Electrochemical Impedance Spectroscopy
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Lecture - 18
Zero/Pole Representation, R_t and R_p

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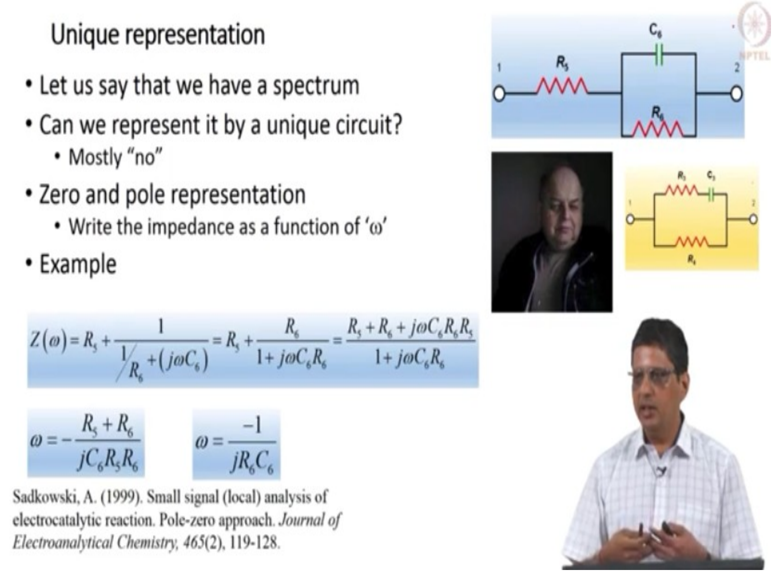

Unique representation

- Let us say that we have a spectrum
- Can we represent it by a unique circuit?
  - Mostly "no"
- Zero and pole representation
  - Write the impedance as a function of 'ω'
- Example

$$Z(\omega) = R_5 + \frac{1}{1/R_6 + (j\omega C_6)} = R_5 + \frac{R_6}{1 + j\omega C_6 R_6} = \frac{R_5 + R_6 + j\omega C_6 R_6 R_5}{1 + j\omega C_6 R_6}$$

$$\omega = -\frac{R_5 + R_6}{jC_6 R_5 R_6} \qquad \omega = \frac{-1}{jR_6 C_6}$$

Sadkowski, A. (1999). Small signal (local) analysis of electrocatalytic reaction. Pole-zero approach. *Journal of Electroanalytical Chemistry, 465*(2), 119-128.

Let us assume a case where you have a data and see whether it can be modeled only by a particular circuit. In very simple case, it is possible but as a whole, it is not possible. If you have only 1 capacitance, get the data, it can be modeled only by a capacitance. If you have only 1 resistance and you get the data, (let us say its noise is low level noise), this can be modeled by a resistor.

If resistance and capacitance are in series, you can model only by these 2 components. Anything, which is complex, you can have multiple circuits, which give you the same result. When you have experimental data with noise, the question arises on how to fit it all. It is possible to represent the data using unique set of numbers. If I write this in complex expression or complex mathematics, you can have what is called 0s and poles.

For example, you write it as a fraction with function z:

$$\frac{f(z)}{g(z)}$$

If you set $f(z)$ to 0, whatever you get are called 0s of this function and if you set g(z) to 0, depending on the type of function, you can get what is called singularity, removable, essential, or poles. Let's not go into the complexities of those now.

Generally, what we get in the denominator will be a polynomial and they will have what is called poles. If we specify the data using 0s and poles, then it does not matter which circuit you use and all of them will give you the same result. This is proposed by Sadkowski.

We write the impedance as a function of angle of frequency. This example, I will write it as R_5 in series with this pair of R_6 and C_6 (refer slide or video for circuit), so I can get the impedance of this R_6 and C_6 parallel element and write this as a function of jω.

$$Z(\omega) = R_s + \frac{1}{\frac{1}{R_6} + (j\omega C_6)} = \frac{R_5 + R_6 + j\omega C_6 R_6 R_5}{1 + j\omega C_6 R_6}$$

If I set the numerator to 0, I will get a value for this. I can get the value, at what frequency would the numerator go to 0 or what frequency would the denominator go to 0. So I can say when

$\omega = -\frac{R_5 + R_6}{jC_6 R_5 R_6}$, the numerator is going to 0 and when

$\omega = -\frac{1}{jC_6 R_6}$, this is the pole. If you give values for resistance saying this is R_5 is 10 Ω, R_6 is 100 Ω, C_6 is 20 μF, you will get value here for ω at each case and the latter one, and in general, it can be complex number. We will say for this arbitrary system, this is the 0, and this is the pole. Then, even if you represent by another combination of resistance and capacitance, they would also have the same 0 and same pole.

