Electrochemical Impedance Spectroscopy
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Lecture - 52
Application - Other Techniques HA, EFM

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Previous class

- Experimental aspects of NLEIS

Today

- Understanding other, related, techniques
  - Background – Corrosion parameter estimation.
  - Tafel analysis of potentiodynamic polarization data, LP, EIS
  - Effect of solution resistance - example
  - Use EIS to calculate correct scan rate for LP - example
  - Understanding Harmonic analysis and Electrochemical Frequency Modulation (EFM)

So in the last class, we saw experimental aspects of NLEIS, so today I want to show you how understanding of EIS and NLEIS can be useful. First, I want to give you some background. If we do corrosion experiments to estimate corrosion parameters, certain standard techniques are used. We have seen this in the introduction part where we discussed about other techniques.

There are certain experiments; one is called potentiodynamic polarization, another is called linear polarization and of course EIS. These three are commonly used to characterize corrosion but these make some assumptions and when the assumptions are violated, the results that we get will not be correct.

I want to give you some examples and after that I also want to give you an introduction to another technique called electrochemical frequency modulation, in fact one more technique called harmonic analysis, which are also proposed to monitor corrosion and we can go through them and see how to interpret the data, what are the limitations of those techniques.

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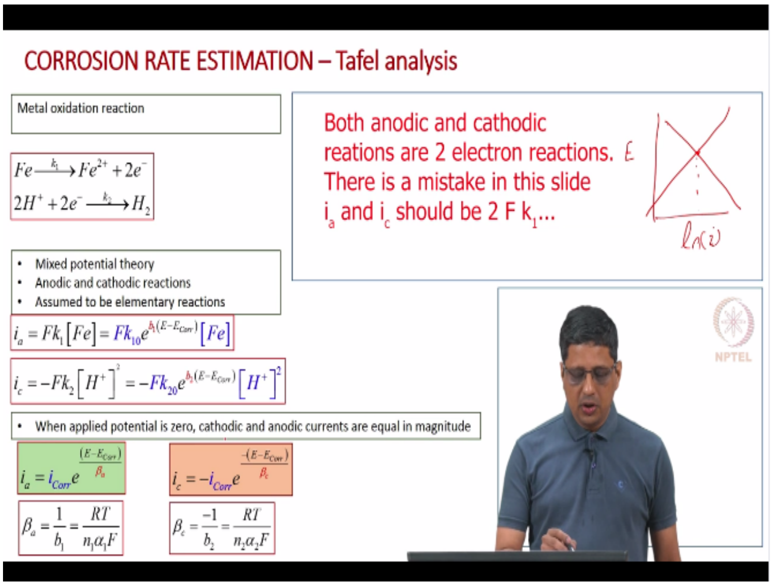

CORROSION RATE ESTIMATION – Tafel analysis

Metal oxidation reaction

$Fe \xrightarrow{k_1} Fe^{2+} + 2e^-$

$2H^+ + 2e^- \xrightarrow{k_2} H_2$

- Mixed potential theory
- Anodic and cathodic reactions
- Assumed to be elementary reactions

$i_a = Fk_1[Fe] = Fk_{10}e^{b_1(E-E_{Corr})}[Fe]$

$i_c = -Fk_2[H^+]^2 = -Fk_{20}e^{b_2(E-E_{Corr})}[H^+]^2$

- When applied potential is zero, cathodic and anodic currents are equal in magnitude

$i_a = i_{Corr}e^{\frac{(E-E_{Corr})}{\beta_a}}$

$i_c = -i_{Corr}e^{\frac{-(E-E_{Corr})}{\beta_c}}$

$\beta_a = \frac{1}{b_1} = \frac{RT}{n_1\alpha_1F}$

$\beta_c = \frac{-1}{b_2} = \frac{RT}{n_2\alpha_2F}$

Both anodic and cathodic reations are 2 electron reactions. There is a mistake in this slide i_a and i_c should be 2 F k_1...

So in corrosion rate estimation, people commonly use what is called Tafel extrapolation, it is called Tafel analysis often. If you imagine that you have metal oxidation, iron oxidizing to iron 2+ and simultaneously H+ reduction to hydrogen, you can imagine that these two reactions are elementary reactions. They may or may not be elementary reactions but let us assume that they are elementary reactions.

First reaction is called anodic, it is oxidation and the second reaction is cathodic. Then, both proceed at the same rate, you will have iron dissolving into the solution and hydrogen ion coming out as hydrogen gas and this is described by what is called mixed potential theory where it is assumed this is potential, this is current in fact log of current and if it is elementary reaction for fixed concentration, we will expect that current is proportional to the exponential of the potential, so log current will be proportional to the potential.

If I take only the anodic reaction, it should be a straight line in this semi-log plot. If I take only cathodic reaction, it will be a straight line but with a negative slope and at this location both of them will have the same rate. So if you put iron in HCl, then I would get corrosion given by this location where cathodic and anodic reactions are equal in magnitude, opposites in sign of course and this is called mixed potential theory.

We assume the cathodic reaction does not influence the anodic reaction and vice versa and these are of course assumed to be elementary reactions. This case, we would normally write anodic reaction as faradaic constant, k1 is the rate constant, Fe here is the concentration or activity of iron because it is solid we can take it as 1 and k1 we would expand it as k1 0 exponential b1 E with reference to corrosion potential.

And the cathodic reaction, we will write it as Fk2 H+ square because it is a second-order reaction with a negative sign of course and again we can expand the k2 and we will keep the concentration. If we assume the concentration of H+ is fixed, it is possible to write this in a simpler form. When we do not apply any potential, the cathodic and anodic reactions are equal in magnitude.

You can rewrite this i corr exponential E-E corr/beta a. Now i corr is going to be Fk1 0 Fe concentration and that is going to be also equal to Fk2 0 concentration of H+ or activity of H+ square okay. This notation which is more common in the corrosion field, beta a is going to be inverse of what we have written as b1 and that is going to be RT/n1 alpha 1 F, n1 here is the number of electrons 2 electrons.

For the cathodic reaction, again it is 2 electron and 2 but it could be a different reaction. Instead of iron going to iron 2+, it could be iron going to iron 3+ in which case n1 will be 3, n2 will still be 2 for this reaction. If you have another cathodic reaction, correspondingly the n number will vary.

So I want you to be familiar with the notation that is used in the corrosion industries. People use beta a and beta c, call it as anodic Tafel slope, cathodic Tafel slope.

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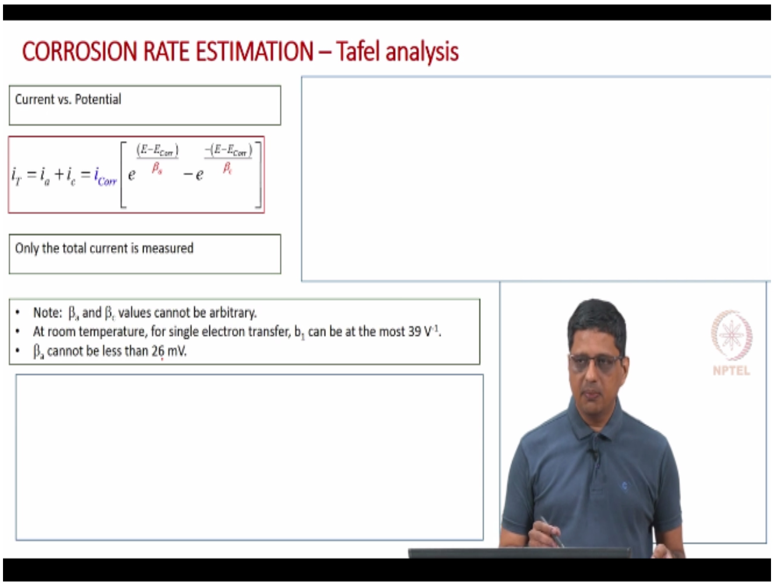

CORROSION RATE ESTIMATION – Tafel analysis

Current vs. Potential

$$i_T = i_a + i_c = i_{Corr}\left[e^{\frac{(E-E_{Corr})}{\beta_a}} - e^{\frac{-(E-E_{Corr})}{\beta_c}}\right]$$

Only the total current is measured

- Note: β_a and β_c values cannot be arbitrary.
- At room temperature, for single electron transfer, b_1 can be at the most 39 V^{-1}.
- β_a cannot be less than 26 mV.

And the total current of course is the sum of this anodic and cathodic currents, it is an algebraic sum. So you get an expression like this and this is what is used for Tafel analysis. What we measure is the total current, when we do the experiments we do not measure the anodic current alone or cathodic current alone, we measure the total current. If we go to very positive potential, we can sometimes say that we can neglect the cathodic current.

It is not likely to be a large number. If you go to very negative potential, we can say the anodic current is negligible, cathodic current is probably equal to the total current or more or less equal to the total current. Now beta a and beta c values cannot be arbitrary because earlier we have seen this right. It is given by RT/n alpha F, R of course is universal gas constant, T is the temperature, F is the Faraday constant, n1 is the number of electrons, alpha is the charge transfer coefficient and that can vary between 0 to 1 okay.

