Electrochemical Impedance Spectroscopy
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Lecture - 21
Simple Electron Transfer Reaction

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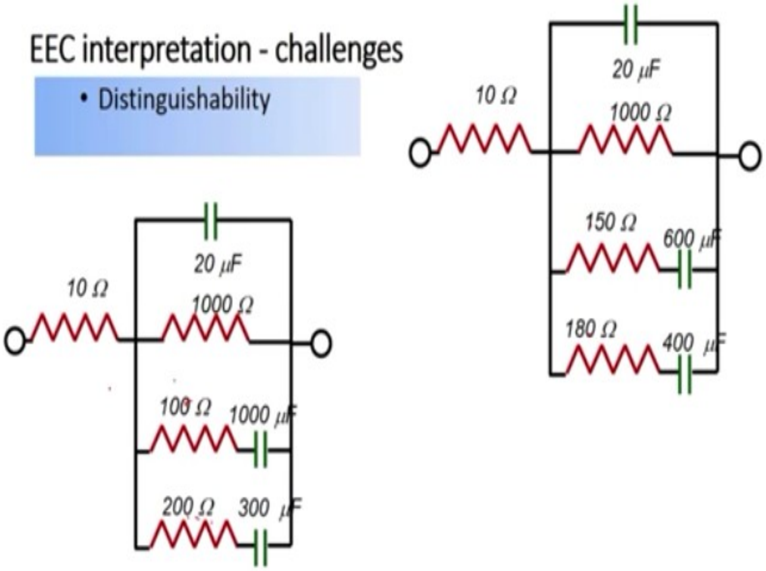

EEC interpretation - challenges

- Distinguishability

In this session we will discuss about what we can do for the physical interpretation of resistance and capacitance when you have a complex reaction.

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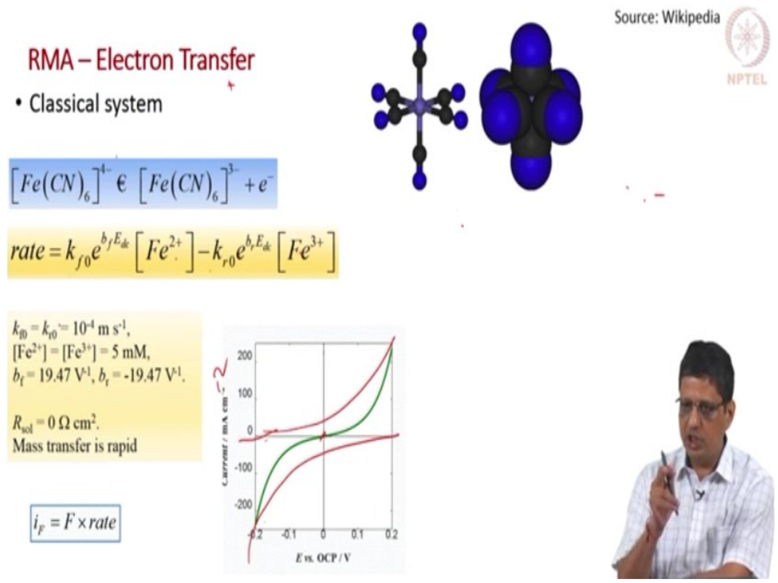

RMA – Electron Transfer

- Classical system

Source: Wikipedia

$[Fe(CN)_6]^{4-} \in [Fe(CN)_6]^{3-} + e^-$

$rate = k_{f0} e^{b_f E_{dc}} [Fe^{2+}] - k_{r0} e^{b_r E_{dc}} [Fe^{3+}]$

$k_{f0} = k_{r0} = 10^{-4}$ m s^{-1},
$[Fe^{2+}] = [Fe^{3+}] = 5$ mM,
$b_f = 19.47$ V^{-1}, $b_r = -19.47$ V^{-1}.

$R_{sol} = 0\ \Omega$ cm^2.
Mass transfer is rapid

$i_F = F \times rate$

$$[Fe(CN)_6]^{4-} \rightleftharpoons [Fe(CN)_6]^{3-} + e^-$$

Consider this reversible reaction. We want to say the impedance spectrum can originate from this reaction and when I make some changes, the reaction has changed accordingly. We would like to assume a reaction say, A going to B actually happens in different steps. A goes to intermediate species, intermediate species goes to the product B or A goes to intermediate (I_1), that intermediate goes to another intermediate (I_2) and then it goes to the product and similarly, the reversible reaction. Another possibility is A can also directly go to I_2. Similarly many possibilities exist. Many of the reactions of importance do not happen in 1 step. If I say 2 hydrogen ions take 2 electrons and form a hydrogen molecule and go out as gas bubble, it does not happen in 1 step. It happens through multiple steps.

$$2H^+ + 2e^- \longrightarrow H_2\,(g)$$

Similarly, oxygen evolution reaction to oxygen reduction reaction do not normally happen in 1 step. They happen through multiple steps. If they happen through multiple steps, can we find out the rates of each step? If you know the slowest step, you can hope to increase it or if you want to suppress something, you can possibly reduce it further. Similarly you can have a better idea in this regard.