So if you want to specify that this is the spectrum which I got and these are the 0s and poles, then you can tells this is the unique way of representing it. The real problem with this is, it is not easy to assign physical meaning to the 0s and poles which means I cannot tell say adsorption is stronger or adsorption surface coverage is more or the film is thicker. It is possible to some level with electrical circuit. So although we know there is a unique way to represent it, you do not find that is used commonly, because of harder physical interpretation.

“Professor - student conversation starts”

Professor: No, once they have the same 0 and pole, that means the spectrum that are coming from there are equal and it does not necessary to mean the system are equivalent. If I have a circuit made out of the resistor and capacitor, as given in the top circuit, we make another circuit as given in the second one, both of them will give you the same impedance at any frequency as long as we have the equivalent values here.

Now from the data, you cannot tell which circuit is the one that is generating it. But you might come up with the top circuit, somebody else might come up with the bottom circuit and then each one may claim, this is the correct circuit, whereas if you represent it as 0s and poles, both of you will get the same number. It is easy to say that both of them are the same number, it is identical result. Does not necessarily mean this generating circuit is identical or generating systems are identical. It just means, there is no ambiguity in figuring out which is the better representation, because we do not ask that question.

“Professor - student conversation ends”

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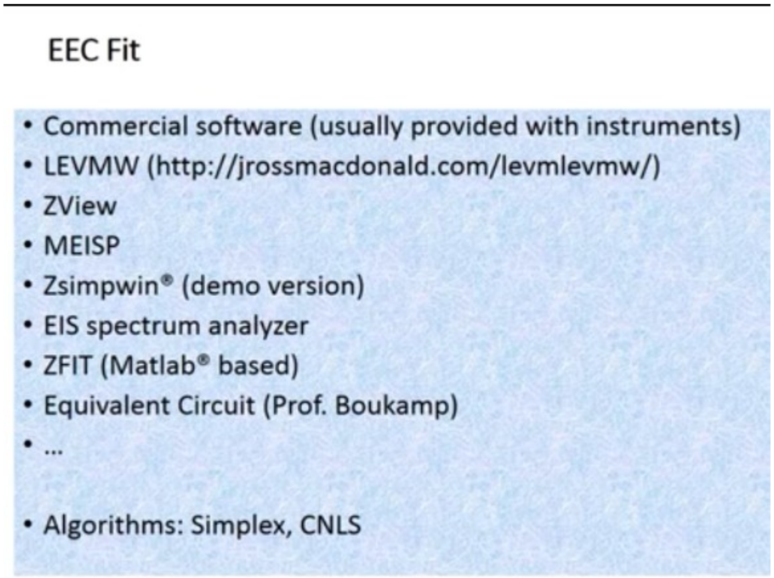

EEC Fit

- Commercial software (usually provided with instruments)
- LEVMW (http://jrossmacdonald.com/levmlevmw/)
- ZView
- MEISP
- Zsimpwin® (demo version)
- EIS spectrum analyzer
- ZFIT (Matlab® based)
- Equivalent Circuit (Prof. Boukamp)
- ...

- Algorithms: Simplex, CNLS

Though there are many software that are available to get these values. There are commercial software that comes with instruments. Publicly, you can get a software from Ross MacDonald’s website, you can get a Zview (maybe a demo version). You can get another software called multiple EIS program, EIS spectrum analyzer Matlab based program ZFIT or ZFITGUI. There is another demo version of a commercial software called Zsimpwin. You can go to the website of Professor Boukamp and get equivalent circuit. They use either simplex or complex non-linear square, called LEVM algorithm. Some of them say, they use the combination. They will use 1 to come to a good initial guess and then the second one to go to the actual optimum. As long as a spectra is simple, I think all of them will work. When spectra is complex, you will have to get the initial values correctly and you will have to do some work to get those initial values. To some level, knowing which circuits are distinguishable or which circuits are equivalent are helpful. Similarly, knowing what to expect at high frequency limit and what to expect at the low frequency limit, helps us simplify and get some initial guesses correctly.

