complex plane plot we would get a semi-circle as you would expect 10 micron centimetre square is a very small values so on the small amplitude perturbation you would get a clean semicircle. Even at the larger amplitude perturbation you would not get a semi-circle for this particular mechanism.

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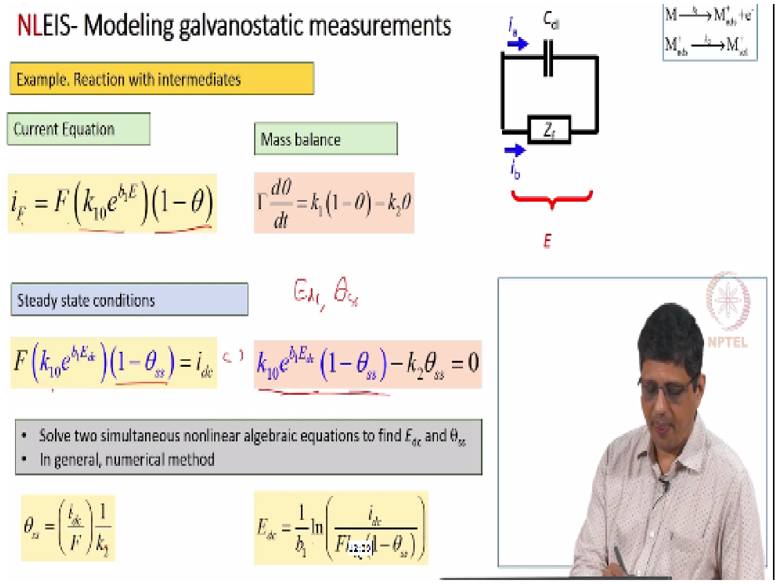

NLEIS- Modeling galvanostatic measurements

Example. Reaction with intermediates

$M \xrightarrow{k_1} M^+_{ads} + e^-$

$M^+_{ads} \xrightarrow{k_2} M^+_{sol}$

Current Equation

$$i_F = F\left(k_{10}e^{b_1 E}\right)(1-\theta)$$

Mass balance

$$\Gamma\frac{d\theta}{dt} = k_1(1-\theta) - k_2\theta$$

Steady state conditions

E_{dc}, θ_{ss}

$$F\left(k_{10}e^{b_1 E_{dc}}\right)(1-\theta_{ss}) = i_{dc}$$

$$k_{10}e^{b_1 E_{dc}}(1-\theta_{ss}) - k_2\theta_{ss} = 0$$

- Solve two simultaneous nonlinear algebraic equations to find E_{dc} and θ_{ss}
- In general, numerical method

$$\theta_{ss} = \left(\frac{i_{dc}}{F}\right)\frac{1}{k_2}$$

$$E_{dc} = \frac{1}{b_1}\ln\left(\frac{i_{dc}}{F k_{10}(1-\theta_{ss})}\right)$$

What happens when you have more complex mechanisms? We will look at the mechanism with intermediate species to step mechanism. We have seen the mass balance equation and we have seen the charge balance equation before so mass balance equation is gamma d theta / dt is k1 1 – theta –k2 theta and the current equation is k1 1- theta only the first equation contributes to the electrons.

Under steady state condition this we replaced E by Edc i/idc this of course are the steady state condition d theta/ dt goes to 0. In this particular example it is possible to rearrange this and write a clear expression for the Edc in general. When you have 2 or more steps it may not be possible to do this and you will have to solve these two equations simultaneously. See we do not know Edc we do not know theta SS.

So, 2 equations 2 unknowns it is possible to solve but they are not linear equations so these are nonlinear algebraic equations which are to solve simultaneously to find Edc and theta SS. You may have mechanisms with two intermediate species you will have an equation for theta SS theta 1 SS and then an equation for Edc. All of them should be solved simultaneously in general you have to use numerical method.

This particular case I can replace k10 e b1 Edc 1 – theta SS which happens to come here also with idc /F. And then I can write theta SS in terms of idc/F 1/k2 so once we know the K2 value once we know the kinetic parameter value and idc of course we know the faraday constant. We can estimate the theta SS and once you know theta SS you can rearrange this equation and write the expression for Edc but in general you might not be able to do this.