So that means beta a cannot be arbitrary in number. At room temperature, if n1 or n2 that is 1 then b1 can vary between 0 to 39 that means beta a has to vary between 26 millivolt to infinite if alpha is 0 but very large number, so it cannot be less than 26 millivolt. When you fit this data, you should be careful, you cannot get an arbitrarily small number for beta a or beta c.

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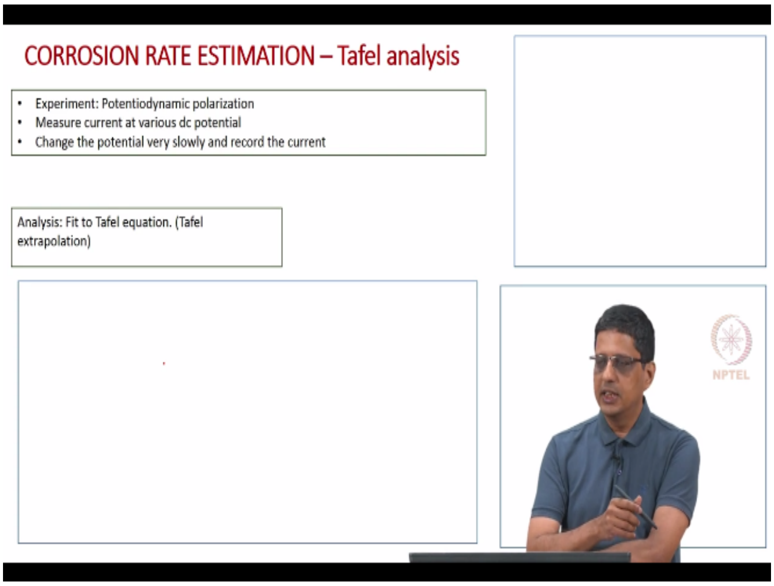

CORROSION RATE ESTIMATION – Tafel analysis

- Experiment: Potentiodynamic polarization
- Measure current at various dc potential
- Change the potential very slowly and record the current

Analysis: Fit to Tafel equation. (Tafel extrapolation)

Now when you do experiments, you will typically go to a dc potential, measure the current and normally you will scan it at a very slow rate and you will analyze the data assuming that it is more or less under steady state condition. You change the potential very slowly and record the current. Ideally, you should go to galvanostatic mode, supply a current, wait for the potential to stabilize and note that or record that.

And then go to next value of the current and proceed but most of the time researchers end up scanning the potential at a slow rate and measuring the current and assuming that the double-layer capacitor does not contribute that much to the total current and then fit it to the Tafel equation, it is often called Tafel extrapolation.

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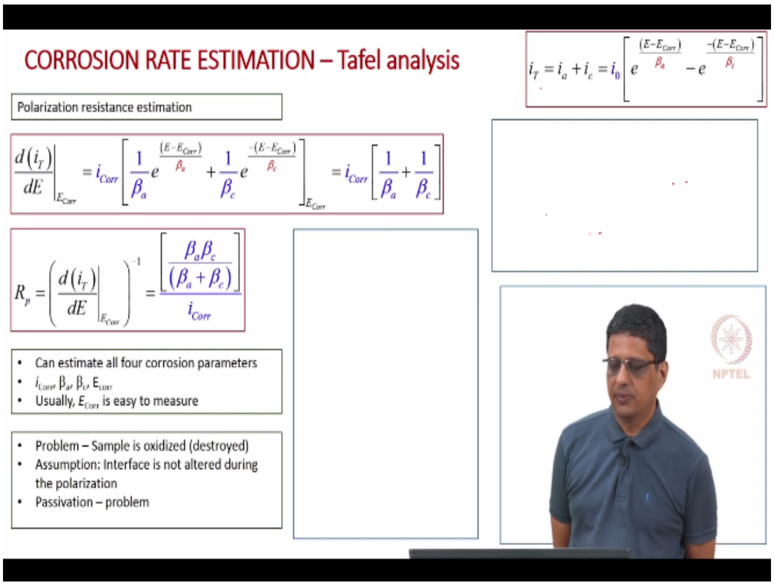

CORROSION RATE ESTIMATION – Tafel analysis

$$i_T = i_a + i_c = i_0\left[e^{\frac{(E-E_{Corr})}{\beta_a}} - e^{\frac{-(E-E_{Corr})}{\beta_c}}\right]$$

Polarization resistance estimation

$$\left.\frac{d(i_T)}{dE}\right|_{E_{Corr}} = i_{Corr}\left[\frac{1}{\beta_a}e^{\frac{(E-E_{Corr})}{\beta_a}} + \frac{1}{\beta_c}e^{\frac{-(E-E_{Corr})}{\beta_c}}\right]_{E_{Corr}} = i_{Corr}\left[\frac{1}{\beta_a} + \frac{1}{\beta_c}\right]$$

$$R_p = \left(\left.\frac{d(i_T)}{dE}\right|_{E_{Corr}}\right)^{-1} = \frac{\left[\frac{\beta_a\beta_c}{(\beta_a+\beta_c)}\right]}{i_{Corr}}$$

- Can estimate all four corrosion parameters
- i_{Corr}, β_a, β_c, E_{corr}
- Usually, E_{Corr} is easy to measure

- Problem – Sample is oxidized (destroyed)
- Assumption: Interface is not altered during the polarization
- Passivation – problem

Essentially, take this data and this is the expression i total is this, you can use commercial software or you can write your own code and get this parameters beta a, beta c, i0 or i corr and E corr. E corr is very easy to get, the other parameters you can model this and get. Now you can also calculate one more term called polarization resistance okay. That is basically di total/dE assuming that you have not scanned it at a fast rate.

Ideally, you have just gone to a dc potential, measure the current, gone to another dc potential, measure the current, measure the steady state current and then if you plot it, if you plot idc versus Edc and this going to be 0 at some potential and that is corrosion potential. The slope at this location should give you di/dE and the inverse of the slope should be the polarization resistance.

So in this case, if you take this expression, if this expression is valid, you can take the derivative and then rearrange it and then show that this di/dE is given by i corr*inverse of beta a and inverse of beta c. So that is essentially you can rearrange it and then write an expression for polarization resistance. Now if I get idc versus Edc, potentiodynamic polarization curve and fit it to this model if it fits well.

Then, I can extract the values of i0, beta a, beta c and E corr and I can estimate the value of polarization resistance. So using this technique, E corr is easy to measure but other 3 parameters can be measured using Tafel extrapolation, potentiodynamic polarization and Tafel extrapolation analysis. Now it takes some time to do these experiments. If you go to large anodic potential, sample will get oxidized or it may corrode very fast and will get destroyed.

We assume that the interface, electrode-electrolyte interface is not altered during the experiment and usually in the cathodic regime, it is not altered but in the anodic regime there is a high likelihood of the surface getting altered. Anyway, if you go to high potential, there good chance it will get destroyed and in some cases it can also passivate, the surface can get passivated at anodic potential.

This Tafel model assumes that reaction proceeds without passivation, so if there is passivation then you cannot use the data acquired in the passive regime and use this model and hope to get corrosion current estimates.

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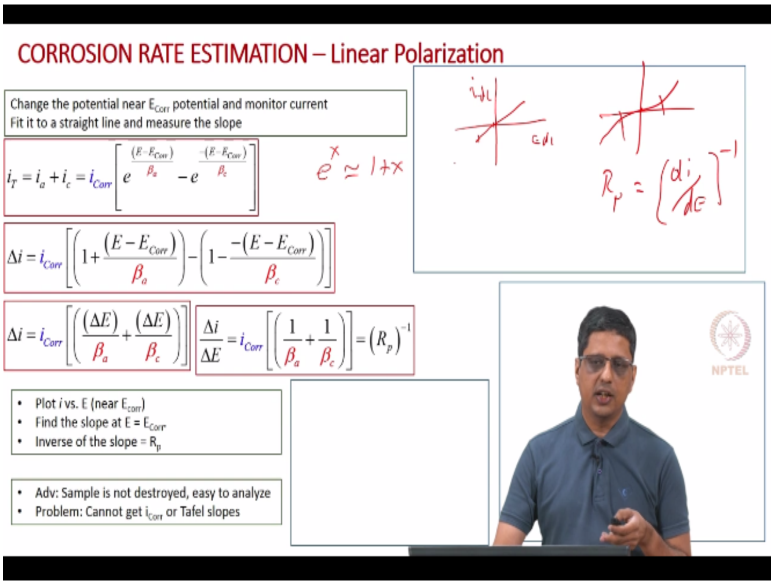

CORROSION RATE ESTIMATION – Linear Polarization

Change the potential near E_{Corr} potential and monitor current
Fit it to a straight line and measure the slope

$$i_T = i_a + i_c = i_{Corr}\left[e^{\frac{(E-E_{Corr})}{\beta_a}} - e^{\frac{-(E-E_{Corr})}{\beta_c}}\right]$$

$$e^x \simeq 1+x$$

$$\Delta i = i_{Corr}\left[\left(1+\frac{(E-E_{Corr})}{\beta_a}\right)-\left(1-\frac{-(E-E_{Corr})}{\beta_c}\right)\right]$$

$$\Delta i = i_{Corr}\left[\left(\frac{(\Delta E)}{\beta_a}+\frac{(\Delta E)}{\beta_c}\right)\right]$$

$$\frac{\Delta i}{\Delta E} = i_{Corr}\left[\left(\frac{1}{\beta_a}+\frac{1}{\beta_c}\right)\right] = (R_p)^{-1}$$

$$R_p = \left(\frac{di}{dE}\right)^{-1}$$

- Plot i vs. E (near E_{corr})
- Find the slope at E = E_{Corr}
- Inverse of the slope = R_p

- Adv: Sample is not destroyed, easy to analyze
- Problem: Cannot get i_{Corr} or Tafel slopes

So another technique that is used in corrosion industry is called linear polarization. In this, we keep the electrode very close to the open circuit potential, corrosion potential. It is slightly disturbed from this, so we hope that the electrode is not altered too much and it will not get destroyed and it is considered as a non-destructive technique. When the electrode is very close to the open circuit potential, the current versus potential, idc versus Edc can be assumed to be a straight line.