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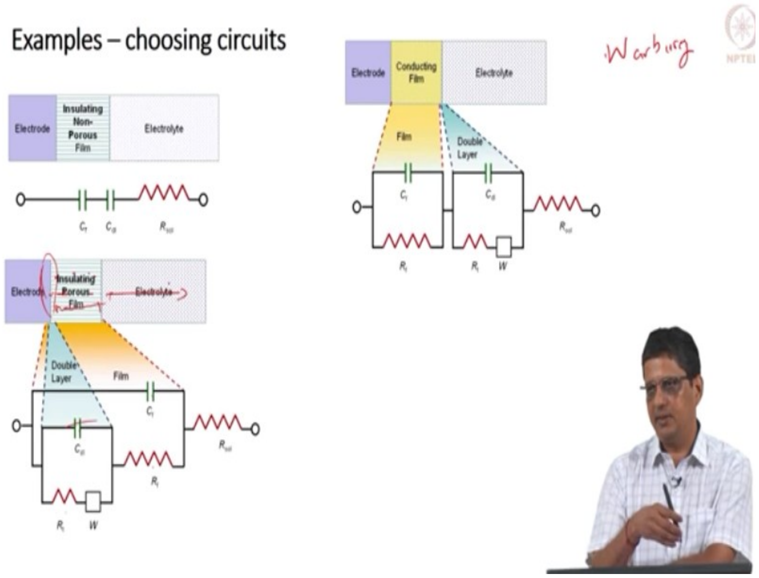

Examples – choosing circuits

Physically, how would you go about choosing a circuit? You have to know something about the system. These are some examples proposed in literature. We have a metal electrode covered by a non-porous insulating film and to the right of it is the electrolyte (refer slide/video). We do not expect any current to pass through it because the insulating film is just going to block everything. You can represent this by one capacitor, another capacitor in series with a solution resistance. When you get this, all that you get here in the data can be modeled by a capacitance and a resistance in series. Because you cannot add the 2 capacitance. You can take the inverse and add them and what will get the inverse of the effective capacitance. Now, assume you coat a film of certain thickness, and you measure the spectrum, and then you coat with a different thickness and you measure the spectrum, you will get a different value. Now you have to interpret that as the sum of 2 capacitances. One of them is fixed, another one is changing. Hopefully you will have another method to measure the thickness and then you can come up with the idea of what is happening here to check whether this is giving you the correct result. You can use it as a validation. If you do not know that the C_f and C_{dl} are arranged like this (as in series here) and C_{dl} remains the same and if you give me 2 spectrum, I cannot tell what the value of C_f and C_{dl} from it. I have to know that these are coming from a system like this and the C_{dl} is the same between these 2 experiments. Therefore, any variation there, I can assign it to C_f. Otherwise, all that I can say is this can be modeled by a resistance in series with a capacitance.

If you have a porous film, which is insulating and the electrolyte is there (as in slide or video), that means some liquid passes through this and reaction can happen at the interface between porous film and electrode. You will have double layer along with reaction and Warburg impedance for mass transfer effect. Porous film means, it is not really flowing freely and concentration of the reactants and products at the interface are not the same as the concentration of the reactant products at the bulk material. Now this is in parallel with film capacitance, also because electrolyte has to go through this, there is some resistance associated with this. So you can use a circuit given by R_f and C_f in combination with C_{dl} and R_t and W, with solution resistance for the remaining bulk. Basically you have to visualize how this would behave and then choose a circuit. For example, if I have a conducting/semiconducting film and it is not porous, reaction happens only at the interface between conducting film and electrolyte. There is no penetration of this electrolyte into this film. I can model the left side conducting film with the resistance and capacitance. The resistance will be low here and that is in series with the reaction that is happening at the interface, double layer, charge transfer resistance, Warburg impedance and so on. Now if you count this, you have similar number of resistance and capacitance here. Let's assume the Warburg impedance is not significant. Then I can model it with resistance in parallel with a capacitance and resistance. So I have to know before hand, what I am looking at, what circuit can physically represent this system, and then I will have to make a guess and model this.

“Professor - student conversation starts”

Student: Sir every time reaction will be represented as resistance or something else?

Professor: No this is assuming that reaction can be represented by a simple resistance. So next, after this, I want to show you how we can get the impedance of a reaction. In a very simple case, we will show the impedance of the reaction can be represented by a simple resistance. In more complex case, we will see how it can be represented.