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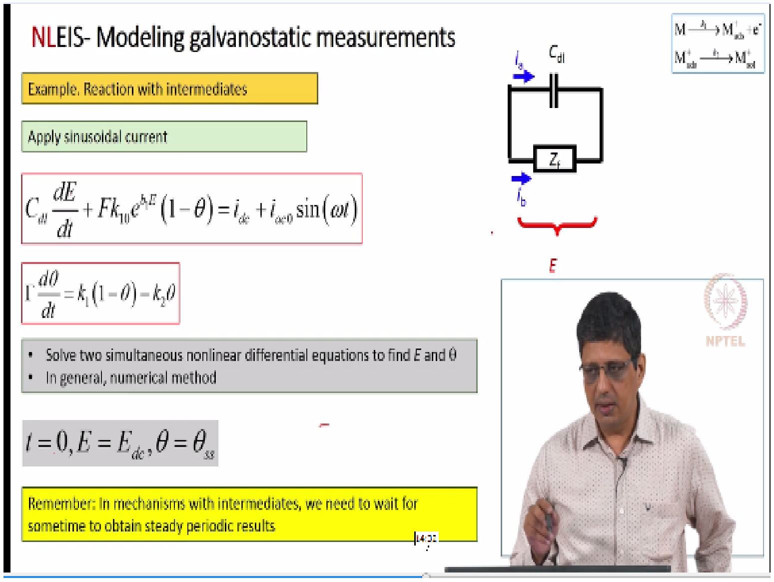

NLEIS- Modeling galvanostatic measurements

Example. Reaction with intermediates

Apply sinusoidal current

$$C_{dl}\frac{dE}{dt}+Fk_{10}e^{b_1E}(1-\theta)=i_{dc}+i_{ac0}\sin(\omega t)$$

$$\Gamma\frac{d\theta}{dt}=k_1(1-\theta)-k_2\theta$$

- Solve two simultaneous nonlinear differential equations to find E and θ
- In general, numerical method

$$t=0, E=E_{dc}, \theta=\theta_{ss}$$

Remember: In mechanisms with intermediates, we need to wait for sometime to obtain steady periodic results

Now if you apply sinusoidal current I take the general equation which is the current to the double layer and current through faraday impedance with the total current. And of course mass balance equation remains the same now these are differential equations nonlinear differential equation independent variable is time dependent variables are e and potential theta. So, we will have to write it as dE/dt = right and side some function of E theta t.

Second equation is d theta/ dt is some function of the E theta and t and then use a programming language or programming environment with the initial condition t = 0 we need to specify what is the value of E. And what is the value of theta and then ask it to integrate whenever we have a mechanism with intermediates or even without intermediates if you have a significant solution resistance or if you have significant mass transfer impedance.

All those cases even for the simple electron transfer reaction in the previous case where we have used pseudo potential static mode we know that we have to apply potential and wait for some time. Let it stabilise and give us steady periodic result and we can take that result if it take data before that it is not going to give me correct value of impedance and it will not take any compare.

Similarly, here we have to wait for some time let the potential be steady periodic and then take data.

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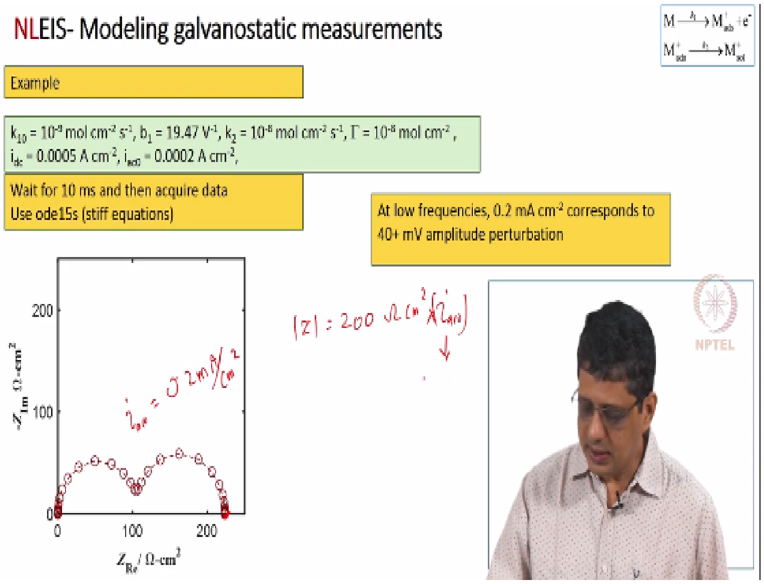