Assume you prepare and characterize a catalyst for a reaction, you want to characterize the reaction occurring through the catalyst. For that, you will have to look at few spectra together and then interpret what is happening in the reaction. In summary, we should be able to interpret the mechanism. That is not very easy. What we have to learn in the beginning is, if we know the reaction, I should be able to tell the corresponding spectrum. Therefore you get an idea for the spectrum corresponding to different types of reactions. In the case of electrical circuits, we found that we will get a particular spectrum corresponding to the capacitor or resistor arranged in the circuit. If you have an arrangement with more capacitors, you will get a spectrum accordingly. Similarly if I get a spectrum, I should be able to model it with a corresponding circuit. Likewise, I would like you to become familiar with the process of first proposing a reaction and proposing rate constant. So if I know the rate constant for a particular reaction, I should be able to generate the spectrum. At different DC potentials, it will give me particular type of spectrum.

The reverse problem can be attempted after knowing how to do the forward problem, because the reverse problem involves optimization. You have to propose a reaction, vary the rate constant and then see whether you can fit all the spectra nicely. In order to do that, you should be able to generate the spectrum if you have the reactions and the rate constant. Only then you can vary something and do the corresponding fitting. If you cannot even generate it, I will not be able to do the optimization.

Initially, I want to start with a simple reaction.

$$[Fe(CN)_6]^{4-} \rightleftharpoons [Fe(CN)_6]^{3-} + e^-$$

Although the species looks complex, reaction is considered simple. It is called ferro/ferri redox couple.

$$K_4[\mathrm{Fe(CN)}_6] \rightleftharpoons K_3[\mathrm{Fe(CN)}_6] + K^+ + e^-$$

K^+ and e^- are not usually written. It is one iron atom surrounded by cyanide molecule. This is considered as simple reaction because this does not need rearrangement of any of these atoms. This $Fe(CN)_6$ whole group gets an electron or gives an electron without any rearrangement. That means it can happen without it adsorbing, going through any rearrangement and coming out. If I take only Fe^{2+} ion, it is usually surrounded by water molecules/ water dipoles. If I want to adsorb it on a surface and remove an electron or if it is Fe^{3+} and I want to add an electron, I have to remove the water molecules. It has to adsorb, it has to spend some time there, remove that water molecule and then get adsorbed on it. When it goes out, it will again get hydrated. In case of ferro/ferricyanide, it does not have that much charge per unit volume because as it has a large molecule and water dipole does not bound strongly to this. It is easy to give or take an electron from it. So this is normally taken as a classical system in many labs. If we suspect something is wrong, we take gold electrode or platinum electrode, introduce it to this redox couple and measure the spectrum. If it comes correctly, the system is well and good. If it does not come correctly, there may be a problem with the reference electrode or the instrument and we have to sort it out.

This reaction can be represented as

$$A \rightleftharpoons B^{+} + e^{-}$$

A and B had different charges and it is a reversible reaction. The forward rate constant is represented as k_f, and reverse is k_r. So the net rate is:

$$\text{Rate} = k_f[Fe^{2+}] - k_r[Fe^{3+}]$$

The square brackets indicate concentration. Activity coefficient is assumed to be 1 here. Net rate is going to be forward minus the reverse. The rate constants will change with potential as it involves electron transfer (forward reaction gives an electron reverse reaction takes an electron). So I am writing the rate as:

$$\text{Rate} = k_{f0}\, e^{b_f E_{dc}}[Fe^{2+}] - k_{r0}\, e^{b_r E_{dc}}[Fe^{3+}]$$

It means $k_f = k_{f0}\, e^{b_f E_{dc}}$ E_{dc} is DC potential. Now we look into the case where we apply only DC potential. Later we can see what happens when you apply AC potential. First we should know what to expect when you apply a DC potential. The notation b_f represents how much the forward rate will increase if I change the potential and b_r tells how much the reverse rate constant will increase or decrease if I change the potential. Now I have taken some values (refer slide or video). It depends of course on the electrode surface. If I take graphite, I will get a different type of reaction or different rates. I have taken the concentration of ferro and ferri to be 5 millimolar. I had taken the value of b_f and b_r to be close to ±20 with inverse of voltage as the units. This b_f is actually going to be:

$$b_f = \frac{n\alpha F}{RT}$$

R is the universal gas constant and T is the temperature in Kelvin. F is the Faradaic constant; n is the number of electrons involved which means it is 1 here. α is called charge transfer coefficient.

Assume α to be 0.5 and b_r is going to be $\frac{-(1-\alpha)F}{RT}$. If I take α to be 0.5, then this is going to be same as the first equation with a negative sign. So I have used some arbitrary temperature values (25 or 28 Celsius to get this value). I have taken solution resistance to be zero.