Student: What is W?

Professor: W here represents what is called Warburg. It is the name of a person who first came up with an expression for mass transfer based impedance. So this is called Warburg impedance.

“Professor - student conversation ends”

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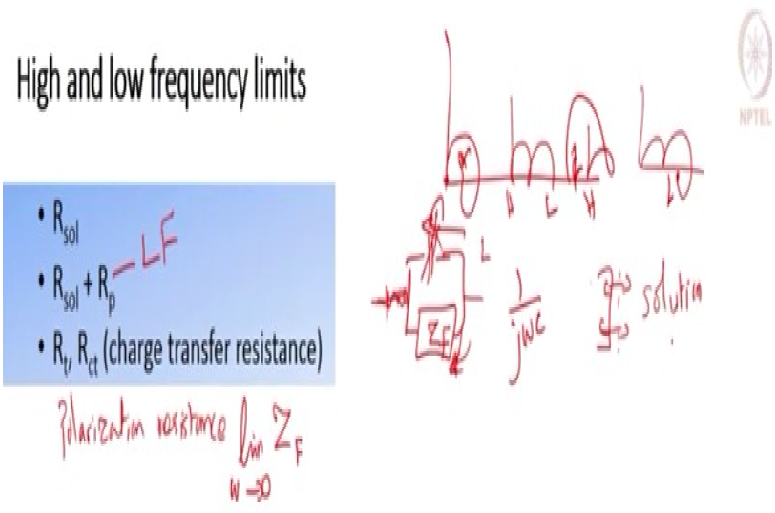

High and low frequency limits

- R_{sol}
- $R_{sol} + R_p$ — LF
- R_t, R_{ct} (charge transfer resistance)

Polarization resistance $\lim_{w \to 0} Z_F$

We have seen some examples for different impedance spectra. We have seen something, which looks like 2 semicircles, 1 semicircle with an inverted loop, 2 semicircle with an inverted loop and many other complicated loops (refer video/slide). Here the starting point is high frequency, and the ending point is the low frequency. High frequency limit is usually the solution resistance. We have seen a case in which you have a resistor, a capacitor and a reaction with a complex impedance which is often called Faradaic impedance (in honor of Michael Faraday). So any electrochemical reaction which is assumed to be kinetic limited and to have no film and mass transfer effect, can be represented like as shown in slide/video (a parallel combination of capacitor and resistor which are in series with another resistor).

When you go to very high frequency, the impedance of the capacitor will be 0 or close to 0 because we know it is going to be given by $1/j\omega C$. That means all the current will pass through the capacitor and not much current will pass through the resistor which is in parallel with the capacitor. That means, only resistance offered is at the solution side. So solution resistance will be the high frequency impedance.

If I go to very low frequency, capacitor will not allow much current to go through because ω tends to 0, $1/\omega$ tends to infinity. So it looks like an open circuit. All the current will go through only the Faradaic process or the electrochemical reaction and the solution resistance as well. So low frequency impedance is going to be solution resistance plus a resistance which is called polarization resistance. Polarization resistance is the Faradaic impedance at the limit of ω tending to 0. It means, if I have a surface and I want to the change the polarity (moving it from whatever voltage it is in i.e. little higher or lower), there will be a corresponding change in current as we do it slowly. So that ratio of change in potential to change in current, when we change it very slowly from whatever value it was originally at, is called polarization resistance. So if I change the potential, it is possible that more species may absorb or less species may absorb. All those processes are taken into account. Overall change in current is given by this Z_f when ω is tending to 0.