NLEIS- Modeling galvanostatic measurements

$M \xrightarrow{k_1} M^{+}_{ads} + e^{-}$

$M^{+}_{ads} \xrightarrow{k_2} M^{+}_{sol}$

Example

$k_{10} = 10^{-9}$ mol cm^{-2} s^{-1}, $b_1 = 19.47$ V^{-1}, $k_2 = 10^{-8}$ mol cm^{-2} s^{-1}, $\Gamma = 10^{-8}$ mol cm^{-2},
$i_{dc} = 0.0005$ A cm^{-2}, $i_{ac0} = 0.0002$ A cm^{-2},

Wait for 10 ms and then acquire data
Use ode15s (stiff equations)

At low frequencies, 0.2 mA cm^{-2} corresponds to 40+ mV amplitude perturbation

$i_{ac} = 0.2\ mA/cm^2$

$|Z| = 200\ \Omega\ cm^2 \times (i_{ac})$

So, I want to show you an example we will take this two-step reaction with single adsorb intermediate we have the kinetic parameters like this. That is k10 is 10 powers – 9 moles per centimetre square per second. The exponent b1 is 19.47 volt inverse and that is essentially saying alpha =.5 K2 is likewise given here the gamma value is given we take a DC current of half milliamps per centimetre squared.

And AC current with an amplitude off 0.2 milli amp per centimetre square now when we apply this DC current + AC current the potential will oscillate the baseline will change and after some time it will settle. In this case it settles after 10 milliseconds for this set of kinetic parameters and this mechanism and to integrate these equations we need to use Ode15s basically these equations are stiff equations.

And after going through the process of integrating getting the potential performing the Fourier transform and then taking the ratio of E1/iac 0 and calculating the phase – 0 phase for the current. We can calculate the impedance and we can plot this is what we get for an ac amplitude iac 0 = 0.0002 A centimetre square and now same equation we can use it with a larger amplitude.

Your does not have to do anything differently we just have to follow the same procedure. I also want you to note the following look at the impedance values at low frequencies. It is little more than 200 ohms centimetre square. So, if we take the impedance value magnitude as roughly 200 ohms centimetre square and then apply current has amplitude of 0.2 milli amp per centimetre square.

The amplitude of this potential oscillation it is going to be a roughly 40 milli volts. 40 milli volts are usually not considered to be in the linear region. One has to verify by changing this amplitude and seeing whether the impedance at any frequency is independent of this amplitude but in general if you say 10 milli volt people normally believe that it is likely to be in the linear region. If you say 40 millivolts there will be questions.

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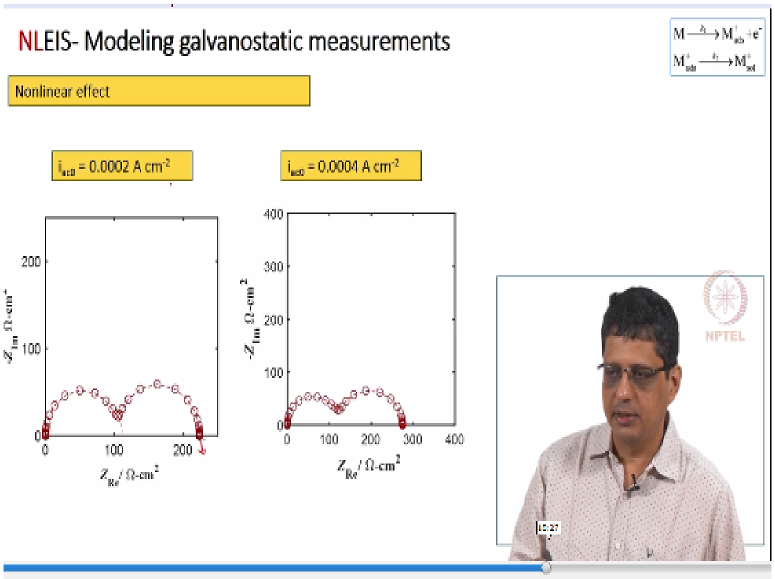