Sometimes, it may not be a straight line even near this OCP open circuit potential, it can be a curved line, it is alright you can fit it to a curve, maybe a quadratic equation, maybe a cubic equation but then take the derivative and find the value of the derivative at this location where current is zero and the inverse of this derivative can still be related to the polarization resistance.

So this Tafel equation or this expression if we expand it Taylor series and then linearize, we can write it as e power x as approximately 1+x and therefore we will get an expression like this you, can rearrange it and then divide by del e, a small change in potential and you can get the expression for polarization resistance. Now what you can measure using this technique is basically del E/del i.

You will not be able to get i corr, beta a and beta c from this experiment and analysis. Essentially, plot i versus E taken near E corr, find the slope, inverse of the slope is polarization resistance but in this technique the sample is likely to be preserved, it is not likely to be destroyed and if it passivates at large anodic potential, we do not have to worry because we do not go to large anodic potential in this technique.

So the problem in this is that you cannot get i corr, you cannot get beta a and beta c, you can get polarization resistance value and if you want to look at the effect of certain chemical for example you have a solution, you have a metal, it corrodes at certain rate, you add a chemical and hope that the chemical acts as an inhibitor, you can find the polarization resistance without the chemical, you can find the polarization resistance with the chemical.

And that will give you an idea of the effectiveness of this chemical okay. So in that sense, it is useful but if you really want to know the corrosion current then you cannot get the corrosion current from this technique.

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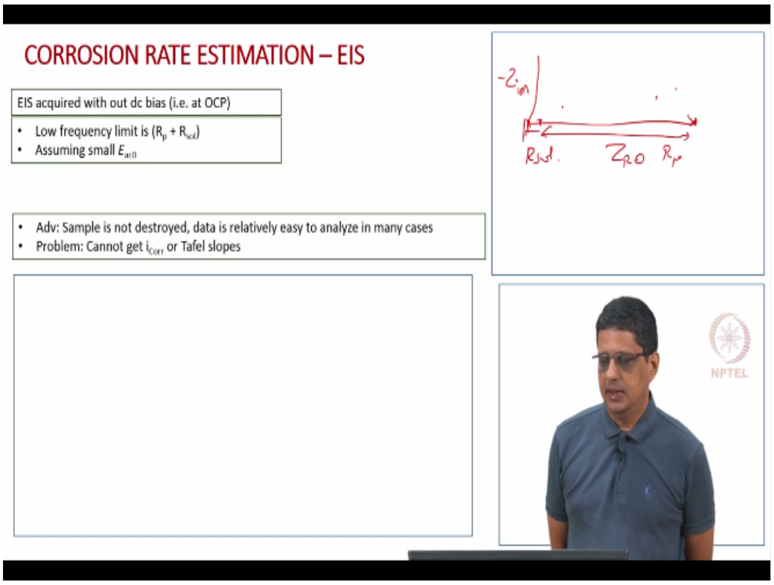

CORROSION RATE ESTIMATION – EIS

EIS acquired with out dc bias (i.e. at OCP)

- Low frequency limit is ($R_p + R_{sol}$)
- Assuming small E_{ac0}

- Adv: Sample is not destroyed, data is relatively easy to analyze in many cases
- Problem: Cannot get i_{Corr} or Tafel slopes

If you use EIS, you can acquire EIS without any dc bias and the low frequency limit will give you the polarization resistance if the solution resistance is negligible. In case, solution resistance is significant, low frequency limit is given by Rp+R solution, so it is an example. In complex plane plot, data may come like this. This is R solution; this is Rp and this point starting from origin that is Rp+R solution.

And you can get the value of Rp without any ambiguity here, so for example you are able to take data only up to this, you can fit it to a circuit and extrapolate and see where it will fit. Of course, if you take data only up to this limit, your confidence will not be that high but you will at least be aware that your confidence is not that high. Here also the sample is not destroyed, it is similar to LP, it is similar to linear polarization but then you cannot get the i corr value from this.

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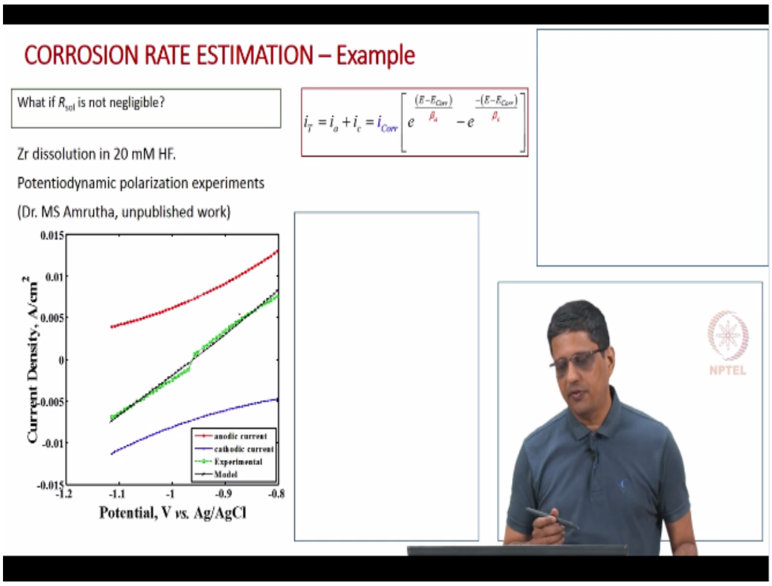

CORROSION RATE ESTIMATION – Example

What if R_{sol} is not negligible?

$$i_T = i_a + i_c = i_{Corr}\left[e^{\frac{(E-E_{Corr})}{\beta_a}} - e^{\frac{-(E-E_{Corr})}{\beta_c}}\right]$$

Zr dissolution in 20 mM HF.

Potentiodynamic polarization experiments

(Dr. MS Amrutha, unpublished work)

So if the solution resistance is not negligible what happens is this okay. This is an example; these experiments were done by one of our research scholars. Zirconium dissolving in solutions containing small concentration of hydrofluoric acid. The green colored dots here show you the experimental data and she has written her one code to model this.

The anodic current is given by the red color line and the cathodic current is given by the blue color line and the total current of course is given by the black color line, does not fit very well, this is current versus potential, this can also be shown as potential versus log of current.

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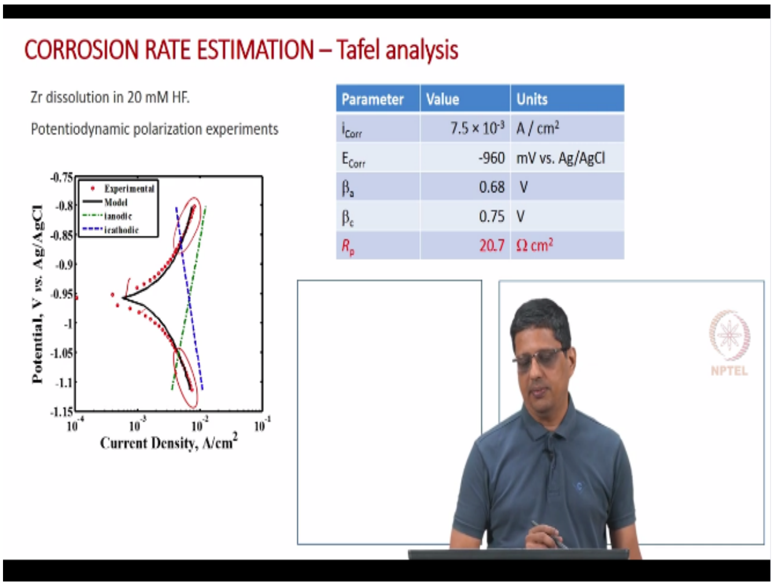

CORROSION RATE ESTIMATION – Tafel analysis

Zr dissolution in 20 mM HF.