Faradaic impedance is basically the impedance offered by electrochemical reactions. So consider another example where we have a solution resistance R_s, resistance offered by the capacitance which is called double layer impedance (even if there is no reaction, AC current can pass through) and resistance offered by the reaction which is called Faradaic impedance. Altogether, we measure the total impedance. But we want to separate out or deconvolute and assign one component as solution resistance, another from double layer and another one from reaction. Usually, we need to understand what is happening in the reaction and that is why we do the impedance spectrum. However, we cannot get the impedance spectra of the reactions alone, we will get it for the system. So this is first step of separating them out. Now I know I can get the polarization resistance if I know the Faradaic impedance and if I measure, it will be the lowest value. But the lowest value at Z_f is not going to be polarization resistance. It is going to be sum of solution resistance and polarization resistance, because the circuit tells us, total impedance that we measure between these 2 points (refer video), it has to go through solution resistance and double layer capacitance. As ω is close to 0, I know that I can neglect the double layer capacitance part and I can say it goes through the bottom part (refer video). So what we measure as the lower frequency impedance, it has to settle at a particular value. If I measure up to half of the semi-circle, I cannot call this as a polarization resistance. I have to see where it settles. That means, I have to go to lower and lower frequency and it remains more or less at the same level, then that is the low frequency impedance and is the sum of polarization resistance and solution resistance. If $R_{solution}$ is very small, you can say low frequency impedance is the polarization resistance. So sometimes in publications or in books, you will see as the low frequency limit is regarded as the polarization resistance. They are implicitly neglecting the solution resistance. So do not take the settling point of impedance spectra as polarization resistance, if this solution resistance is not close to 0. Another thing to be noted is the charge transfer resistance.

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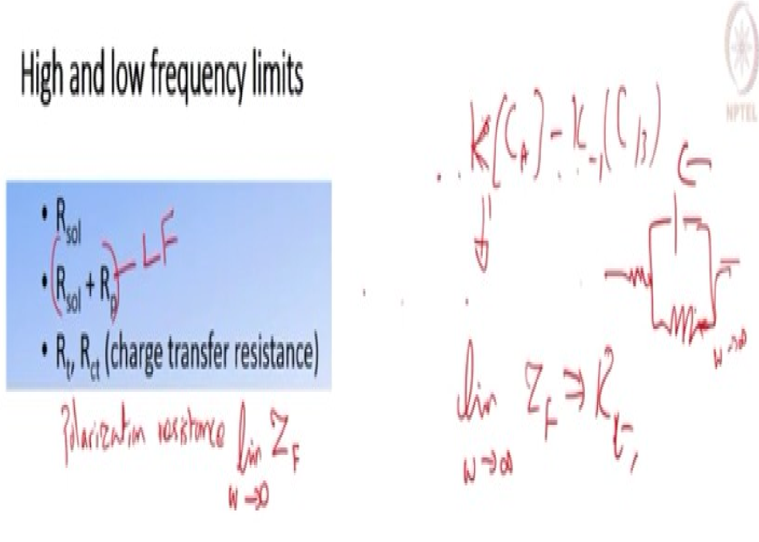

High and low frequency limits

- R_{sol}
- $(R_{sol} + R_p)$ – LF
- R_t, R_{ct} (charge transfer resistance)

Polarization resistance $\lim_{\omega \to 0} Z_F$

$K(C_A) - K_{-1}(C_B)$

$\lim_{\omega \to \infty} Z_F \to R_{t}$

You have rate constant K. You can have other terms like concentrations of species (C_A, C_B etc.), K_1, K_{-1}, or you can have other intermediates in a more complex reaction. Whenever we change the potential, the rate constant changes and it is supposed to change exponentially as in K_1= $K_0 e^{\frac{n\alpha F}{RT}}$ and in similar way K_{-1}= $K_0 e^{\frac{-n\alpha F}{RT}}$. There are different ways of representing this for forward reaction and reverse reaction, they are going to have exponential relationship as seen above. In one case, it will increase and in another case, it will decrease. If I change the perturbation or the sinusoidal potential very fast, ω will be tending to infinity and all current will go through the capacitor since it offers almost 0 impedance in this case. Then I can see only R solution. Now let us assume, we can separate the capacitor and parallel resistor from solution resistance, I want to find out what happens to Faradaic impedance when ω tends to infinity. When ω tends to infinity, the Faradaic impedance will tend towards a resistance, called charge transfer resistance denoted as R_t or R_{ct}. For a given system, if I go to high frequency, it will tend towards a resistance value which depends on what happens to K_1 and K_{-1}, as we change the potential. Let us assume that you have an electrode on one side and a solution on the other. Let us say mass transfer is also playing a role. If I increase the potential at the electrode, one of the species will get consumed, another species will get produced. So whichever gets produced will diffuse out and whichever is consumed, will diffuse in. If I increase and decrease the potential very fast, for example 100 KHz, within 1 second it goes 10 power 5 times. Species will not diffuse in and out that fast. It cannot cope up with this speed. However, the rate constant will still go up and down. So effectively, everything else will remain same, only the rate constant will change. When a species adsorbs or desorbs in a system, at this particular frequency, it cannot adsorb and desorb that fast. And at the limit of infinite frequency, it definitely will not cope up with the speed. Whereas the rate constant, it is directly related to the potential. So whenever we increase the potential, the rate constant will also increase or decrease. When you apply a slow change, the faradaic impedance is the polarization resistance. When you apply a fast change, it will tend toward a simple resistance and that is charge transfer resistance. If the electrochemical process is very simple, I can represent faradaic resistance using a simple resistance. At any frequency, it will give me the same resistance. Therefore, in this particular case, charge transfer resistance and polarization resistance, will be the same. I get only one resistance for all frequencies. Therefore, the upper limit and lower limit will be the same number. This sometimes causes confusion. Sometimes people represent a system with the low frequency limit as charge transfer resistance and/or high frequency limit as polarization resistance. It is not correct.