Mass transfer is assumed to be rapid which means concentration of 3 & 2 will not be different. When I apply a potential, it will still remain the same. Whatever is consumed will be replenished very quickly and whatever is produced will go out quickly. Therefore concentration is maintained uniformly everywhere. If I calculate the rate and multiply the rate with Faradaic constant, net rate will tell how many electrons are released. Faradaic constant will tell how to convert this to current in coulombs. Rate is moles/cm^{2}time^{-1}. So after multiplication with faradaic constant, I will get amperes (coulombs/unit time/cm^2).

In the linear scale, when we plot current versus potential, we will get a graph as shown in slide. This first term is going to exponentially increase and here it goes towards zero (refer video 10:05). b_r is negative, which means the second term is given by the line at the bottom. Algebraic sum of these two gives us the green color line which goes through zero (refer slide or video). At E_{dc} to be 0, k_{r0} and k_{f0} are equal and Fe^{2+} and Fe^{3+} are equal. Although b_r & b_f are different, e power zero voltage will give me 1 in both cases. Therefore net current becomes zero in this case which also means I cannot write k_{f0} and k_{r0} as independent.

When E_{dc} is 0, the net current has to be 0. That is how we want to choose the reference for DC. So the current which passes through 0 is called open circuit potential and the DC potential should be written with respect to that potential not with respect to reference electrode, because if you change the reference electrode, the potential will change.

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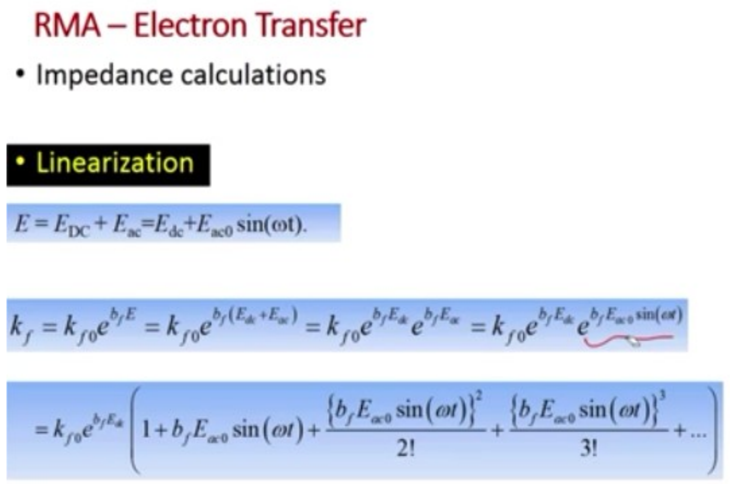

RMA – Electron Transfer

- Impedance calculations

- Linearization

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

$$k_f = k_{f0}e^{b_f E} = k_{f0}e^{b_f(E_{dc}+E_{ac})} = k_{f0}e^{b_f E_{dc}}e^{b_f E_{ac}} = k_{f0}e^{b_f E_{dc}}e^{b_f E_{ac0}\sin(\omega t)}$$

$$= k_{f0}e^{b_f E_{dc}}\left(1 + b_f E_{ac0}\sin(\omega t) + \frac{\{b_f E_{ac0}\sin(\omega t)\}^2}{2!} + \frac{\{b_f E_{ac0}\sin(\omega t)\}^3}{3!} + \dots\right)$$

Now I want to apply AC potential and calculate the impedance. If you apply AC potential, I can write the potential as DC+AC. I will write DC as E_{dc}. I will write AC component as the amplitude, so in our notation E_{ac0} is the amplitude.

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

So I will call this curve as AC curve (refer video). E_{ac0} is the amplitude. E_{ac} is a function of time. If I write the rate constant, I can expand it as function of potential. I can expand that as DC and AC. I can separate the DC and AC because they are in the power term and then I can expand E_{ac} as E_{ac0}sine ωt.

$$k_f = k_f e^{b_f E} = k_{f0} e^{b_f (E_{dc}+E_{ac})} = k_{f0} e^{b_f E_{dc}} e^{b_f E_{ac}} = k_{f0} e^{b_f E_{dc}} e^{b_f E_{ac0}\sin(wt)}$$

k_{f0} can be large or small. $b_f E_{dc}$ can be large or small. However we are assuming E_{av0} is a small number and correspondingly $b_f E_{ac0}$ becomes a small number. That means in the previous graph, we can see zero voltage for DC. Consider 0.1 and 0.2 voltage in the graph. I can apply sinusoidal voltage in those points. I am not making any assumptions regarding DC voltage. I want to make an assumption that E_{ac0} is a small voltage. If I apply 5 millivolt, 10 millivolt, or even 20 millivolt, you might get spectrum in the linear regime with reasonably good signal-to-noise ratio. If I apply 1 millivolt, for many systems, it will be in the linear regime. However we may not get a good signal to noise ratio.

To summarize, we found the reversible reaction with A going to B. We can write the rate constant as a function of potential. We assume that the concentration of these 2 reactants and products do not change with time. They are replenished very quickly as soon as they are consumed or produced. Diffusion is assumed to be fast and on the surface, the concentration remains the same. We also found that if you apply DC+AC, you can split the potential into DC component and AC component.