Potentiodynamic polarization experiments

Parameter	Value	Units
i_{Corr}	7.5×10^{-3}	A / cm^2
E_{Corr}	-960	mV vs. Ag/AgCl
β_a	0.68	V
β_c	0.75	V
R_p	20.7	Ω cm^2

And this is just the same data and the model data with potential versus model current, potential versus current density and you can see that the fit is not that good. Black color line is the model, near this region it is deviating, that is not too bad but even when the current is large it shows some difference and if you estimate the parameters, i corr is 7.5 milliamps per centimeter square.

You get certain value for E corr, beta a, beta c and the polarization resistance coming from this is nearly 21 ohm centimeter square.

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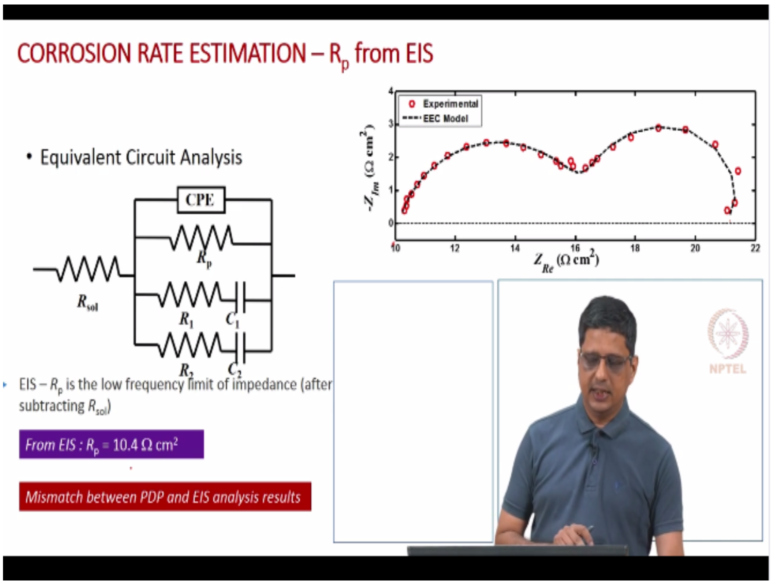

CORRORSION RATE ESTIMATION – R_p from EIS

- Equivalent Circuit Analysis

- EIS – R_p is the low frequency limit of impedance (after subtracting R_{sol})

From EIS : R_p = 10.4 Ω cm^2

Mismatch between PDP and EIS analysis results

Now if you do impedance analysis, if you take EIS data, this is what we get. Just note that the x axis or the Z real goes from 10 to 22 ohms and the imaginary –Z imaginary goes from nearly 0 to 4 ohms. You can fit it to an equivalent circuit and get the polarization resistance. Right now, I would not worry about the details of what circuit is meaningful for this, we will just say that this circuit fits this data well and the polarization resistance can be estimated.

And you can see the solution resistance plus polarization resistance is about 21 ohms. The polarization resistance alone is about 11 ohms; it is 10.4 ohm centimeter square. So obviously this is quite different from what we got from Tafel analysis. So there is a mismatch between potentiodynamic polarization data and analysis versus impedance data.

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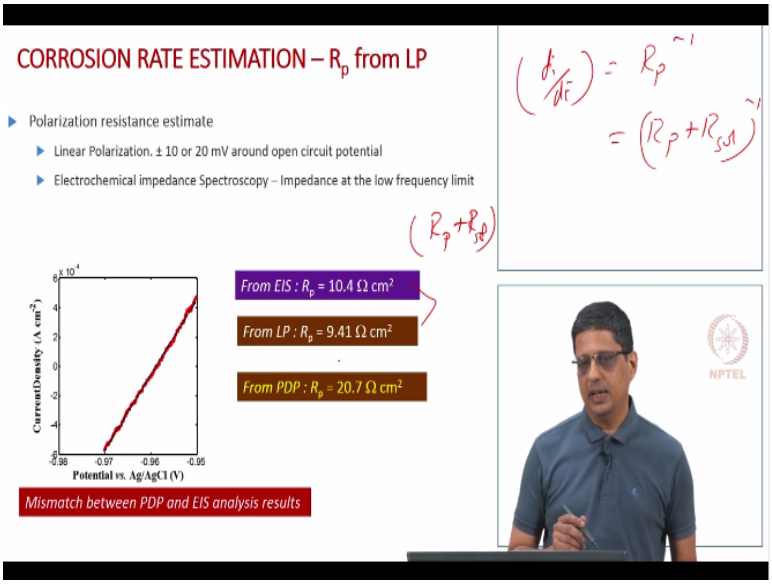

CORROSION RATE ESTIMATION – R_p from LP

- Polarization resistance estimate
  - Linear Polarization. ± 10 or 20 mV around open circuit potential
  - Electrochemical impedance Spectroscopy – Impedance at the low frequency limit

$$\left(\frac{di}{dE}\right) = R_p^{-1} = (R_p + R_{sol})^{-1}$$

$(R_p + R_{sol})$

From EIS : R_p = 10.4 Ω cm²

From LP : R_p = 9.41 Ω cm²

From PDP : R_p = 20.7 Ω cm²

Mismatch between PDP and EIS analysis results

Now we can do polarization experiments, linear polarization experiment typically +or-10 millivolt around the open circuit potential and that sort of equivalent to impedance at low frequency limit. If you do polarization experiment, we get 21 ohm again. First thing to note is polarization experiment analysis and the Tafel extrapolation; they all assume solution resistance is 0.

But what you get out of those, what you get out of this is Rp+R solution, so the polarization resistance in linear polarization comes out to be close to 9.5 ohms, which is sort of close to 10.4 ohms. So between the EIS and linear polarization, one can say that the data is similar. Potentiodynamic polarization gives you 21 ohms, so linear polarization gives you di/dE and we would normally write it as Rp inverse.

But in reality it should be written as Rp+R solution inverse. Since solution resistance is close to 10 ohms, linear polarization data will give you the polarization resistance as close to 9.5 ohms. The actual slope, if you take the inverse of the actual slope that is going to be close to 20 ohms. Now potentiodynamic polarization data, the first simplest step is to take the estimate of Rp and say that is actually equal to Rp+R solution.

Then, get the R solution value from impedance spectra, subtract it, then the value of Rp that you get is going to be close to the correct value.

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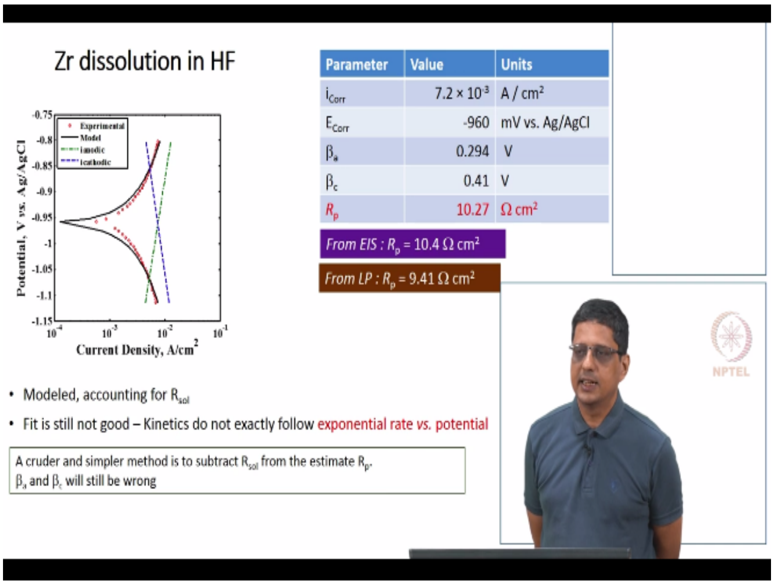

Zr dissolution in HF

Parameter	Value	Units
i_{Corr}	7.2×10^{-3}	A / cm^2
E_{Corr}	-960	mV vs. Ag/AgCl
β_a	0.294	V
β_c	0.41	V
R_p	10.27	Ω cm^2

From EIS : R_p = 10.4 Ω cm^2

From LP : R_p = 9.41 Ω cm^2

- Modeled, accounting for R_{sol}
- Fit is still not good – Kinetics do not exactly follow exponential rate *vs.* potential

A cruder and simpler method is to subtract R_{sol} from the estimate R_p.
β_a and β_c will still be wrong

There is a more appropriate way of handling this. When we apply a potential, some part of the potential is dropped across the solution and some part of that is dropped across the interface. The analysis normally assumes that all the potential drop occurs at the interface but you can incorporate the solution resistance effect by saying the actual potential across the interface is little less than the potential that we apply and put it in the solution.

So i total which is on the left side also comes on the right side, it is an implicit equation but it is possible to handle this. You can then use an optimization program and get these values. So we have used an optimization program, which accounts for solution resistance and then if you calculate the value that comes to be 10.3 ohm centimeter square which is comparable to what you get from impedance spectra or from the linear polarization.