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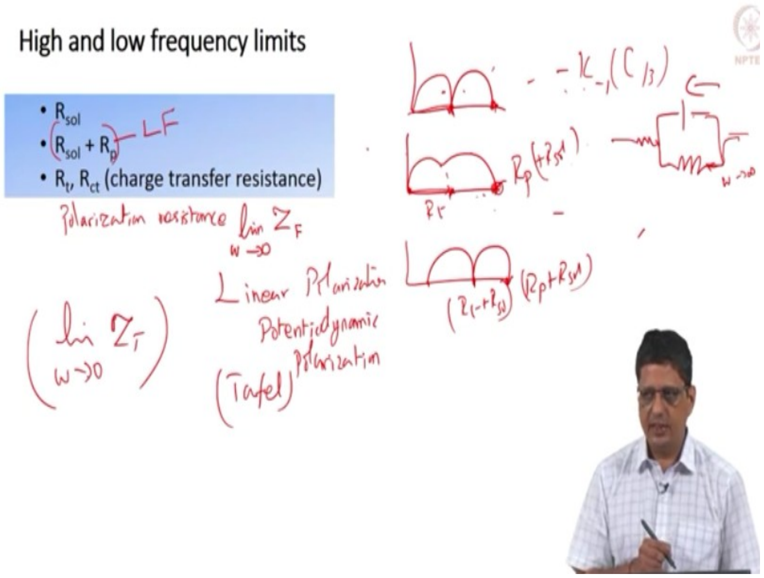

High and low frequency limits

- R_{sol}
- $(R_{sol} + R_p)$ — LF
- R_t, R_{ct} (charge transfer resistance)

Polarization resistance $\lim_{w \to 0} Z_F$

$\left(\lim_{w \to 0} Z_T\right)$

Linear Polarization

Potentiodynamic Polarization

(Tafel)

Let's take an example where impedance spectra is as shown in the above slide. We have taken enough number of points and we know where it settles. That will be R_p+$R_{solution}$ and if solution resistance is negligible, I can say it is R_p. The extension of 1st loop as referred in the video, where it settles is going to be R_t from the start of the spectra. That means this values R_t+$R_{solution}$. If the solution resistance is negligible, it is going to be only R_t. If the solution resistance is significant, the impedance will be R_t+$R_{solution}$. This impedance after 2nd loop will be R_p+$R_{solution}$. R_t can be obtained only via impedance measurement. You will not get it using other techniques, such as linear polarization or potentiodynamic polarization, which is often analyzed using a particular type of analysis called Tafel analysis or Tafel extrapolation which will give you Rp. They also assume that solution resistance is negligible and ω is tending to 0. Z_{total} is all you get from linear polarization and Tafel extrapolation. If solution resistance is 0, it will become equal to:

$$\lim_{\omega \to 0} Z_f = R_p .$$

If you want to get R_t, you have to get it via only impedance measurement and you should clearly separate out polarization resistance and charge transfer resistance. They will be the same only in very few cases which means the values will be the same but the definition will be different.