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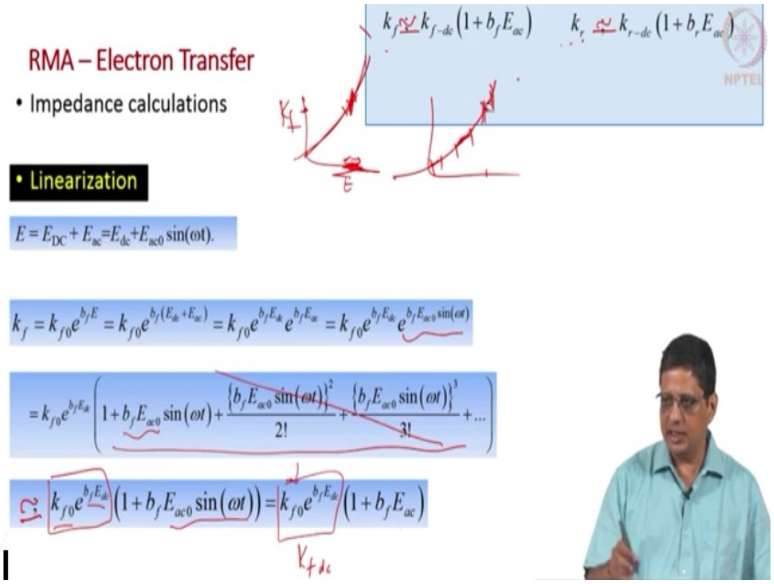

RMA – Electron Transfer

- Impedance calculations

• Linearization

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

$k_f = k_{f0}e^{b_f E} = k_{f0}e^{b_f(E_{dc}+E_{ac})} = k_{f0}e^{b_f E_{dc}}e^{b_f E_{ac}} = k_{f0}e^{b_f E_{dc}}e^{b_f E_{ac0}\sin(\omega t)}$

$= k_{f0}e^{b_f E_{dc}}\left(1 + b_f E_{ac0}\sin(\omega t) + \cancel{\frac{\{b_f E_{ac0}\sin(\omega t)\}^2}{2!} + \frac{\{b_f E_{ac0}\sin(\omega t)\}^3}{3!}} + \dots\right)$

$\approx \boxed{k_{f0}e^{b_f E_{dc}}}\left(1 + b_f E_{ac0}\sin(\omega t)\right) = \underbrace{\boxed{k_{f0}e^{b_f E_{dc}}}}_{K_{f\,dc}}\left(1 + b_f E_{ac}\right)$

$k_f \approx k_{f-dc}(1 + b_f E_{ac}) \quad k_r \approx k_{r-dc}(1 + b_r E_{ac})$

If you take the AC component of k_f, e^x, can be written as Taylor series and x here is $b_f E_{ac0}$sine (ωt) and sine is going to be between ±1. If $b_f E_{ac0}$ is a small number, I can truncate it after 2nd term of taylor series expansion. Therefore I can write that e^x is approximately equal to 1+x. This is called linearization. E_{dc} need not be small. It can be small or large. We are neither making any assumptions about E_{dc} nor k_{f0}. The assumption we make to bring the current expression to the final form (refer video or slide to understand the derivation) is that $E_{ac0}b_f$ is a relatively small number.

$$k_f \approx k_{f0}e^{b_f E_{dc}}(1 + b_f E_{ac0}\sin(wt)) = k_{f0}e^{b_f E_{dc}}(1 + b_f E_{ac})$$

I can write the first part as k_f at DC potential of E_{dc} and I can write E_{ac0}sin (ωt) as E_{ac}. E_{ac} is a time dependent function and E_{ac0} is a constant. So I will write k_f as:

$k_f \approx k_{f-dc}(1 + b_f E_{ac})$ and k_r as:

$k_r \approx k_{r-dc}(1 + b_r E_{ac})$

It means if I apply a DC potential, k_f will have a value accordingly. If I change it a little (up and down as shown in video), k_f is expected to change only a little and that can be linearized. If I change the potential a lot, this relationship will not be linear. So k_f as a function of E_{dc} is actually a curve. It is an exponential curve. At a small variation, I can say it has a linear relationship. So even if I have an exponential curve, at a particular E_{dc}, you will get a corresponding slope. In another E_{dc}, it will be having a slightly different slope. However, in small regions where the curve is linear, I can assume it to have a linear relationship. All of them will not have the same slope, but I can approximate at each DC with some slope. If I choose a larger region, it means I am assuming E_{ac0} as a large value and the approximation will be a poor. When it is small value, the approximation holds good. So I am making it piecewise linear. If I choose the pieces to be small pieces, it is good. If I choose them to be large ones, it would not be good.