I want you to note that the fit is still not good even after accounting for solution resistance and that is likely because the hydrogen evolution reaction or the zirconium dissolution, neither of them are elementary reactions. So we do not expect the kinetics to follow exponential rate versus potential all the time. This will give you an idea of what the corrosion rate is going to be.

For comparison with other situation, this is probably useful to get the absolute value of corrosion current and estimate the weight loss or corrosion loss, this is probably not going to be the best choice but then if you have to make an estimate in a short time, this is probably a good choice. So this is a more appropriate method, you can always take the polarization resistant estimate and subtract the solution resistance; you will get a better estimate for Rp.

But the values of beta a and beta c that you get from the previous case will not be correct okay. So it is better to use the proper equation which accounts for solution resistance or potential drop across the solution and calculate the value of beta a and beta c and i corr and then calculate the value of polarization resistance.

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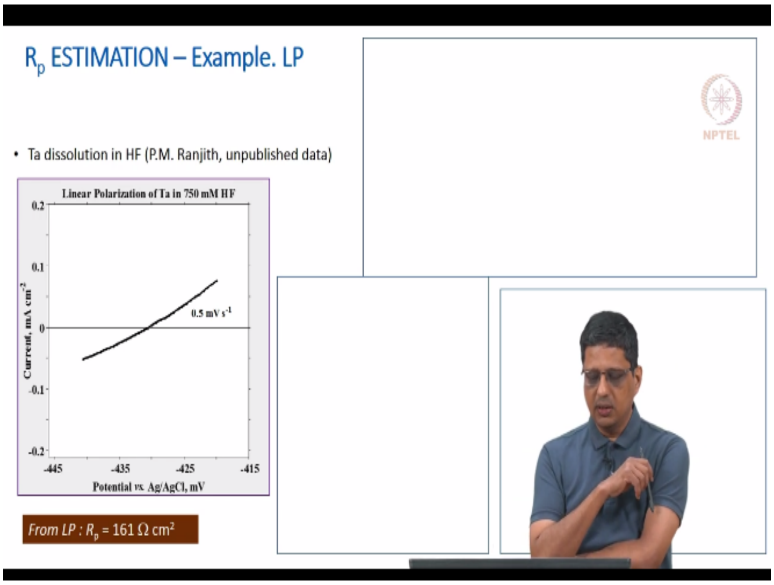

R_p ESTIMATION – Example. LP

- Ta dissolution in HF (P.M. Ranjith, unpublished data)

From LP : $R_p = 161\ \Omega\ cm^2$

Next, I want to show you another example okay. This is done by another of our research scholar Ranjith. This is for tantalum dissolving in hydrofluoric acid in 750 millimolar of hydrofluoric acid if you take tantalum and monitor the current as a function of potential with the scan rate of 0.05 millivolts per second, you can get this data and from this data you can get a polarization resistance of 161 ohm centimeter square.

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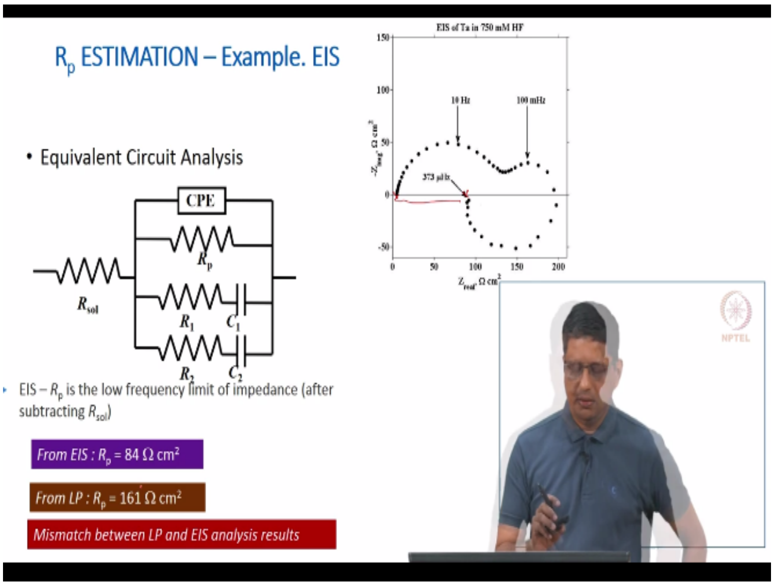

R_p ESTIMATION – Example. EIS

- Equivalent Circuit Analysis

- EIS – R_p is the low frequency limit of impedance (after subtracting R_{sol})

From EIS : $R_p = 84\ \Omega\ cm^2$

From LP : $R_p = 161\ \Omega\ cm^2$

Mismatch between LP and EIS analysis results

Now if we take impedance data, what we get is shown here. Solution resistance is not that large, maybe 10 ohms. The polarization resistance is going to be <100 ohms, so we see a much lower polarization resistance in this case from impedance data compared to the polarization resistance from the linear polarization experiment and that cannot be explained using the solution resistance.

So what do we do? This equivalent circuit we have used, from this you can visually see that it is going to be <100 ohm centimeter square. You can actually calculate it and show that it is 84 ohm centimeter square. It is nearly half of what you get from linear polarization data and that makes you think why is it different. The mismatch between LP and EIS is quite large.

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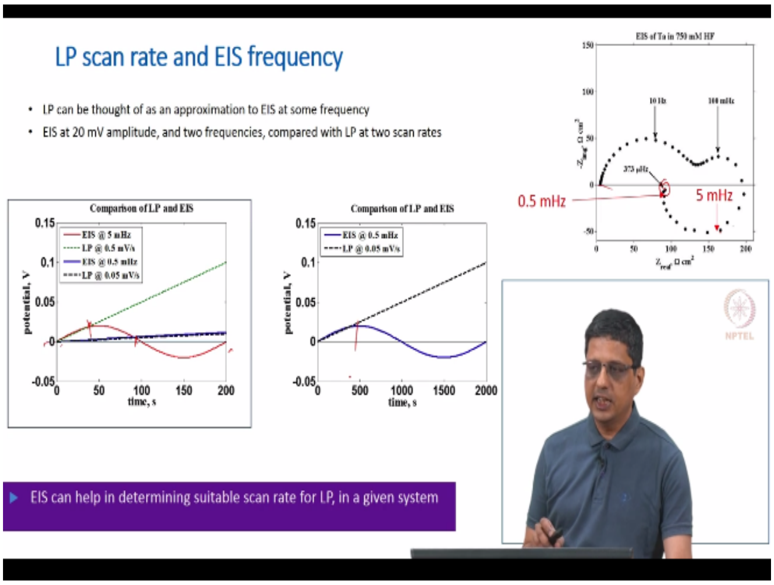

LP scan rate and EIS frequency

- LP can be thought of as an approximation to EIS at some frequency
- EIS at 20 mV amplitude, and two frequencies, compared with LP at two scan rates

▶ EIS can help in determining suitable scan rate for LP, in a given system

Now you can visualize linear polarization as EIS experiment at some frequency. Now if we do EIS with 20 millivolt amplitude and compare two frequencies and two scan rates in linear polarization. Now if you are going to do linear polarization, potential will change at 0.5 millivolts per second. If you go for 0 to 200 second, this is how the potential would change. That is given by the green color line, dash line.

If you are doing EIS experiments at 5 millihertz and 20 millivolts amplitude, the amplitude and frequency both are important okay. Then, if you look the red color line which shows the sinusoidal potential is more or less overlapping with the green color line, not exactly but it is somewhat similar up to nearly one-quarter of this cycle. This is one full cycle, half cycle and this is one-fourth of a cycle.

EIS at 5 millihertz, this is 0.3 millihertz, 5 millihertz come somewhere here. So if I do linear polarization experiment at 0.5 millivolts per second, that is similar to doing EIS at 5 millihertz and at 5 millihertz this data has not settled, it has not come to the real axis. So I cannot take this data and tell that that is going to be low frequency limit and that is going to be polarization resistance.

So looking at this EIS data, anybody can tell somewhere here the impedance has settled, somewhere here the value is probably 180 ohms, you know you can actually calculate the number, maybe 200 ohms but you can definitely say it has not settled there. At close to 0.5 millihertz, I can claim that this data is settled and this is probably the polarization resistor or polarization resistance and solution resistance put together.

Now if I draw a sinusoidal wave of 0.5 millihertz goes from 0 to 2000 seconds and draw a linear polarization at the rate of 0.05 millivolts per second, this is how it will appear. That means one-fourth of a cycle will roughly match with the linear polarization. So if I do 0.05 millivolts per second, linear polarization at point 0.05 millivolts per second, then I should expect to see a polarization resistance close to 84.

So normally one would think 0.5 millivolts per second is low enough for linear polarization experiments but looking at the EIS data helps you understand what scan rate is suitable or sufficiently low to perform LP experiments for a given system okay. So EIS helps us identify or choose a scan rate for linear polarization experiment.