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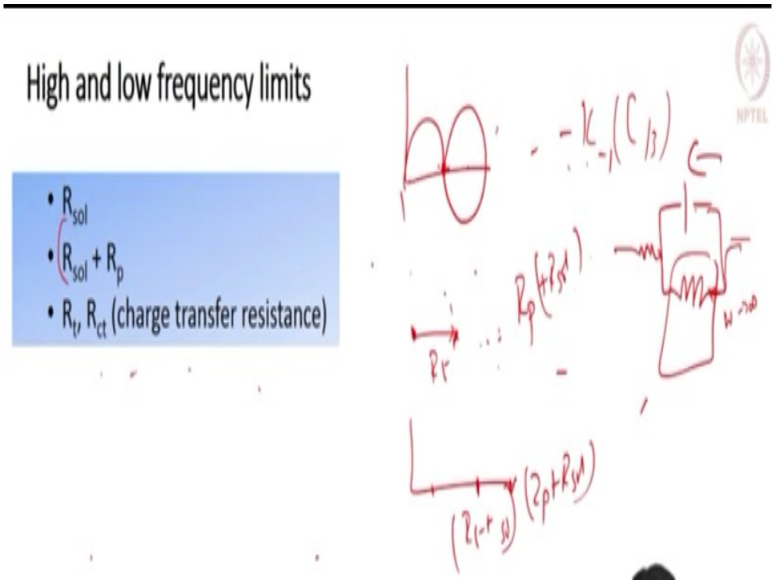

High and low frequency limits

- R_{sol}
- $R_{sol} + R_p$
- R_t, R_{ct} (charge transfer resistance)

"Professor - student conversation starts"

(Refer video)

Meaning I can get 100 ohm. For that system, charge transfer resistance is 100 Ω or 100 Ω cm^2. Polarization resistance is also 100 Ω cm2. It does not mean the definition of charge transfer resistance and polarization resistance are the same.

It is quite possible. (…) the spectrum. This is solution resistance. Low frequency settles here. Let us say solution resistance is 0. Now if I go to this and say I want to note this impedance at low frequency, I want to know this impedance at high frequency. The value is the same. I will give you another example. It comes and settles here. We will get the same number, but it does not mean the meaning of polarization resistance and charge transfer, cannot be used interchangeably.

"Professor - student conversation ends"

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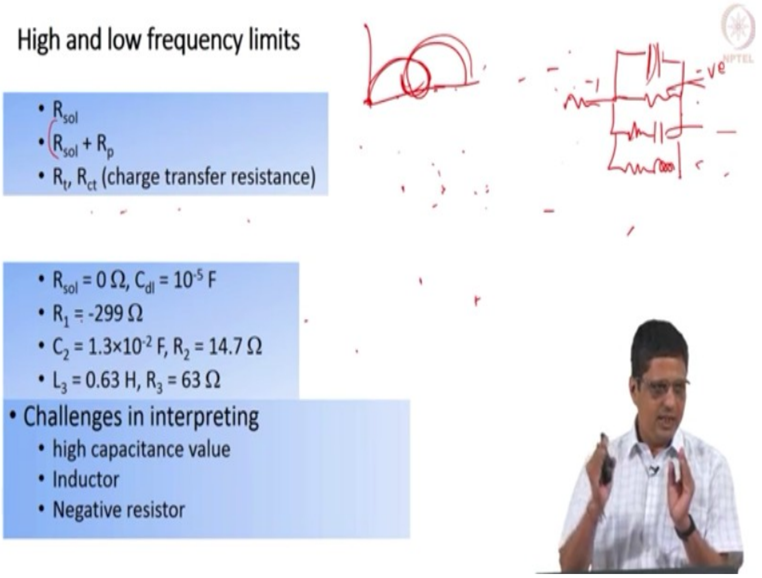

High and low frequency limits

- R_{sol}
- $R_{sol} + R_p$
- R_t, R_{ct} (charge transfer resistance)

- $R_{sol} = 0\ \Omega$, $C_{dl} = 10^{-5}$ F
- $R_1 = -299\ \Omega$
- $C_2 = 1.3\times10^{-2}$ F, $R_2 = 14.7\ \Omega$
- $L_3 = 0.63$ H, $R_3 = 63\ \Omega$

- Challenges in interpreting
  - high capacitance value
  - Inductor
  - Negative resistor