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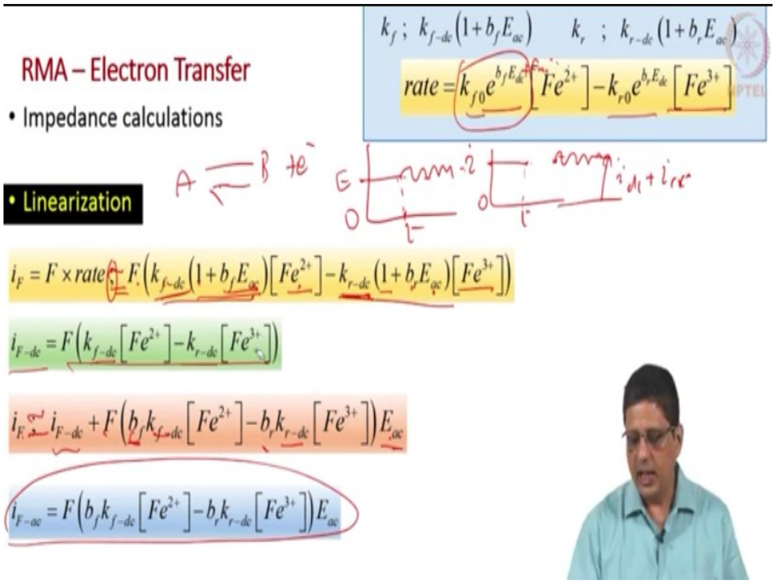

RMA – Electron Transfer

- Impedance calculations

$k_f ;\ k_{f-dc}(1+b_f E_{ac})$ $k_r ;\ k_{r-dc}(1+b_r E_{ac})$

$rate = k_{f0}e^{b_f E_{dc}}[Fe^{2+}] - k_{r0}e^{b_r E_{dc}}[Fe^{3+}]$

- Linearization

$i_F = F \times rate ; F(k_{f-dc}(1+b_f E_{ac})[Fe^{2+}] - k_{r-dc}(1+b_r E_{ac})[Fe^{3+}])$

$i_{F-dc} = F(k_{f-dc}[Fe^{2+}] - k_{r-dc}[Fe^{3+}])$

$i_F \simeq i_{F-dc} + F(b_f k_{f-dc}[Fe^{2+}] - b_r k_{r-dc}[Fe^{3+}])E_{ac}$

$i_{F-ac} = F(b_f k_{f-dc}[Fe^{2+}] - b_r k_{r-dc}[Fe^{3+}])E_{ac}$

Now I can write the rate.

$$rate = k_{f0}e^{b_f E_{dc}}[Fe^{2+}] - k_{r0}e^{b_r E_{dc}}[Fe^{3+}]$$

The above relation is valid at DC condition and when I do not have any AC component. If I have AC, the current is Faradaic constant multiplied by the rate because net rate tells us the number of electrons produced by this reaction. So this is approximately equal to:

$$i_F = F \times rate\ ;\ F(k_{f-dc}(1+b_f E_{ac})[Fe^{2+}] - \mathrm{k}_{\mathrm{r-dc}}(1+b_r E_{ac})[Fe^{3+}])$$

When it is in DC condition, I can use the first equation. When it is in AC condition, I should use E_{ac0} sine (ωt). As I can use the approximation with the assumption that E_{ac0} is small, I can say approximately that the net current at AC condition has components $k_f Fe_2$ and $k_r Fe_3$.

Now consider the DC current. DC current is easy to calculate and it is a simplified version.

$$i_{F-dc} = F(k_{f-dc}[Fe^{2+}] - k_{r-dc}[Fe^{3+}])$$

When I use AC along with DC, I will get a current. I can write it as $I_{dc} + I_{ac}$. So when I apply only DC potential, I will get a DC current. If I superimpose AC potential, the current will also start moving up and down. Assume I give DC potential, the net current I get is i (refer plot in the video). The x-axis is time and up to this time I am giving DC, I will get DC current here. So this is not 0, 0 may be here. This is some value and this is another value. Here I start giving AC potential on top of DC. Then I will start getting AC current. There is going to be a transient. From here to here I am going to skip it. It is going to look like this (refer video). So the net current in this case is I_{dc}+I_{ac}. So DC part is going to be $Fk_{fdc} \times 1 \times Fe^{2+}$ and $Fk_{rdc} \times 1 \times Fe^{3+}$ because that is going to be a constant. AC part is going to be the remaining part. $i_{F-ac} = F(\mathrm{b_f}\, k_{f-dc}[Fe^{2+}] - b_{r-dc}[Fe^{3+}])E_{ac}$ (Refer video for better understanding). So net current can be split it into AC and DC components.