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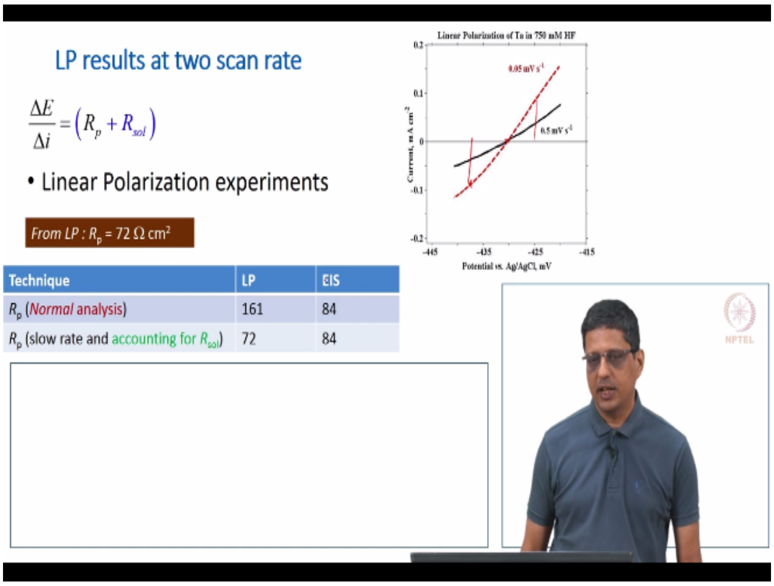

LP results at two scan rate

$$\frac{\Delta E}{\Delta i} = \left(R_p + R_{sol}\right)$$

- Linear Polarization experiments

From LP : $R_p = 72\ \Omega\ cm^2$

Technique	LP	EIS
R_p (*Normal* analysis)	161	84
R_p (slow rate and accounting for R_{sol})	72	84

So out here if you see current versus potential, 0.5 millivolts per second is the black color line. If I go to a slower scan rate, I actually see the current is more; more meaning either magnitude is more. That means the slope is more, inverse of the slope is less and the estimate from this says 72 ohm centimeter square, which is lot better compared to 161 ohm centimeter square. So slow rate and accounting for R solution, we get 72 ohm versus 84.

It is still not exact match but it is close enough. Without looking at the correct scan rate, if you just do it at 0.5 volts, 0.5 millivolts per second saying in literature lot of people use this therefore I use this then you will not be able to explain the difference between the polarization resistance obtained using EIS and obtained using linear polarization.

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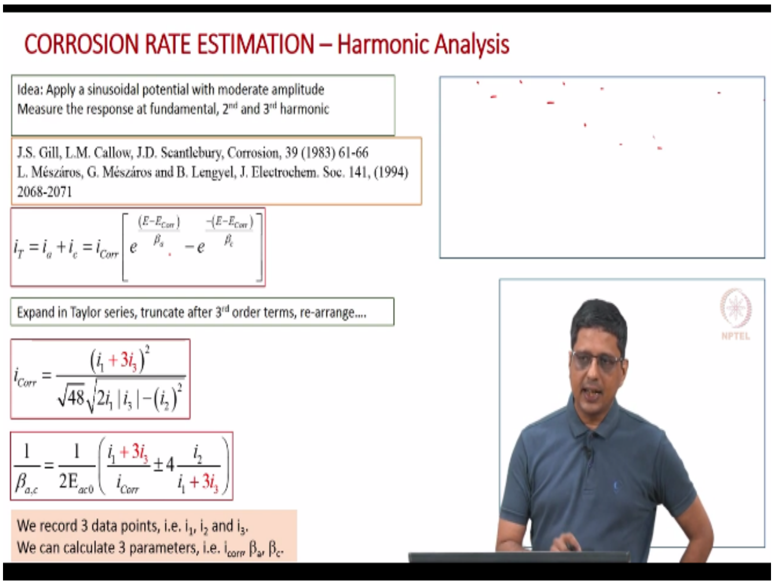

CORRosion RATE ESTIMATION – Harmonic Analysis

Idea: Apply a sinusoidal potential with moderate amplitude
Measure the response at fundamental, 2nd and 3rd harmonic

J.S. Gill, L.M. Callow, J.D. Scantlebury, Corrosion, 39 (1983) 61-66
L. Mészáros, G. Mészáros and B. Lengyel, J. Electrochem. Soc. 141, (1994) 2068-2071

$$i_T = i_a + i_c = i_{Corr}\left[e^{\frac{(E-E_{Corr})}{\beta_a}} - e^{\frac{-(E-E_{Corr})}{\beta_c}}\right]$$

Expand in Taylor series, truncate after 3rd order terms, re-arrange....

$$i_{Corr} = \frac{(i_1+3i_3)^2}{\sqrt{48}\sqrt{2i_1|i_3|-(i_2)^2}}$$

$$\frac{1}{\beta_{a,c}} = \frac{1}{2E_{ac0}}\left(\frac{i_1+3i_3}{i_{Corr}} \pm 4\frac{i_2}{i_1+3i_3}\right)$$

We record 3 data points, i.e. i_1, i_2 and i_3.
We can calculate 3 parameters, i.e. i_{corr}, β_a, β_c.

Next, I want to describe a technical harmonic analysis okay. The idea is this, we normally apply a sinusoidal potential, monitor the current and we know the frequency at which you apply the potential, we do Fourier transform, we do phase sensitive detection any case you want to find the component of the current at that frequency okay. What if we apply little larger sinusoidal potential okay moderate amplitude?

Measure the response at second and third harmonic. If you apply a large amplitude perturbation, you will definitely get a good signal at second and third harmonic, you might get some signal at even higher harmonic but if you apply at moderate amplitude, if you assume that this equation is valid okay, you can do the following okay. This was proposed in 83 and also extended in 94.

If we take this, expand this in Taylor series and then write the current as i0 corresponding to dc i1 sin omega t+i2 sin 2 omega t+phi. Of course, it may become cosine okay+i3 etc. Then, after expanding this and doing some algebraic rearrangement, one can show that the i corr is going to be related to i1, i2 and i3. Beta a and beta c can also be obtained from this. Originally, it was given as i1 square but then later I think (()) (29:49) et al showed that it has to be corrected.

And there is a term 3 i3 which has to be added to this to get the correct expression for corrosion parameter, corrosion parameters i corr, beta a and beta c. Now since we measure i1, i2 and i3, it is possible to estimate three parameters, i corr, beta a and beta c. This is obtained by taking this expression, expand in Taylor series, truncate after three terms and then rearrange. Since we record three points, three data points we can calculate three parameters.

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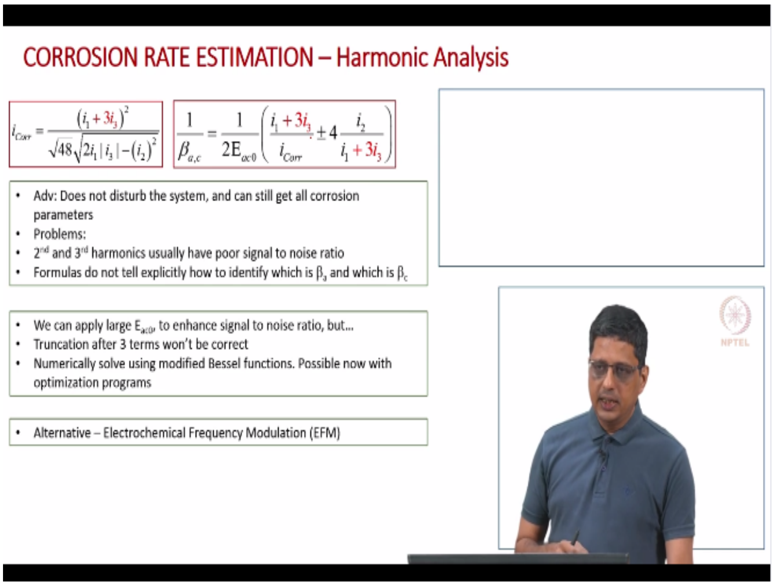

CORROSION RATE ESTIMATION – Harmonic Analysis

$$i_{Corr} = \frac{(i_1 + 3i_3)^2}{\sqrt{48}\sqrt{2i_1|i_3| - (i_2)^2}}$$

$$\frac{1}{\beta_{a,c}} = \frac{1}{2E_{ac0}}\left(\frac{i_1 + 3i_3}{i_{Corr}} \pm 4\frac{i_2}{i_1 + 3i_3}\right)$$

- Adv: Does not disturb the system, and can still get all corrosion parameters
- Problems:
- 2nd and 3rd harmonics usually have poor signal to noise ratio
- Formulas do not tell explicitly how to identify which is β_a and which is β_c

- We can apply large E_{ac0}, to enhance signal to noise ratio, but...
- Truncation after 3 terms won't be correct
- Numerically solve using modified Bessel functions. Possible now with optimization programs

- Alternative – Electrochemical Frequency Modulation (EFM)

Now the advantage is it is still not very large amplitude, it is not like potential in polarization. You can stay within 20, 30 millivolts so you do not disturb the system that much and you can still get all the corrosion parameters that is i corr, beta a, beta c whereas with linear polarization and impedance spectroscopy, you can get only RP. Now there is a problem, the second and third harmonics are usually small.