NLEIS- Modeling galvanostatic measurements

$M \xrightarrow{k_1} M^{+}_{ads} + e^{-}$

$M^{+}_{ads} \xrightarrow{k_2} M^{+}_{sol}$

Nonlinear effect

$i_{ac0} = 0.0002\ A\ cm^{-2}$

$i_{ac0} = 0.0004\ A\ cm^{-2}$

Regardless if it change it from 0.2 2 milli amps per centimetre square 2.4 milli amp per centimetre square what happens if you run the same code get the spectrum and you can see this is little more than 200 this is the low frequency value Rp value here is more than what we got in this case. So, this is close to 300 more than 250 this is probably less than 250 and likewise the charge Trans resistance is little more than a 100 ohms centimetre square here.

And this is probably a little higher value here you can see that that is a difference so nonlinear efforts do come in of course it is possible for us to simulate an estimate or calculate what one would get under galvanostatic as measurements for this particular reaction and for set of kinetic parameter values.

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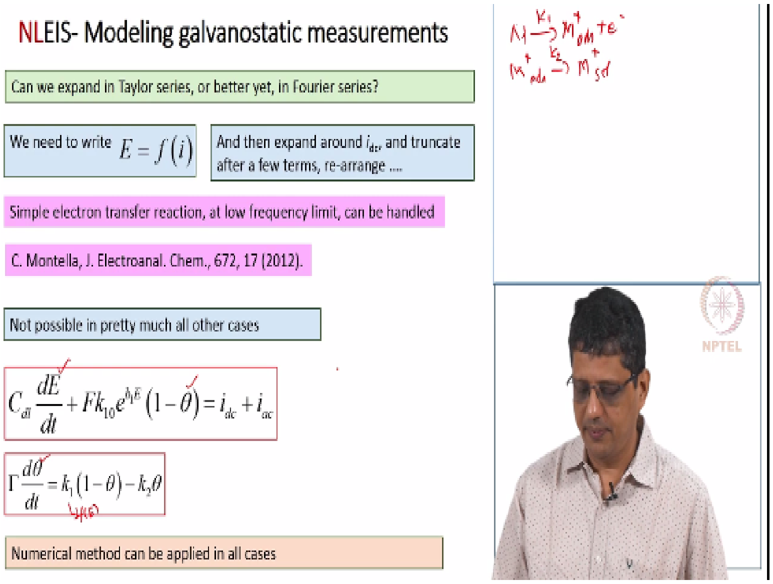

NLEIS- Modeling galvanostatic measurements

Can we expand in Taylor series, or better yet, in Fourier series?

We need to write $E = f(i)$

And then expand around i_{dc}, and truncate after a few terms, re-arrange ....

Simple electron transfer reaction, at low frequency limit, can be handled

C. Montella, J. Electroanal. Chem., 672, 17 (2012).

Not possible in pretty much all other cases

$$C_{dl}\frac{dE}{dt} + Fk_{10}e^{b_1 E}\left(1-\theta\right) = i_{dc} + i_{ac}$$

$$\Gamma\frac{d\theta}{dt} = k_1\left(1-\theta\right) - k_2\theta$$

$f(\theta)$

Numerical method can be applied in all cases

$M \xrightarrow{k_1} M^+_{ads} + e^-$

$M^+_{ads} \xrightarrow{k_2} M^+_{sol}$

Now a question earlier when we analysed it potential static mode or pseudo potential static a measurement. We showed that you can start with Taylor series expand too few terms truncate and then rearrange and write it in Fourier series. Or in some cases you might be able to write directly in Fourier series and get the components fundamental second harmonic third harmonic and so on now we can do that here for galvanostatic measurement.