Previously we have taken some examples. I want to look at the numbers again. Solution resistance can be 10 ohm or 0 ohm. Double layer capacitance is 10^{-5} Fcm^2 (this is a reasonable number) and this is for a circuit, which look like as in slide (or refer video). We got R_1 and this is modeled by a circuit, where you have solution resistance, double layer capacitance and a resistor parallel to it. Then we put additional one resistance and a capacitor in series as shown in slide. Then we included a resistance and inductance as shown in the above slide. The first part can be modeled by capacitance and resistance. This is what we normally use. The middle loop is inductive loop, therefore I will use a resistance and inductance for it. 2nd loop is a capacitive loop and I will use a resistance and capacitance. If we just use this circuit and then do not realize that the value of 2nd resistance (refer video) has to be negative, you will have a problem. You would not be able to fit it correctly. It may almost fit. However, if you measure the parameters, you will see that the uncertainty in the parameter is very high and you will see that if I use equivalent circuit with capacitors and resistor instead of inductor, allowing for negative values, you can get better fit. This 2nd capacitance comes as $1.3*10^{-2}$ F that is 13 mF and resistance is 15 Ω. You get the inductance as 0.63 H, which is actually large inductance. We cannot explain the high capacitance values. It does not mean we can store lot of energy here. It means that the spectrum can be generated by a circuit as shown in figure. It does not mean the electrochemical reaction has the capacity to store this much energy or it has an effective inductance of this much value.

Also, it does not mean that there is any magnetic field associated with this and/or you have a negative resistance. It also does not mean that the current will go in the opposite direction, if you apply potential in one direction.

So we have difficulty in explaining this from the circuit. We can fit it to a circuit, but what do we make out of these numbers. As we look at the reference electrode, we say that I cannot measure the potential of a single electrode, but I can measure the potential of 2 electrodes together knowing that one is fixed. Any change that I apply, it happens to only 1 electrode. That's how we interpret the result. Likewise if I change the system a little, these values will change accordingly. That is better than not knowing anything about these numbers although it has problems associated with it.

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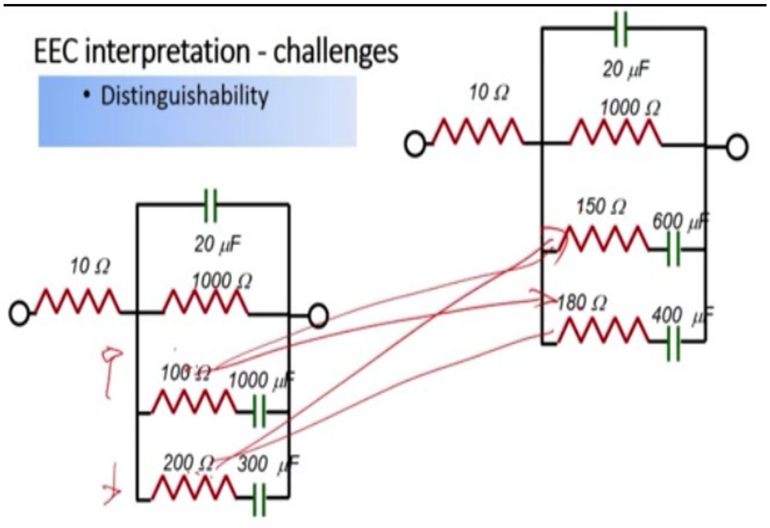

EEC interpretation - challenges

- Distinguishability

When you fit the data, the numbers were randomly made up. When you get system like what we considered, another software will tell you, some of parameters can move up and or some other can move down or so on. Another software may give different set of values to each parameters. They are the same. Let us assume you change the concentration or you change the DC offset and you will get a different spectrum. Now you can fit it to a circuit (as shown in slide there are 2 circuits). The resistance from 1st circuit has moved from 100 to 150 in the 2nd circuit and capacitance has decreased from 200 to 180. When the resistance goes from 100 Ω to 150 Ω, the capacitance decreases. If it takes a given system and alter something, if one of the resistance goes up, the associated capacitor will go down in magnitude. Let us also take the case where 100 Ω has become 180. It means it has increased a lot and 200 has become 150 (refer video). It is moving in the same direction. However, it has moved much more than what you would interpret if you are taking the first resistance goes to the first resistance of 2nd circuit and you never know which one is going to be the top or bottom (refer video for better understanding). It is not easy to interpret electrical circuits or changes in the circuit, when you have a complex spectrum. When you have very simple spectrum, it is easy to interpret. If you have a spectrum and you move the reference electrode a little bit, solution resistance will change. You can interpret that change. If you have a reaction and by adding some chemical, adsorption is altered, the spectrum pattern will remain the same, but the values will be changing. The physical interpretation of resistance and capacitance will be meaningful in a simple system. However, it is not possible when you have complex reaction.