The impedance that we measure using the experimental setup is differential impedance. I give a small sinusoidal and it will give a resulting current and we can find out the sinusoidal oscillation there. I am not looking at E/i. I am looking at E_{ac}/i_{ac}, which means I should get rid of DC components. If I take E_{ac} divided by i_{ac} here, I will get

$$\frac{E_{ac}}{i_{F-ac}} = \frac{1}{F(\mathrm{b_f}\, k_{f-dc}[Fe^{2+}] - b_{r-dc}[Fe^{3+}])}$$

So for this reaction, we can calculate the impedance coming from this reaction. In order to do that, we need to calculate E_{ac}/i_{ac}. E_{ac} is what we apply, I_{ac} is coming from the reaction rate. To calculate i_{ac} we need to calculate the reaction rate and you need the rate constant. The rate constant depends on potential. So the rate constant changes with E_{ac}. And it is actually exponentially related to E_{ac}. We are just truncating it saying E power x can be approximated as 1+x. With that it is easy to get the analytical expression. Now this E_{ac}/i_F is called Faradaic impedance as it is obtained from Faradaic current. This does not depend on ω as there is no ω in this. This is basically a simple resistor. If I draw current DC current as a function of DC potential, it goes like this (refer video). If this is my E_{dc}, I get a current here. It will actually go via zero. This slope gives me di/dE. Inverse of the slope is going to be dE/di and that will give me a constant value. That resistance is going to be the Faradaic impedance for this particular reaction. That is the resistance at 0 frequency, infinite frequency, any intermediate frequency. If I keep the DC potential here, this is going to have a different slope. I will get a different value because K_{fdc} will be different and b_f is a constant. We are assuming that we are using the same solution for Fe^{2+} and Fe^{3+}. So that is also going to be a constant. K_{fdc} depends on E_{dc}. If I superimpose that at 1 potential, I am going to get 1 impedance. If I superimpose at another potential, I will get a different impedance.

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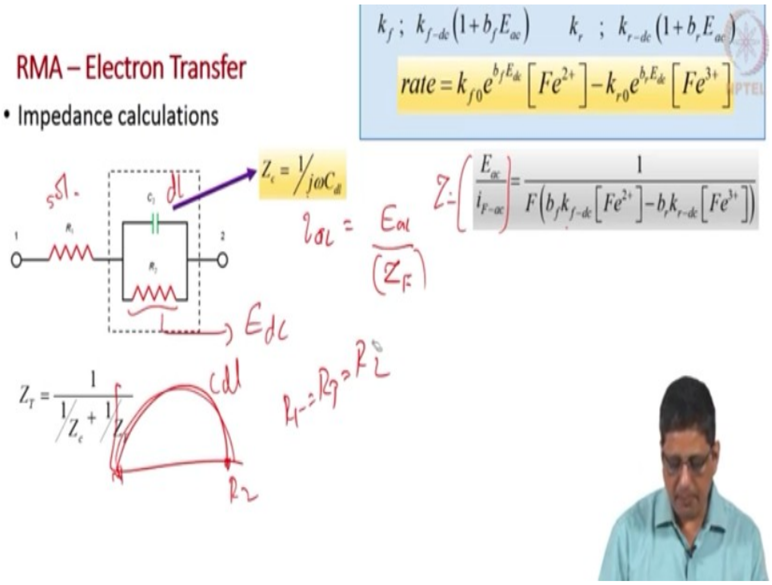

RMA – Electron Transfer

- Impedance calculations

$$k_f \;;\; k_{f-dc}\left(1+b_f E_{ac}\right) \qquad k_r \;;\; k_{r-dc}\left(1+b_r E_{ac}\right)$$

$$rate = k_{f0}e^{b_f E_{dc}}\left[Fe^{2+}\right] - k_{r0}e^{b_r E_{dc}}\left[Fe^{3+}\right]$$

$$Z_c = \frac{1}{j\omega C_{dl}}$$

$$Z = \left(\frac{E_{ac}}{i_{F-ac}}\right) = \frac{1}{F\left(b_f k_{f-dc}\left[Fe^{2+}\right] - b_r k_{r-dc}\left[Fe^{3+}\right]\right)}$$

$$i_{ac} = \frac{E_{ac}}{(Z_F)}$$

$$Z_T = \frac{1}{\frac{1}{Z_c} + \frac{1}{Z}}$$

All the data in general can be modeled using this circuit (refer video) where R_1 is the solution resistance, this is the double layer capacitance (C_{dl}). This is one resistance (parallel to C_{dl}) which depends only on E_{dc} and assuming solution concentrations are remaining the same and the electrode is the same. Z Faraday will not depend; i will depend. In this particular example i_{ac} is related to E_{ac} by:

$$i_{ac} = \frac{E_{ac}}{Z_F}$$

This is proportional to E_{ac} which means Z is a constant and this is correct when we use small amplitude perturbation in. That is one. Second, for this reaction, when you have more complex reaction, it would not be simplified like a resistor. You will have much more complex patterns there. Assume I increase the sinusoidal perturbation, which means I have 1 DC voltage, say 0.1 voltage with respect to OCP (open circuit potential). It has a non-zero DC current. I applied 5 millivolt, I will get an impedance spectrum. If I apply 10 millivolt, I will probably get same impedance spectrum. If I apply 20 millivolts, it may deviate a little. If I apply 100 millivolts, it will change, that means the approximations which we use there are no longer valid. If I use a large amplitude perturbation, I cannot make the approximation that e^x is 1+x. So if I use large amplitude perturbation, you have to solve the actual equation that is going to be valid even for small amplitude, and it is harder. So we most of the time want to say that perturbation is small. I can linearize and solve and get analytical expressions. In this case, the analytical expression is at a given DC, this impedance can be represented by a resistor. At a different DC, it can be represented by another resistor, still a constant value for that DC. So the impedance spectrum that I get out of this will look like this (refer video). Solution resistance is marked here, r_2 here and C_{dl} will give me the high frequency loop here. As it is a simple resistor whether I go to zero frequency or infinite frequency or anything in between, I get the same resistance. Here it so happens. R_t and R_p will have the same value. Capacitor has $1/j\omega C_{dl}$ and you can get the total impedance by adding the capacitor and R_2, assuming solution resistance is zero. So I can write an expression for total impedance. If I am using a programming language, I will write separate expressions for impedance part for the Faradaic process. I have separate expression for the capacitor. I can add them in the correct way.

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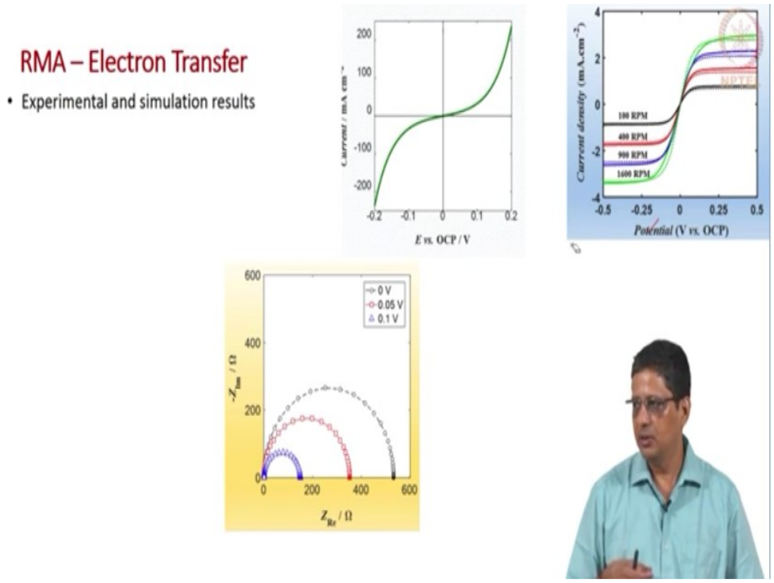

RMA – Electron Transfer

- Experimental and simulation results

At different E_{dc}s, at 0 voltage, I get one semicircle, 50 millivolts of DC, I get another semicircle, 100 millivolts of DC, I get another semicircle (refer slide or video). This is what would happen if our solution resistance is 0, if our perturbation amplitude is small and if diffusion is not playing a significant role. DC current will look like this (refer video). This is what we have calculated previously. I also want to show you what happens when you actually do this process.

If I take ferro/ferri solution and measure the current as a function of potential, it does not go exponentially. It goes up and then saturates (refer the next figure in video). Here in the coloured lines,one of them is experimental and another is model data. Later we will see how to calculate it in the presence of diffusion. Different RPM will have different current levels. So even if you go to high RPM, it does not go as exponential, 1600 is actually moderate. You can go to few thousands. It will still settle, because diffusion will become rate limiting. In ferro/ferri reaction, even if you go to 5000, 6000 RPM, diffusion will not be so fast that you can ignore the contribution from mass transfer. You can ignore the resistance from mass transfer. So if I take the impedance of this, this is how it looks (refer video).

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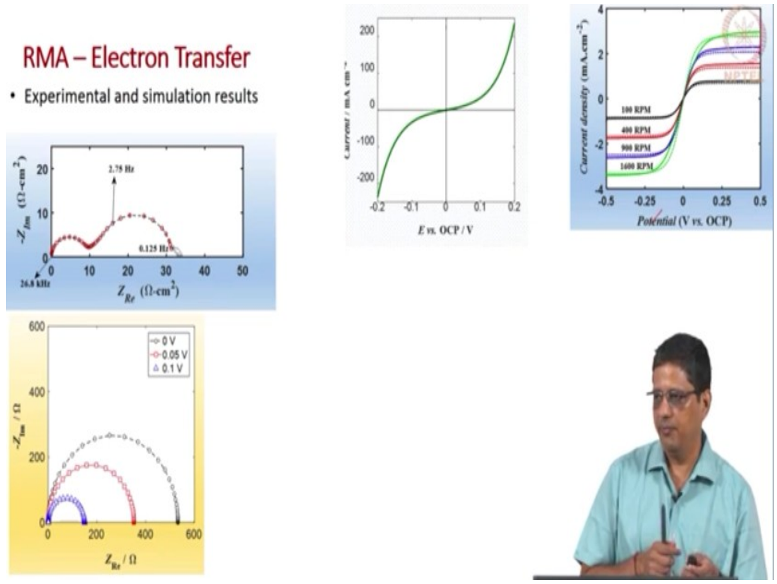

RMA – Electron Transfer

- Experimental and simulation results

The first semicircle is actually coming from the reaction. Second is not a semicircle, it looks like a distorted semicircle. It is not a distorted semicircle either. It is almost like a 45° line here with a curve here and we will give a proper expression for this which is possible to derive. So mass transfer is present. We make the assumption that mass transfer resistance is not that significant, so that we can derive this equation. When mass transfer is coupled with this, it is not that easy. For simple reaction, you can derive. For anything more complex, it is very difficult.