So in presence of noise, getting good quality, reliable data from this is not that easy. So we have poor signal-to-noise ratio and if I say I will crank up the voltage, I will get better signal-to-noise ratio, then we cannot truncate the Taylor series after three terms, it is still possible to analyze assuming that the basic equation is valid but you will have to get expression in terms of modified Bessel functions and use some numerical method or optimization program to extract the parameters okay.

There is no expression which will give you i corr, beta a, beta c in a fashion similar to this. You will have to use an optimization program and get this. Another thing is this particular analysis does not tell you which is beta a which is beta c okay. It just tells you plus or minus and you will have to have some idea about the system but actually if you measure the phase, it should be possible to tell which is beta a and which is beta c.

If you do not measure the phase, you will have to have some idea of whether cathodic reaction is fast or slow or anodic reaction is fast or slow compared to the cathodic reaction. So we can apply large amplitude perturbation but truncation is not going to be correct and it is possible to do numerical program and optimization and get these parameters but it is not very straightforward. So another technique that suggested is called electrochemical frequency modulation okay.

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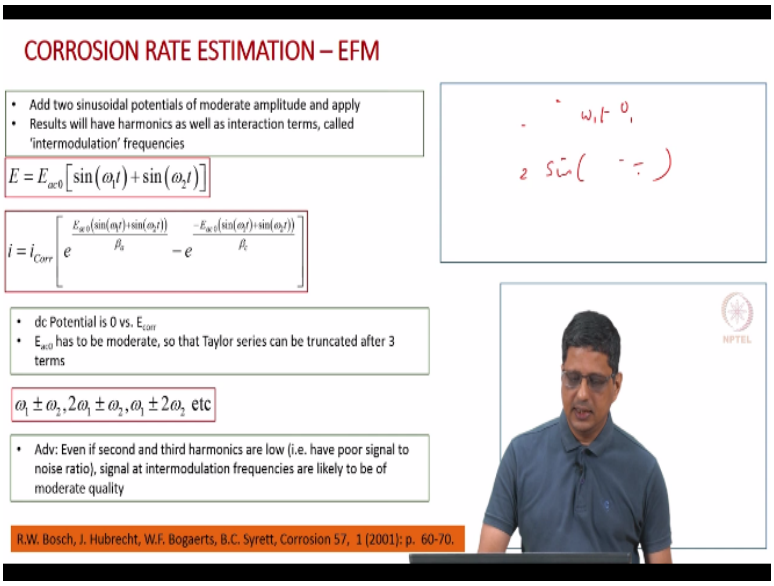

CORROSION RATE ESTIMATION – EFM

- Add two sinusoidal potentials of moderate amplitude and apply
- Results will have harmonics as well as interaction terms, called 'intermodulation' frequencies

$$E = E_{ac0}\left[\sin\left(\omega_1 t\right) + \sin\left(\omega_2 t\right)\right]$$

$$i = i_{Corr}\left[e^{\frac{E_{ac0}\left(\sin(\omega_1 t)+\sin(\omega_2 t)\right)}{\beta_a}} - e^{\frac{-E_{ac0}\left(\sin(\omega_1 t)+\sin(\omega_2 t)\right)}{\beta_c}}\right]$$

- dc Potential is 0 vs. E_{corr}
- E_{ac0} has to be moderate, so that Taylor series can be truncated after 3 terms

$$\omega_1 \pm \omega_2, 2\omega_1 \pm \omega_2, \omega_1 \pm 2\omega_2 \text{ etc}$$

- Adv: Even if second and third harmonics are low (i.e. have poor signal to noise ratio), signal at intermodulation frequencies are likely to be of moderate quality

R.W. Bosch, J. Hubrecht, W.F. Bogaerts, B.C. Syrett, Corrosion 57, 1 (2001): p. 60-70.

This was suggested in 2001 by Bosch et al. The idea is this, instead of giving one sinusoidal potential, you can give two sinusoidal potential simultaneously, add them up and apply, again use moderate amplitude okay. Now what will happen is you will get the results, you will get second harmonic, you will get third harmonic for each of these frequencies. In addition, you will also get something called intermodulated frequency or interaction effects.

So the potential is not just sinusoidal, it is Eac0 sin omega 1t+sin omega 2t and you can again expand this. We do not apply any dc bias, so it is going to be at open circuit potential. This has to be moderate so that Taylor series can be truncated after three terms. Now the results you get will contain omega 1, 2 omega 1, 3 omega 1, omega 2, 2 omega 2, 3 omega 2. In addition, omega 1 +or-omega 2, 2 omega 1 +or-omega 2, omega 1 +or-2 omega 2.

And of course even higher ones but will say that they are negligible. As long as the amplitude is moderate, it should work okay. In general, one should be able to use this technique with even different amplitudes for these different sinusoidal waves, different frequencies. That is instead of saying it is Eac0 I can write Eac0 1 sin omega 1t possibly even +phi 1+Eac0 2 sin omega 2t+phi 2.

But then it becomes very complex and it is not necessary but it is just possible you should be aware of that. Now the advantage over the harmonic analysis is this. Even if higher harmonics are small, at least it is possible to get reasonable magnitude for the intermodulation frequencies okay. They are likely to be of moderate quality, moderate signal-to-noise ratio. So hopefully we will get accurate estimates of i corr, beta a and beta c.

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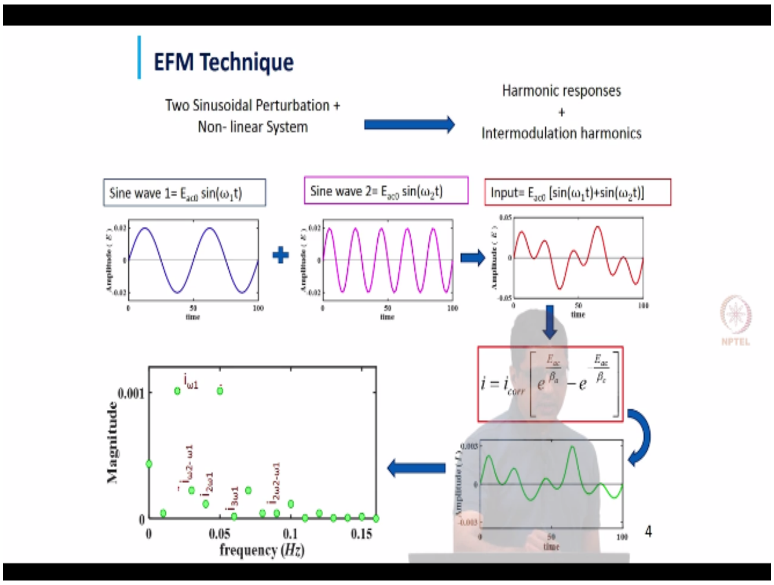

EFM Technique

Two Sinusoidal Perturbation + Non- linear System → Harmonic responses + Intermodulation harmonics

Sine wave 1= $E_{ac0}\sin(\omega_1 t)$

Sine wave 2= $E_{ac0}\sin(\omega_2 t)$

Input= $E_{ac0}[\sin(\omega_1 t)+\sin(\omega_2 t)]$

$$i = i_{corr}\left[e^{\frac{E_{ac}}{\beta_a}} - e^{-\frac{E_{ac}}{\beta_c}}\right]$$

So just a quick representation of how it is done. We have two sinusoidal perturbation, we take a nonlinear system, we take two sinusoidal perturbations, add them together. This is how an example wave would appear and if you apply to a system which follows this expression, then the current would appear like what is shown in the green color line here and then subject it to FFT, you will get magnitude versus frequency a dc i omega 1 i omega 2.

These are intermodulation frequency results, this is second harmonic, this is third harmonic, so you can see that this is of course a noise free system, ideal system but results at intermodulation frequency will have little better signal-to-noise ratio.