In order to do that earlier we always wrote current as a function of potential and then we changed the potential we said this E is going to be Edc + Eac and we could write this in Taylor series by expanding around Edc. So, we would rate this as x + h where x is the equivalent of Edc h is the equivalent of Eac and then truncate of the certain number of terms rearranged now in order to do the same thing here and the galvanostatic measurement.

We should be able to write first potential as a function of current in general and then say this can be written as idc +iac for our sinusoidal current variation. And then say I can expand this in

Taylor series and so on. The problem is in most of the cases you will not be able to do this if we have a very simple electron transfer reaction at low frequencies. It is possible to write this in terms of certain functions called Lambert W functions.

And that has been published in 2012 but in general if you take any reaction it is not possible to write like this. It is not possible to write an explicit function E as a function of current so as an example if you consider this reaction of M going to M+ adsorb + electron M+ adsorb going to M+ solution. We will call the first one as K1 and second constant as K2. This we have seen few minutes ago.

The governing equations are given here first is a nonlinear ordinary differential equation. It is written in terms of the dependent variable E and the dependent variable theta. The second equation is also an ordinary differential equation. It is written in terms of theta and of course K1 is a function of potential K2 in this case is independent of potential. So, this is a couple differential equation nonlinear ordinary differential equations.

We do not have an analytical solution for this in most of the cases we will not get it so it will not be possible for us to write E as a function of I which case we would not be able to expand in Taylor series or right in Fourier series and so on. Whereas numerical method can be applied in all cases it is going to be time consuming to write the code. It is going to be time consuming to run the code but you will get a clear answer for the nonlinear galvanostatic measurement.

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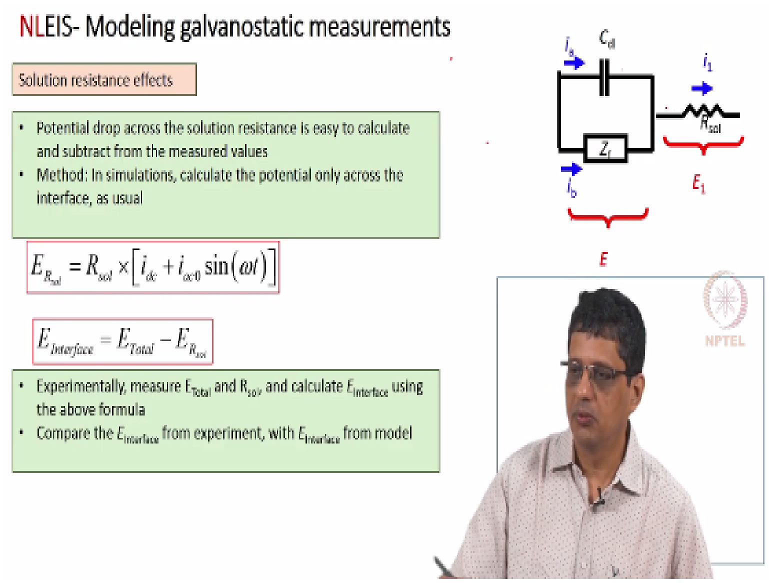

NLEIS- Modeling galvanostatic measurements

Solution resistance effects

- Potential drop across the solution resistance is easy to calculate and subtract from the measured values
- Method: In simulations, calculate the potential only across the interface, as usual

$$E_{R_{sol}} = R_{sol} \times \left[i_{dc} + i_{ac0} \sin(\omega t) \right]$$

$$E_{Interface} = E_{Total} - E_{R_{sol}}$$

- Experimentally, measure E_{Total} and R_{sol}, and calculate $E_{Interface}$ using the above formula
- Compare the $E_{Interface}$ from experiment, with $E_{Interface}$ from model

Next what happens if solution assistance is there it is not negligible now this is easy to handle in case of pseudo galvanostatic measurement one potential drop across the solution resistance is easy to measure you can go to high frequencies measure the impedance. This is in complex plane plot you can fit this part to resistance capacitor are constant phase element and resistor as long as we are in that high and mid frequency region.