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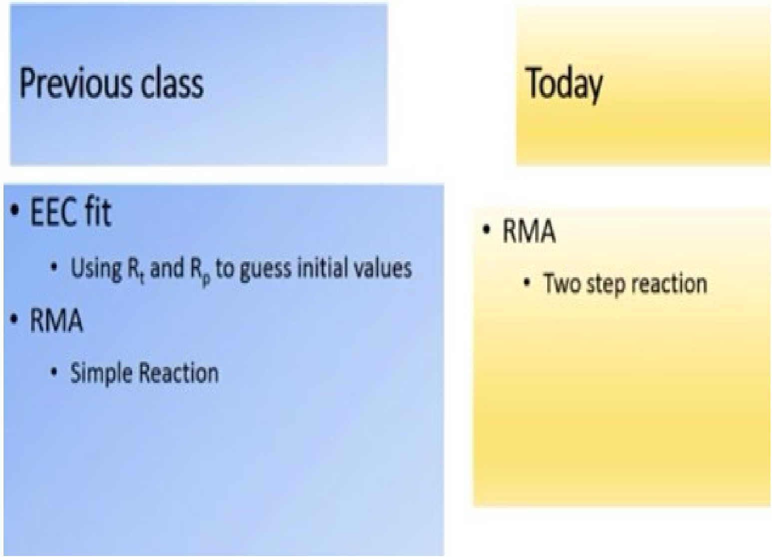

Previous class

- EEC fit
  - Using R_t and R_p to guess initial values
- RMA
  - Simple Reaction

Today

- RMA
  - Two step reaction

In the previous session, we have seen some examples with EEC and how we can use the polarization resistance and charge transfer resistance to guess initial values and we have also seen the derivation of impedance equation and current potential equation for a simple reaction. Now I want to show you the derivation of impedance for a reaction with 2 steps.

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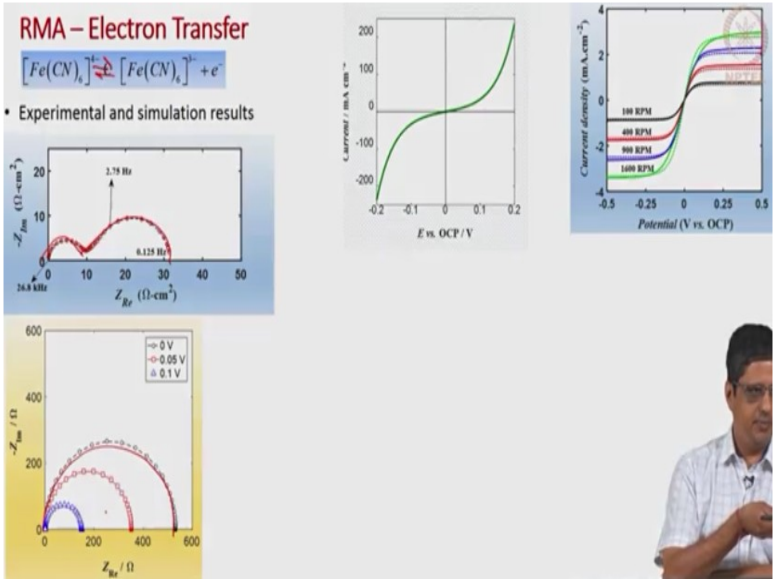

RMA – Electron Transfer

$[Fe(CN)_6]^{4-} \rightleftharpoons [Fe(CN)_6]^{3-} + e^-$

- Experimental and simulation results

To summarize the previous topics; we have seen the reaction A going to B with an electron transfer. If you calculate the impedance at various DC potentials, we saw that we will get semicircles with different diameters. The calculations also showed that, if you calculate the current versus potential, it is going to go as exponential when you are far away from 0. When you are at 0 potential or at the equilibrium potential, it is going to be 0. This is what you predict if diffusion is not rate limiting and only kinetics are rate limiting and we also saw examples where we showed that, when you measure at different RPM, current will increase with potential and then saturate due to diffusion. Similarly, if you go to the negative potential, current will decrease and then saturate. Likewise, if you measure the impedance, it is going to show you 1 semicircle corresponding to the charge transfer process that is corresponding to the kinetics. And then another loop which is not really semicircle that comes from diffusion. So diffusion is not really completely neglected. It cannot be neglected when you are actually measuring for this particular reaction. So whatever we are calculated or the equations we have derived or assuming the diffusion is very fast, we are going to do few more examples where diffusion is considered to be very fast and therefore mass transfer resistance is negligible.