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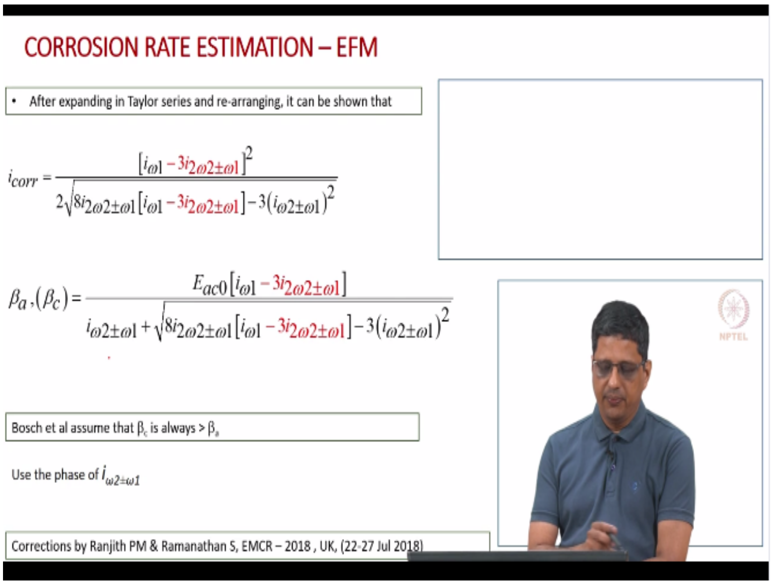

CORROSION RATE ESTIMATION – EFM

- After expanding in Taylor series and re-arranging, it can be shown that

$$i_{corr} = \frac{[i_{\omega 1} - 3i_{2\omega 2\pm\omega 1}]^2}{2\sqrt{8i_{2\omega 2\pm\omega 1}[i_{\omega 1} - 3i_{2\omega 2\pm\omega 1}] - 3(i_{\omega 2\pm\omega 1})^2}}$$

$$\beta_a,(\beta_c) = \frac{E_{ac0}[i_{\omega 1} - 3i_{2\omega 2\pm\omega 1}]}{i_{\omega 2\pm\omega 1} + \sqrt{8i_{2\omega 2\pm\omega 1}[i_{\omega 1} - 3i_{2\omega 2\pm\omega 1}] - 3(i_{\omega 2\pm\omega 1})^2}}$$

Bosch et al assume that β_c is always > β_a

Use the phase of $i_{\omega 2\pm\omega 1}$

Corrections by Ranjith PM & Ramanathan S, EMCR – 2018 , UK, (22-27 Jul 2018)

And after expanding what Bosch et al have proposed is given in the black color font here but our group has identified some small mistake there and that correction is given in the red color font here. So i corr has to be corrected, beta a and beta c has to be corrected. Bosch et al have assumed that beta c is always >beta a but if you monitor the phase it should be possible to identify which is beta a and which is beta c.

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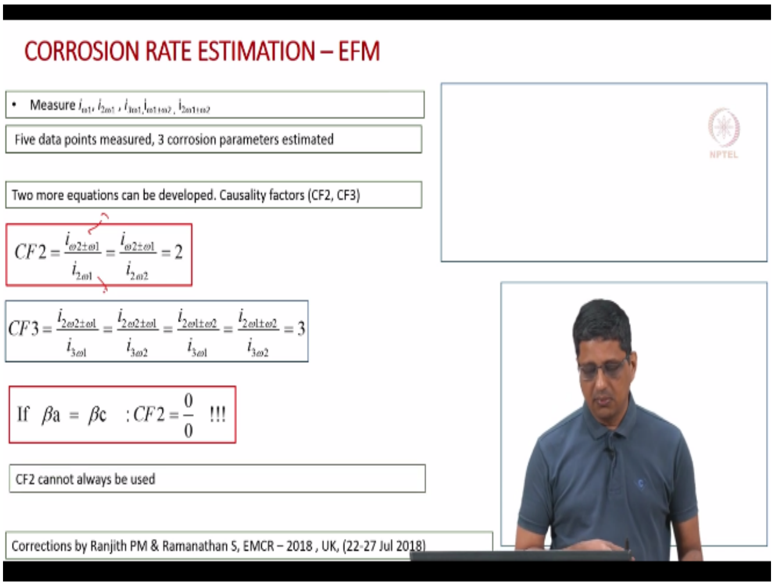

CORROSION RATE ESTIMATION – EFM

- Measure $i_{\omega 1}$, $i_{2\omega 1}$, $i_{3\omega 1}$, $i_{\omega 1\pm\omega 2}$, $i_{2\omega 1\pm\omega 2}$

Five data points measured, 3 corrosion parameters estimated

Two more equations can be developed. Causality factors (CF2, CF3)

$$CF2 = \frac{i_{\omega 2\pm\omega 1}}{i_{2\omega 1}} = \frac{i_{\omega 2\pm\omega 1}}{i_{2\omega 2}} = 2$$

$$CF3 = \frac{i_{2\omega 2\pm\omega 1}}{i_{3\omega 1}} = \frac{i_{2\omega 2\pm\omega 1}}{i_{3\omega 2}} = \frac{i_{2\omega 1\pm\omega 2}}{i_{3\omega 1}} = \frac{i_{2\omega 1\pm\omega 2}}{i_{3\omega 2}} = 3$$

$$\text{If } \beta a = \beta c \quad : CF2 = \frac{0}{0} \quad !!!$$

CF2 cannot always be used

Corrections by Ranjith PM & Ramanathan S, EMCR – 2018 , UK, (22-27 Jul 2018)

Now we measure minimum 5 data points, we measure i omega 1, second harmonic, third harmonic and omega 1 +or-omega 2, 2 omega 1 +or-omega 2. Go back to the previous expression, out here if you look at i corr, if you look at beta a, beta c, you have a i omega 1 and that is supposed to be equal to, actually i omega 1 is supposed to be equal to i omega 2 in terms of the magnitude okay.

We do not use i of 2 omega 1 or i of 3 omega 1 or 3 omega 2 or 2 omega 2. We do not use the higher harmonics to estimate this. That means if the higher harmonics have little poor signal-to-noise ratio, you should still be able to get a decent estimate for the i corr, beta a and beta c. Since we measure at least 5 data points, omega 1, second harmonic and third harmonic, we should be able to get few more expressions.

We have got 3 corrosion parameters, i corr, beta a, beta c. We can develop two more relationship and these are called as Causality factor by the authors. So one relationship uses second harmonic, another uses third harmonic, so if we take the ratio of i omega 2 +or-omega 1 to second harmonic, it should come as 2 and if we take the third harmonic, it should come as 3 and they call the Causality factor 2 and 3.

However, if beta a is equal to beta c, then you would get an expression saying 0/0, obviously you will have some noise in the system, so unless the instrument is very precise you are likely to get some small value here and some small value here which means the ratio would not be 2, it will be some number, random number or arbitrary number okay but causality factor 3 is probably reliable.

If CF 2 comes as different from 2, you may or may not have to throw away the information. If CF 3 comes to be significantly different from 3, then maybe that analysis is not reliable.

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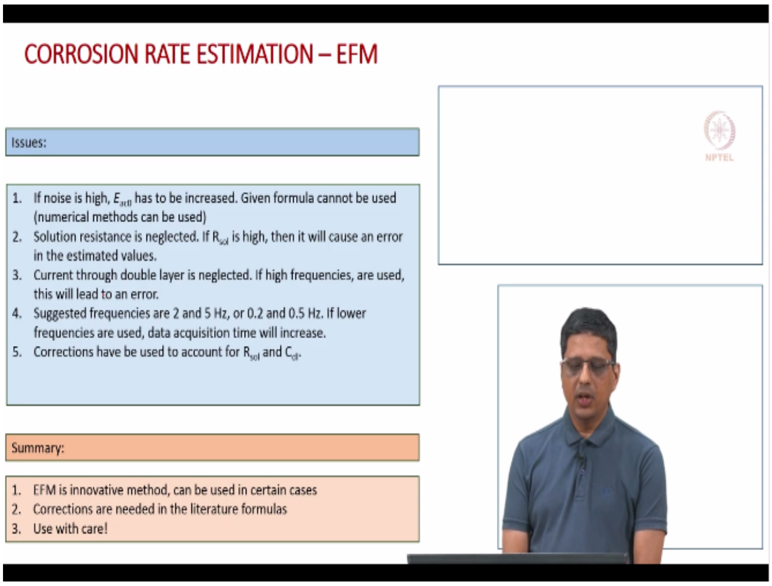

CORROSION RATE ESTIMATION – EFM

Issues:

1. If noise is high, E_{ac0} has to be increased. Given formula cannot be used (numerical methods can be used)
2. Solution resistance is neglected. If R_{sol} is high, then it will cause an error in the estimated values.
3. Current through double layer is neglected. If high frequencies, are used, this will lead to an error.
4. Suggested frequencies are 2 and 5 Hz, or 0.2 and 0.5 Hz. If lower frequencies are used, data acquisition time will increase.
5. Corrections have be used to account for R_{sol} and C_{dl}.

Summary:

1. EFM is innovative method, can be used in certain cases
2. Corrections are needed in the literature formulas
3. Use with care!

If the noise is high, you will have to increase the perturbation potential, Eac0 has to be increased and this formula cannot be used but you can expand in modified Bessel function and use optimization program to get it, always assuming that the Tafel expression is still valid okay. Now if solution resistance is high, this will definitely cause an error and that is lot more challenging to model okay.

In this case, it is assumed that the current through the double-layer is negligible. If the frequency chosen is small, it will be okay. What is small? Maybe 1 millihertz is usually small enough okay but it will take long time and if you want to acquire this data quickly, you will have to go to a little higher frequency.

Typically, 2 and 5 Hertz are used, sometime 0.2 and 0.5 Hertz are used and double-layer capacitance current may not be always negligible okay and corrections have to be employed to account for solution resistance and double-layer capacitance okay. So in summary, this is a new method, it can be used in certain cases. Usually, when corrosion current is large, this is good and corrosion current is small and if the noise is high, you will have problem in interpreting this data correctly.

So corrections are needed to the literature formula even under the assumption that solution resistance is negligible and double-layer capacitance is not contributing that much to the current and you have to use it with care okay. We will stop here today.