Not low enough in frequency region in any case it is easy to measure the solution resistance. In simulations pseudo have to do anything differently we assumed that solution resistance is not playing a role. We do not even worry about them solution the systems and the calculation they can use the same circuit. Calculate the potential across this interface without worrying about the solution resistance.

So, far applied current which is idc+ iac and we can calculate the potential across the interface based on our model. We know this is AA or capacitance we know this is a faraday competence and we have an expression relating the potential to the curtain so we can calculate the potential across the interface. When we do experiments we can measure only the total potential across the system.

So, it includes a solution resistance what the measure is the sum of E + E1 or we can call it test E interface + E solution. Now E solution is easy to estimate. We know the solution resistance the assistance we know the current we are applying therefore is solution can be calculate. Now we know the total measured value and we can calculate the potential drop across the resistance across the solution.

So, we can calculate or estimate what is the experimental value for the potential drop across the interface. All that we need to do is compare the model prediction for the E interface with the experimental value of an interface and if they match or we can say that model is probably a good model to choose. So, in terms of calculation in terms of simulations we do not have to do anything differently in terms of experiment.

We need to measure the solution resistance and we need to measure the total potential drop across this system cell which is what normally we would get from that potential static. So, handling solution resistance is lot easier when we are doing the calculations in the galvanostatic mode.

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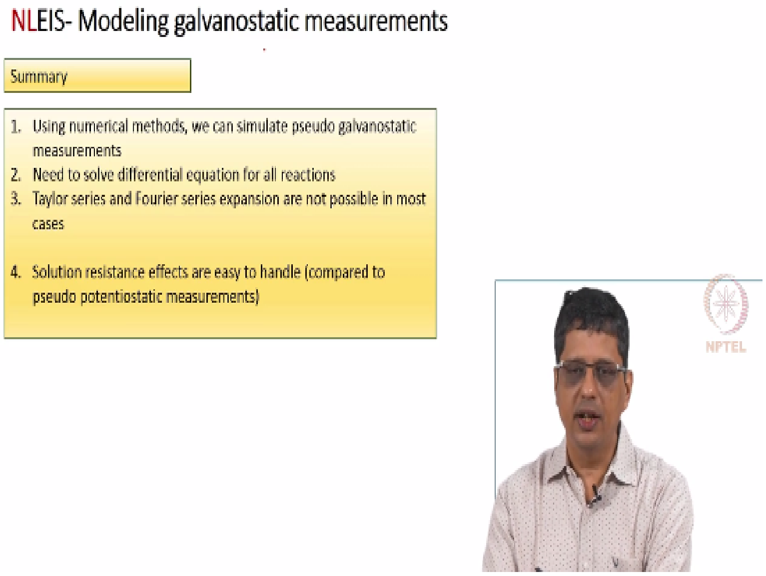

NLEIS- Modeling galvanostatic measurements

Summary

1. Using numerical methods, we can simulate pseudo galvanostatic measurements
2. Need to solve differential equation for all reactions
3. Taylor series and Fourier series expansion are not possible in most cases
4. Solution resistance effects are easy to handle (compared to pseudo potentiostatic measurements)

So, in summary using numerical method we can simulate pseudo potential strategic experiments. We can also simulate pseudo galvanostatic experimental measurements. Okay in case of potential static measurements if we have simple electron transfer reaction we do not have a differential equation. At least for the cases we have seen till now. In case of pseudo galvanostatic measurement.

You will have a differential equation to solve but then as long as you are using numerical method it is quite possible to solve. Taylor series and Fourier series expansions are not that easy or not possible in majority of the cases. So, numerical simulations pretty much the only method as well as I know that you can use to handle or model pseudo galvanostatic measurements and in this case solution resistance effects are easy to handle at least compared to what we had to do in case of potential static measurements. Okay we will stop here today.